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Emmanuel Mousset

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Joint PhD degree in Environmental Technology

Docteur de l'Université Paris-Est
Spécialité : Science et Technique de l'Environnement

Dottore di Ricerca in Tecnologie Ambientali

Degree of Doctor in Environmental Technology

Thèse - Tesi di Dottorato - PhD thesis

Emmanuel MOUSSET

INTEGRATED PROCESSES FOR REMOVAL OF PERSISTENT ORGANIC POLLUTANTS: SOIL WASHING AND ELECTROCHEMICAL ADVANCED OXIDATION PROCESSES COMBINED TO A POSSIBLE BIOLOGICAL POST-TREATMENT

Defended on December, 2nd 2013

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Erasmus Joint doctorate programme in Environmental Technology for Contaminated Solids, Soils and Sediments (ETeCoS^3)

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List of Abbreviations

1,2-DCB	1,2-dichlorobenzene
1,2,4-TMB	1,2,4-trimethylbenzene
2-NB	2-nitrobiphenyl
2,4-D	2,4-dichlorophenoxyacetic acid
2,4-DANT	2,4-diamino-4-nitrotoluene
2,4-DNT	2,4-dinitrotoluene
2,6-DANT	2,6-diamino-4-nitrotoluene
4-ADNT	4-amino-2,6-dinitrotoluene
4-NP	4-nonylphenol
α-CD	Alpha-cyclodextrin
γ-CD	Gamma-cyclodextrin
Ac-β-CD	Acetyl-beta-cyclodextrin
ACE	Acenaphthene
ACY	Acenaphthylene
ADEME	Agence De l'Environnement et de la Maitrise de l'Energie
ANT	Anthracene
AO	Anodic Oxidation
AOPs	Advanced Oxidation Processes
BaA	Benzo(a)anthracene
BaP	Benzo(a)pyrene
BB	Butylbenzene
BbF	Benzo(b)fluoranthene
BDD	Boron-Doped Diamond
β-CD	Beta-cyclodextrin
BghiP	Benzo(g,h,i)perylene
BkF	Benzo(k)fluoranthene
BOD_5	Biochemical Oxygen Demand after 5 days
BRGM	Bureau de Recherches Géologiques et Minières
BTEX	Benzene, Toluene, Ethylbenzene, Xylene
BuOH	Buthanol
CB	Chlorobenzene

CEC	Cationic Exchange Capacity
CECs	Commission of the European Communities
CDs	Cyclodextrins
CHRY	Chrysene
CMC	Critical Micelle Concentration
CMCD	Carboxymethyl-beta-cyclodextrin
COD	Chemical Oxygen Demand
CSTR	Continuously Stirred Tank Reactor
CV	Cristal Violet
dBahA	Dibenzo(a,h)anthracene
DDT	Dichlorodiphenyltrichloroethane (1,1,1-trichloro-2,2-bis (4-chlorophenyl) ethane
DEC	Decane
DMCD	Heptakis-2,6-di-o-methyl-beta-cyclodextrin
DNA	Deoxyribonucleic acid
DNAPL	Dense Non-Aqueous Phase Liquid
DOM	Dissolved Organic Matter
DSA	Dimensionally Stable Anode
DTPA	Diethylene Triamine Pentaacetic Acid
EAOPs	Electrochemical Advanced Oxidation Processes
EB	Ethylbenzene
EC_{50}	Half maximal Effective Concentration
EDCD	Ethylene diamine beta-cyclodextrin
EDTA	Ethylene Diamine Tetraacetic Acid
EEA	European Environment Agency
EF	Electro-Fenton
EtOH	Ethanol
FAME	Fatty acid methyl esters
FLA	Fluoranthene
FLE	Fluorene
GAC	Granular Activated Carbon
GCD	Glycine-beta-cyclodextrin
GluCD	Glutamic acid-beta-cyclodextrin

HCB	Hexachlorobenzene
HOCs	Hydrophobic Organic Compounds
HP-α-CD	Hydroxypropyl-alpha-cyclodextrin
HP-γ-CD	Hydroxypropyl-gamma-cyclodextrin
HPCD	Hydroxypropyl-beta-cyclodextrin
HPLC	High Performance Liquid Chromatography
HRT	Hydraulic Retention Time
IARC	International Agency for Research on Cancer
INERIS	Institut National de l'EnviRonnement industriel et des rISques
I-CA-720	Igepal CA-720
I(1,2,3-c,d)P	Indeno(1,2,3-c,d)pyrene
M-biodiesel	Marketed-biodiesel
m-parathion	Methyl-parathion
m,p-XYL	m,p-xylene
MCD	Methyl-beta-cyclodextrin
MeOH	Methanol
MF	Mefenacet (2-(2-benzothiazolyloxy)-N-methyl-N-phenylacetamide)
MGP	Manufactured Gas Plant
Mod-β-CD_{12}	Modified monosubstituted beta-cyclodextrin with an amphiphilic chain of twelve carbons
Mod-β-CD_{12} (2.4)	Modified beta-cyclodextrin with an amphiphilic chain of twelve carbons and substitution degree of 2.4
MW	Molar Weight
n-But	n-butylamine
NACs	Nitroaromatic compounds
NAP	Naphthalene
NAPL	Non-Aqueous Phase Liquid
NBZ	Nitrobenzene
NFL	Norflurazon
NIS	Non-Ionic Surfactant
NMR	Nuclear Magnetic Resonance
NOM	Natural Organic Matter
OM	Organic Matter

o-XYL	o-xylene
PAHs	Polycyclic Aromatic Hydrocarbons
PCBs	Polychlorinated biphenyls
PCDDs	Polychlorinated dibenzo-p-dioxins
PCDFs	Polychlorinated dibenzo furans
PCP	Pentachlorophenol
PFR	Plug-flow Reactor
PHE	Phenanthrene
POPs	Persistent Organic Pollutants
Pt	Platinum
PYR	Pyrene
RAMEB	Randomly methylated beta-cyclodextrin
RDX	Hexahydro-1,3,5-trinitro-1,3,5-triazine
SBR	Sequential Biological Reactor
SD	Substitution Degree
SDS	Sodium Dodecyl Sulfate
SF	Soil Flushing
S-FAME	Synthesized FAME
SOeS	Service de l'Observatoire et des Statistiques
SOM	Soil Organic Matter
SW	Soil Washing
TCB	1,2,3-Trichlorobenzene
TCE	Trichloroethene
TCP	2,4,6-trichlorophenol
TeCE	Tetrachloroethene
TeCP	Tetrachlorophenol
THF	Tetrahydrofuran
TNS	6-(p-toluidino)naphthalene-2-sulfonic acid
TNT	2,4,6-trinitrotoluene
TOC	Total Organic Carbon
TOL	Toluene
UNDEC	Undecane
USEPA	United States Environmental Protection Agency

VOCs	Volatile Organic Compounds

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Abstract

Soils contaminated by hydrophobic organic pollutants like Polycyclic Aromatic Hydrocarbons (PAHs) are a common concern since they are extremely difficult to remove and their potential toxicological impacts are significant.

As an alternative to traditional thermal or physical treatments, soil washing and soil flushing processes appear to be conceivable and efficient approaches, especially for higher level of pollution. However, the treatment of highly loaded soil washing/flushing solutions is another challenge to overcome. In that way, a new integrated approach is suggested: soil washing/flushing processes combined to an Electrochemical Advanced Oxidation Process (EAOP) in a combination with a recirculation loop (to save extracting agents) and/or a biological post-treatment step (to minimize energy cost).

Extraction efficiency of the extracting agent like hydroxypropyl-beta-cyclodextrin (HPCD) is compared to the traditional non-ionic surfactant Tween 80 in synthetic and real soil washing solutions. A new simple fluorescent sensitive and selective quantification method is developed to monitor Tween 80 oxidation. Two EAOPs were compared: Electro-Fenton (EF) and Anodic Oxidation (AO). Platinum (Pt) (in EF process) and Boron-Doped Diamond (BDD) (in both treatment) anodes are the respective electrodes employed to recycle effluents and to consider a biological post-treatment, respectively. Regarding the extracting agent recovery, the biodegradability evolution of effluent and the energy consumption (in kWh (kg TOC)$^{-1}$) during EAOP, HPCD is more advantageous than Tween 80. However, in terms of extraction efficiency, costs of extracting agents and impact on soil respirometry, Tween 80 is much more efficient. By considering all these advantages and drawbacks, Tween 80 could still appear to be the best option.

Keywords: Soil washing, Polycyclic Aromatic Hydrocarbons (PAHs), Cyclodextrins, Surfactants, Electrochemical Advanced Oxidation Processes (EAOPs), Degradation, Biodegradability.

Résumé

Les sols contaminés par les polluants organiques hydrophobes tels que les Hydrocarbures Aromatiques Polycycliques (HAPs) constituent un problème majeur puisqu'ils sont difficilement éliminés et leurs impacts toxicologiques restent significatifs.

Comme alternative aux procédés thermiques et physiques traditionnels, les procédés de lavages de sol *in situ* et *ex situ* apparaissent être une solution envisageable et efficace et particulièrement pour les fortes pollutions. Cependant, le traitement des solutions fortement chargées de lavages de sol est une autre barrière à surmonter. Une nouvelle approche combinée est proposée pour répondre à ce problème: les procédés de lavages de sol *in situ*/*ex situ* combinés à un Procédé Electrochimique d'Oxydation Avancée (PEOA) avec possibilité de recirculer l'effluent (pour réutiliser l'agent extractant) et/ou de combiner avec un post-traitement biologique (pour minimiser le coût énergétique).

L'efficacité d'extraction de l'agent extractant tel que l'hydroxypropyl-beta-cyclodextrine (HPCD) est comparé au traditionnel tensioactif non-ionique dénommé Tween 80, dans les solutions synthétiques et réelles de lavages de sol. Une nouvelle méthode sensible d'analyse du Tween 80, basée sur la fluorescence, est développée pour suivre l'oxydation du Tween 80. Deux PEOAs sont comparés : l'Electro-Fenton (EF) et l'Oxydation Anodique (OA). Les anodes de platine (Pt) (dans le procédé EF) et de Diamant Dopés au Bore (BDD) (dans les deux procédés) sont respectivement utilisées pour étudier la recirculation des effluents et la possibilité d'une combinaison avec un post-traitement biologique. Concernant la réutilisation des agents extractants, l'évolution de la biodégradabilité des solutions et l'énergie consommée (en kWh (kg COT)$^{-1}$) pendant les PEAOs testés, l'HPCD est trouvée être plus avantageuse que le Tween 80. En revanche, en terme d'efficacité d'extraction, de coût des agents extractants et d'impact sur la respirométrie du sol, le Tween 80 paraît être plus avantageux. En prenant en compte tous ces avantages et inconvénients, le Tween 80 pourrait être retenu comme la meilleure solution.

Mots clés: Lavages de sol, Hydrocarbures Aromatiques Polycycliques (HAPs), Cyclodextrines, Tensioactifs, Procédés Electrochimiques d'Oxydation Avancée (PEOAs), Dégradation, Biodégradabilité.

Sintesi

Suoli contaminati da inquinanti organici idrofobici, come gli idrocarburi policiclici aromatici (IPA), rappresentano una preoccupazione comune, essendo estremamente difficili da rimuovere e avendo un impatto tossicologico potenziale molto elevato.

Come alternativa ai trattamenti termici o fisici tradizionali, i processi di "soil washing" e "soil flushing" appaiono i più idonei ed efficienti soprattutto in caso di alti livelli di inquinamento. Tuttavia il trattamento delle soluzioni concentrate prodotte dai processi di "soil washing" e "soil flushing" risulta un problema di non semplice soluzione. A tal riguardo un nuovo approccio integrato è stato proposto nel presente lavoro di tesi: "soil washing" e "soil flushing" accoppiati a un processo di ossidazione avanzata elettrochimica (electrochemical advanced oxidation process - EAOP) con un ricircolo per il recupero degli agenti estraenti e/o uno stadio di post-trattamento biologico (per minimizzare i costi energetici).

L'efficienza di estrazione dell'agente estraente hydroxypropyl-beta-cyclodextrin (HPCD) è stata confrontata con quella del surfatante non ionico tradizionale Tween 80 per il soil washing di suoli artificiali e reali. Un nuovo metodo di quantificazione selettiva basato sulla fluorescenza è stato proposto per monitorare l'ossidazione del Tween 80 e sono stati confrontati due EAOP: electro-Fenton (EF) e ossidazione anodica (Anodic Oxidation - AO). Anodi di Platino (Pt) (nel processo EF) e Boron-Doped Diamond (BDD) (in entrambi i processi) sono stati utilizzati come elettrodi, rispettivamente, per ricircolare gli effluenti o effettuare un post-trattamento biologico. Con riguardo al recupero dell'agente estraente, l'evoluzione della biodegradabilità dell'effluente ed il consumo di energia (in kWh (kg TOC)$^{-1}$) nel corso del processo di EAOP, l'HPCD si è dimostrato più vantaggiso rispetto al Tween 80. Tuttavia, in termini di rendimenti di estrazione, costi dell'agente estraente e impatto sulla respirometria del suolo, il Tween 80 è molto più efficiente. Prendendo in considerazione tutti i vantaggi e gli svantaggi, il Tween 80 risulta essere ancora la migliore opzione disponibile.

Parole chiave: soil washing, idrocarburi policiclici aromatici (IPA), ciclodestrine, tensioattivi, processi di ossidazione avanzata elettrochimica (POAEs), degrado, biodegradabilità.

Samenvatting

Bodems verontreinigd met hydrofobe organische stoffen zoals polycyclische aromatische koolwaterstoffen (PAK) zijn een belangrijk milieuprobleem omdat ze zeer moeilijk te verwijderen zijn en aanzienlijk potentiële toxicologische gevolgen hebben.

Als alternatief voor de traditionele thermische of fysische bodembehandelingen, lijken bodemwas / -spoel processen een mogelijke en efficiënte benadering, vooral voor de meer vervuilde bodems. De behandeling van de hoogvervuilde bodemwas / -spoel vloeistoffen is echter nog een andere uitdaging. Daarom wordt een nieuwe, geïntegreerde benadering voorgesteld: het combineren van een bodemwas / -spoel behandeling met elektrochemisch geavanceerde oxidatieprocessen (EAOP) in combinatie met een recirculatie stroom (om de extraheermiddelen op te slaan) en / of een biologisch nabehandelingstap (om de energiekosten te minimaliseren).

De extractie efficiëntie van hydroxypropyl-beta-cyclodextrine (HPCD) werd vergeleken met de traditionele niet-ionogene oppervlakteactieve stof Tween 80 in synthetische en echte bodemwasoplossingen. Een nieuwe, eenvoudige fluorescentie-gevoelige en selectieve kwantificatie methode werd ontwikkeld om de oxidatie van Tween 80 te monitoren. Twee EAOPs werden vergeleken: electro-Fenton (EF) en anodische oxidatie (AO). Anodes van platina (Pt) (in het EF-proces) en boor gedopeerde diamant (in beide behandelingsprocessen) zijn de respectievelijke elektroden die gebruikt werden om afvalwater te recyclen en een biologische nabehandeling te overwegen. Wat betreft de recovery van het extractiemiddel, de evolutie van de biologische afbreekbaarheid van het effluent en het energieverbruik (in kWh (kg TOC) $^{-1}$) gedurende de EAOP behandeling, was HPCD voordeliger dan Tween 80. Echter, in termen van de extractie-efficiëntie, kosten van het extractieagens en de impact op de bodemrespirometrie, is Tween 80 veel efficiënter. Na afweging van de voor- en nadelen lijkt Tween 80 nog steeds de beste optie.

Trefwoorden: Bodem wassen, polycyclische aromatische koolwaterstoffen (PAK), Cyclodextrines, Surfactantia, elektrochemische geavanceerde oxidatie processen, Afbraak, Biologische afbreekbaarheid.

CHAPTER 1

Introduction

CHAPTER 1

1.1 Background

1.1.1 Overview on polluted sites in Europe

The remediation of contaminated sites is a common concern and represents a challenge for the next years since the number of polluted sites increases together with human activities. In the last two decades, the number of potentially contaminated sites increased six or seven times in most of the developed countries (Swartjes, 2011). The European Environment Agency (EEA) estimated that over 3,000,000 sites are potentially contaminated in Europe in 2006 and around 250,000 contaminated sites among them may need urgent remediation (EEA, 2007). Probably, the number of sites has increased until now (Swartjes, 2011). A number of 5,129 potentially contaminated sites are listed in France in 2013 (BASOL, 2013). The main causes of sites contamination are antropogenic activities and most of these sites are located close to or in urban areas. Nowadays, the awareness of European countries about the practical, social and financial impacts of contaminated sites is increasing. Soil remediation represents a great economic stakes with a market value of 57 billion euros in Europe according to the Commission of the European Communities (CECs) (CECs, 2006) and especially 651 million in France in 2011 (SOeS, 2013). Moreover, there is an increase of 10% contaminated sites each year in France since 1996.

1.1.2 Targetted pollutants

The most common pollutants in contaminated sites in Europe are mineral oil and heavy metals according to EEA (2007). In France, hydrocarbons (32% of sites) are the most usual pollutants (BASOL, 2013). Then lead (15%) and Polycyclic Aromatic Hydrocarbons (PAHs) (13%) are the second and the third contaminants found in French soils, respectively. Since, PAHs are widely present in polluted soils, particular interests were brought to PAHs contaminants in this thesis.

1.1.2.1 Origins of PAHs contamination

PAHs are chemical compounds made of two or more fused aromatic rings. They are ubiquitous in environment and are mainly produced through formation of fossil energy

(petroleum and coal), through incomplete combustion of Organic Matter (OM) (heating oil, incineration, vehicles, forest fires,…) or through use of creosote for wood protection (INERIS, 2005). Their main origin is anthropogenic and natural source like forest fires and volcanic eruptions are less important (Srogi et al. 2007).

1.1.2.2 Physicochemical properties of PAHs and their environmental fate

The environmental fate of PAHs compounds is directly related to their physicochemical properties. The latter are depending especially on their molar weight (MW) and their structure. The main physicochemical properties are gathered in Table 1.1. Their nonpolar and hydrophobic properties with a high octanol/water partition coefficient (Log K_{ow}) make them persistent in the environment. Moreover, their high carbon partition coefficient (Log K_{oc}) makes them strongly bound to soil, which is the main sink, since PAHs can be adsorbed to Soil Organic Matter (SOM) concentrated in fine particles. Furthermore, their low Henry constant values (H) and low vapor pressure when the molar weight increases make them non-volatile. Only light PAHs having a low molar weight (2 aromatic rings) can be considered as semi-volatile with a relatively higher water-solubility. The PAHs density is higher than 1 and they are considered as dense non-aqueous phase liquid (DNAPL).

1.1.2.3 Toxicity

The PAHs toxicity can be explained by intercalation of the PAH aromatic ring system into the DNA duplex (Cai et al., 2013). This formation of DNA adducts is a key event in mutagenicity and carcinogenicity by PAHs (WHO, 2010). Sixteen of them are listed as priority substances by the Environmental Protection Agency of United States (USEPA): naphthalene (NAP), acenaphthene (ACE), acenaphthylene (ACY), fluorene (FLE), phenanthrene (PHE), anthracene (ANT), fluoranthene (FLA), pyrene (PYR), benzo(a)anthracene (BaA), chrysene (CHRY), benzo(b)fluoranthene (BbF), benzo(k)fluoranthene (BkF), benzo(a)pyrene (BaP), dibenzo(a,h)anthracene (dB(ah)A), benzo(g,h,i)perylene (BghiP) and indeno(1,2,3-c,d)pyrene (I(123-cd)P). Some of these PAHs are classified by the International Agency for Research on Cancer (IARC) as carcinogenic to humans (group 1) like BaP, as probably carcinogenic to humans (group 2A) like dB(ah)A and dibenzo(a,l)pyrene, as possibly carcinogenic to humans (group

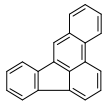
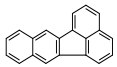
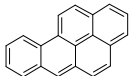
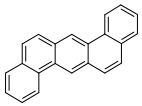
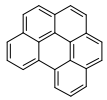
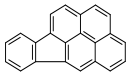
2B) like BaA, BbF, benzo(j)fluoranthene, BkF, benzo(c)phenanthrene, CHRY, dibenzo(a,i)pyrene, dibenzo(a,h)pyrene and I(123-cd)P (WHO, 2010).

1.1.2.4 Regulations about PAHs-contaminated soils

The soil quality criteria of the sixteen PAHs listed by USEPA about PAHs-contaminated soils disposal in some countries in the world are listed in Table 1.2. Since no worldwide rules exist at the world scale and European scale about contaminated-soil disposal, there is heterogeneity of the threshold values concerning the PAHs pollutants. However, a soil directive is in progress for European countries. Most of the countries give national threshold values for the most toxic one according to IARC like BaP that has usually the lowest authorization level. Other countries like France give only a threshold value for all the PAHs contents that is 50 mg kg^{-1} for landfill disposal (for inert wastes). Denmark gives the lowest restriction value for total PAHs that is 1.5 mg kg^{-1} for sensitive land use.

Table 1.1. Some physicochemical properties of the 16 PAHs listed by USEPA.

PAHs	Chemical structure	Formula	MW (g mol^{-1})	Density[c]	Water-Solubility at 25°C (mg L^{-1})[a]	Boiling Point (°C)[b]	Log K_{ow}[a]	Log K_{oc}[c]	Vapor pressure (20°C) (Pa)[d]	Henry constant (H) at 25°C (Pa m^3 mol^{-1})[c]
NAP		$C_{10}H_8$	128.2	1.162	3.2×10^{1}	218	3.4	3.15	3.7×10^{1}	4.9×10^{1}
ACY		$C_{12}H_8$	152.2	1.194	3.9×10^{0}	280	4.1	1.40	4.1×10^{0}	-
ACE		$C_{12}H_{10}$	154.2	1.024	3.4×10^{0}	279	4.3	3.66	1.5×10^{0}	1.5×10^{1}
FLE		$C_{13}H_{10}$	166.2	1.203	1.9×10^{0}	298	4.2	6.20	7.2×10^{-1}	9.2×10^{0}
PHE		$C_{14}H_{10}$	178.2	1.172	1.3×10^{0}	340	4.4	4.15	1.1×10^{-1}	4.0×10^{0}
ANT		$C_{14}H_{10}$	178.2	1.240	7.0×10^{-2}	340	4.5	4.15	7.8×10^{-2}	5.0×10^{0}
FLA		$C_{16}H_{10}$	202.3	1.236	2.6×10^{-1}	375	5.2	4.58	8.7×10^{-3}	1.5×10^{0}
PYR		$C_{16}H_{10}$	202.3	1.271	1.4×10^{-1}	393	5.3	4.58	1.2×10^{-2}	1.1×10^{-3}
BaA		$C_{18}H_{12}$	228.3	1.174	1.0×10^{-2}	438	5.6	5.30	6.1×10^{-4}	2.0×10^{-2}
CHRY		$C_{18}H_{12}$	228.3	1.274	2.0×10^{-3}	448	5.6	5.30	8.4×10^{-7}	1.0×10^{-2}

BbF		$C_{20}H_{12}$	252.3	-	1.5×10^{-3}	481[c]	6.6	5.74	6.7×10^{-5}	5.0×10^{-2}
BkF		$C_{20}H_{12}$	252.3	-	8.0×10^{-3}	480	6.8	5.74	4.1×10^{-6}	6.9×10^{-2}
BaP		$C_{20}H_{12}$	252.3	1.282	3.8×10^{-3}	495	6.0	6.74	2.1×10^{-5}	5.0×10^{-2}
dB(ah)A		$C_{22}H_{14}$	278.3	1.252	5.0×10^{-4}	524[c]	6.0	6.52	9.2×10^{-8}	4.8×10^{-3}
BghiP		$C_{22}H_{12}$	276.3	1.329	3.0×10^{-4}	500	7.0	6.20	2.3×10^{-5}	1.4×10^{-2}
I(123-cd)P		$C_{22}H_{12}$	276.3	-	2.0×10^{-4}	533[c]	7.7	6.20	1.3×10^{-8}	2.9×10^{-2}

[a] Manoli and Samara (1999)

[b] Martens and Frankenberger (1995)

[c] INERIS (2005)

[d] Mackay et al. (1992)

Table 1.2. Soil quality criteria for PAHs-contaminated soils disposal in several countries in the world (Venny et al., 2012).

Country	Site designation	PAHs (mg kg^{-1})																
		NAP	ACE	ACA	FLE	ANT	PHE	FLA	PYR	BaA	CHRY	BaF	BkF	BaP	dB(ah)A	I(123-cd)P	BghiP	Total PAHs
United States	Land disposal	-	4	3	4	4	3	8.2	8.2	8	8	3	3	8	8		2	
Canada	Agricultural					3		50						20				
	Residential/park land					3		50						20				
	Commercial					32		180						72				
	Industrial					32		180						72				
The Netherlands	General	0					1	2.6		0	11		2	0			8	
Denmark	Sensitive land use													0	0			1.5
	Ecotoxicological quality criteria													0				1
Norway	General													1				
France[(a)]	Landfill (inert waste)																	50
Sweden	Less sensitive land use (industrial and commercial areas,…)	15	15	15	20	20	20	20	20	10	10	10	10	10	10	10	10	
Australia	Residential with gardens and accessible soil													1				20
	Residential with minimal access to soil													4				80
	Parks													2				40
	Commercial/Industrial													5				100
China	Exhibition sites for common usage	54			210	2300	2300	310	230	0.33	9	0.9	0.9	0.3	0.33	0.9	230	
Thailand	Habitat and agriculture													0.6				
	Other purposes													2.9				

(a) Decree of October, 28th 2010 about landfilling of inert wastes

1.1.3 Which soil treatment use?

1.1.3.1 Comparison of the usual treatments for organic-contaminated soil

Different typical treatments for organic-contaminated soils are listed in Table 1.3. These data were published by French public organization such as "Bureau de Recherches Géologiques et Minières" (BRGM) (Colombano et al., 2010) and "Agence De l'Environnement et de la Maitrise de l'Energie" (ADEME) (Cadière et al., 2011). Physical processes, physico-chemical treatments, thermal treatments and biological techniques are compared according to three key factors: robustness and maintenance, time of remediation, average relative costs. The costs represent the total costs from the beginning to the end of the remediation process (consulting, site meeting, treatments, maintenance…). About the cost in euro per ton of treated soils, it has to be added for *ex situ* treatments the costs of excavation and transport that are in average 7 €t^{-1} and 0.2 € t^{-1} km^{-1}, respectively (Cadière et al., 2011).

1.1.3.2 Determination of the studied treatment

The physical processes like containment and landfilling do not remove the pollutant from the soil but only avoid the expansion of the pollution. The soil washing (SW) with water process is not efficient enough since PAHs pollutants are hydrophobic and strongly sorbed into soil. Table 1.3 shows that thermal treatments are usually more expensive and energy consuming. Biological treatments are generally slow and not efficient enough with xenobiotics compounds like heavy PAHs (Colombano et al., 2010). Physico-chemical treatments like solidification/stabilization do not treat the soil but only restrain the pollution diffusion. The other physicochemical ones are able to treat the soil and can be quicker than the biological treatments especially when the level of contamination is high but the chemicals added need to be environmentally friendly.

Though the robustness and the maintenance are not the best point of SW and SF processes, the costs and time of remediation for PAHs-contaminated soils can still be competitive with the other techniques (Colombano et al., 2010). Moreover, it is more environmentally friendly than the thermal treatments, assuming that the enhancing agents used are biodegradable.

Table 1.3. Typical main soil remediation processes for organic-contaminated soils (Colombano et al., 2010)[(a)] and (Cadière et al., 2011)[(b)].

Remediation Techniques			Robustness and maintenance[(a)]	Time of remediation[(a)]	Relative costs[(a)]	Costs (€t^{-1})[(b)]
Physical processes	*In situ*	Containment	+++	+	+++	15-40
	Ex situ on site or off site	SW with water	+++	+++	++	nd
	Ex situ off site	Landfill (hazardous wastes)	+++	+	+++	75-195
Physico-chemical treatments	*In situ*	Chemical oxidation	++	+++	++	25-50
		SF	++	++	++	nd
		Solidification/stabilisation	+++	+++	+++	70-150
	Ex situ on site or off site	Chemical oxidation	+++	+++	++	nd
		SW	++	++	++	15-60 (on site)
		Solidification/stabilisation	+++	+++	+++	40-200 (off site)
Thermal treatments	*In situ*	Heating	+++	+++	++	nd
		Vitrification	+++	+++	++	nd
	Ex situ on site or off site	Incineration	++	+++	+	150-400 (off site)
		Thermal desorption	++	+++	++	65-110 (off site)
		Vitrification	+++	+++	++	nd
Biological treatments	*In situ*	Enhanced/monitored natural attenuation	++	++	+++	nd
		Bioventing	+++	++	+++	5-35
	Ex situ on site or off site	Biopile	+++	++	+++	15-60 (on site)
		Landfarming	+++	++	+++	15-60 (on site)
		Composting	+++	++	+++	15-60 (on site)

One "+" means a low robustness, high maintenance, long time of remediation and high costs. Two "++" and three "+++" mean a medium and a good quality of the criteria, respectively.

Considering these aspects, in the present work SW and SF treatments are studied. These techniques are developed in the sub-section 1.2.1.2.

1.1.3.3 Issues

Since SW and SF processes only permit to extract PAHs from solid matrix to liquid matrix, a post-treatment is needed to treat the highly loaded solutions. An integrated approach is suggested in this work and explained in the following section 1.2.

1.2 Objectives

1.2.1 Integrated process

1.2.1.1 Presentation of the innovative integrated approach

The integrated process described in Fig. 1.1 consists of combining SW/SF processes with an electrochemical advanced oxidation process (EAOP) as an alternative to traditional separation techniques (Activated carbon, membrane processes, filtration…) and chemical oxidation (Chlorine, ozone, H_2O_2, etc). The possibility to save the extracting agent after the electrochemical treatment and to recirculate the treated solution is carried out. Since the electrochemical treatment can be energy consuming, the possibility to transform the initial biorecalcitrant compounds to more biodegradable one in order to treat them with a possible biological post-treatment is also studied.

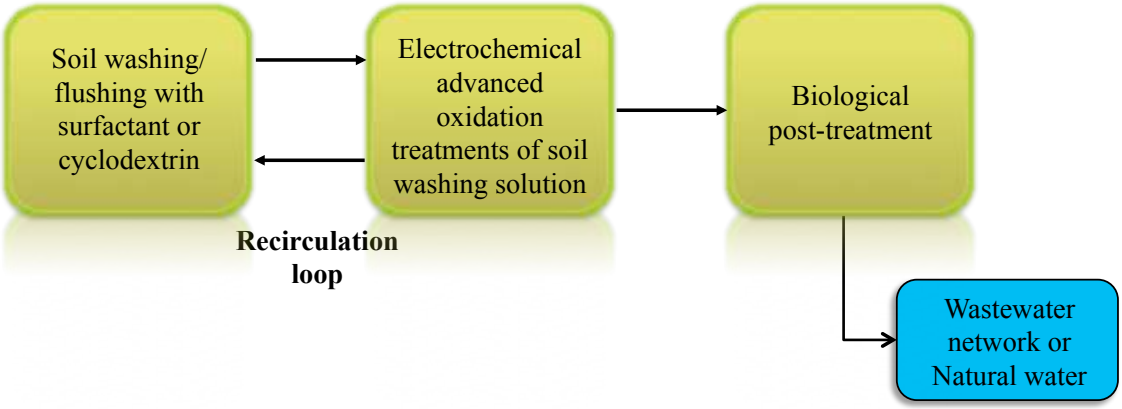


Fig. 1.1. *Innovative integrated process: SW combined to EAOP with a recirculation loop and / or a possible biological post-treatment.*

1.2.1.2 Presentation of each unit of the process

Only the main information are mentioned in this sub-section since these processes are described more in details in Chapter 2 and followings.

1.2.1.2.1 SW/SF process

- SW process

SW is an *ex situ* process that can be applied on site or off site in a specific platform of soil treatment. It consists of a study in a reactor by mixing a certain quantity of soil with a certain volume of solution containing the extracting agents (surfactants or biosurfacants, co-solvents, chelates, cyclodextrins,…). Different parameters are previously studied at laboratory scale like solid/liquid ratio, contact time, age of contaminated soil, kind of extracting agent, concentration of solubilizing agents and soil characteristics.

- SF process

SF is an *in situ* process. The percolation of a flushing solution containing the extracting agent through a column containing the soil is performed at laboratory scale. The different parameters usually studied are the surface flow rate, the soil characteristics, the volume of flushing solution, the concentration of solubilizing agent, the contact time and the age of contaminated soil.

1.2.1.2.2 Electrochemical advanced oxidation processes (EAOPs)

EAOPs have been developed recently especially to degrade recalcitrant organic pollutant in a clean way (electron as a main reagent) through the production of hydroxyl radicals ($^{\bullet}OH$). These powerful oxidizing agents (E° = 2.80 V vs SHE) are especially efficient to degrade aromatic rings (10^8 – 10^{10} M^{-1} s^{-1}) like PAHs. Two EAOPs techniques emerged in the last decade and were performed in this work: electro-Fenton (EF) and anodic oxidation (AO).

- EF process

EF is a process developed simultaneously by Oturan's group in University of Paris-Est and Brillas's group in University of Barcelona. This AOP has been rewiewed by Brillas

et al. (2009). It consists of the *in situ* generation of H_2O_2 via O_2 reduction at the cathode and the regeneration of the catalyst Fe^{2+} via the reduction of iron(III). This catalyst (Fe^{2+}, Fe^{3+}, iron oxide) is added at the beginning of the treatment at a very low quantity (~ 10^{-3} mM). Hydroxyl radicals are therefore formed through the Fenton reaction:

$$Fe^{2+} + H_2O_2 + H^+ \rightarrow Fe^{3+} + H_2O + {}^{\bullet}OH \qquad (1.1)$$

Compared to traditional Fenton treatment, no sludge is produced, no reagent is added, except iron at calalytic quantity and electrolytes, and the kinetic of oxidation are quicker (Oturan, 2000).

- AO process

AO is an EAOP that allow generating ${}^{\bullet}OH$ at high O_2-overvoltage anode (M) through the reaction:

$$M + H_2O \rightarrow M({}^{\bullet}OH) + H^+ + e- \qquad (1.2)$$

This process has been reviewed by Panizza and Cerisola (2009). The emergent anode Boron-Doped Diamond (BDD) exhibited excellent oxidation power when used at this process. The main advantages of this technique are that no reagent is added and the mineralization rates can be very high (Comninellis and Guohua, 2011).

1.2.1.2.3 Biological post-treatment

The biological post-treatment of the SW solutions previously treated by electrochemical treatment in order to enhance effluent biodegradability is suggested in the integrated process. It has to be noted that no biological post-treatment were applied in the present work and only biodegradability and toxicity assays were performed. The combination between EF or AO treatments and biological post-treatment will need to be studied in further works.

1.2.2 Novelty of the project

SW/SF processes are already applied at industrial scale. The traditional techniques used for SW solutions are separation process like filtration on activated carbon filter. However, the separation methods do not degrade the pollution, the filters need to be regenerate and another treatment is finally needed to take care about the pollution. Currently, to the best of our knowledge, no combination exists between SW/SF

processes and EF or AO treatments. Moreover, many studies from laboratory scale to pilot-scale already exist about EAOPs treatment using the improperly name "electro-Fenton". However, most of them do not apply the same technique but rather Fered-Fenton (continuous addition of H_2O_2) or electrochemical peroxidation (ECP) (sacrificial iron anode and H_2O_2 addition) or Anodic Fenton Treament (AFT) (similar to ECP with divided cells) treatments that are different (Brillas et al., 2009). The main drawbacks of these techniques is that reagents are added in high quantity and large volume of sludge is produced in ECP and AFT processes.

Concerning the combination of EF or AO with a biological post-treatment, only two recent studies evoke it at a laboratory scale (Mansour et al., 2011; Estrada et al., 2012). These studies deal with different topic than the one discussed here. They focused on pharmaceutical compounds at low initial load.

Besides, there is one technique called "bioelectro-Fenton" developed in China (Zhu and Ni, 2009; Feng et al., 2010). However, this process is different than the one suggest in this work. It consists of combining in a divided cell a kind of EF process with microbial fuel cell. The main drawback of this process is that the kinetic of degradation and mineralization are very low, i.e. several couple of hours and around hundred hours, respectively.

1.3 Structure of the thesis

The structure of the thesis is described in Fig 1.2 and is related to the following topic of this thesis:

"Integrated processes for removal of persistent organic pollutants: SW and electrochemical advanced oxidation processes combined to a possible biological post-treatment."

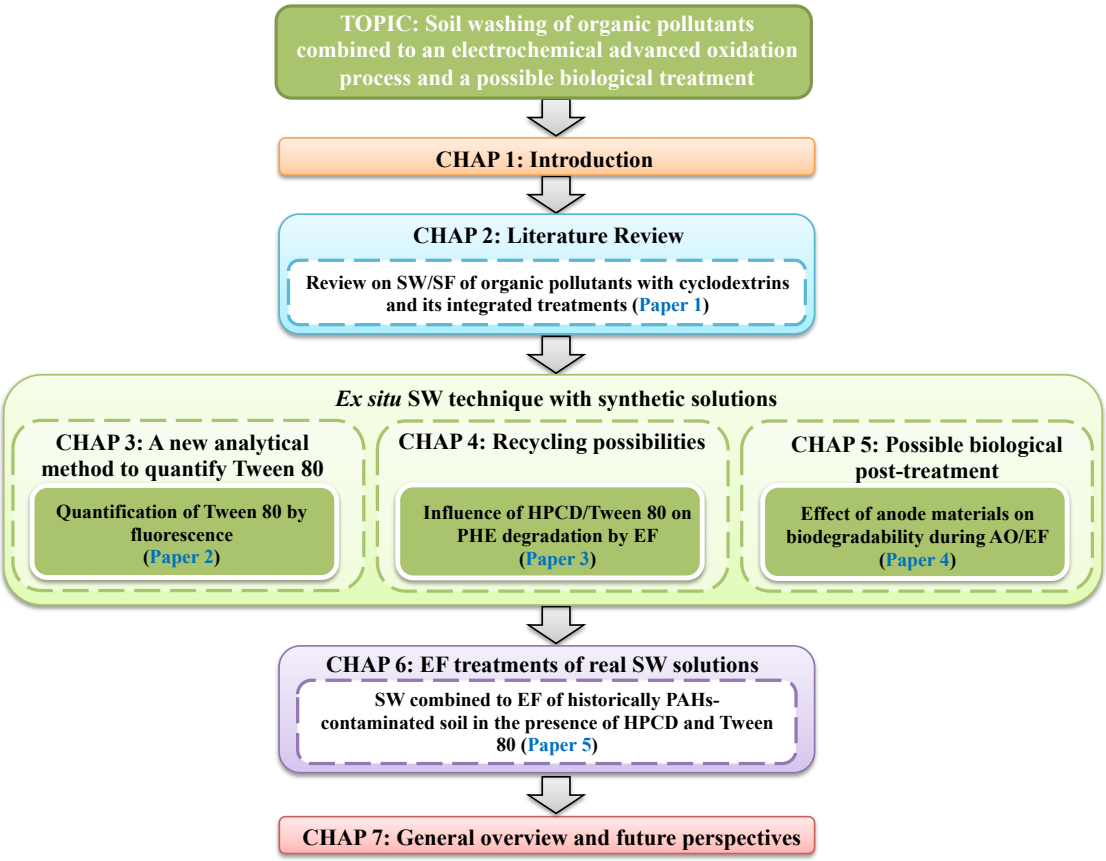


Fig. 1.2. *Structure of the thesis.*

The thesis book is composed of seven chapters:

- Chapter 1: Introduction. It evokes background information about contaminated sites and soils, about selected pollutants (properties, toxicity, legislative rules, and usual applied treatments), the treatment selected, the issues and the innovative project as a suggestion.
- Chapter 2: Literature review. In this review paper accepted in *Critical Reviews in Environmental Science and Technology* is presented the use of cyclodextrins in SW and SF processes. They are compared to other extracting agents like surfactants, co-solvent and less traditional agents (DNA,…). Integrated techniques with SW/SF using cyclodextrins are also mentioned at the end of the review. The promising use of EAOPs like EF is notably highlighted.

Then the three following chapters are related to a part of the research that has been done during the thesis with synthetic SW solution, *i.e.* with only a representative PAH pollutant and a representative surfactant or cyclodextrin.

- Chapter 3: A new analytical methods to quantify Tween 80. This work has been published in *Agronomy for Sustainable Development* journal. A new fluorescent method has been developed to quantify Tween 80 and has been applied for the other research studies.
- Chapter 4: Study of SW recycling possibilities. This study has been accepted (currently published online) in *Water Research*. The possibility to recycle HPCD and Tween 80 SW solution after an EF treatment are performed.
- Chapter 5: Influence of anode materials on toxicity and biodegradability. This research paper has been submitted to *Applied Catalysis B: Environment*. Different anode materials were tested and the biodegradability and toxicity of the SW solutions treated by EF or AO in the presence of cyclodextrin were measured.

The following chapter is related to research work in real SW solutions.

- Chapter 6: EF treatment of real SW solutions. SW of historically PAHs-contaminated soils in the presence of HPCD and Tween 80 are performed. This chapter allows comparing with results obtained in synthetic solutions. This study will be submitted in *Journal of Hazardous Materials*.

Finally, the last chapter discusses about the research that has been done during the thesis and highlights the main key points to remember from this research.

- Chapter 7: General overview and future perspectives. A general discussion is given about Chapter 3 to 6 by comparing results with synthetic and real SW solutions. A short cost-benefit study is also performed to compare the two extracting agents, HPCD and Tween 80. The future perspectives that could be expected at laboratory scale and larger scale are then mentioned.

All the papers published, accepted or submitted and related to the PhD work are listed in Appendix 1. All the conferences attended during the PhD are also listed.

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CHAPTER 2

Literature Review

This chapter has been published as:

Mousset, E., Oturan, M. A., van Hullebusch, E. D., Guibaud, G., Esposito, G. (2014). Soil washing/flushing treatments of organic pollutants enhanced by cyclodextrins and integrated treatments: state of the art. *Critical Reviews in Environmental Science and Technology* (*in press)* doi:10.1080/10643389.2012.741307.
(http://www.tandfonline.com/doi/abs/10.1080/10643389.2012.741307#.Ujp8VLy0x7g)

CHAPTER 2

A detailed literature review is needed before taken up the following research work described from chapter 3 to 6.

In this chapter is reviewed the use of cyclodextrins in soil washing (SW) and soil flushing (SF) processes compared to the use of other extracting agents (surfactants, co-solvents,…). The combination of cyclodextrins in SW/SF treatments with other processes (advanced oxidation processes, separation techniques,…) are also evoked.

Soil washing/flushing treatments of organic pollutants enhanced by cyclodextrins and integrated treatments: state of the art

Abstract

Soils contaminated by hydrophobic organic pollutants are a common concern since they are extremely difficult to remove and their potential toxicological impacts are significant. As an alternative to traditional pump-and-treat technologies, soil washing and soil flushing are conceivable and efficient approaches. Extracting agents like cyclodextrins are compared to traditional surfactants, co-solvents and less conventional agents. Ability of cyclodextrin derivatives to form a ternary pollutant-cyclodextrin-iron complex allows discussing about promising integrated treatments requiring modified Fenton treatments like electro-Fenton process with or without combination to a biological step and a recirculation loop.

Keywords: organic pollutants; soil remediation; soil washing; soil flushing; cyclodextrins; recycling; Fenton; electro-Fenton.

2.1 Introduction

The remediation of polluted soils is a part of challenges of the coming years not only in a scientific and technical aspect but also in a social (rehabilitation of former industrial sites in ecodistrict) and economic level (markets of soil rehabilitation). In particular, the soil contamination of hazardous hydrophobic organic compounds (HOCs), which are considered as neutral, non-polar or slightly polar in nature, comprise aliphatic hydrocarbons, halocarbons, formates, esters, branched alkanes, alcohols, acids and aromatic hydrocarbons. These kinds of compounds are an environmental concern because they are commonly detected in the environment and may strongly sorb onto soil in unsaturated zone or be retained in the underneath saturated zone (Chu and Chan, 2003). This feature makes them less bioavailable, while it simultaneously limits conventional remediation measures. The natural attenuation of HOCs is often very slow in soil and treatments are required to remove these polluants. HOCs removal from soils and aquifers by biological treatments such as phytoremediation are not costly but require more time (Colombano et al., 2010). Traditional pump and treat technique is also a time consuming remediation technique due to the low water solubility of HOCs water (Zhou and Zhu, 2005). In contrast, thermal treatment like incineration to remove non-volatile organic compounds (VOCs) or thermal desorption and pyrolisis for VOCs are expensive even if it is quick and efficient (Colombano et al., 2010). Thus, cost-effective remediation of these contaminants is needed in complicated matrices such as soil (Lindsey et al., 2003).

As an alternative to water-based elution techniques, the method in which HOCs can be transfered to a mobile phase that results in an increase in HOCs mobility and apparent solubility in water is considered as a promising remediation technology (West and Harwell, 1992; Boving et al., 1999). Since water solubility is the controlling removing mechanism, additives are used to enhance efficiencies. These additives can reduce the treatment time while enhancing treatment efficacy compared to the use of water alone.

An ideal extracting agent would interact very weakly with soil components, enhance the mobility of the target contaminant, and be generally non-toxic and biodegradable (Stegmann et al., 2001). Despite those considerations, co-solvents and surfactants are the most conventional extracting agents being studied since the beginning of the efforts in this area (Gomez et al., 2010). However, in more recent years, cyclodextrins (CDs)

have been proposed as an alternative agent in order to enhance the removal of organic compounds from soil (Ko et al., 1999). As a result of molecular complexation phenomena CDs were before widely used in many industrial products, technologies and analytical methods. The negligible cytotoxic effects of CDs are an important attribute in applications such as drug carrier, food and flavours, cosmetics, packing, textiles, separation processes, environment protection, fermentation and catalysis (Del Valle, 2004).

Thus, it appears that CDs are getting very interesting as an extracting agent especially when combined with specific treatments of soil washing (SW) solution. However, according to our knowledge, some recent reviews were published about general applications of cyclodextrins (Del Valle et al., 2004; Landy et al., 2012) but no detailed reviews about their applications in SW and soil flushing (SF) have been published yet. That is the reason why this review focuses on this topic. However, it is limited to the extraction of organic pollutants in order to be as exhaustive as possible though CDs are also known to have the ability to extract heavy metals from soils, which is particularly interesting in the treatment of mixed pollution (Wang and Brusseau, 1995b; Brusseau et al., 1997b; Chatain et al., 2004; Skold et al., 2008; Hoffman et al., 2010; Wang et al., 2010).

The main physicochemical properties of CDs and their solubilization are discussed in a first part and compared with traditional surfactants. In a second section is presented the extraction efficiency and impact of diverse parameters (sorption of CDs, soils characteristics, laboratory parameters) on SW and SF enhanced by CDs, comparing with other extracting agents used in the same conditions. After HOCs desorption with extracting agents through solid–liquid equilibrium, the HOCs present in the collected solution have to be degraded in a second stage by an adequate treatment, which is discussed in a third section. Among these treatments, ongoing researches and perspectives with electro-Fenton (EF) process with or without combination to a biological step, and a recirculation loop have been discussed in a fourth section.

2.2 Overall properties of CDs

In this section different general properties of CDs that are widely discussed in different papers and reviews on CDs (Saenger, 1980; Szejtli, 1982; Duchene, 1991; Connors, 1997; Szejtli, 1998; Liu and Guo, 2002; Del Valle, 2004) are summarized.

2.2.1 Structure and physicochemical properties of CDs

Cyclodextrins, also known as cycloamyloses, cyclomaltoses and Schardinger dextrins (Villiers, 1891; Eastburn and Tao, 1994), are produced as a result of intramolecular transglycosylation reaction from degradation of starch by cyclodextrin glucanotransferase (CGTase) enzyme (Szejtli, 1998). The first reference to a substance that later proved to be a cyclodextrin was published by Villiers (1891) by digesting starch with *Bacillus amylobacter*. Between 1900 and 1911, Schardinger (1903) isolated a new organism, called *Bacillus macerans*, capable of producing large amounts of crystalline dextrins (25-30%) from starch whose given names were "crystallised dextrin α" and "crystallised dextrin β". Around 1950, X-ray crystallography studies determined that CDs are molecules with a hydrophilic outside, which can dissolve in water, and an apolar cavity, which provides a hydrophobic matrix, described as a 'micro heterogeneous environment' (Szejtli, 1989). Thus, they possess a cage-like supramolecular structure, which is the same as the structures formed from cryptands, calixarenes, cyclophanes, spherands and crown ethers (Del Valle, 2004).

2.2.1.1 Native CDs

The three main native CDs used industrially consist of cyclic oligosaccharides with six (α-cyclodextrin (α-CD)), seven (β-cyclodextrin (β-CD)) or eight (γ-cyclodextrin (γ-CD)) glucopyranose units (formula $C_6H_{10}O_5$) linked by α-(1,4) bonds (Dass and Jessup, 2000). The physicochemical characteristics of these three native CDs are given in Table 2.1.

A nuclear magnetic resonance (NMR) study highlighted the chair conformation of the glucopyranose unit (Szejtli, 1982). All the polar hydroxyls (-OH) groups are located on the external shape. Primary alcohol function (located on C6) is positioned on the smallest rim of the wreath-shaped truncated cone. Secondary alcohol functions (in position C2 and C3) are located on the opposite rim, which is the largest. The apolar oxy group (-O-) formed by the bond between two glycopyranose units is directed toward the inside of the cavity. This structure allows having an internal apolar (hydrophobic) cavity, when the external shape is polar (hydrophilic). This amphiphilic behaviour allows forming water-soluble inclusion complex with HOCs (Matsunaga et al., 1984; Szejtli, 1998).

Table 2.1. Some physicochemical properties of native cyclodextrins.

Properties	α-CD	β-CD	γ-CD
Number of glucopyranose units	6	7	8
Formula	$C_{36}H_{60}O_{30}$	$C_{42}H_{70}O_{35}$	$C_{48}H_{80}O_{40}$
Anhydrous molecular weight (g mol^{-1})	972	1135	1297
Solubility in water at 25°C (g L^{-1})	145	185	232
Outer diameter (nm)	0.146	0.154	0.175
Cavity diameter (nm)	0.47-0.53	0.60-0.65	0.75-0.83
Cavity length (nm)	0.79	0.79	0.79
Cavity volume (nm^3)	0.174	0.262	0.427
pK at 25 °C	12.33	12.20	12.08
Hydration	n = 6-7	n = 10-12	n = 7-13

They are often depicted by a toroidal shape with an internal cavity whose dimensions vary according to the glucopyranose units (Fig. 2.1) (Szejtli, 1998).

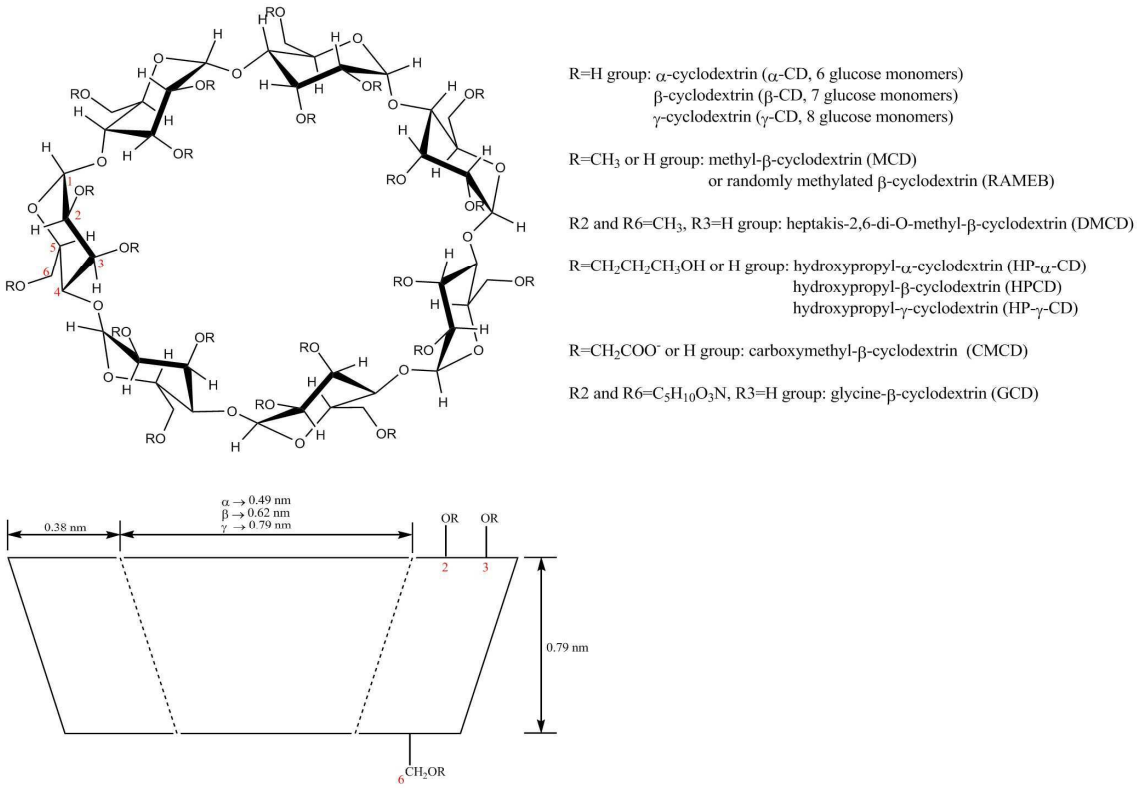

Fig. 2.1. *Structure of some native and derivative cyclodextrins used in SW/SF processes.*

The water solubility of these CDs is presented at 25 °C in the following order: β-CD (18.5 g L^{-1}) < α-CD (145 g L^{-1}) < γ-CD (232 g L^{-1}) (Szejtli, 1998). β-CD has a limited

water solubility compared to α-CD and γ-CD. This can be explained by the formation of hydrogen bonds between hydrogen atom and oxygen atom from secondary alcohol groups (C2 and C3), which gives a rather rigid structure (Paginton, 1987). These bonds cannot be completely effective with the two other CDs because of their different number of glycopyranose units. α-CD can have four hydrogen bonds instead of six in β-CD and γ-CD is a noncoplanar, more flexible structure (Szejtli, 1998).

2.2.1.2 Derivative CDs

Although β-CD is the most accessible, the least expensive and generally the most useful (Del Valle, 2004), it has also a limited water solubility that minimizes the applications (Suzuki and Sasaki, 1979), especially in SW/SF processes. Alkylation of β-CD hydroxyls leads to increase in solubility, and this phenomenon has constituted one motivation for carrying out such chemical modifications (Connors, 1997). Some widely studied and used water-soluble β-CD derivatives that can be applied in soil remediation include hydroxypropyl-β-CD (HPCD) (substitution by hydroxypropyl groups ($-C_3H_7O$)), methyl-β-CD (MCD) (substitution by methyl groups ($-CH_3$)) and carboxymethyl-β-CD (CMCD) (substitution by carboxymethyl groups ($-CH_2COOH$)). These CDs have a relatively large water solubility ranging from 100 to 1000 g L^{-1} (Eastburn and Tao, 1994; Singh et al., 2002).

2.2.1.3 Chemical stability of CDs

The stability of native and derivative CDs is generally not significantly influenced by pH and temperature at standard conditions. According to Stella and Rajewski (1997), hydrolysis of CDs can be effective at pH below 1 and at temperature superior to 80 °C, whereas alcoholate CD ion (more soluble than neutral CDs) can be formed at pH higher than 12.

2.2.2 Environmental impacts

2.2.2.1 Biodegradability of CDs

Since CDs are seminatural products, produced from a renewable natural material, starch, by a relatively simple enzymic conversion (Szejtli, 1998), Verstichel et al. (2004) proved that the three naturally occurring CDs (α-, β- and γ-CD) were completely

and readily biodegradable in a controlled composting biodegradation test at 58 °C. However, chemical modification of these basic CDs by acetylation or methylation may reduce strongly the biodegradability. Fully acetylated-α-CD, fully acetylated-β-CD, and randomly methylated-β-CD (RAMEB) with a substitution degree (SD) of 13 showed no sign of degradation during 45 days of controlled composting, but diminishing the SD makes it possible to increase the biodegradation rate of CDs which can be seen with HPCD (Verstichel et al., 2004).

The CDs involved in the study of Fenyvesi et al. (2005) were biodegraded by soil microorganisms from non-polluted site in the following order (with the half-life time in brackets): α-CD (17.5 days) ≈ β-CD (17.5 days) ≈ Ac-β-CD (17.5 days) > γ-CD (20 days) > cellulose (35 days) > peracetyl-α-CD (62 days) > peracetyl-β-CD (65 days) > HPCD (122 days) >> RAMEB (no biodegradation). For derivatives of β-CD, Oros et al. (1990, 2001) found several plant-associated bacteria (*Agrobacterium*, *Bradyrhizobium*, *Xanthomonas* and *Corynebacterium*) as well as soil fungi (*Trichoderma* species) metabolising β-CDs as sole carbon source with the following biodegradability order: unsubstituted > carboxymethyl > hydroxypropyl > polymethyl. HPCD (Fava et al., 1998) and RAMEB were found to be almost non-biodegradable (20% for HPCD (Verstichel et al., 2004) and ≈ 0% for RAMEB (Fenyvesi et al., 2005)) in standard uncontaminated soil with standard biodegradability test (ISO 17556 (2001)). However, they are biodegraded slowly from real soils historically contaminated with hydrocarbons, since the microflora of these soils was adapted to the xenobiotics compounds. Particularly the *Trichomonas* species seems to have strong degrading capacity toward the substituted CDs (Verstichel et al., 2004).

2.2.2.2 Toxicity of CDs

All toxicity studies have demonstrated that orally administered CDs are practically non-toxic, due to lack of absorption from the gastrointestinal tract (Irie and Uekama, 1997). In general, the natural CDs and their hydrophilic derivatives are only able to permeate lipophilic biological membranes, such as the eye cornea, with considerable difficulty. Even the somewhat lipophilic RAMEB does not readily permeate lipophilic membranes, although it interacts more readily with membranes than the hydrophilic cyclodextrin derivatives (Totterman et al., 1997). Furthermore, a number of safety evaluations have shown that γ-cyclodextrin, HPCD, sulphobutylether-β-CD, sulphated-

β-CD and maltosyl-β-CD appear to be safe even when administered parenterally. However, toxicological studies have also shown that the parent α- and β-cyclodextrin and the MCD are not suitable for parenteral administration (Del Valle, 2004). Besides, some studies demonstrated that CDs present no toxicologic effect or inhibition effect on soil microflora (Fava et al., 1998; Reid et al., 2000).

In order to compare with other extracting agents in the same conditions during a recent SW study, Rosas et al. (2011) have shown that HPCD can be considered as non-toxic and biodegradable compound. Moreover, Tween 80, considered as a nonionic surfactant (NIS), is toxic at concentrations higher than 20 g L^{-1}. However, the toxicity of surfactant varies considerably according to their molecular structure. Biodegradation of NIS is difficult when the hydrophobic chain of the molecule is branched, an aromatic group is present within the hydrophobic part, or ethoxylate chain length of hydrophilic portion is important (Paria et al., 2008). For instance, some NIS like Brij 30 and Triton X-100 were found to be toxic at lower concentration (Rosas et al., 2011). The ecotoxicities of Brij 30 and Triton X-100, in terms of half maximal effective concentration (EC_{50}) determined by the exposition to *Vibrio fisheri*, are 0.5 and 48 mg L^{-1}, respectively. Specifically, Brij 30 ecotoxicity is very high and is even slightly higher than the ecotoxicity value obtained for p-cresol (EC_{50} = 1.5 mg L^{-1}), meaning that this surfactant is clearly ruled out in spite of its high p-cresol extraction percentage (Rosas et al., 2011). In another study, Tween 80 is found to be less toxic to *Mycobacterium spp. KR2* than other surfactants following the rank: Tween 80 < Brij 35 < Brij 30 < linear alkane sulfonate (LAS) < tetradecyl trimethyl ammonium bromide (TDTMA) (Jin et al., 2007).

2.2.3 Ability to solubilize: inclusion complex formation

The main interest in CDs lies in their ability to form inclusion complexes with several compounds (Hedges, 1998; Baudin et al., 2000; Koukiekolo et al., 2001; Lu and Chen, 2002; Del Valle, 2004), which is discussed below.

2.2.3.1 Inclusion complex formation

Several hypotheses have been proposed as responsible, solely or in combination, for CD complex formation and stability. They were reviewed by different research teams (Atwood et al., 1984; Connors, 1997; Liu and Guo, 2002) and summarized as below:

- Relief of conformational strain,
- Exclusion of cavity-bound high-energy water,
- Hydrophobic interactions,
- Hydrogen-bonding interactions,
- van der Waals interactions,
- Charge-transfer interactions.

Many studies favour the steric factor and the host/guest model taking into account thermodynamic interactions between the different components of the system (cyclodextrin, guest, solvent). The first factor depends on the relative size of the cyclodextrin to the size of the guest molecule or certain key functional groups within the guest, since complex formation is a dimensional fit between host cavity and guest molecule (Munoz-Botella et al., 1995). Moreover, the lipophilic cavity of cyclodextrin molecules provides a microenvironment into which appropriately sized non-polar moieties can enter to form inclusion complexes (Loftsson and Brewster, 1996). Furthermore, in aqueous solution, appropriate "guest molecules" which are less polar than water can readily substitute water molecules, which are energetically unfavored (polar-apolar interaction) in CD cavity. The "driving force" of the complex formation is the substitution of the high-enthalpy water molecules by an appropriate "guest" molecule, providing a favourable net energetic driving force that pulls the guest into the cyclodextrin. Once inside the cyclodextrin cavity, the guest molecule makes conformational adjustments to take maximum advantage of the weak van der Waals forces that exist (Del Valle, 2004). However, no covalent bonds are broken or formed during formation of the inclusion complex (Schneiderman and Stalcup, 2000).

2.2.3.2 Solubilization ability of different organic compounds

The number of glucose units determines the internal diameter of the cavity and its volume, while the height of the cyclodextrin cavity (0.79 nm) is the same for all three main types (Table 2.1). Based on these dimensions, α-CD can typically complex low molecular weight molecules or compounds with aliphatic side chains, β-CD will complex aromatics and heterocycles and γ-CD can accommodate larger molecules such as macrocycles and steroids (Del Valle, 2004).

As solubilization experiments are often a preliminary step before SW/SF studies, a large number of research papers have published (Appendix 2.1) about the ability of CDs to enhanced the solubilization (compared to water alone) of many kinds of HOCs like Polycyclic Aromatic Hydrocarbons (PAHs) (Wang and Brusseau, 1993; Wang and Brusseau, 1995a; Wang et al., 1998; Shixiang et al., 1998; Ko et al., 1999; Badr et al., 2004; Veignie et al., 2009; Wang et al., 2010; Yang et al., 2010; Wu et al., 2010; Sales et al., 2011), pesticides (Wang and Brusseau, 1993; Villaverde et al., 2005a; Villaverde et al., 2005b; Zeng et al., 2006; Villaverde et al., 2007; Bian et al., 2009; Wan et al., 2009; Guo et al., 2010), nitroaromatic compounds (NACs) (Sheremata and Hawari, 2000; Cai et al., 2006; Chen et al., 2006), benzene, toluene ethylbenzene and xylene (BTEX) (Carroll and Brusseau, 2009), chlorinated solvents such as trichloroethene (TCE) and tetrachloroethene (TeCE) (Boving et al., 1999; Yang et al., 2006; Skold et al., 2008), pentachlorophenol (PCP) and 2,4,6-trichlorophenol (TCP) (Hanna, 2003; Hanna et al., 2004a), nonylphenol (Kawasaki et al., 2001), polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzo furans (PCDFs) (Cathum et al., 2007).

Native CDs have generally less potential of solubilization than the derivative ones. Among the modified CDs, CMCD displays a lower solubilization power compared to HPCD because of the former's higher polarity near the ends of the cavity due to the presence of the carboxyl groups (Brusseau et al., 1997b). Thus, the following order of solubilization efficiency can be usually obtained: RAMEB or MCD > HPCD > β-CD > α-CD > γ-CD (Hanna et al., 2004a; Villaverde et al., 2007). This reflects the effect of the size of the CD cavity (between the native CDs), and also the presence of different organic groups in the CD molecule (comparing the results of β-CD, RAMEB and HPCD) on the formation of the different inclusion complexes (Villaverde et al., 2007). Besides, the SD has to be taken into account since the solubility of HOC in the modified CDs solutions changed due to the SD of the CD as observed for example with HPCD (SD = 0.6, 0.8 and 1.0) (Kawasaki et al., 2001). The length of the chain in modified monosubstituted β-CD with an amphiphilic chain (Mod-β-CD_{12} and Mod-β-CD_{12} (2.4)) plays also a role in solubilisation ability. A longer chain induces a lower concentration of solubilized contaminant (Sales et al., 2011). This is probably due to the interaction of the hydrocarbon chain with the cavity.

Another factor that can affect the stability of the complex is the ionic strength. Several researchers have reported that the presence of ions in the aqueous phase lowers the

partitioning of ionizable molecules with the organic phase (Westall et al., 1985; Jafvert et al., 1990; Johnson and Westall, 1990). This is in accordance with the data reported by Hanna et al. (2004a) in which PCP solubilization decreases when the ionic strength increases. However, the solubilization capacity of CDs for non-ionisable organic compounds, such as PAHs, biphenyl, 1,2,3-trichlorobenzene (TCB), etc., is not affected by high concentrations of salts in the aqueous phase, because cations do not interact significantly with the low-polarity cavity of CDs (Wang and Brusseau, 1995b; Ko et al., 1999; Badr et al., 2004).

The pH effect on the stability constant (see Eq. (2.2)) is directly linked to the ability of the organic compound to be ionized and its acidity constant value. In case of organic ionisable compounds (PCP, TCP, phenol, etc.), neutral species form a more stable complex with CDs than the ionic form, which is more hydrophilic (Buvari and Barcza, 1988; Hanna, 2003; Hanna et al., 2004a).

Furthermore, CDs, as do surfactants and cosolvents, generally cause a greater relative solubility enhancement for more-hydrophobic compounds (Wang and Brusseau, 1993; Brusseau et al., 1994; Augustijn et al., 1994; Shiau et al., 1994; Bizzigotti et al., 1997; McCray and Brusseau, 1998; Badr et al., 2004). However, the actual apparent solubilities can be larger for less-hydrophobic compounds because of their higher aqueous (non-enhanced) solubilities.

By comparing solubility enhancement of HOCs with different surfactants, CDs have usually less solubilisation ability than traditional surfactants. This ability is usually ten times lower depending on the CDs and surfactants structures. For instance molar solubilisation ratio (MSR) of naphthalene in the presence of Mod-β-CD_{12} or Tween 80 are 0.089 and 0.184 respectively (Sales et al., 2011). A table giving molar solubilisation ratio (MSR) of organic pollutants in the presence of surfactants is available in the review of Paria et al. (2008).

2.2.3.3 Equilibrium equation

Most frequently the host/guest ratio is 1:1, which is the simplest and most frequent case for different applications (Szejtli, 1998). By considering this 1:1 ratio, a thermodynamic equilibrium is established between dissociated and associated species, which is expressed as follows (Blyshak et al., 1989; Singer et al., 1991):

$$CD + S \leftrightarrow CD\text{-}S \tag{2.1}$$

$$K_S = \frac{[CD-S]}{[CD][S]} \tag{2.2}$$

where K_s is the complex stability (or equilibrium) constant also known as K_{CW} (Wang and Brusseau, 1993; Kawasaki et al., 2001) or K_{CD} (Hanna, 2003), i.e. the partition coefficient of S between the CD and water, [CD] is the concentration of cyclodextrin, S is the substrate (guest molecule) and [S] its concentration, CD-S is the CD/guest complex formed and [CD-S] its concentration.

However 2:1, 1:2, 2:2, or even more complicated associations and higher order equilibria can exist, almost always simultaneously (Connors, 1995; Connors, 1997; Szejtli, 1998). Thus, the stability constant (K_s) is better expressed as $K_{m/n}$ to indicate the stoichiometric ratio of the complex, which can be written as follow (Higuchi and Connors, 1965a; Hirayama and Uekama, 1987):

$$mL + nS \leftrightarrow (L_mS_n) \tag{2.3}$$

(a-mx)(b-nx) *(x)*

$$K_{m/n} = \frac{[x]}{[a-mx]^m[b-nx]^n} \tag{2.4}$$

where L is the ligand considered to be the CD and S the substrate which is the guest.

Besides, several studies demonstrated that the apparent solubility of HOCs in aqueous CD solutions increases linearly with the concentration of CD (Pitha and Pitha, 1985; Singer et al., 1991; Wang and Brusseau, 1993; Brusseau et al., 1994; Bizzigotti et al., 1997; McCray and Brusseau, 1999). This result confirms the use of the simple model with 1:1 ratio, which gives a linear relationship (obtained from Eqs. (2.1) and (2.2)) between total aqueous-phase concentration (S_t) of the guest molecule and cyclodextrin concentration (Wang and Brusseau, 1993):

$$S_t = S_0\left(1 + \frac{K_S}{(1+K_S S_0)}[CD]_0\right) \tag{2.5}$$

with

$$[CD\text{-}S] = S_t - S_0 \tag{2.6}$$

$$[CD] = [CD]_0 - (S_t - S_0) \quad (2.7)$$

and

$$E = S_r = \frac{S_t}{S_0} \quad (2.8)$$

where S_0 and $[CD]_0$ are the initial concentrations of S and CD respectively, S_r is the relative aqueous-phase concentration, which is equivalent to the enhancement factor E.

When S_t is plotted against $[CD]_0$, K_s can be determined from the following equation (Higuchi and Connors, 1965b):

$$K_S = \frac{\left(\frac{1}{S_0}\right)(S_t - S_0)}{\left([CD]_0 - (S_t - S_0)\right)} = \frac{slope}{S_0(1 - slope)} \quad (2.9)$$

with

$$slope = \frac{(S_t - S_0)}{[CD]_0} \quad (2.10)$$

When low-solubility organic compounds are used (*i.e.* $K_s*S_0 << 1$), some authors suggested simplifying Eq. (2.5); and then the following equation can be used (Wang and Brusseau, 1993):

$$S_t = S_0\left(1 + K_S[CD]_0\right) \quad (2.11)$$

Then if E or S_t is plotted against $[CD]_0$, K_s can be obtained from the slope in the first case, and from the slope/S_0 in the second case.

Sometimes more complicated ratio can be taken into account as suggested in study of Kawasaki et al. (2001) in which 1:2 to 1:4 ratios were considered between different CDs and 4-nonylphenol (4-NP).

2.3 Soil remediation with CDs and other extracting agents

Borrowed from minerals processing industry (Esposito et al., 2002), SW (*ex situ on site* or *off site* treatment) and SF (*in situ* treatment) technologies with suitable extractants have shown as a potential alternative to some of the conventional techniques for the remediation of contaminated soils (USEPA, 1990). Principally, adding suitable extractants/chemical agents to the contaminated soil can enhance the apparent

solubilization/extraction/dissolution of the contaminants. The two steps involved in the extraction of a compound from the solid matrix are desorption from the binding site in (or on) the solid matrix followed by elution from the solid phase into the extraction fluid (Kubatova et al., 2002). Under controlled conditions, this may result in efficient and cost-effective contaminant removal (Maturi and Reddy, 2008). Several classes of extractants that are being studied for SW/SF include surfactants, co-solvents, cyclodextrins, chelating agents, dissolved organic matter (DOM), deoxyribonucleic acid (DNA), fatty acid methyl esters (FAME), vegetable oil (USEPA, 1990; Wood et al., 1990; Abumaizar and Smith, 1999; Tanada et al., 1999; Boving and Brusseau, 2000; Chu and Chan, 2003; Gao et al., 2003). Besides, soil composition as well as types of contaminants can limit the effectiveness of SW/SF-based remediation (Maturi and Reddy, 2008). There are also different limitations of SW compared to SF techniques which are exposed in this section.

2.3.1 SW process

Ex situ SW, which is operated in batch system at a certain solid/liquid ratio, is commonly used for treating contaminated soils by separating the most contaminated fraction of the soil for disposal. This *on site* or *off site* process allows not only to treat all the contaminated soil in a wide quantity without taking care of soil heterogeneity but also to treat mixed contamination, i.e. HOCs and heavy metals in the same time (Colombano et al., 2010). Moreover, SW requires less time of contact compare to SF processes.

Appendix 2.2 lists and summarizes the different CDs SW studies found in literature, including the soils' characteristics, the lab parameters and the HOCs removal efficiency by using CDs and other extracting agents in some cases.

2.3.1.1 Removal efficiency of organic pollutants

2.3.1.1.1 Different pollutants treated in soils by CDs

CDs have ability to extract widely studied organic pollutants like PAHs. β-CD enhancement of PAH extraction was compared to HPCD (Badr et al., 2004; Khodadoust et al., 2005; Maturi and Reddy, 2008) and MCD (Petitgirard et al., 2009). In all the cases, HPCD and MCD appeared to be greatly more efficient than β-CD to extract

PAHs from soil. It may be due to the higher stability of the 1:1 inclusion complexes of HPCD and MCD compared to β-CD (Khodadoust et al., 2005; Maturi and Reddy, 2008). Another reason is the larger solubility of HPCD and MCD compared to that of β-CD (Petitgirard et al., 2009). According to Navarro et al. (2007), γ-CD is also less efficient than MCD at the same concentration. For instance, MCD (1%) is able to extract 13% of phenanthrene (PHE) whereas γ-CD (1%) can only remove 2%. The removals of PAHs by both HPCD and MCD were similar and they were effective to enhance PHE extraction (70% with 4% of CDs) (Gomez et al., 2010). Glycine-β-cyclodextrin (GCD) was also efficient to remove PAHs from contaminated soil, since 79% of PHE was removed at 40 g L^{-1} using 4% GCD (Wang et al., 2010). Interestingly, there was also a significant inverse relationship between the CDs extractable fraction for each of the PAHs and their respective Log K_{ow} values, *i.e.* CD extraction efficiency decreased with increasing PAH ring number (Badr et al., 2004; Navarro et al., 2007; Hua et al., 2007; Papadopoulos et al., 2007; Petitgirard et al., 2009; Gao et al., 2009; Latawiec and Reid, 2009; Gong et al., 2010; Wu et al., 2010). This observation can be explained by the fact that low-ring PAHs are more soluble in water than high-ring PAHs and they are better protected against the high polarity of water in β-CD than pyrene (Petitgirard et al., 2009).

Some well-known pesticides were also studied. For instance, with β-CD extraction of norflurazon (NFL), 100% desorption was obtained in all cases except in one soil, for which herbicide desorption was not higher than 62% (with 20 mg L^{-1} NFL initial concentration) (Villaverde et al., 2005a). Some results show that α- and ϒ-cyclodextrin (0.01 M) greatly increased (100% extracted) the removal of NFL previously adsorbed on a loamy sand soil (Villaverde et al., 2005b), proving the potential use of these three native CDs for remediation of pesticide-contaminated soils. About mefenacet (MF: 2-(2-benzothiazolyloxy)-N-methyl-N-phenylacetamide), it was observed that the presence of proper concentration of β-CD (4.25 mM) can greatly enhance the transfer of herbicide from soil phase to aqueous phase, with extraction efficiency between 90 and 100% (Guo et al., 2010). To extract lindane from real soil and model soil, γ-CD had better performance in both cases (6.5 - 7 fold increase); this is probably because it has the biggest cavity volume comparing it to α-CDs, and β-CDs, which had similar behaviors removing lindane from contaminated soils (3.5 - 4 fold increase), compared to water CDs free performance (Bartolo et al., 2008). PCP, usually used as a biocide,

can be efficiently extracted by cyclodextrin from soil (Hanna et al., 2004b; Hanna et al., 2005). When the CD concentration was 5 mmol L^{-1}, an extraction of about 70% of PCP adsorbed on soil was observed, whereas only 37% was removed when water was used as the washing solution (Hanna et al., 2004b). In a tetrachlorophenol (TeCP) study, when CMCD concentration was optimum (40 mM), an extraction of about 80% of TeCP previously adsorbed on soil was observed, whereas it is only 33% when water is used alone as the washing solution (Chatain et al., 2004). Hexachlorobenzene (HCB) extraction efficiency appears to be low (8.5% and 2%) with β-CD (1%) in spiked soil with no organic matter (OM) (Yuan et al., 2006) and with MCD (100 g L^{-1}) (10%) in kaolin soil (Wan et al., 2009), respectively. A better efficiency (18%) is notified in HCB really contaminated soil with high OM (7.1%) (Wan et al., 2009).

NACs such as hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) and 2,4,6-trinitrotoluene (TNT) and its metabolites like 4-amino-2,6-dinitrotoluene (4-ADNT), 2-amino-4,6-dinitrotoluene (2-ADNT), 2,4-diamino-4-nitrotoluene (2,4-DANT), and 2,6-diamino-4-nitrotoluene (2,6-DANT) are also extracted with CDs. The heptakis-2,6-di-o-methyl-β-cyclodextrin (DMCD) performed consistently better results than the HPCD for desorption of all NACs tested (TNT, 4-ADNT, 2,4-DANT) from illite and topsoil (Sheremata and Hawari, 2000). This may be explained by the high surface activity of DMCD as compared to the case of the HPCD that has negligible surface activity (Frömming and Szejtli, 1994). However, HPCD (5%) was widely effective (81%) in removing 2,4-dinitrotoluene (2,4-DNT) from kaolin soil (Khodadoust et al., 2006). Furthermore, the extraction efficiency of RDX from a spiked soil reaches 87% with 10% HPCD, which proves that HPCD is effective enough as an RDX extracting agent (Hawari et al., 1996). Moreover, TNT recovery from TNT spiked soil was improved by a 2.1-fold factor when using a 5 mM MCD flushing solution as compared to a distilled water flushing solution. These results reveal that MCD is an efficient washing agent for TNT removal from soil (Yardin and Chiron, 2006).

After one washing step at 10% of CD concentration, an increased quantity of Polychlorinated biphenyls (PCBs) was mobilized with the RAMEB formulation (42%) relative to the HPCD formulation (24%) for identical conditions of equilibration (Ehsan et al., 2007). RAMEB is more efficient than HPCD in these conditions.

Considering PCDDs and PCDFs, their removal efficiencies reached their maximum values of 45%, 50%, 73%, 96% and 80% using α-CD, β-CD, hydroxypropyl-α-

cyclodextrin (HP-α-CD), HPCD and hydroxypropyl-γ-cyclodextrin (HP-γ-CD), respectively, after 28 days of batch experiment (Cathum et al., 2007). HPCD performed very well in extracting PCDDs/PCDFs from the spiked contaminated soil relative to other CDs.

42% of p-Cresol was extracted from a spiked soil with 1% HPCD (10 g L^{-1}) that is widely better than water alone (almost 0%) as washing agent (Rosas et al., 2011).

Finally, all the CDs have shown better results as a washing agent to extract HOCs from soil, compared to water alone. However derivatives of CDs appear to have better extracting enhancement than the native ones. Among the modified CDs, HPCD and MCD have good and close performances and the choice between them should be greatly determined by their respective costs (Gomez et al., 2010). That is why HPCD is the most studied in CDs SW papers.

2.3.1.1.2 Comparison between CDs and other extracting agents

- *Comparison between CDs and surfactants*

Surface active agents or « surfactants » are amphiphilic molecules having both a hydrophobic (apolar group) tail and a hydrophilic (polar group) head (Rosen, 2004). When dissolved in water at low concentrations, surfactant molecules exist as monomers. As the concentration of surfactant increases, there is a critical concentration beyond which surfactant monomers start aggregating to form self-assemblies called micelles. The concentration at which this occurs is known as the "Critical Micelle Concentration" (CMC). CMC is a function of surfactant structure, composition, temperature, ionic strength, and the presence and types of organic additives in the solution (Rosen, 2004; Edwards and Liu, 1994). There are two general mechanisms by which surfactant enhances desorption of HOCs in a soil/aqueous system, i.e. mobilization which occurs below the CMC (sub-CMC) through a soil rollup mechanism, and solubilization, by lowering the surface and interface tension, which occurs above the CMC (supra-CMC) (Deshpande et al., 1999). Whereas relatively little HOC solubility enhancement typically occurs in sub-CMC surfactant solutions, comparatively larger amounts of HOC can be solubilized within micelles at bulk solution surfactant concentrations greater than the CMC (Edwards and Liu, 1994). Another parameter that describes the surfactants properties is the hydrophile-lipophile

balance (HLB), which is determined by the hydrophilic part/hydrophobic part ratio. The HLB value increases with the hydrophilic behavior (Tiehm, 1994).

Depending on the nature of the hydrophilic group, surfactants can be classified as anionic, cationic, zwitterionic, and non-ionic (NIS) (Rosen, 2004). Anionic and nonionic surfactants are mostly used for SW or SF (Mulligan et al., 2001). Between the NIS, which are better solubilizing agents than ionic ones because of their lower CMC value (Paria, 2008) and their better cost-effectiveness (Alcantara et al., 2008; Wang and Keller, 2008), Tween 80, Triton X-100 and Brij 35 are widely studied.

Maximum PHE removals were 33.6% with Igepal CA-720 (I-CA-720) and 52% with Tween 80 for the spiked kaolin soil (Maturi and Reddy, 2008). In comparison to two contaminated manufactured gas plant (MGP) site soils (soils A and D), the maximum removal were 100% and 100% for Soil A, and 72.6% and 48.3% for Soil D in the presence of surfactants I-CA-720 and Tween 80, respectively (Maturi and Reddy, 2008). Tween 80 performed better than I-CA-720 in kaolin and Soil A, while I-CA-720 performed better than Tween 80 in Soil D. These variations in the removal of PHE from the three soils may be attributed mainly to their differences in their clay and organic contents (Maturi and Reddy, 2008). To compare with HPCD (10% concentration) that was much better than β-CD, the maximum removal of PHE were 44%, 96%, and 23% from kaolin and the two naturally contaminated soils (Soil A and D respectively) (Maturi and Reddy, 2008). Thus, HPCD gives lower results than Tween 80 to remove PHE from the three soils and better results in kaolin soil compared to Igepal. This is in accordance with previous results showing that non-ionic surfactants (I-CA-720 and Tween 80) are effective in removing PHE (75% and 53% respectively) on the contrary to CDs (HPCD and β-CD) that were less effective to remove this contaminant (22.5% and 1% respectively) (Khodadoust et al., 2005). Gong et al. (2010) also concluded that HPCD (10%) gives lower results than Tween 80 (10%) and Triton X-100 (10%) to enhance washing of PAHs contaminated soil. Wu et al. (2010) showed 20% to 40% of difference of efficiency between Tween 80 and HPCD at 10% concentration in all the soils (spiked soil and real contaminated soil). Moreover, each of nine aqueous test surfactants (Tween 20, Tween 40, Tween 80, Tween 85, Brij 98, Triton 405, Triton X-301, Triton XQS 20, sodium dodecyl sulfate (SDS)) (concentration of 3%) proved to be superior to extract PAHs compared to a wash with RAMEB (concentration of 10%) under similar conditions (Yuan and Marshall, 2007).

The solubilizers used by Rosas et al. (2011) showed that extraction percentages of p-cresol varied between 42%, 45%, 55% and 58% for HPCD, Triton X-100, Brij 30 and Tween 80, respectively. Tween 80 (1%) showed promising results in removing HCB from soil compared with β-CD (1%) (Yuan et al., 2006).

However, HPCD (60 mM) is more effective than Brij 700 (5.25 mM) for PAHs extraction (Latawiec and Reid, 2009). Moreover, the anionic surfactant SDS was less effective (21.7%) than MCD (28.3%) and HPCD (45.4%) to extract RDX from a spiked soil, at the same initial concentration of washing agent (1%) (Hawari et al., 1996). Furthermore, β-CD could be a more effective washing agent for desorption of MF compared with Tween 80 at the same initial concentration, since the adsorbed β-CD had a weaker affinity for MF than the adsorbed Tween 80 (Guo et al., 2010).

The removal efficacies of HOCs are eventually less effective with CDs compared with surfactant in most of the cases studied in CDs SW papers.

- *Comparison between CDs and co-solvents*

Since the water solubility of many organic contaminants is the controlling removal mechanism, the additives are being used to increase the solubility of the organic contaminant in the washing liquid. For this reason, the use of solvents has also been investigated, often using low molecular alcohols (methanol (MeOH), ethanol (EtOH) and butanol (BuOH)) or other water miscible or partially water miscible organic compounds like n-butylamine (n-But) and tetrahydrofuran (THF). These kinds of solvents, when dissolved in water, reduce the polarity of the aqueous phase and increase the solubility of HOCs (Boving and Brusseau, 2000). The increase in rate of mass transfer to the aqueous phase leads to the redistribution of contaminants in sites exhibiting slow desorption rates as well as those exhibiting fast rates (Bonten et al., 1999). They also can reduce interfacial tension between the water and the contaminant, which may result in direct mobilization of HOCs (Pazos et al., 2010). Besides, it may cause the organic carbon associated with the soil to swell, thereby increasing HOCs availability (Fu and Luthy, 1986).

THF was found to be ineffective for the removal of PHE from all three soils (Two MGP soils and one spiked kaolin soil) (Maturi and Reddy, 2008). Khodadoust et al. (2005) confirm that ineffectiveness with 3% of PHE removal (with 20% THF). To compare,

HPCD (10%) is much more efficient whereas β-CD (1%) gives same results as THF in both cases.

n-But resulted in increased removal of PHE with an increase of its concentration (Khodadoust et al., 2005; Maturi and Reddy, 2008). The maximum removal of PHE was 46%, 100%, and 18% for kaolin and two MGP Soils, respectively, using 20% n-But (Maturi and Reddy, 2008). One of MGP Soil is a sandy soil with less clay content, which allowed better desorption of PHE as compared to the kaolin and the other MGP Soil. Khodadoust et al. (2005) obtained a removal efficiency of 4% with 5% n-But, increasing to 30% with 20% n-But (Khodadoust et al., 2005). HPCD (10%) gives similar results whereas β-CD (1%) is completely ineffective in both cases.

Among the alcohols, MeOH (100%) is a relatively largely better extracting agent than HPCD (10%) (Gong et al., 2010), knowing that the study is carried out at equivalent soil/active ingredient ratio. Buthanol (BuOH) (100%, equivalent to 10.8 M) showed better results by removing PAHs in really contaminated soil and less efficient extraction with spiked soil compared to HPCD (60 mM) (Latawiec and Reid, 2009), though the range of concentration are not the same. BuOH extraction method is additionally the most rapid technique (Latawiec and Reid, 2009). Khan et al. (2011) as well as Swindell and Reid (2006) suggested that HPCD and BuOH extraction techniques had different extraction efficiencies. The difference in the extraction efficiencies of HPCD and mild organic solvents might be due to the fact that CDs can form inclusion complexes between the cyclodextrin macromolecule and organic moiety that can subsequently enhance the water solubility of low-polarity organic compounds (Blyshak et al., 1988).

- *Comparison between CDs and chelating agents*

Due to their strong complexing ability with multivalent cation, chelating agents have been used to enhance the efficiency of SW. EDTA (ethylene diamine tetraacetic acid) is a popular chelating agent that has been widely studied for removing heavy metals from soils because of its high chelating ability (Lo and Yang, 1999; Lee and Kao, 2004; Zhang and Lo, 2006). The efficacy of chelant-aided extraction depends upon the soil pH and soil type (Ghestem and Bermond, 1998). Though they are widely used to extract heavy metals, few studies compared their efficiency to solubilize HOCs with other extracting agents (Khodadoust et al., 2005; Maturi and Reddy, 2008).

The contaminant removal efficiencies with two chelants, EDTA and DTPA (diethylene triamine pentaacetic acid), in three soils, kaolin soil and two MGP soils, show poor affinity of chelants for the removal of phenantherene from the tested soils (Maturi and Reddy, 2008). As expected, in the study of Khodadoust et al. (2005), both chelating agents were ineffective in the removal of PHE with removal efficiency less than 4% at all the concentrations. None of the chelating agents were able to solubilize or desorb PHE from the soil, as they are ligands and could not form any stable complexes with PAHs (Khodadoust et al., 2005). HPCD (10%) is much more efficient (Khodadoust et al., 2005; Maturi and Reddy, 2008) and β-CD (1%) efficiency is better according to Maturi and Reddy (2008) than the study of Khodadoust et al. (2005) study that gives same results as for chelants EDTA and DTPA.

- *Comparison between CDs and Fatty acid methyl esters (FAME)*

FAME are the major constituents of biodiesel and are produced based on the use of renewable agricultural materials as feedstock (Marchetti et al., 2007; Yagiz et al., 2007). Commercial and synthetized biodiesels are made by transesterification of vegetable oil (like soybean oil) with MeOH (Wu et al., 2010). The methyl esters of biodiesel have less molecular weight and are less viscous than their parent vegetable oil compounds (Shumaker et al., 2007). As an oleophilic agent, biodiesel has the potential to solubilize HOCs from contaminated soils (von Wedel, 2000).

Synthesized FAME (S-FAME) (100%), marketed-biodiesel (M-biodiesel) (100%) and biodiesel (100%) present higher PAHs removals than HPCD (10%), especially for pyrene and benzo(a)pyrene, demonstrating that HPCD was less efficient to remove high concentrations of high molar weight PAHs with more than four rings from the spiked and really contaminated soils, at equivalent soil/active ingredient ratio (Gong et al., 2010; Wu et al., 2010).

- *Comparison between CDs and vegetable oil*

Vegetable oils have long been used as carriers for hydrophobic herbicides, before being used in SW studies (Bogan et al., 2003). Vegetable oils are hydrophobic compounds composed by complex mixtures of numerous organic compounds, which are largely composed of triglycerides (93-99%), with smaller amounts of phospholipids, free fatty acids, unsaponifiables and tocopherols (Przybylski, 2005). The phospholipids, fatty

acids and neutral lipids present in vegetable oil contribute to the surfactant effect (Desai and Banat, 1997), which promotes the mobility and displacement of the contaminants and subsequent desorption from the soil matrix (Pizzul et al., 2007).

A SW study highlights that soybean oil (100%) gives better extraction than HPCD (10%) in spiked soils and really contaminated soil, at equivalent soil/active ingredient ratio (Gong et al., 2010).

- *Comparison between CDs and deoxyribonucleic acid (DNA)*

Recently, utilization of DNA in the field of environmental cleanup has been studied, since the toxicity of such HOCs is often associated with their high affinity for DNA, which can induce mutations in living systems (Lesko et al., 1968; Wolfe et al., 1987). Binding is generally attributed to the intercalation of planar HOCs like PAHs in the hydrophobic spaces between adjacent base pairs of the DNA molecule (Boyland and Green, 1964; Wolfe et al., 1987). An extension of the application of DNA in the field of soil remediation was also evaluated. At 1% DNA concentration, PAHs like PHE, anthracene, and pyrene extractions are higher than those with MCD (1%) and β-CD (1%) (Navarro et al., 2007).

2.3.1.1.3 Synergistic effects

Wan et al. (2009) demonstrated that HCB recovery from really contaminated soil was greatly enhanced when using MCD combined with 30% EtOH. For instance, up to 45% of HCB was recovered by this system at 100 g L^{-1} (10%) MCD, relative to that of 18% with MCD alone at the same concentration. MCD combined with 30% EtOH increased monotonically from 10% to 45% as MCD concentration increased. The maximal absolute synergy was achieved at the MCD concentration of 80 g L^{-1} (8%), followed by a slight decrease at 100 g L^{-1} (10%). Besides, much more significant increase as well as synergistic increase in HCB recovery from kaolin was achieved compared with natural soil. Up to 72% of HCB was recovered from kaolin, relative to 44% of that from really contaminated soil by the same solution system. As it has been demonstrated, the sorption-desorption behavior of HOCs on soils is governed by soil organic matter (SOM) (Grathwohl, 1990; Huang and Weber Jr, 1997; Luthy et al., 1997; Xia and Ball, 1999). Therefore, soil characteristics, especially the organic content, greatly affect the synergistic effect of MCD/EtOH system on contaminants removal. Higher synergistic

effect can be achieved for soils with lower organic contents, i.e. kaolin soil (Wan et al., 2009).

2.3.1.2 Parameters impacting the removal efficiencies

Different parameters impacting the removal efficiencies are listed in this section. The recovery efficiency depends on the distribution of HOCs between soil, aqueous phase, sorbed extracting agent and cavity of CDs or micellar surfactant phases, which are influenced by operating parameters at laboratory scale. Moreover, the differences between apparent solubilisation obtained in batch experimental conditions (section 2.3.2.) and the removal efficiencies reached after SW can be explained by the following parameters.

2.3.1.2.1 Sorption of CDs into soil

During the desorption process of organic pollutants, the possible sorption of CDs onto soils is an important parameter which could affect the removal efficiency of pollutants from contaminated soils.

Appendix 2.3 depicts the different CDs sorption experiments found in literature, as a function of soils' characteristics, lab parameters, models used and percentages of sorption compared to other mentioned extracting agents.

- *Comparison between the CDs*

β-CD sorption on soil has been shown by Perez-Martinez et al. (1999) and demonstrated by the group of Villaverde (Villaverde et al., 2006; Villaverde, 2007). According to their studies, β-CD sorption is not negligible in almost all the case whatever the soil characteristics and the β-CD concentration (Villaverde, 2007). Other studies confirm this β-CD sorption (Morillo et al., 2001; Badr et al., 2004; Guo et al., 2010; Wang et al., 2010). According to Villaverde et al. (2006), the influence of β-CD on NFL mobility and availability depends on the concentration and the irreversible sorption of β-CD in soils. The sorption of β-CD is dependant on the soil clay content and SOM content (Badr et al., 2004; Guo et al., 2010). If the concentration of β-CD is less than 0.1 mM, most of the β-CD molecules would be adsorbed due to the irreversible sorption behaviour onto soil particles, leading to the formation of a coating, which acts as a

bridge between NFL and the soil surface. This mechanism is retarding the mobility of the herbicide (Villaverde et al., 2006).

Several studies show that HPCD sorption into soil is negligible (Ko et al., 1999; Zeng et al., 2006) or almost negligible (Tick et al., 2003; Badr et al., 2004). Other works have shown that HPCD (that has negligible surface activity) was not significantly sorbed by kaolinite, illite or topsoil, though sorption of CDs is clay content dependant (Ko et al., 1999; Sheremata and Hawari, 2000). Badr et al. (2004) affirm that the SOM favors the HPCD sorption as well as the retention of organic compounds. Besides, the very low values of the fractions of HPCD sorbed on sand ruled out the affinity of the HPCD towards sand (De Lisi et al., 2007).

A low Carboxymethyl-β-cyclodextrin (CMCD) sorption (4%) to soil was observed though a relatively high OM content (6.5%) (Chatain et al., 2004).

Adsorption isotherms have shown that the methyl-β-cyclodextrin (MCD) fraction sorbed is still less than 2%, which is negligible according to the estimated error on concentration measurements (Petitgirard et al., 2009).

GCD, which is synthesized by the reaction of beta-cyclodextrin with glycine in the presence of KOH and epichlorohydrin, was suggested to be applied for the simultaneous removal of organic pollutants and heavy metals from co-contaminated soils (Wang et al., 2010). In the same study, the sorption of GCD onto soils appears to be low (below 3.5%) when the percentage of OM content is around 3.1%.

DMCD was selected by Sheremata and Hawari (2000) for its high surface activity. This CD was sorbed by topsoil (high OM content and low clay content) at 2.2% of total CD mass and sorbed by illite (negligible OM content and very high clay content) at 9.9% of total CD mass. DMCD seems to be fewer dependents on the OM content of the soil.

To compare, the sorption efficiencies of GCD onto soil are lower than those of β-CD onto soil, because the water-solubility of GCD is higher than β-CD (Wang et al., 2010), which may favor the interactions with SOM. The comparable results observed with HPCD compared to β-CD (Badr et al., 2004) could also be explained with the same reason, as the water-solubility of HPCD is widely higher than β-CD. HPCD was not sorbed by either illite or topsoil unlike DMCD (Sheremata and Hawari, 2000).

- *Comparison between CDs and surfactants*

Among the widely studied surfactants like Tween 80, Triton X-100 and Brij 35, several studies have shown that the sorption onto soil of Tween 80 increases with the increase of initial Tween 80 concentration until the saturation sorption capacity was reached (Zeng et al., 2006; Guo et al., 2009; Guo et al., 2010). The influence of the soil properties on the sorption capacity of NIS like Tween 80 followed the order: clay content > OC content > cationic exchange capacity (CEC) content (Manuel and Cano, 1996; Mata-Sandoval et al., 2002; Guo et al., 2010). This suggests that SOM is not always the dominant phase and the sorption of NIS may be governed by the sorption of molecules occurring at the soil-water interface. The clay surface, the polyethoxylate chain of the surfactant and the polar groups of SOM are together responsible for its sorption (Mata-Sandoval et al., 2002). For Tween 80 and Brij 35, 99% of surfactant molecules are sorbed onto the soil particles at lower concentrations (Zeng et al., 2006). Some studies (Sun et al., 1995; Ko et al., 1998; Lee et al., 2000; Zeng et al., 2006) found NIS sorption occurring above the Critical Micelle Concentration (CMC) value, which is in contrast with other papers (Liu et al., 1992; Brownawell et al., 1997) that found the sorption of NIS reaching a plateau close to their CMC values. However, Lee et al. (2000) demonstrated that NIS uptake on soils with high OM reached a plateau at concentrations around two times the nominal CMC in pure water. This observed disparity is attributed to the fact that the NIS tested is not molecularly homogeneous, and its micelle formation takes place over a range of surfactant mass fractions across the nominal CMC (Zeng et al., 2006). Many other papers and reviews describe and confirm the ability of the surfactants to adsorb onto soil (Tsomides et al., 1995; Joshi and Lee, 1996; Haigh, 1996; Boving and Brusseau, 2000; Paria, 2008), requiring higher concentration of surfactants. However, most of the mineral surfaces are negatively charged in neutral pH aqueous solution, and consequently, anionic surfactants and NIS are expected to be less sorbed than cationic surfactants (Deshpande et al., 1999). Discussion of equilibrium partitioning theory in the case of surfactant was reviewed by Laha et al. (2009).

Some studies compared the surfactants and CDs sorption into soil in the same conditions. Thus, β-CD showed a larger sorption loss than Tween 80 in a comparable molar concentration range (Guo et al., 2010). After reaching soil maximal sorption capacity, described by the Langmuir isotherm, Tween 80 present in the aqueous

solutions as micelles could not be adsorbed by the soil particles any more. In contrast to β-CD whose adsorption model is linear. In addition, by fitting with a Langmuir model, the maximum of HPCD sorption into soil (q_{max} = 0.021 mg g^{-1}) is much lower than the Tween 80 (q_{max} = 14.2 mg g^{-1}) and Brij 35 sorption (q_{max} = 5.13 mg g^{-1}) (Zeng et al., 2006). Rosas et al. (2011) also observed that HPCD hardly sorbed to soil compared to the three NIS Tween 80, Brij 30 and Triton X-100. In Brusseau et al. (1994) study, Triton X-100 was significantly sorbed by soil, whereas HPCD was not.

The sorption of CD by soils is finally much less than that of many surfactants (Edwards et al., 1991; Zeng et al., 2006), except for β-CD. As the soil sorption of organic contaminants is usually predominated by interactions with the fraction of organic carbon in soil (f_{OC}) (g of organic carbon per g of soil) (Huang and Weber Jr, 1997; Weber Jr et al., 1998; Xing, 2001), sorbed CD molecules would increase the effective fraction organic carbon content of the soil (f_{OC}^{*}), and could also increase contaminant sorption (Badr et al., 2004). This may also significantly increase the amount of extracting agent required to remediate a contaminated site (Ko et al., 1999). This is beneficial for CDs when strong decontaminate sorption by porous media is undesirable (Badr et al., 2004). Therefore, CDs that do not sorb appreciably to solid phases may be effective in a wide variety of SW/SF applications to remove sorbed HOCs from contaminated subsurface systems (Ko et al., 1999).

2.3.1.2.2 Impact of soil characteristics

HOCs partition into hydrophobic microenvironments, with a tendency to be strongly bound with clay minerals and SOM, was investigated by several authors (Gauthier et al., 1986; Herbert et al., 1993; Tanaka et al., 1997; Chin et al., 1997; Luthy et al., 1997; Paria et al., 2008; Guo et al., 2010).

It is also interesting to study the behaviour of CDs according to soils characteristics, as it was shown to strongly impact their ability to sorb. At various β-CD concentrations, Villaverde et al. (2005a) determined a clear relationship between the physicochemical characteristics of the soils and the β-CD concentration necessary to desorb the contaminant from each soil. The soil with the highest sorption capacity for the pollutant, reached a minimum desorption compared with the other soils, even upon addition of the maximum β-CD concentration used (10 mM) (1.13%) (Villaverde et al., 2005a).

Moreover, Bartolo et al. (2008) observed that CDs had better performances in model soil than in real soil, which is probably due to the lack of OM in model soil with which contaminants can interact and form bonds. Furthermore, due to its higher hydrophobicity than naphthalene (NAP), PHE is strongly sorbed on both soils whose compositions differ only for their SOM value (almost same percentage of sand, silt and clay), according to Badr et al. (2004). This leads to low desorption rates compared to that of NAP whatever the extracting agent used. For both compounds, the soil, which has a greater sorption capacity towards the hydrophobic compounds due to its relatively higher OM content, explains the lower release of pollutants from this soil, whatever the washing solution used.

2.3.1.2.3 Effect of laboratory parameters

- *Effect of spiked and aged contaminated soil*

The concentrations of the desorbing fraction of PAHs clearly decreased after 16 weeks by the use of HPCD (Gao et al., 2009). According to Khan et al. (2011), at lower pyrene level (i.e., 1.07 mg kg^{-1}), the percentage extractability of HPCD did not change significantly even after 222 days ageing as compared with values at 0 day. However, in case of higher pyrene levels (i.e., 9.72, 88.4, and 429 mg kg^{-1}), significant reduction in percentage HPCD extractability of pyrene was observed even after 69 days ageing time, with respect to values at 0 days. This is in accordance with results of Puglisi et al. (2007), who found that HPCD extractability of PHE was significantly reduced as a consequence of ageing. Villaverde et al. (2007) also demonstrated this ageing effect on HOC desorption. They observed no extraction efficiency difference of NFL by β-CD between 1 and 15 days ageing but a decrease of efficiency after 30 days ageing. This suggests that a minimal time of ageing is required to observe its effects. Furthermore, Wan et al. (2009) noted that HCB really contaminated soil experienced a much longer ageing process than kaolin, which means a dramatically stronger interactions and sequestration between the contaminant and soil in comparison of kaolin, as Huang and Weber Jr (1997) also demonstrated before.

As SW is often studied at laboratory scale, it is important to note that the type of contamination (spiked soil or naturally contaminated soil) is directly related to the ageing of contamination and pollutant concentration (Wu et al., 2010). HOC removal efficiency from the spiked and aged soils might be quite different due to the ageing

effect of HOC in the historically contaminated soil. Due to sequestration of PAHs in the weathered soil, PAHs mass transfer processes from the spiked and aged soils might be quite different (Gong et al., 2010). For instance, PAHs extraction with HPCD is much better in spiked soil than in really contaminated soil (Latawiec and Reid, 2009; Gong et al., 2010; Wu et al., 2010). Thus, it is of importance to investigate HOCs removal from aged contaminated soils, since hydrophobic contaminants solubilization from artificially contaminated soils is always unrealistically high when compared to that from aged contaminated soils (West and Harwell, 1992).

- *Effect of successive washing and solid/liquid ratio*

When RAMEB and HPCD were used as mobilizing agents, the second and third SW experiments with recycled cyclodextrin increased PCB mobilization by 35% and 17% of the PCB initial load, respectively (Ehsan et al., 2007). Moreover, no significative differences of extraction efficiency were noticed between fresh or unfresh reagent used in successive extractions (Ehsan et al., 2007), which allows saving CDs.

The efficacy of successive washing is partly related the solid/liquid ratio. An increase quantity of extracting solution with a constant mass of soil usually provides an enhancement of recovery efficiency. Among the CDs SW studies, 10 and 20% are the most frequent solid/liquid ratios (or pulp density) used. Besides, when Rosas et al. (2011) varied the ratio from 20 to 100%, the optimal ratio of 29% (1/3.5) appeared to be the most efficient ratio to remove p-cresol from soil.

- *Pollutant soil content*

In spiked soils, the pesticide NFL removal with β-CD, α-CD and γ-CD increases when the initial concentration of the pesticide in soil increases (Villaverde et al., 2005a; Villaverde et al., 2005b; Villaverde et al., 2006). Moreover, in PAHs really contaminated soil, the increase of pollutant concentrations from 52.8 to 996.9 mg kg^{-1} implies an increased total PAHs removal by the HPCD (Wu et al., 2010). The HOCs concentrations in soil appear to be an important factor affecting their removal from the contaminated soil.

- *CDs concentration*

As expected, in most of the cases the removal efficiencies increase with an increase concentration of CDs, confirming the results about the solubility enhancement in section 2.2.3.2. For instance, the removal efficiencies of PHE increase dramatically with increasing GCD concentrations (5 to 40 g L^{-1}) (0.5 to 4%) (Wang et al., 2010). Besides, PHE desorption was evaluated increasing when the cyclodextrin (MCD and HPCD) concentration increased from 0.1 to 4% (Gomez et al., 2010). This is in accordance with some other works about PAHs contaminated soil with HPCD (1 to 10%) (Maturi and Reddy, 2008; Wu et al., 2010), MCD (0 to 50 g L^{-1}) (0 to 5%) (Petitgirard et al., 2009) and β-CD (0.05 to 1%) (Maturi and Reddy, 2008). Similar results are obtained in PCB and HCB contaminated soils with β-CD (1 to 5 mM) (0.11 to 0.57%) (Hanna et al., 2004b) and MCD (0 to 100 g L^{-1}) (0 to 10%) (Wan et al., 2009), respectively.

An optimal value of CD concentration can be found in some papers. For example, the extraction efficiency of TeCP from soil initially increases with increasing CMCD concentration up to a maximum value (40 mM of CMCD) (6%) and then reaches a plateau (Chatain et al., 2004). Moreover, the 1 and 2% HPCD solutions were as effective as the 5% HPCD solution in extracting the 2,4-DNT from the kaolin and glacial till soils, respectively (Khodadoust et al., 2006). A plateau is observed at around 4 mM (0.45%) of β-CD (Guo et al., 2010) and 5% of HPCD (Hawari et al., 1996) in MF and RDX contaminated soil, respectively. Maturi and Reddy (2008) observed a decrease in PHE removal at high HPCD concentration in one really contaminated soil, which was also contaminated by heavy metals. They suggest that it may be due to the formation of complexes with other dissolved soil metals.

Khodadoust et al. (2005) observed a different behaviour, as the removal efficiency of PHE by HPCD was 42% at a concentration of 1% and it decreased to 10% at a concentration of 3%. This decrease might be due to heterogeneities in the PHE concentrations in the field soil. The removal efficiency thereby increased to 21% at a concentration of 10%.

- *Contact time*

The applied contact time appears to vary from 4 hours to 28 days depending on the study. The most frequent applied time is 24 hours and then 20 and 48 hours. Besides,

some papers studied the effect of applied contact time. Rosas et al. (2011) have shown that the optimal time for p-cresol desorption is 48 hours, the time when the plateau begins. Bartolo et al. (2008) evaluated an optimal contact time of 75 hours for lindane extraction whereas 28 days was required as optimal time to enhance PCDDs/PCDFs desorption according to Cathum et al. (2007).

2.3.1.3 Desorption modeling of SW in lab scale study

Classic and well-known models are commonly used for desorption in SW lab scale study. Sheremata and Hawari (2000) adapted Freundlich adsorption isotherm to describe equilibrium desorption data for NACs in soil. In order to take into consideration the soils-HOCs-solubilizing agent interactions, Guo et al. (2010) suggested the model using the water-soil partition coefficient (K_d), considering that surfactant and solubilizer molecules alter the characteristics of the soil and the aqueous phase. Wang et al. (2010) tried to fit a pseudo-first-order and a pseudo-second-order desorption kinetic model. They concluded that desorption of PHE with GCD from contaminated soil follows a pseudo-second-order kinetic model. However, desorption extraction data of p-cresol were well described by the model containing a pseudo first-order equation (Khalladi et al., 2009; Rosas et al., 2011).

2.3.2 SF process

In-situ technologies have become very attractive for treating contaminated soils and groundwater because of lower cost, no need of a preliminary excavation step, less disruption to the environment, and reduced worker exposure to hazardous materials (Villaverde et al., 2005a). Moreover, enhanced-flushing technologies, based on flushing the contaminated zone with chemical agents to increase contaminant mobility, have shown promise as an alternative to the basic pump and treat technique (Boving and Brusseau, 2000). It is also important to note that the delivery of the active ingredient to contaminated soils and aquifers is difficult to manage and to monitor the treatment efficiency. Regardless the extracting agents, low recovery efficiencies will be obtained in low permeability soil and high heterogeneity containing different layers having different properties (SOM, permeability, clay lenses,…).

Appendix 2.4 lists and summarizes the different CDs SF studies found in literature, including the soils characteristics, the lab parameters and the HOCs removal efficiency by using CDs and other extracting agents in some case.

2.3.2.1 Removal efficiency of organic pollutants

2.3.2.1.1 Different pollutants treated in soils by CDs

PAHs were investigated in some flushing studies. CMCD significantly enhanced the removal of NAP from soil, as 70% of the initial NAP was removed by 2 g L^{-1} (0.2%) CMCD solution after 160 pore volumes of flushing (1.6 L in total) (Jiradecha et al., 2006). Besides, CMCD (1%) solution enhanced removal of PHE with almost 100% of removal after 12 and 42 pore volumes of flushing in a Borden soil and Hayhook soil, respectively (Brusseau et al., 1997b). HPCD (10%) significantly enhanced mass removal of NAP (97.7%) after 10 days, after the water flush had become virtually ineffective at removing mass for this compound (McCray and Brusseau, 1998). Moreover, given a large value of OM, the impact of HPCD on NAP transport in the Mt. Lemmon soil is remarkable, according to Brusseau et al. (1994). Furthermore, the total PHE removal with aqueous solutions of 1% HPCD attained a value of almost 70% after 6 days (Gomez et al., 2010). Brusseau et al. (1994) also observed this HPCD effectiveness. Indeed, pyrene could be almost totally removed with just 1 pore volume of solution containing 10 g L^{-1} (1%) of HPCD whereas approximately 1800 pore volumes of water would be required to remove the same mass of pyrene under the same conditions. Viglianti et al. (2006) demonstrated that the removal efficiencies of PAHs with three CDs can be ranked in the following order: MCD > HPCD >> β-CD, which is consistent with the complexation equilibrium constants available in the literature (Viglianti et al., 2006). In the same study the modified CDs (MCD and HPCD) had closing performance.

Regarding pesticides, Villaverde et al. (2007) tried to approach a more realistic environment when they studied NFL. They eluted columns initially with distilled water, with the aim to simulate the herbicide drainflow losses because of rainfall. With a following β-CD flushing step, the removal efficiencies were greatly enhanced (2 times) reaching 80 to 90% by comparing with a β-CD flushing treatment without a previous water flush. About lindane, CDs have similar behaviors as in SW, *i.e.*, γ-CD displays the best performance and α-CD, and β-CDs have similar behaviors, but the percentage

removals are still low (Bartolo et al., 2008). Morillo et al. (2001) observed that the percentage of the herbicide 2,4-dichlorophenoxyacetic acid (2,4-D) eluted with β-CD (0.01 M) (1.13%) reached 100 % after 1 L of flushing solution. HPCD (10%) allowed extracting 78% of 1,2-dichlorobenzene (1,2-DCB) in 10 days with a total volume equal to 65,400 L at field scale application (McCray and Brusseau, 1998).

The total flushing volume necessary to remove residual saturation by TCE and TeCE was reduced substantially with HCPD and MCD compared to water flushing (Boving et al., 1999; Boving and Brusseau, 2000). Due to its less polar character and its impact on interfacial tension, MCD proved to be more effective than HPCD to remove both TCE and TeCE, though it is similar to HPCD to remove TCE (Boving et al., 1999). A later study from the same team shows better TCE removal with MCD compared to HPCD (Boving and Brusseau, 2000). However, MCD caused mobilization in some experiments, whereas HPCD did not (Boving et al., 1999). A more recent study demonstrated that HPCD flushing solution achieved 48% removal of TeCE. This was calculated by comparing the peak TeCE concentrations (1,300 mg L^{-1} with CD solution), measured immediately after the maximum cyclodextrin concentrations (15%) were attained, to the average concentrations measured in the water flush conducted prior to the CD flushing (60 mg L^{-1}) and based on the equivalent of 33 L of TeCE removed by HPCD flushing compared to the initial volume of TeCE present prior to the flushing (68.6 L) (Tick et al., 2003).

CMCD significantly enhanced the removal of 2,4-DNT from soil, as 73% of the initial 2,4-DNT was removed after 140 pore volumes of 2 g L^{-1} of CMCD flushing solution (Jiradecha et al., 2006).

CV, considered as a synthetic dye, is not removed by HP-α-CD whereas MCD is the most efficient to remove it (De Lisi et al., 2007).

HPCD (10%) allowed extracting between 70 and 80% of BTEX and its derivatives except with 1,2,4-trimethylbenzene (1,2,4-TMB) (39%), in 10 days at field scale application (McCray and Brusseau, 1998).

Alkane hydrocarbons like decane (DEC) and undecane (UNDEC) were not well extracted by HPCD (10%) compared with the other compounds removed in the same study (McCray and Brusseau, 1998). This reflects that 8 pores volume is not enough to produce a large reduction of mass for these more hydrophobic compounds (DEC and

UNDEC). If the CD flushing had been longer, the mass-removal percentages for these compounds would have been similar to those obtained for the less-hydrophobic compounds (McCray and Brusseau, 1998).

Finally, the enhanced-transport effect coupled with observations of no retardation or pore exclusion of the CDs, suggest that CDs have potential for use in subsurface remediation efforts (Brusseau et al., 1994). Among the modified CDs, which have better enhancement ability than the native ones, HPCD is the most used in research papers about CD flushing experiments and MCD proved to have slightly higher efficiency than HPCD.

2.3.2.1.2 Comparison between CDs and other extracting agents

- *Comparison between CDs and surfactants*

The retardation factor for PHE transport in a sandy soil was reduced from a value of 234 to 8 in the presence of a 2 g L^{-1} solution of Triton which is similar to that observed for HPCD (Brusseau et al., 1994).

According to Boving and Brusseau (2000), the two anionic surfactants (SDS 5%) and DOWFAX 8390 (5%) have better performance than HPCD (5%) to remove TCE from a spiked soil by comparing the total volume of flushing solution. However, the total number of pore volume is lower with MCD (5%) than DOWFAX and higher with MCD compared to SDS, which indicates that MCD had better performance than HPCD and Dowfax, but lower performance compared to SDS.

While surfactants may obtain comparable results, reduction of interfacial tension may cause partial mobilization of immiscible liquid like TCE, during the first pore volumes (Pennell et al., 1994; Boving and Brusseau, 2000) and frequently emulsification (Okuda et al., 1996; Bai et al., 1997), which is not observed for CDs flushing (Brusseau et al., 1994).

- *Comparison between CDs and co-solvents*

The results of 50% EtOH flushing experiment showed widely better extraction than HPCD or MCD with 40 pore volumes for 95% of TCE removal (Boving and Brusseau, 2000). However, it is specified that a 50% solution has to be used for EtOH because a 5% solution had negligible effect on TCE solubilization compared with CDs, surfactant

or DOM. Moreover, co-solvent flushing has shown mobilization at the beginning of this treatment. This phenomenon was not observed for CDs flushing.

- *Comparison between CDs and dissolved organic matter (DOM)*

Recently used for subsurface remediation (Johnson and Amy, 1995; Lesage et al., 1995), DOM generally refers to suspended solids from soils, sediments, or sewage effluent and to dissolved organic macromolecules such as humic acid. These substances have hydrophobic as well as hydrophilic parts and they can facilitate the transport of HOCs (Boving and Brusseau, 2000).

By comparing the total volume of flushing solution, DOM (5%) is better than HPCD (5%) but less efficient than MCD (5%) (Boving and Brusseau, 2000).

2.3.2.1.3 Synergistic effects

The mixed CD solution (CMCD (0.5%) and HPCD (0.5%)) increased the removal of PAHs like PHE as compared to the CMCD solution. For example, 86% of the initial mass was removed by the CMCD/HPCD solution after 20 pore volumes of flushing, compared to 66% for the CMCD solution (Brusseau et al., 1997b). This synergistic effect has shown promising results.

2.3.2.2 Parameters impacting the removal efficiencies

2.3.2.2.1 Sorption of CDs into soil

Brusseau et al. (1994) showed that HPCD retardation factors (defined in section 2.3.2.4) obtained from column studies were equal to 1 for both a low organic carbon content (0.29%, Borden sand) and high organic carbon content (12.6%, Mount Lemmon soil), indicating negligible sorption of HPCD. They also stated that the retardation results agreed with their batch sorption data. In Villaverde (2007) column experiment, higher β-CD sorption implies lower NFL availability for leaching. This is explained by β-CD soil sorption where this surfactant would act as a bridge between NFL molecules and the soil surfaces. Perez-Martınez et al. (1999) observed also a delay effect in 2,4-D leaching in soil with higher adsorption of β-CD.

Regarding the surfactant in SF experiment, once the capacity has been reached (generally after one pore volume) there will be no further net loss.

2.3.2.2.2 Impact of soil characteristics

Brusseau et al. (1994) argued that the reduced effectiveness of HPCD for enhancing transport in their soil is due to its much larger organic carbon content (12.6%) compared with other soils at low OM content. The same team has shown a decrease of the efficiency (around 22%) when the SOM content increases from 0.1 to 2.4% (Brusseau et al., 1997b).

Besides, Villaverde et al. (2007) results were mainly related to soil texture, that is to say, soils with a high sand content (56.7% and 49.8%) showed the highest percentage of percolation and the soil with only a 16.7% in sand content (with higher clay and silt contents) showed a very low extraction capacity, knowing that the OM content of the three soils was similar. Thus, from sandy to clay soil, a decline in leached loads of pollutant was observed (Renaud et al., 2004).

In *in situ* soil remediation, the effectiveness of extracting agent application largely depends on the physico-chemical properties and texture of soils, and therefore preliminary studies about the contaminated soils should be carried out.

2.3.2.2.3 Effect of laboratory parameters

- *CDs concentration*

The increase of CD concentration from 10 to 100 g L^{-1} involved a linear increase in PAHs released from natural contaminated soil (Viglianti et al., 2006). Besides, a significant enhancement effect, compared to water flushing of PAHs, is observed only when the concentration of HPCD is greater than 0.01 g L^{-1}, which is determined as the minimal CD required concentration (Brusseau et al., 1994). An increase of the methyl-parathion (m-parathion) removal efficiency is also observed with the increase of HPCD concentration from 0.5 to 5 g L^{-1} (Zeng et al., 2006). However, Jiradecha et al. (2006) observed that adding more CMCD did not significantly improve the total NAP removal. For example, 70% of the initial NAP was removed by 2 g L^{-1} CMCD solution and 72% was removed by 5 g L^{-1} of CMCD solution after 160 pore volumes of flushing. It may be due to the diffusion of the contaminants from the soils to the bulk liquid which was rate limited. Furthermore, adding more CMCD also did not significantly improve the total 2,4-DNT removal. For instance, 73% and 75% of the initial 2,4-DNT was removed after 140 pore volumes of 2 and 5 g L^{-1} CMCD solution flushing, respectively

(Jiradecha et al., 2006). When the CDs reach their maximum concentrations, the initial concentration increases for all contaminants (McCray and Brusseau, 1998). The concentration decrease exhibited by most compounds is believed to be partly due to the impact of decreasing mole fractions on dissolution. The final decreases in contaminant concentrations to very small values occur as the CD concentration decreases.

- *Temperature*

The evolution of extracted concentrations of PAHs versus time was similar for all experiments, independently from temperature or CD type (HPCD, MCD or β-CD) (Viglianti et al., 2006). Despite the temperature is an important process parameter, it is really noticeable that the extraction seems not very sensitive to temperature variation (5, 20 and 35 °C). As enhancement of aqueous solubility of PAHs is caused by the complexation reaction, the very low dependence on the temperature is probably due to the fact that the increase of PAHs aqueous solubility with temperature (Whitehouse, 1984) is counterbalanced by a destabilization of PAH/CD complexes. These complexes have a negative enthalpy of formation (for example, about – 4 kcal mol^{-1} for anthracene-β-CD complexe), and thus tend to be dissociated with the increasing temperature. This is very interesting for a possible industrial application, though more work in this field is needed to confirm this behavior, because others methods (organic solvents, surfactants) present a clear decrease of efficiency with decreasing temperature (Krauss and Wilcke, 2001).

- *Volume of flushing solution and successive SF*

Different volumes of flushing solution are applied depending mainly on the study scale and lab parameters. However, a trend appears in most of the CDs SF studies: the plot of relative contaminant concentration in effluent as a function of number of pore volume follows a breakthrough curve (Boving and Brusseau, 2000; Boving et al., 1999; Brusseau et al., 1994; Brusseau et al., 1997b). For instance, in HPCD flushing experiments by Boving and Brusseau (2000), the concentration of TCE in the column effluent increased in less than two pore volumes to an essentially constant value. After the steady state, by flushing the column with several tens of pore volumes, the effluent concentration began to decrease in an approximately linear fashion and continued until less than 1% of the initial mass of NAPL (non-aqueous phase liquid) remained in the

column. In the study of Viglianti et al. (2006), the PAHs extraction increased when total volume of flushing solution increased from 1 to 5 pore volume.

PAHs extracted quantities increased almost linearly with the overall quantity of CD used at increased volume of flushing solution and constant mass of soil (Viglianti et al., 2006). Moreover, considering the flow rate of the flushing solution, in 6 days, the ratio soil/flushing solution (55 g of soil per L of solution) was similar to that attained at shake flask scale in Gomez et al. (2010) experiments. These results confirm the good correlation between the experiments at shake flask and column scales.

The effect of successive SF is directly related to the applied volume of flushing solution and the column pore volume. Thus, after five successive extractions for β-CD and HPCD and three for MCD at a constant soil/flushing solution ratio for each step, cumulated quantities of extracted PAHs seem to follow a quasi-linear trend with the increase of flushing solution used, which confirms experiments at various soil/flushing solution ratios (Viglianti et al., 2006).

- *Surperficial velocity*

Various superficial velocities are being used from very low rate like 9.82 x 10^{-4} mL min^{-1} cm^{-2} to high rate like 222 mL min^{-1} cm^{-2}. However, De Lisi et al. (2007) observed that decreasing the surface flow rate from 1.33 to 0.11 mL min^{-1} cm^{-2} leads to a detectable increase of Cristal Violet (CV) removal from the solid surface. Nevertheless, below this value the contaminant extraction yield did not improve.

- *Vertical vs horizontal flow*

Boving, McCray and Brusseau's team usually placed the column in a horizontal position to mimic typical groundwater flow conditions (Boving et al., 1999; Boving and Brusseau, 2000; McCray and Brusseau, 1998). In most of the other CD flushing studies, the vertical way was most frequently chosen (Morillo et al., 2001; Tick et al., 2003; Viglianti et al., 2006; Villaverde et al., 2006; De Lisi et al., 2007; Petitgirard et al., 2009; Gomez et al., 2010;). By studying the effect of gravitational forces in vertical position vs horizontal position, Boving et al. (1999) observed no difference between the two kinds of flow. The comparison of the 5% HPCD flushing experiments conducted under vertical (downward) and horizontal flow conditions with TeCE as the immiscible liquid revealed that the mass-normalized removal rates were approximately the same for

both experiments. As expected there is no impact of gravitational forces, since there were no mobilization and displacement of soluble TeCE.

- *Contact time*

In batch equilibrium tests, the contact times of the HOC with the extracting solution are considered to be very rapid, where as a limitation in transport of the active ingredient to the sorption sites occurs in soil column and field experiments.

Among the published data from CD flushing experiments, the contact time can vary from few days (Petitgirard et al., 2009) until one or two months (Tick et al., 2003), depending on the scale of the study. As this time is directly related to the flow rate and the volume of CD solution applied, the total removal efficiency increases when the applied time increases, giving a breakthrough curve (McCray and Brusseau, 1998; McCray and Brusseau, 1999; Villaverde et al., 2007). Whatever the age of soils contamination, a CD solution (10 g L^{-1}) removed without constraint the fraction of aged PAHs contaminated soil after 38 days of contact with flushing solution (Brusseau et al., 1997b).

Besides, a flow interruption technique (Brusseau et al., 1989; Brusseau et al., 1997a) was used to investigate possible mass-transfer constraints, *i.e.*, rate-limited solubilization. This method involves the interruption of flow during the experiment. If the dissolution of an organic contaminant is rate-limited, one can expect an increase in the effluent concentration after the flow is resumed. Flow interruption during the HPCD experiments of Boving and Brusseau (2000) indicated instantaneous dissolution during the steady state phase, i.e., no significant change in the TCE effluent concentration after the flow was resumed.

2.3.2.3 SF processes at field scale

The 3 m x 4.6 m area cell studied by Tick et al. (2003) is located on the Dover Air Force Base (Delaware, USA). The cell was enclosed by sealed 9.5-mm thick steel sheets that were driven into the clay layer. Approximately 7 pore volumes (85,000 L) of the 15% cyclodextrin solution were pumped through the cell at an average flow rate of 1-2 L min^{-1} during 54 days of injection. HPCD flushing solution achieved 48% removal of TeCE, corresponding to an enhancement factor of 21.7.

Blanford et al. (2001) have conducted a field experiment at Air Frorce Plant-44 in Tucson, Arizona (USA) (Figure 2.2).

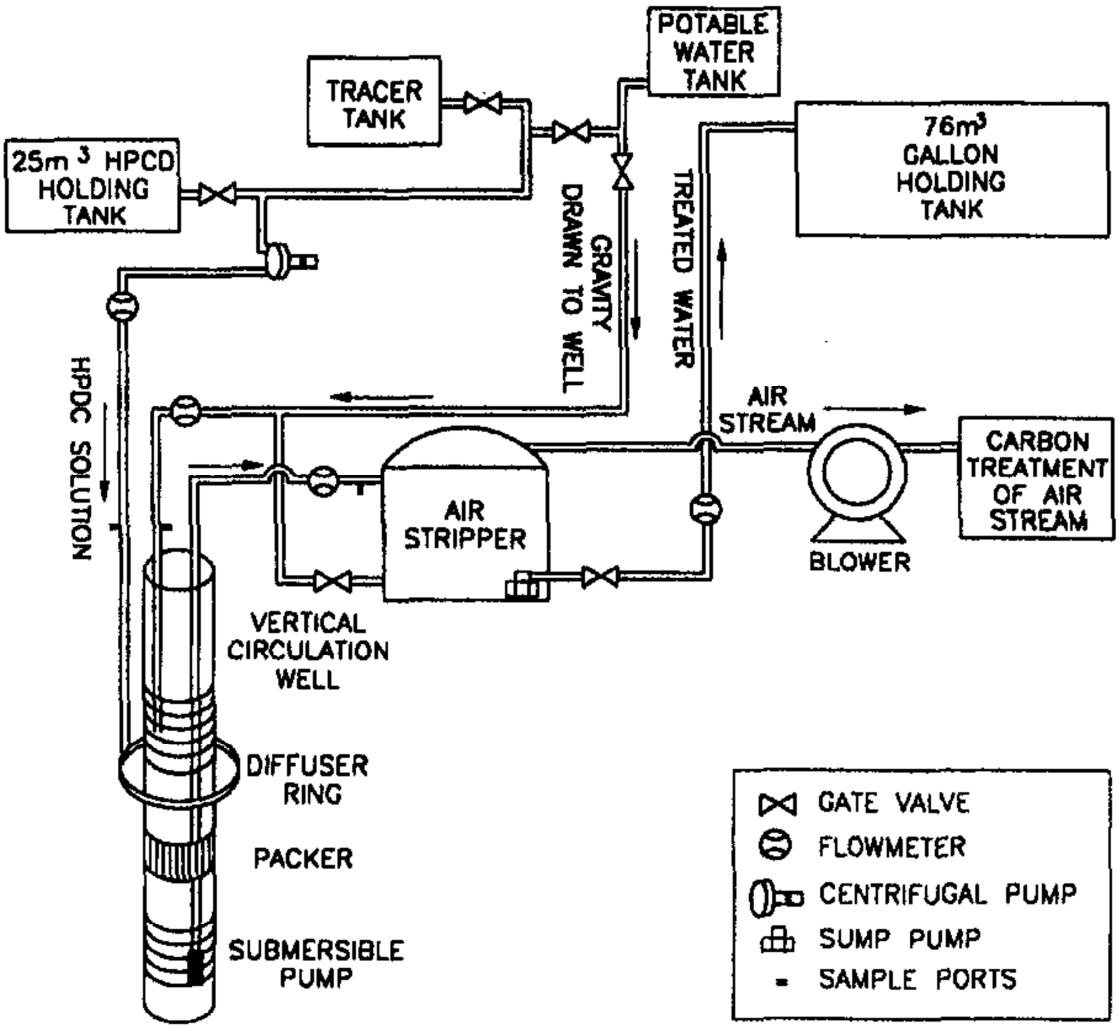

Fig. 2.2. *Schematic representation of an experimental setup for SF pilot tests (From Blanford et al., 2001).*

The pilot tests were conducted in the vicinity of former unlined disposal pits that received waste solvents like TCE. A vertical circulation well was installed to a depth of 55.15 m, screened by stainless steel. During the CD flushing test, approximately 4 m^3 of HPCD (20%) solution was injected at a flow rate of 7.6 L min^{-1}. The TCE extraction increased abruptly to about 0.8 mg L^{-1} compared to 0.3 mg L^{-1} in water flush test, corresponding to an enhancement factor of 3.

Another field site was studied by McCray and Brusseau's team (McCray and Brusseau, 1998; McCray and Brusseau, 1999), which is located in the Weber River Valley, approximately 25 miles north of Salt Lake City, USA. The unit of concern is a shallow, unconfined aquifer that consists of fine-to-coarse sand interbedded with gravel and clay stringers and is approximately 9 m thick. The natural groundwater elevation at the site fluctuates between 5.5 and 7.5 m below ground surface. A line of four injection wells and a line of three extraction wells, both normal to the direction of flow, were used to generate a steady-state flow field. Approximately 8 pore volumes of the 10% cyclodextrin (HPCD) solution (approximately 65,500 L total) were pumped through the cell at a rate of 4.54 L min^{-1} for 10 days, using a horizontal flow field. The CD flushing appears to have been very effective in reducing soil-phase mass for most of the target contaminants during the 8 pore volumes flush (McCray and Brusseau, 1998). For example, the mass of TCE is reduced by more than 90%. The masses of the other targets were reduced by more than 70% with the exception of 1,2,4-TMB, DEC, and UNDEC, which are the most hydrophobic target contaminants. The 8 pore volumes were insufficient to produce a large reduction of mass for the more hydrophobic compounds under the existing conditions. However, the removal of all the compounds were greatly enhanced by the CD flushing compared to water flushing. The cyclodextrin solution increased the aqueous concentrations of all the targeted contaminants to values from about 100 to more than 20,000 times during the water flush. For most contaminants, the effluent concentrations exhibited large initial increase followed by a decrease to a somewhat constant value. These asymptotic concentrations indicate that the NAPL-phase contaminant was not completely removed at the end of the SF. However, the solubility enhancements were still quite large for all contaminants after the asymptotic concentrations were reached, indicating that mass removal was still being enhanced by the CD flushing. Finally, the average reduction in soil-phase concentrations with CD flushing for all the target contaminants was 41% (McCray and Brusseau, 1998).

Similar results have been finally reported in all these filed-tests in which Brusseau's team from the Universtiy of Arizona (USA) was involved. Moreover, it is useful to compare the removal efficiency of contaminants observed during the pilot test of CD flushing to that expected based on laboratory experiments. Blanford et al. (2001) concluded that there is a perfect correlation between the degree of enhancement

projected from laboratory studies and the degree of enhancement measured from their pilot-tests. Furthermore, the enhancement factor determined for the field test of Tick et al. (2003) is essentially identical to the expected value obtain from laboratory data reported by Boving et al. (1999), indicating that the maximum possible solubility enhancement was obtained, showing the similarity between the two different scale tests.

2.3.2.4 Desorption modeling of SF

Different models to predict and to quantify desorption of HOCs are suggested in some CD flushing papers and reviewed in this section.

- *Complexation/solubilization theory*

The performance of the CD solution in terms of enhancing contaminant removal from a soil can be evaluated using the complexation/solubilization theory (Brusseau et al., 1997b). For organic compounds, the expected enhanced-removal factor can be calculated using the following equation:

$$\frac{C_m}{C_0} = 1 + \sum_i K_{C_i} X_i \qquad (2.12)$$

where C_m is the measured maximum solute concentration in the effluent (mg L^{-1}), C_0 is the initial aqueous concentration of the contaminant (mg L^{-1}), K_{c_i} is the partition coefficient of the solute between the specific CD and water (L kg^{-1}), and X_i is the aqueous concentration of the specific cyclodextrin (kg L^{-1}).

For instance, measured K_c values for PHE were 75.4 L kg^{-1} for CMCD and 1680 L kg^{-1} for HPCD (Brusseau et al., 1997b). The measured enhanced-removal factors for PHE were similar to the expected values for the CMCD/Hayhook soil and CMCD/Borden soil systems. However, the measured enhancement factors were significantly smaller than the expected values for the CMCD+HPCD/Hayhook and CMCD+HPCD/surface soil systems, because the initial sorbed mass of PHE was not sufficient to meet the maximum solubilization enhancement of HPCD, which has a much stronger solubilization enhancement as compared to CMCD.

- *Raoult's law model*

During flushing (or washing) experiments, the dissolution from the NAPL to water

phase can be expressed by following Raoult's law:

$$C_{aq} = X \times \sigma \times S \tag{2.13}$$

where C_{aq} is the compound molar aqueous concentration; X is the compound molar fraction within the NAPL; σ is the compound activity coefficient within the NAPL; S is the compound aqueous solubility. σ can be taken equal to 1, which implies that NAPL is considered as ''ideal''. X can be expressed as:

$$X = \frac{C_S \times MW_{NAPL}}{C_{NAPL,s} \times MW} \tag{2.14}$$

where C_s is the compound massic concentration in soil; $C_{NAPL,s}$ is the NAPL massic concentration in soil; MW is the compound molecular weight; MW_{NAPL} is the NAPL molecular weight.

As the molecular weight of the NAPL cannot be measured, the common range for coal tar (200-1000 g mol^{-1}) can be used. $C_{NAPL,s}$ is based on Lane and Loehr's works (Lane and Loehr, 1992; Lane and Loehr, 1995) who assumed that the Total Organic Carbon (TOC, mg kg^{-1}) detected in the soil is equivalent to the amount of TOC in the tar, and that the NAPL (tar) has an average TOC of 71%, which gives:

$$C_{NAPL,s} = \frac{TOC}{0.71} \tag{2.15}$$

Based on the relations (2.13) - (2.15) the aqueous concentration of a single PAH solubilized from a multiple-component NAPL can be expressed as:

$$C_{aq} = \frac{(0.71 \times C_s \times MW_{NAPL} \times S)}{(TOC \times MW)} \tag{2.16}$$

This model can predict HOC (such as PAH) aqueous concentration in pure water, but this concentration is considerably enhanced in presence of CDs. The apparent HOC aqueous concentration in presence of CDs could also be estimated. The apparent solubility of HOCs like PAHs in aqueous CD solutions has been observed to increase linearly with the CD concentration (Wang and Brusseau, 1993; Brusseau et al., 1994; McCray et al., 2001). The apparent HOC aqueous concentration $C_{aq,app}$ is the sum of free HOC form, and the CD-complexed form [CD/HOC] (Viglianti et al., 2006):

$$C_{aq,app} = C_{aq} + C_{[CD/HOC]} \tag{2.17}$$

Thus,

$$C_{aq,app} = C_{aq}\left(1 + K_{CW}C_{CD}\right) \tag{2.18}$$

where C_{aq} is the compound aqueous concentration calculated with equation (2.16); K_{CW} is the compound partition coefficient between CD and water or stability constant; C_{CD} is the CD aqueous concentration. Concentration of extracted HOC present in the flushing solutions ($C_{aq,app}$) can be estimated by Eq. (2.18), based on a HOC aqueous concentration estimated by the previous model and the partition between CD and water equilibrium constant, available in the literature.

Linearity curves observed by Viglianti et al. (2006) for PAHs release with CD concentration, corroborates this theoretical approach. A very good fit is observed between predicted and experimental PHE concentrations for the whole range of CD concentration, while about one fold divergence for anthracene values. This could be caused by a non-ideal NAPL, which could invalidate the use of Raoult's law (McCray and Brusseau, 1999; Majhoub et al., 2000).

- *Desorption with soil/water partition coefficient (K_p)*

To estimate NAPL compound aqueous concentration obtained in the flushing (or washing) of this type of contamination, a desorption model using soil/water partition coefficients can be used. Lane and Loehr (1995) developed this method in which the soil/water partition constant K_p can be found in literature:

$$K_p = K_{OC} f_{OC} = \frac{C_s}{C_{aq}} \tag{2.19}$$

where K_{OC} is the organic carbon partition coefficient; f_{OC} is the organic carbon fraction present in the soil. C_s can be detailed as:

$$C_s = C_{s,0} - C_{aq}\frac{L}{S} \tag{2.20}$$

where $C_{s,0}$ is the compound initial concentration in soil; L/S, mass of water (L) in contact with the mass of soil (S) ratio. Then, C_{aq} is given by relations (2.19) and (2.20):

$$C_{aq} = \frac{C_{s,0}}{K_{OC} f_{OC} + \frac{L}{S}} \tag{2.21}$$

Viglianti et al. (2006) also adapted this model and took into account the presence of CD by inserting eq (2.21) into relation (2.18). The linearity of the curves observed corroborates also this theoretical approach.

- Advective-dispersive transport: retardation factor calculation

Brusseau et al. (1994) suggest the following equation to describe one-dimensional advective-dispersive transport of solute in a homogeneous porous medium under conditions of saturated, steady-state water flow:

$$R\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2} - v\frac{\partial C}{\partial x} \qquad (2.22)$$

where C is the compound concentration in solution (mg L^{-1}) ; x is the distance (m) ; v is the average pore-water velocity ($v = \frac{q}{n}$, where q is Darcy velocity and n is porosity, m s^{-1}) ; t is the time (s) **;** R is the retardation factor ($1+\left(\frac{\rho}{n}\right)K_d$) ; K_d is the equilibrium sorption constant (dm^3 kg^{-1}) ; ρ is the bulk density of the soil (kg dm^{-3}), and D is the longitudinal dispersion coefficient (m^2 s^{-1}).

The effect of CD on the transport of organic compounds is accounted for by modifying the retardation factor in the following manner. The concentration of solute in the aqueous phase consists of both dissolved and complexed (associated with the CD) species. Thus, C is defined as:

$$C = C_d\left(1 + XK_c\right) \qquad (2.23)$$

where C_d is the concentration of dissolved compound (mg L^{-1}); X is the concentration of CD in solution (kg L^{-1}) and K_c is the equilibrium constant describing distribution of organic compound between CD and the aqueous phase (L kg^{-1}) (which can be obtained from solubilization experiments). The modified sorption equation is then obtained by substituting Eq. (2.23) into an isotherm equation of the form $S = K_d C_d$:

$$S = \frac{K_d C}{1 + XK_c} \qquad (2.24)$$

With the assumption that the organic compound-CD complex is not sorbed by the soil, which can be possible (Ko et al., 1999; Tick et al., 2003; Badr et al., 2004; Chatain et al., 2004; Zeng et al., 2006), the modified retardation factor is given by:

$$R = 1 + \frac{\rho K_d}{n\left(1 + XK_c\right)} \tag{2.25}$$

This equation is an equivalent form as those developed to account for facilitated transport by DOM and surfactants (Bengtsson et al., 1987; Kan and Tomson, 1990).

According to Brusseau et al. (1994), predicted values of retardation factors (calculated from Eq. (2.25)) are within 10% of the measured values, with the exception of anthracene and trichlorobiphenyl. These results suggest that the impact of HPCD on solute transport can be accurately quantified with the simple modified retardation factor.

- Model for an eluted dye: Cristal violet (CV)

A correlation between the dye CV incorporation efficiency by CDs extraction in the aqueous phase and its function in the transport of CV through the sand column at a flow rate of 1.5 mL min^{-1} was given by De Lisi et al. (2007):

$$mt_{CV} = \left(-65 \pm 12\right) + \left(29 \pm 3\right)\log K_{cpx} \tag{2.26}$$

where K_{cpx} is the equilibrium constant for the CV/CD inclusion complexes formation and mt_{cv} is the maximum CV extracted (expressed as percent CV removed fraction). This equation predicts that CDs with K_{cpx} values less than 180 M^{-1} are not recommendable for removing CV from sand at a flow rate of 1.5 mL min^{-1} (De Lisi et al., 2007).

2.4 CDs SW/SF integrated with other treatments

Since the enhanced SW or SF processes only permit to extract the pollutant but not to destroy it, a post-treatment is needed. Few data are available in literature about integrated treatments with CDs in SW and SF. They are reviewed in the following section in which coupling between SW/SF and treatments using Fenton's reagent is firstly mentioned. Secondly, integrated treatments trying to regenerate CDs in order to reuse them in a recirculation loop are discussed.

2.4.1 SW/SF-Fenton's reagent treatments

Advanced oxidation processes (AOPs, (Glaze et al., 1987)), which involve the *in-situ* generation of a very powerful oxidizing agent such as hydroxyl radical ($^{\bullet}OH$) (E° = 2.80 V/SHE; (Latimer, 1952)), have shown promising and environmentally friendly methods to popular AOP is that based on the Fenton's reagent (a mixture of H_2O_2 and Fe^{2+} ion) to produce hydroxyl radical $^{\bullet}OH$ according to equation (2.27) (Brillas et al., 2009; Pignatello et al., 2006). In order to treat the soil washed solutions, various and improved techniques of Fenton treatments are evoked in this section.

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO^- + {}^{\bullet}OH \qquad (2.27)$$

2.4.1.1 Fenton reaction

Soil remediation techniques based on the basic Fenton's treatment have been found to be inefficient due to the high reactivity of the reagents with soil constituents (Li et al., 1998; Wang and Brusseau, 1998; Lindsey and Tarr, 2000a; Lindsey and Tarr, 2000b; Lindsey and Tarr, 2000c), since the $^{\bullet}OH$ generated by Eq. (2.27) are non-selective reagent and will be consumed by several wasting reactions, particularly by the OM contents of the soil. It has been illustrated that natural organic matter (NOM) inhibits Fenton degradation by complexing iron and pollutants into spatially separate microenvironmental sites (Shiavello, 1987; Lindsey and Tarr, 2000a; Lindsey and Tarr, 2000c).

CDs show promise of providing an effective means to improve the efficiency of Fenton degradation. Indeed, beyond the fact that CDs can desorb and solubilize HOCs from solids matrix, they can form a ternary complex with iron and the hydrophobic pollutant, which allow effective direct $^{\bullet}OH$ radical reaction towards contaminants (Figure 2.3) (Lindsey et al., 2003; Zheng and Tarr, 2004; Hanna et al., 2005; Zheng and Tarr, 2006; Veignie et al., 2009).

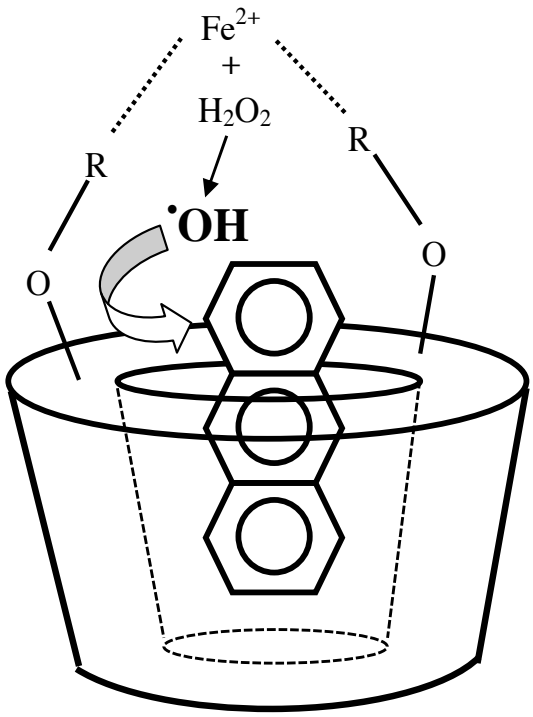

Fig. 2.3. *Ternary complex formation (Fe^{2+}-CD-HOC) (R group depends on the kind of cyclodextrin).*

Lindsey et al. (2003) demonstrated the CD-iron complex formation by observing differences in absorbance spectra for β-CD, CMCD, Fe^{2+}, and iron–cyclodextrin mixtures. The ternary complex formation improves the degradation rate of the pollutant by minimizing the detrimental effect of non-pollutant scavengers such as mannitol (Veignie et al., 2009) or humic acid and chloride (Lindsey et al., 2003) as a result of some radicals formed close to the complex, which permit a direct degradation of the pollutant (Lindsey et al., 2003). This is interesting for more realistic samples which would likely have other materials present in washed water solution from SW/SF for example, such as dirt and grime (oils, dust, metal particles, etc), in which the use of CDs will likely minimize the interference of non-pollutant radical scavengers present in the system.

Fenton chemistry generally requires low pH to maintain iron solubility and prevent formation of iron oxides and hydroxides. However, the use of chelating agents allows higher pH conditions (Sun and Pignatello, 1992; Sun and Pignatello, 1993). In these systems, the CD chelated the iron, allowing the Fenton reaction to be carried out at near neutral pH (Lindsey et al., 2003).

Furthermore, naturally occurring iron minerals (hematite a-Fe_2O_3, goethite a-FeOOH, magnetite Fe_3O_4 and ferrihydrite) from soil may catalyse the decomposition of H_2O_2 and promote Fenton-like reactions without a supplementary soluble iron (Tyre et al., 1991; Kulik et al., 2006). Since CDs like CMCD can complex with iron, Fenton-like treatment of soil extract solution with CD would not necessary need addition of iron salt.

CDs have different efficiency to form this complex, depending on the groups present on the external shape. The most reasonable sites for metal binding to HPCD are the hydroxyl groups located on the ends of the cavity as metal binding by hydroxyl groups has been reported for mono- and disaccharides (Kaiwar et al., 1994; Geetha et al., 1995). Furthermore, differences between the β-CD–Fe^{2+} and CMCD–Fe^{2+} spectra indicate that iron is coordinated to different functional groups with each CD (Lindsey et al., 2003). For β-CD, the iron is likely coordinated by hydroxyl group on the rim of the CD, while for CMCD, oxygen in the carboxyl group is likely responsible for iron binding. However, alcohol groups are relatively weak ligands compared to the carboxylic acid groups (Zheng and Tarr, 2006). Thus, HPCD, β-CD and α-CD have weak metal bindings compared to CMCD, which minimize the ternary complex formation (iron-CD-HOC). This is in accordance with results of Lindsey et al. (2003) showing a better efficiency of Fenton degradation of some HOCs (phenol, PAHs and PCBs) with CMCD compared to β-CD solution. In addition Veignie et al. (2009) reported that the Fenton degradation efficiency of BaP increases in the following order: β-CD, RAMEB and HPCD, as the methylation could hinder interactions between iron and hydroxyl groups of the RAMEB.

2.4.1.2 Photo-Fenton process

Photo–Fenton process is carried out by applying ultraviolet (UV) light to a Fenton process. The coupling of fenton's reagent with UV irradiation provides further benefits to the overall treatment efficiency: (i) generation of additional $^{\bullet}OH$ through the photo-reduction of $Fe(OH)^{2+}$ ions (predominant form of iron(III) at pH 3) (Eq. (2.28)), (ii) generation of additional $^{\bullet}OH$ through the photolysis of H_2O_2 (Eq. (2.29)) respectively (Sun and Pignatello, 1993; Pignatello et al., 2006, Boufia-Chergui et al., 2010), (iii) catalysis of the Fenton reaction (Eq. (2.27) by continuous generation of Fe^{2+} ions, and

(iv) elimination of sludge formation, since a catalytic amount of Fe^{2+} introduced into the system:

$$Fe(OH)^{2+} + hv \rightarrow Fe^{2+} + {}^{\bullet}OH \quad (2.28)$$

$$H_2O_2 + hv \rightarrow 2{}^{\bullet}OH \quad (2.29)$$

One the other hand, the generation of UV radiations requires an excessive economical cost that constutues one of the major drawbacks of this process. Recent convincing works use sunlight as a free and renewable energy source in order to reduce operating costs (Gernjak et al., 2003; Kavitha and Palanivelu, 2004; Brillas et al., 2009).

Yardin and Chiron (2006) ran experiment with MCD (5 mM) as flushing agent to extract TNT from spiked soil and treated the washed solution with photo-Fenton process. A factor of 1.3 increases in apparent degradation rate constant was observed in the presence of MCD with respect to TNT degradation in distilled water. Thus, MCD has a beneficial effect on TNT degradation rates in complex solutions containing high amounts of hydroxyl radical scavengers. Moreover, when injecting into a phenyl column TNT alone and a TNT ferrous ion mixture in a mobile phase containing 95% of a 5 mM MCD solution, they observed a dramatic shift in retention times (Rt = 4.5 min instead of Rt = 13.8 min). These changes in retention times could be ascribed to the formation in solution of a ternary complex (TNT-CD-iron). The beneficial effect of MCD on TNT degradation rate can be ascribed to the formation of a ternary TNT-cyclodextrin-iron complex as already discussed in the previous part. Besides, soil extract solution mineralization was not completed at the end of the treatment time with only 60% abatement of the initial TOC during 11h of treatment time. However, no potential toxic aromatic intermediates were left in the treated solution.

2.4.1.3 EF process

The most popular technique among the coupling between electrochemistry and AOP is the EF process, in which H_2O_2 is generated at the cathode with O_2 or air feeding while an iron catalyst (Fe^{2+}, Fe^{3+}, or iron oxides) is added to the effluent to produce oxidant ${}^{\bullet}OH$ at the bulk solution via Fenton's reaction (Oturan, 2000; Brillas et al., 2009). Compared to chemical Fenton process, the EF process permits to minimize the use of reagent since the production of H_2O_2 is *in-situ* and a catalytic amount of soluble iron is enough because it is continuously electro-regenerated at the cathode. Thanks to these

enhancements, higher degradation rate and mineralization degree of organic pollutants and no sludge production are observed.

Hanna et al. (2005) degraded synthetic solution containing PCP and HPCD (5 mM) with EF process. Based on the scavenging effect of HPCD, one would expect a strong decrease in the PCP degradation rate, since HPCD alone has a higher reactivity than PCP alone against hydroxyl radicals: k_{abs}(HPCD) > k_{abs}(PCP). However compared with that of the PCP alone reaction a 5-fold increase in apparent rate constant of PCP degradation was observed. This experiment clearly shows that HPCD increases the efficiency of pollutant degradation; PCP degradation quickly occurred even in the presence of large HPCD excess. The kinetic data of Murati et al. (2009) permit to note a slight decrease in apparent rate constant (k_{app} = 0.48 min^{-1}) in case of synthetic solution prepared with 1 mM MCD and TNT with respect to TNT degradation in distilled water (k_{app} = 0.54 min^{-1}), even in presence of a large excess of MCD. The beneficial effect of HPCD on PCP and MCD on TNT degradation rate might be explained by the formation of a ternary pollutant-cyclodextrin-iron complex as suggested before. To provide indirect evidence of this complex formation, absorbance spectrum of HPCD-Fe^{2+}, HPCD-PCP and HPCD-PCP-Fe^{2+} mixtures were analysed (Hanna et al., 2005). Upon addition of Fe^{2+} into a PCP-HPCD mixture, the absorbance spectrum exhibited several changes including a shift and an increase in the 200–240 nm absorbance region. These different changes could confirm the formation of a ternary complex. Besides, 100% PCP degradation and 90% Chemical Oxygen Demand (COD) abatement of a solution containing mainly 0.77 mM of PCP extracted from soil and 4.7 mM of HPCD were achieved after 11 h electrolysis (at applied current of I = 200 mA, corresponding to a charge of 8000 C) (Hanna et al., 2005).

All these results make the coupling of enhanced solubilization by CD with modified-Fenton treatment a promising approach for HOCs contaminated soil remediation.

2.4.2 Combined physico-chemicals techniques with CDs' regeneration

A critical component of full-scale application of any enhanced-solubilization technology is cost-effectiveness, which may depend in large part on the ability to recycle the extracting agent during the project. Such an evaluation at different scale was discussed in this section.

2.4.2.1 Air stripping and granular activated carbon

Tick et al. (2003) suggested a field-scale demonstration including the recycling and reuse of CD using an in-line, real-time configuration, as it is essential to evaluate the practicability of recycling the remedial flushing solution to increase efficiency and decrease material costs. The initial CD flushing solution comprised approximately 21,000 L of 15% HPCD which was recycled approximately 3 times during the demonstration. The extraction-well effluent was passed through a 7-tray air stripper to remove TeCE. The off-gas was passed through a series of granular activated carbon (GAC) reactors to remove remaining TeCE. The treated effluent was directed to the primary storage tank, from which it was reinjected into the test cell. Concentrations of TeCE in the re-injected water averaged approximately 0.1 mg L^{-1}, compared to TeCE initial concentration (1,300 mg L^{-1}) in the extraction effluent. This indicates that the in-line treatment system was up to 99.99% effective at removing TeCE from the 15% HPCD flushing solution.

This recirculation method for TCE removal was prior tested at field-scale by (Blanford et al., 2001) and the airstripping system removed 98.00% of the TCE from the 10% HPCD solution and 99.98% from the water solution with the following conditions: TCE concentration of 5 mg L^{-1}, influent solution flow rate of 30 L min^{-1}, and an air flow rate of 13,000 standard L min^{-1}.

Thus this process is efficient even in HPCD solution but only for VOCs.

2.4.2.2 Colza oil

Petitgirard et al. (2009) observed that MCD can be easily and economically regenerated by contact with natural oil like colza oil, included in a continuous soil treatment with an ascending flushing mode. This liquid-liquid extraction allowed the regeneration of CD by concentrating the pollutants (PAHs) in the organic phase with a small loss of carrier and fast kinetics of PAHs transfer. After two days of homogeneous washing of the soil, the decontamination was almost complete (96-98%), using a 10 mM solution of β-CD. To reduce the amount of MCD loss in the oil phase, they set a low colza oil fraction, by using a micro-emulsion or by impregnating an organic membrane with the oil. The latter is more economical and robust. This process strongly reduces the contaminated

volumes to be treated and the polluted oil can be destroyed in cement plants as suggested by Petitgirard et al. (2009).

2.4.2.3 Heterogeneous photocatalysis: TiO_2/UV

In order to reuse the same flushing solution, Petitgirard et al. (2009) suggested first to release PAHs from the contaminated aqueous solution by heterogeneous photocatalysis using TiO_2 suspensions (1 g L^{-1}) saturated with dioxygen. Basically, this AOP consists of the mineralization of organic compounds occurring through a multistep process involving the attack of organic molecules by reactive oxidizing species, in particular $^{\bullet}OH$, formed during UV irradiation of the semiconductor particles (TiO_2) (Fabbri et al., 2009; Herrmann, 2010).

Slow degradation rates for the PAHs are described by Petitgirard et al. (2009), which is similar to those obtained for their direct photolysis (Fasnacht and Blough, 2002). CDs have an inhibitory effect on the photodegradation of PAHs, because the degradation of PHE carried out in the same conditions without MCD is complete within 30 min (Petitgirard et al., 2009) while it is not achieved in presence of MCD even after 200 min.

These results are in accordance with Hanna et al., (2004b) for which a 90-min irradiation time is sufficient to achieve complete removal of PCP in water, while PCP decay is only 70% in 2 mM CD solution and less than 30% in 5 mM CD solution. Thus, the PCP degradation depends on CD concentration. These results show that CD is also degraded during the photocatalytic process and that the reactivity of hydroxyl radicals toward both molecules is different. The presence of more organic charge (i.e., more CD) as a competitive agent towards the oxidizing species (hydroxyl radicals) may explain the inhibitor effect of CD on the degradation rate of PCP (Hanna et al., 2004b). The same team suggests another hypothesis with the existence of a rapid equilibrium between PCP and CD to form a PCP-CD complex, which implies that the photodegradation of PCP in water may be measurably inhibited when this compound is enclosed in the apolar cavity of CD. Petitgirard et al. (2009) suggest that the CD-HOC complex degradation occurs probably at the TiO_2 surface.

These results confirm that regeneration of soil extract solutions by heterogeneous photocatalysis approach is not enough sufficient.

2.4.2.4 Electrochemical treatment

Gomez et al. (2010) examined the possibility to recycle the washing solution as well as to check the efficiency of this solution in another washing process. Thus, an electrochemical treatment is suggested to treat the exhausted washing solution enriched in PHE in order to destroy the pollutant. In this treatment the application of an electric current between two electrodes induces redox reactions, mainly oxidation on anode surface resulting in the destruction of the organic compound (Sanroman et al., 2004; Alcantara et al., 2008). The oxidation mechanisms involved in this technology include direct electrooxidation, hydroxyl radical-mediated oxidation, and oxidation mediated by oxidants generated during the treatment of the salts contained in the waste (Canizares et al., 2007).

In Gomez et al. (2010) study the electrochemical treatment was carried out in a cubic Plexiglass cell, with a working volume of 0.4 L, by using graphite electrodes with an immersed area of 52 cm^2 and an electrode gap of 8 cm. A constant potential difference of 5 V was applied, which is one of the optimal parameters determined by Gomez et al. (2009). The pH was around 3 and temperature was set at 25 °C during the treatment. The total degradation of PHE (15-20 mg L^{-1} initially) was achieved after 1 day of treatment. In order to determine the removal capacity of the solution after electrochemical treatment in shake flask, it was determined that the level of PHE removal attained with the reused solution was 3% lower than the value obtained with new HPCD solution. Thus, it is clear that electrochemical treatment for the removal of pollutants from the washing solution is a potentially effective technology for reusing CD in SW process.

2.5 Ongoing researches and perspectives

2.5.1 Potential use of EF process

As demonstrated by Lindsey et al. (2003) and other research teams (Zheng and Tarr, 2004; Hanna et al., 2005; Hanna et al., 2005; Yardin and Chiron, 2006; Zheng and Tarr, 2006; Veignie et al., 2009; Murati et al., 2009), during Fenton and modified-Fenton treatments with CD there is a formation of a ternary complex between iron, CD and HOC which allows effective direct $^{\bullet}OH$ radical reaction towards contaminants. This suggests that CD should be almost not degraded during the electrolysis and then could

be reused for a SW step. For instance, in the study of Murati et al. (2009), the TOC value at 20 min (time to achieve the oxidation of TNT by EF process) is almost the same as the initial TOC value, showing that the mineralization has almost not started and CD is not well degraded. Moreover, thanks to the advantages reviewed in 2.4.1.3 section (very few quantity of soluble iron and in situ H_2O_2 generation) and those expressed in 2.4.1.1 section (possibility to operate without adding iron which could come from the soil extract solution and ability to work at near neutral pH thanks to ternary complex form between iron, CD and pollutant), the EF treatment which is very clean, simple and cost-effective process, can constitutes a promising alternative for treating SW/SF effluents.

Further experiments need to be done in order to confirm the potential use of EF process to remove HOCs from washed water solutions and reuse the CD solution in other SW/SF steps.

2.5.2 SW/SF-Fenton's reaction processes-Biological treatments

It was established that pre-oxidation of recalcitrant pollutant like PAHs by Fenton/modified-Fenton treatments leads to oxidation products that are more soluble in water and also with better availability to microorganisms (Martens and Frankenberger Jr, 1995; Lee et al., 1998; Nam et al., 2001; Chamarro et al., 2001; Lee and Hosomi, 2001). The combination of chemical oxidation and biodegradation has a great advantage over either of the two treatments alone in the remediation of organic contaminants. This combined treatment has been successfully applied in wastewater purification (Nam et al., 2001; Goi and Trapido, 2004; Kulik et al., 2006). Fenton pre-treatment followed by biodegradation resulted in a substantial decrease in the required oxidant dosage and enhanced contaminants biodegradation rates in wastewater contaminated with organic compounds (Carberry and Benzing, 1991).

However, hydroxyl radicals could oxidize only the solubilised HOC (Veignie et al., 2009). Without CD, the very low aqueous solubility of 5- and 6-rings PAHs limits the quantity of soluble PAHs and therefore the efficiency of Fenton's reaction. Rafin et al. (2009) observed that in the presence of CD, when Fenton's treatment was combined with benzo(a)pyrene (BaP) biodegradation with *Fusarium solani* (a fungus), a beneficial effect on benzo(a)pyrene degradation was obtained in comparison with chemical oxidation alone (with or without CD) or with biodegradation alone (with or

without CD), for 12 days of incubation. Besides, the quantity of solubilized BaP differed between both CDs: HPCD is more efficient than RAMEB. HPCD appears to be a better choice as it allows not only a rapid supply of BaP, when the fungus is able to degrade it, but also permits Fenton's degradation at low H_2O_2 concentrations compatible with fungal growth. Moreover, the low pH requirement (pH 3) for optimum Fenton reaction made the process incompatible with biological treatment and posed potential hazards to the soil ecosystem where the reagent was used (Nam et al., 2001). In order to overcome such limitation, a modified Fenton-type reaction can be performed at near neutral pH by using ferric ions and agents with chelating properties such as CDs like CMCD (Lindsey et al., 2003). Furthermore, hydrogen peroxide is a widely used biocide for disinfection, sterilization and antisepsis in various fields and can be also incompatible with biological process unless it is used below a lethal limit as suggested by Rafin et al. (2009). Another way is to combine EF with a biological treatment as suggested but not demonstrated by Murati et al. (2009). Based on previous explanation, the EF process allows an *in situ* production of hydrogen peroxide, without adding more catalytic soluble iron that would come from the soil and could be operated at near neutral pH. Thus, EF process could be implemented to enhance the soil washed solution biodegradability and be combined with a final biological step. This last integrated process needs further confirming studies.

Furthermore, some studies evoke other beneficial effects of CDs during these kinds of integrated treatments, not only by enhancing the solubility (and so the bioavailability) of the HOCs (Wang et al., 1998) during a SW/SF step but also by increasing the biodegradability of HOCs during a biological treatment (Fava et al., 1998; Wang et al., 1998; Steffan et al., 2001). Indeed, the microbial population present in PAHs-contaminated soil was found to utilize β-CD (Bardi et al., 2000), while the indigenous microflora in a PCB-contaminated soil can use of γ-CD and HPCD as sole carbon source (Fava et al., 1998). RAMEB was slowly biodegraded by aerobic microorganisms isolated from PCBs-contaminated soil, when RAMEB was then used as sole carbon and energy source (Fava et al., 2003).

Besides, most of integrated treatments combining Fenton/modified-Fenton treatment with biodegradation are conducted by applying a chemical oxidation prior to condition organic contaminants for biodegradation (Goi and Trapido, 2004; Kulik et al., 2006). Rafin et al. (2009) suggest a simultaneous chemical and biological treatment that might

have great advantages over a remediation strategy based on a sequential application. Such a process would be more cost-effective as well as more compatible with soil integrity and especially indigenous microorganisms' activity in polluted soils, instead of introducing microorganisms into chemically treated-soil.

2.6 Conclusions

Many advantages of CDs used in SW/SF treatments and integrated treatments are detailed in this review.

Firstly, the native CDs like α-CD, β-CD and γ-CD are semi-natural, readily biodegradable and non-toxic. Although β-CD is the most accessible, less expensive and generally the most useful among the native ones, it has also a limited water solubility that minimizes its applications and increases its soil sorption. That is why derivative β-CDs like HPCD, CMCD and MCD were marketed and proved to be widely more water-soluble and more efficient. Though modified CDs are less biodegradable than the native ones in uncontaminated soil tests, they are biodegraded from real soil historically contaminated, since the microflora of soil was long adapted to the xenobiotics compounds.

Secondly, CDs are able to form stable inclusion complex relying on different driving force, which allow enhancing the water solubilization of many HOCs (PAHs, pesticides, NACs, BTEX, etc). Thanks to this solubilization ability and to their low sorption onto soils, CDs can relatively well enhance extraction of pollutants from contaminated soils during SW or SF processes. Derivatives CDs appear to have better extracting ability than the native ones. Among the modified CDs, HPCD and MCD have good and close performances, however, due to their respective costs, HCPD is the most frequently used in laboratory or pilot scale. Synergistic effects could also be considered between HPCD and CMCD in order to enhance this efficiency of extraction. Field-scale experiments have shown promising results as a preliminary step before industrial applications.

Compared with other conventional extracting agents, NIS proved to have better extraction efficiency. However, these more toxic compounds are affected by precipitation or sorption onto soil, requiring larger amount and causing possible damage for soil integrity. Surfactants may also form high-viscosity emulsions that are difficult

to remove. Moreover, the solubilization effect of co-solvents, which are also widely studied, is usually not significant until their volume-fraction concentrations are above 10%. Besides, both co-solvents and surfactants cause partial mobilization of immiscible liquid during SF process whereas CDs do not.

Since a post-treatment is needed after SW/SF processes, CDs proved their ability to form a ternary pollutant-cyclodextrin-iron complex, capable, when using modified-Fenton treatments such as EF for disposal of soil extract solutions, of directing the hydroxyl radicals towards reaction with the pollutant, minimizing the detrimental effect of non pollutant hydroxyl radical scavengers and increasing the pollutant elimination rate. Thus, it allows EF process not being limited by the presence of non-pollutant compounds coming from SW/SF step. Moreover, the advantages of EF process cumulated to the advantages of CDs could make this process clean and cost-effective since CD solution could be reused. Furthermore, CDs can also enhance the biodegradability of HOCs since these host/guest molecules can be used as carbon and/or energy source by some microorganisms. Therefore, a final biological step could be also considered after a modified-Fenton treatment of soil washed solution that would just enhance biodegradability of solution.

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CHAPTER 3

A New Analytical Method to Quantify Tween 80

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CHAPTER 3

The quantification of Tween 80 is needed to study its behavior (compared to cyclodextrins) in soil washing (SW) batch experiments containing the surfactant. However, no practical and sensitive enough quantification approach was proposed in the literature. A new method is then suggested in this chapter.

A new micelle-based method to quantify the Tween 80 surfactant for soil remediation

Abstract

In this study, we report a new and simple quantification method for monitoring of the surfactant Tween 80, which is widely employed to enhance remediation of contaminated soils. It is based on the enhancement of the TNS (6-(p-toluidino)naphthalene-2-sulfonic acid) fluorescence by formation of micelles between Tween 80 and TNS. The calibration curve ($F = 3.1123 (\pm 0.12) \times [\text{Tween } 80] + 7.1849 (\pm 2.33)$) fit well ($R^2 = 0.995$) the established linear model, with a detection limit of 0.13 μM and a quantification limit of 0.39 μM. This method showed significantly better performances in quantification of Tween 80 compared to the methods used so far, such as UV absorbance and Total Organic Carbon (TOC) measurements. In addition, we demonstrated that the measurements using this new technique are not impacted (3.5% maximum) by the presence of oxidation by-products (formed during oxidation by electro-Fenton process) or Hydrophobic Organic Compounds (HOCs) present in solution. Fluorescence measurements of soil washing solution with a real contaminated soil show almost no impact (4% maximum) on Tween 80-TNS micelle analysis. The analytical method proposed for Tween 80 analysis in this paper could replace conventional method currently used, because it is quite simple, highly sensitive and more selective.

Keywords: Micelle; Fluorescence quantification; Soil Organic Matter; Hydrophobic Organic Contaminants; By-products; Electro-Fenton.

3.1 Introduction

Surface-active agents or "surfactants" are amphiphilic molecules having both a hydrophobic (apolar group) tail and a hydrophilic (polar group) head (Rosen, 2004). When dissolved in water at low concentrations, surfactant molecules exist as monomers. When the concentration of surfactant increases, there is a critical concentration beyond which surfactant monomers start aggregating to form self-assemblies called micelles. The concentration at which micelle formation occurs is known as the Critical Micelle Concentration (CMC). CMC is a function of surfactant structure, composition of the solution, temperature, ionic strength, and the presence and types of organic additives in the solution (Edwards and Liu, 1994; Rosen, 2004). Depending on the nature of the hydrophilic group, surfactants can be classified as anionic, cationic, zwitterionic and non-ionic (Rosen, 2004).

Surfactants have several applications not only in soap and detergent industry but also in medicine, and as extracting agents in chemistry and in environmental technology, especially in soil and groundwater remediation (Mulligan et al., 2001; Paria, 2008).

In surfactant-enhanced remediation of contaminated soil, anionic and non-ionic surfactants are mostly used (Mulligan et al., 2001) especially to extract hydrophobic organic contaminants since they are strongly sorbed to soil. These pollutants are also known to be persistent in the environment and have potential toxicity effect (Gascon et al., 2013). Among the non-ionic surfactants, which are better solubilizing agents than anionics and cationics ones because of their lower CMC value, their lower sorption into soil (Paria, 2008) and their better cost-effectiveness (Alcantara et al., 2008; Wang and Keller 2008), Tween 80 is widely studied and employed (Gomez et al., 2010; Lopez-Vizcaino, 2012; Torres et al., 2012). Moreover, Tween 80 is getting more and more interesting since it can enhance also phytoremediation of contaminated soils (Gao et al. 2007). Furthermore, a more recent study shows the potential benefit of Tween 80 in contaminated soil bioremediation by enhancing the interaction between organic pollutants and bacteria (Zhang and Zhu 2012).

It seems to be very interesting to quantify the surfactant evolution during soil remediation process, in particular, its sorption into soil and its degradation during a bioremediation process or a water treatment of soil washing (SW)/Soil flushing (SF) solution containing such surfactant. Its ability to be reused during a SW/SF treatment

can then be studied. Several analytical methods already exist to quantify general surfactants like gas chromatography method, gravimetric method, flow-injection methods and dynamic surface tension detection (Yang and Synovec, 1996). These methods are based on the liquid–liquid extraction and have low sensitivity and selectivity (Yang et al., 2000). Few techniques were developed to quantify non-ionic surfactants and especially Tween 80. There are colorimetric measurements, cobalt thiocyanate active substances method and potassium picrate active substances method (Yeom et al., 1995), direct UV absorbance at a wavelength of 234 nm (Ko et al., 1998; Ko and Schlautman, 1998; Zhu and Zhou, 2008) and Total Organic Carbon (TOC) (Ahn et al., 2008). These methods are not satisfying when studying solutions containing other organic molecules (like organic pollutants, other Organic Matter (OM) or oxidation by-products) that can absorb in the same range of wavelength and whose carbon are also taken into account in TOC values. High performance liquid chromatography method (with derivatization of stationary phase) was also experimented using a complexing agent such as phenyl isocyanate to produce a UV active derivative upon reaction with the ethoxylate group. However, at low concentrations (below 0.6 g L^{-1}), the accuracy of measurement was unacceptable (Yeom et al., 1995). One other method was developed to quantify Tween 60 surfactant based on fluorescence enhancement of tetraphenylporphyrin (Yang et al., 2000). However, this method is not selective and efficient enough when it is applied for Tween 80 quantification. That is the reason why in this study, a new fluorimetric method to quantify Tween 80 is suggested. This is a quick, simple and highly sensitive method, which is more selective to Tween 80. It is based on the enhancement of the fluorescence of TNS by forming Tween 80-TNS micelles. According to the best of our knowledge, such a method has never been reported in the literature. TNS is a compound already used for cyclodextrins (host/guest molecules) quantification by fluorescence (Hanna et al., 2005).

In the present study, surfactant fluorimetric quantification is carried out. It is based on the theory about micelles formation and fluorescence detection. Comparisons were performed between UV absorbance, TOC and fluorescence measurement methods of Tween 80 during electro-Fenton (EF) degradation in the presence of a Hydrophobic Organic Compounds (HOCs) representative from the Polycyclic Aromatic Hydrocarbons (PAHs) family, namely phenanthrene (PHE). The EF process is an emerging advanced oxidation process that consists of a coupling between

electrochemistry and Fenton process (Eq. 3.1) since the Fenton's reagent is electrochemically *in situ* generated (Oturan, 2000).

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO^- + {}^{\bullet}OH \qquad (3.1)$$

EF process appears to be a good alternative technique compared to classical chemical Fenton process. It permits to minimize the use of H_2O_2 reagent that is generated *in-situ* and continuous regeneration of soluble iron (Fe^{2+}, Fe^{3+}, or iron oxides) from a catalytic amount added initially to the solution (Sirés et al., 2007) if needed.

Since the fluorescence measurements of this study are done in the humic acid-like region (Chen et al., 2003), it is also interesting to study the impact on fluorescence of Soil Organic Matter (SOM) extracted during a SW process in the presence of Tween 80. Figure 3.1 schematizes the main objectives of the present study.

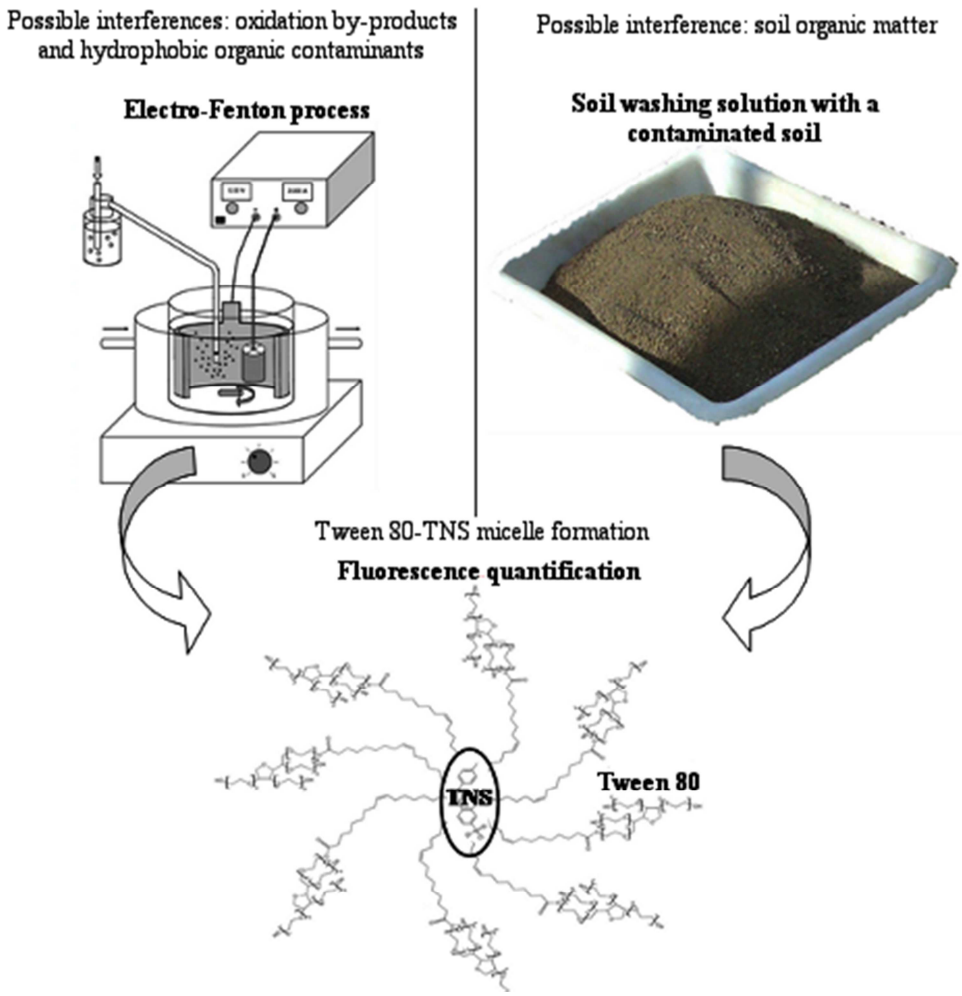

Fig. 3.1. *Schematic representation of possible interferences studied on Tween 80 quantification by fluorescence spectroscopy in the presence of TNS.*

3.2 Materials and methods

3.2.1 Chemicals

Tween 80 (polyoxyethylene (20) sorbitan monooleate; $C_{64}H_{24}O_{26}$; Molar weight: 1310 g mol^{-1}), TNS (6-(p-toluidino)naphthalene-2-sulfonic acid sodium), PHE (> 99.5%), methanol (> 99.9%, analytical grade) and sodium sulfate were purchased from Aldrich (USA). Heptahydrated ferrous sulfate ($FeSO_4$•$7H_2O$), and sulfuric acid were supplied by Acros (USA) at analytical grade. In all experiments, deionised water from a Millipore Simplicity 185 (resistivity > 18 MΩ cm) system was used.

3.2.2 Oxidation treatment

EF experiments were performed at room temperature (22 ± 1°C), in a 0.40 L undivided glass electrochemical reactor at current controlled conditions. The cathode was a 150 cm^2 carbon-felt piece (Carbone-Lorraine, France). The anode was a 5 cm height cylindrical (i.d. = 3 cm) Platinum (Pt) grid, which is centred in the cell and surrounded by cathode covering the inner wall of the cell. An inert electrolyte (Na_2SO_4 at 0.150 M) was added to the medium. Since too much foam is formed during bubbling system, the solutions containing Tween 80 were not saturated with O_2. The electrochemical cell is monitored by a power supply HAMEG 7042-5 (Germany) and applied current was set to 1000 mA. Solutions were stirred continuously by a magnetic stirrer. A heat exchanger system was used to keep the solution at constant room temperature by using fresh water. The pH of initial solutions was set at the optimal value of 3.0 (± 0.1) by the addition of aqueous H_2SO_4 (1 M) solution. In these experiments $FeSO_4$•$7H_2O$ was added at catalytic amount (0.2 mM). Tween 80 (750 mg L^{-1}) was used in the presence of PHE in excess (17 mg L^{-1} initially).

3.2.3 SW process

The polluted soil was sampled from a PAHs and aliphatic hydrocarbons contaminated site. Before its utilization, the soil was sieved under 2 mm and homogenized by a sample divider (Retsch, Germany). The soil has the following particle size distribution: clay (< 2 μm): 19.7%, fine silt (2-20 μm): 23.3%, coarse silt (20-50 μm): 7.5%, fine sand (50-200 μm): 12.3%, coarse sand (200-2000 μm): 37.1%. It has the other following characteristics: pH (water): 8.3, OM content: 4.71%, total PAHs (16

compounds) content: 1,090 mg kg^{-1}, aliphatic hydrocarbons (C10-C40) content: 850 mg kg^{-1}.

The SW experiment was performed in a 500 mL bottle at a soil/liquid ratio equal to 10% (40 g/ 400 mL). A Tween 80 solution (10 g L^{-1}) was used and the mixture was rotated in a Rotoshake RS12 (Gerhardt, Germany) at 10 rotations per minute for 24 h. Then the particles settled for 12 h and the supernatant was filtered with a 0.7 μm glass microfiber filter (Whatman GF/F, England). The supernatant was diluted 15,000 times, and analyzed by excitation-emission matrix fluorescence spectroscopy, with or without adding TNS compound (1.7×10^{-6} M).

3.2.4 Analytical procedures

All absorbance determinations were carried out with a Perkin Elmer (USA) Lambda 10 UV/VIS spectrometer. Calibration curve of Tween 80 was performed at a wavelength of 245 nm that is found to be the optimal wavelength giving the maximal absorbance intensity.

The TOC values were determined by catalytic oxidation using a Shimadzu (Japan) V_{CSH} TOC analyser. Calibrations were performed by using the potassium hydrogen phthalate solutions as standard. All samples were acidified to pH 2 with H_3PO_4 (25%) to remove inorganic carbon. The injection volumes were 50 µL. All samples values are given with a coefficient of variance below to 2%.

The Tween 80 concentration was proposed to be determined with fluorescence (Kontron Instruments SFM 25 spectrofluorometer, USA) by analysing the Tween 80-TNS micelles formed with excitation and emission wavelength of 318 nm and 428 nm respectively. Since TNS is photosensitive, TNS and the diluted samples are therefore stored in dark conditions at the room temperature (22 ± 1 °C).

In the aim to study the possible interferences of PHE, its oxidation by-products and SOM, excitation-emission matrix fluorescence spectroscopy analyses were performed. The samples were first diluted with ultra-pure water at the same dilution factor to be comparable. Fluorescence spectra of the sample were measured using a Shimadzu (Japan) RF-5301 PC spectrofluorophotometer. Spectra were collected with subsequent scanning of emission spectra from 220 to 550 nm by varying the excitation wavelength

from 220 to 450 nm at 12 nm increments using high sensitivity. The software Panorama Fluorescence 2.1 was employed for handling excitation-emission matrix data.

The PHE degradation was followed by reversed phase with a high performance liquid chromatography coupled with a diode array detector from Dionex (USA). The detection was carried out at the wavelength of 249 nm. The mobile phase was a mixture of water/methanol (22:78 v/v) at the flow rate of 0.8 mL min^{-1} (isocratic mode), giving a 6.9 min of retention time for PHE. A reversed-phase C-18 end capped column (Purospher®, Merck, Germany) placed in an oven set at 40°C was used.

3.3 Results and discussion

3.3.1 Tween 80 quantification

3.3.1.1 Theory

It is assumed that the surfactant does not complex with (*i.e.,* solubilize) the substrate TNS, except when the former is in the form of micelles and that complexation between the substrate and the micelle is in a 1:1 stoichiometric ratio.

To establish a relation between fluorescence measured and the concentration of surfactant in solution, one can start from the partitioning model of the organic compounds between micelles and monomeric solution, which quantify the surfactant solubilization. The micelle phase/aqueous phase partition coefficient (K_{mw}) is based on the mole fraction ratios, *i.e.* the ratio of mole fraction of the compound in the micellar pseudophase (X_m) to the mole fraction of the compound in the aqueous pseudophase (X_a). K_{mw} also can be defined as (Paria 2008):

$$K_{mw} = \frac{X_m}{X_a} = \frac{C_m}{C_a} = \frac{S - S_{CMC}}{(C_S - CMC + S - S_{CMC})(S_{CMC} V_W)} \qquad (3.2)$$

where C_m is the concentration of the hydrophobic solute in the micelle, C_a is its concentration in the aqueous phase, CMC is the critical micelle concentration, S is the apparent solubility of organic compound at surfactant concentration C_S (C_S > CMC), S_{CMC} is the apparent solubility of the organic compound at the CMC, V_w is the molar volume of water, *i.e.*, 1.805 x 10^{-3} L mol^{-1} at 22°C.

As the concentration of surfactant and TNS are low, the following equations (3.3) and (3.4) can be written (Rouessac et al., 2004):

$$F = kI_0 S \quad (3.3)$$

$$F_0 = kI_0 S_{CMC} \quad (3.4)$$

where F and F_0 are the emission fluorescence referred to S and S_{CMC} respectively, k is a constant (depending on the equipment and the compounds studied) and I_0 is the radiation intensity of excitation.

The fluorescence of the surfactant (Tween 80) alone is considered to be equal to zero (data not shown).

By replacing relations 3.3 and 3.4 in equation 3.2 we can get a linear equation (3.5) between F and C_s:

$$F = a \times C_S + b \quad (3.5)$$

with $a = \dfrac{F_0 V_W K_{mw} kI_0}{kI_0 - K_{mw} F_0 V_W}$ and $b = F_0 - \dfrac{F_0 V_W K_{mw} kI_0}{kI_0 - K_{mw} F_0 V_W} CMC$

3.3.1.2 Calibration curve

Different excitation and emission wavelengths were investigated out with the spectrofluorometer and finally the highest sensibility was obtained at 318 nm for excitation and 428 nm for emission. Each sample was diluted in TNS (5 x 10^{-5} M). By plotting the emission fluorescence as a function of the Tween 80 concentration, a good R^2 value was reached (Fig. 3.2).

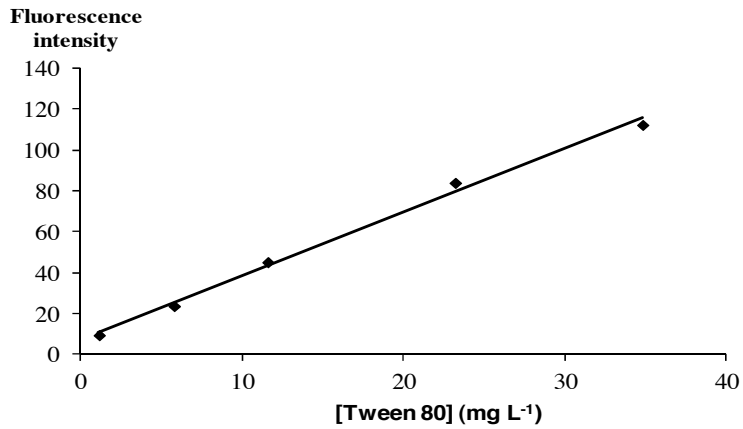

Fig. 3.2. *Calibration curve of Tween 80 determined by fluorescence (Excitation-Emission: 318-428 nm) in the presence of TNS (5 × 10^{-5} M),*

The suggested linear model between fluorescence measurement of Tween 80-TNS micelles and Tween 80 concentration fit well (R^2 = 0.995) the experimental calibration curve (F = 3.1123 (± 0.12) × [Tween 80] + 7.1849 (± 2.33)).

According to the good fitting (R^2 = 0.995) of the calibration curve, this fluorimetric method was then used in the following experiments. As expected, the linear curve does not intercept the ordinate axis. According to the model, this value corresponds to the fluorescence of TNS alone and depends also on the CMC and other parameters described above. It is noticed that the calibration curve is also relevant for Tween 80 concentration below the CMC (15.7 mg L^{-1} (Rosas et al., 2011)) in contrast to the assumption considered in the model. It was mentioned by several authors that only few surfactant monomers (below CMC) are able to slightly solubilize hydrophobic organic molecules (Edwards and Liu, 1994; Deshpande et al., 1999).

The fluorimetric method provided, for Tween 80 analysis, a detection limit of 0.13 µM (0.10 mg C L^{-1}) and a quantification limit of 0.39 µM (0.30 mg C L^{-1}). Comparatively, the detection limit and the quantification limit were 3.18 µM (2.44 mg C L^{-1}) and 9.64 µM (7.40 mg C L^{-1}) respectively for UV absorption method and 0.27 µM (0.21 mg C L^{-1}) and 0.85 µM (0.65 mg C L^{-1}) respectively for TOC method. The detection limit and quantification limit were calculated according to Zhu et al. (2012) and Oliveri and Di Bella (2011) respectively. These results highlight clearly the advantage of the proposed fluorimetric method.

3.3.2 Comparison between different methods for Tween 80 quantification during oxidative degradation

Figure 3.3 illustrates the UV-absorbance spectra of Tween 80, PHE and Tween 80 in the presence of PHE. It highlights the overlap between each spectrum, which restrains the use of this method to quantify Tween 80. The same behavior was observed during Tween 80 degradation alone, since some oxidation by-products absorb in the same range of wavelength (data not shown). For that reason, UV absorbance was not selected for measurement in EF degradation.

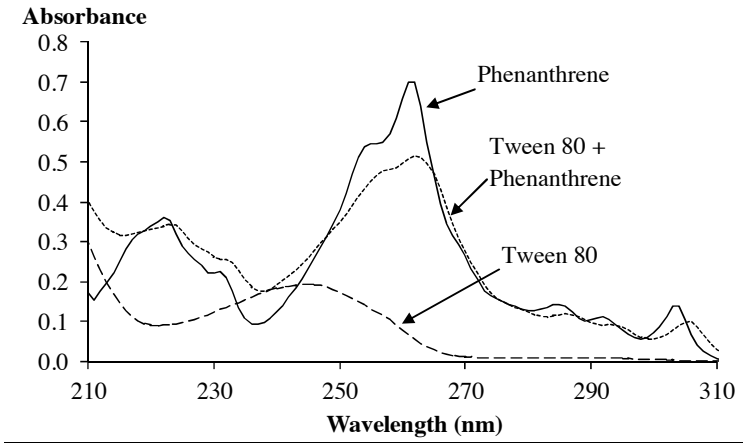

Fig. 3.3. *UV absorbance spectra of Tween 80 (750 mg L^{-1}), PHE (2 mg L^{-1}), and Tween 80 (750 mg L^{-1}) with PHE (2 mg L^{-1}).*

Figure 3.4 represents excitation-emission matrix spectra of EF treatment of PHE (2 mg L^{-1}) with Tween 80 (750 mg L^{-1}) initial solution at first before treatment and then after 2 hours of treatment with or without TNS. The more the colour is warm, the higher the fluorescence intensity is. It can still be considered that Tween 80 has no fluorescence without the presence of TNS, and that the fluorescence of TNS alone is negligible. It is obvious that there is almost no impact of PHE and oxidation by-products on fluorescence of TNS-Tween 80 complex. Several other samples were analyzed during all the treatment and the percentages of fluorescence of PHE and oxidation by-products were not more than 3.5% compared to fluorescence of TNS-Tween 80 complex.

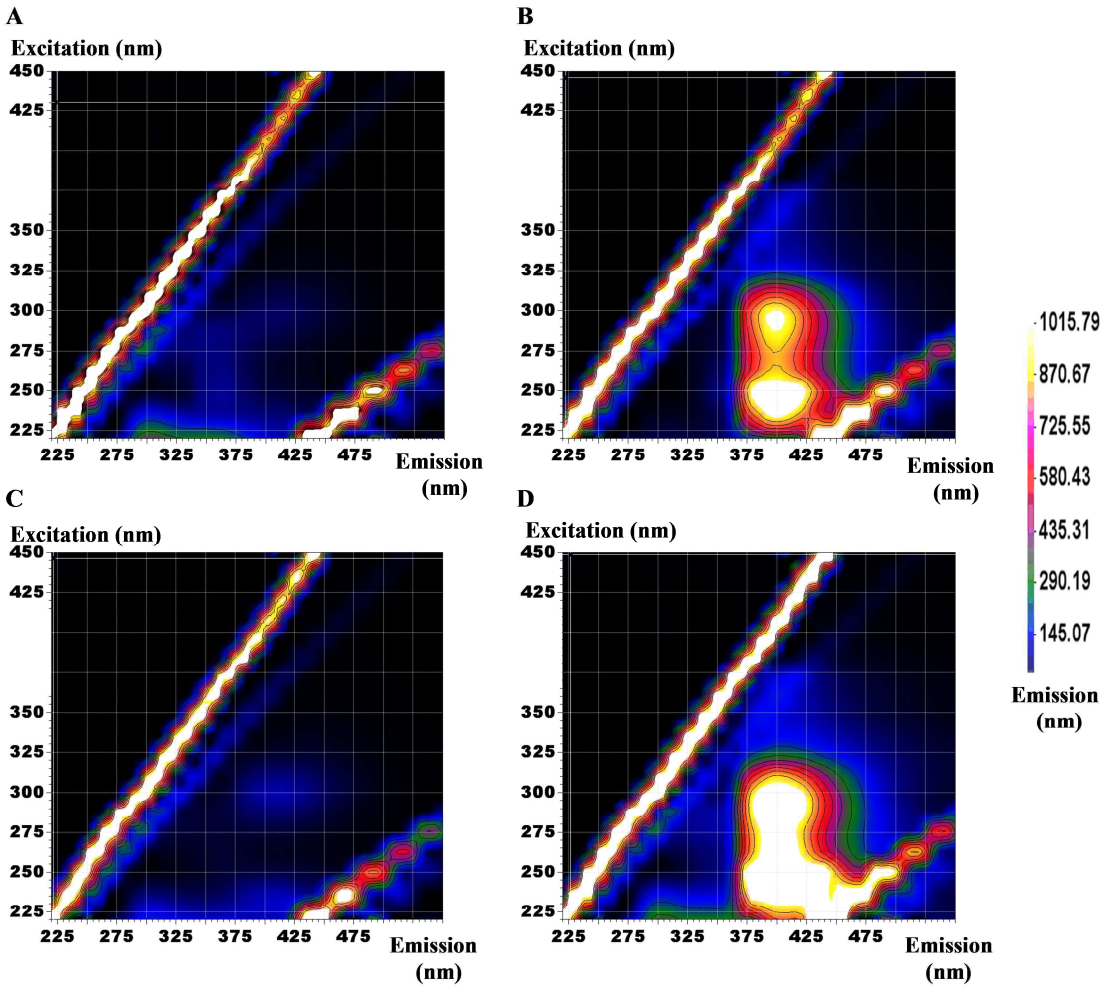

Fig. 3.4. *Excitation-emission matrix spectra of EF treatment of PHE (2 mg L^{-1}) with Tween 80 (750 mg L^{-1}) initial solution at initial treatment (A and B) and after 2 hours of treatment (C and D) without TNS (A and C) and with TNS (B and D). [Fe^{2+}] = 0.2 mM, [Na_2SO_4] = 0.150 M, V = 400 mL, pH 3, Pt anode and I = 1000 mA.*

Figure 3.5 depicts the EF degradation of Tween 80 in the presence of PHE as a hydrophobic organic contaminant representative. Its oxidative degradation during EF treatment was followed by TOC and fluorescence measurements. Since TOC values take into account all the carbons present in the solution, all the Tween 80, PHE and oxidation by-products are considered, leading to a higher value compared to fluorescence data. It is also important to note that the degradation of Tween 80 quantified by fluorescence can follow a pseudo-first order kinetic model (k_{app} = 0.0056 min^{-1}; R^2 = 0.971), which is also notified with PHE degradation (k_{app} = 0.016 min^{-1}; R^2 = 0.994) (Fig. 3.5). This kinetics model was largely observed in oxidative degradation studies in which hydroxyl radicals are involved (Brillas et al., 2009). This can also ensure the quality of the fluorescence measurements.

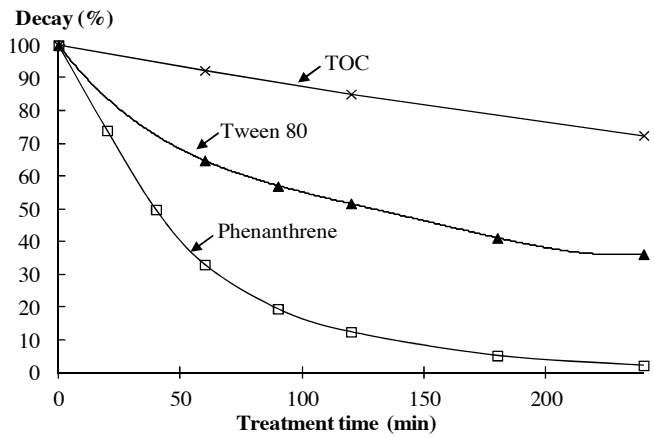

Fig. 3.5. *TOC values (×) and degradation kinetic of Tween 80 (750 mg L^{-1}) (▲) and PHE (17 mg L^{-1}) (□) during EF treatment. [Fe^{2+}] = 0.2 mM, [Na_2SO_4] = 0.150 M, V = 400 mL, pH 3, Pt anode and I = 1000 mA.*

3.3.3 Interference of soil OM on fluorescence detection

It is demonstrated that humic acid-like substances show fluorescence intensity in the following region: excitation: 250-360 nm/emission: 380-480 nm (Chen et al., 2003). Since humic substances represent generally 70% to 90% of the soil OM, their contribution to fluorescence signal should be assessed. Figure 3.6 depicts excitation-emission matrix spectra of SW solution from a real contaminated soil. The fluorescence of SW solution without TNS was much lower than in the presence of TNS and represents only 4.0% of the fluorescence of Tween 80-TNS mixture. By still considering that Tween 80 and TNS have a negligible fluorescence if they are not in the same solution, it can be assumed that SOM do not interfere significantly on Tween 80-TNS complex fluorescence in the operated diluted ratio. This is probably due to the high sensitivity of the method.

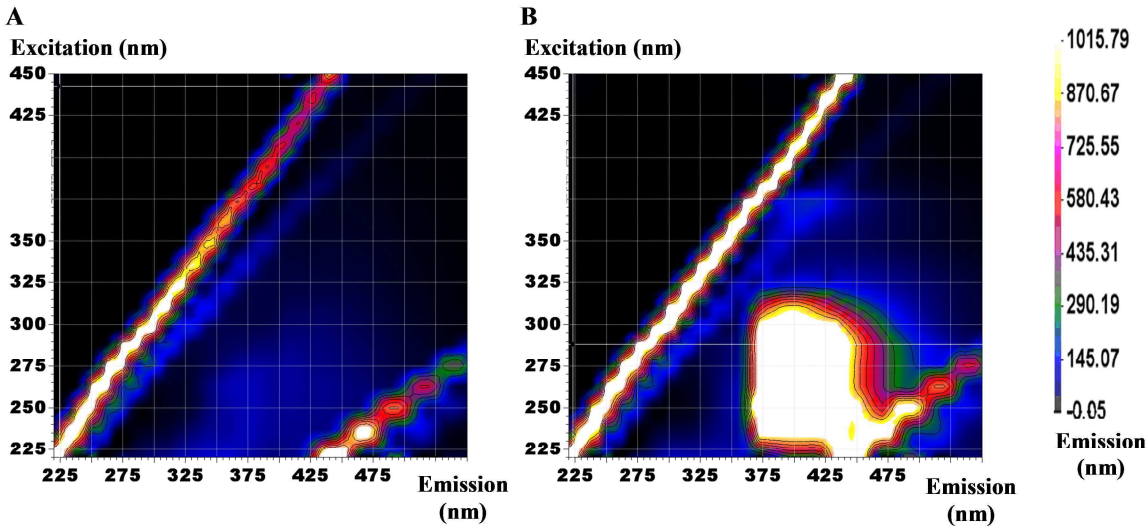

Fig. 3.6. *Excitation-emission matrix spectra of SW solution by using Tween 80 (10 g L^{-1}) without the addition of TNS (A) and in the presence of TNS (1.7×10^{-6} M) (B). OM content: 4.71%, total PAHs content (16 PAHs): 1,090 mg kg^{-1}, aliphatic hydrocarbons (C10-C40) content: 850 mg kg^{-1}, pH of SW solution: 8.0, soil/liquid ratio: 40 g/400 mL, contact time: 24 h.*

3.4 Conclusions

For this new Tween 80 fluorimetric analysis method, with an excitation-emission wavelength of 318-428 nm, the suggested linear model between fluorescence measurement of Tween 80-TNS micelles and Tween 80 concentration fit well (R^2 = 0.995) the experimental calibration curve (F = 3.1123 (± 0.12) × [Tween 80] + 7.1849 (± 2.33)). This method has a detection limit of 0.13 μM and a quantification limit of 0.39 μM. The UV absorbance and TOC analysis have demonstrated much lower performance and selectivity than the fluorescence quantification proposed when it is aimed to follow the decay of Tween 80. Such lower performance is due to interference with other organic compounds present in solution (oxidation by-products, PHE). The degradation curve of Tween 80 during EF process determined by the fluorescence method follows the pseudo-first order kinetic model (k_{app} = 0.0056 min^{-1}; R^2 = 0.971), even in the presence of hydrophobic organic compounds and oxidation by-products. The fluorescence intensity of PHE and by-products are insignificant in this range of concentration (< 3.5%). SOM has a negligible impact (< 4.0%) due to the operated diluted ratio and the high sensitivity of this method. These results validate the performance of the fluorescence quantification of Tween 80 surfactant by using TNS compound.

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CHAPTER 4

Study of Soil Washing Recycling Possibilities

This chapter has been accepted for publication as:

Mousset, E., Oturan, N., van Hullebusch, E. D., Guibaud, G., Esposito, G., Oturan, M. A. (2014). Influence of solubilizing agents (cyclodextrin or surfactant) on phenanthrene degradation by electro-Fenton process – study of soil washing recycling possibilities and environmental impact. *Water Research*, 48, 306-316

CHAPTER 4

One of the aims of the innovative integrated process suggested in this work is the possibility to oxidize the pollutant by minimizing the degradation of solubilizing agent in order to reuse it for soil washing (SW)/flushing (SF) processes. Thus, this possibility is studied in this chapter. Representative compounds from cyclodextrin and surfactant families are compared during an EF experiment containing a representative PAH.

The work in this chapter was partly presented during the summer school that was held in Naples (2011):

- E. Mousset, E. D. van Hullebusch, M. A. Oturan, J. Mouton, J-M. Riom, G. Guibaud, G. Esposito, Cyclodextrins enhanced remediation of soil polluted by hydrophobic organic pollutants and electro-Fenton treatment. Summer school: biological and thermal treatment of municipal solid waste, Naples (Italy), May, 2011. (http://www.iat.unina.it/summerschool/home.html).

Influence of solubilizing agents (cyclodextrin or surfactant) on phenanthrene degradation by electro-Fenton process – study of soil washing recycling possibilities and environmental impact

Abstract

One of the aims in soil washing (SW) treatment is to reuse the extracting agent and to remove the pollutant in the meantime. Thus, electro-Fenton (EF) degradations of synthetic SW solutions heavily loaded with phenanthrene (PHE) (Chemical Oxygen Demand (COD) from 1,400 ± 20 mg O_2 L^{-1} to 11,150 ± 160 mg O_2 L^{-1}) were suggested for the first time. Two solubilizing agents hydroxypropyl-beta-cyclodextrin (HPCD) and Tween 80 were chosen as cyclodextrin (CD) and surfactant representatives, respectively. In order to regenerate HPCD and to degrade the pollutant simultaneously, the following optimal parameters were determined: $[Fe^{2+}]$ = 0.05 mM (catalyst), I = 2000 mA, and natural solution pH (around 6), without any adjustment. Only 50% of Tween 80 (still higher than the Critical Micelle Concentration (CMC)) can be reused against 90% in the case of HPCD while PHE is completely degraded in the meantime, after only 180 min of treatment. This can be explained by the ternary complex formation (Fe^{2+}-HPCD-organic pollutant) (equilibrium constant K = 56 mM^{-1}) that allows $^{\bullet}OH$ to directly degrade the contaminant. This confirms that Fe^{2+} plays an important role as a catalyst since it can promote formation of hydroxyl radicals near the pollutant and minimize HPCD degradation. After 2 h of treatment, HPCD/PHE solution got better biodegradability (BOD_5/COD = 0.1) and lower toxicity (80% inhibition of luminescence of *Vibrio fischeri* bacteria) than Tween 80/PHE (BOD_5/COD = 0.08; 99% inhibition of *V. fischeri* bacteria). According to these data, HPCD employed in this suggested integrated approach gave promising results in order to be reused whereas the pollutant is degraded in the meanwhile.

Keywords: PAHs; HPCD; Tween 80; Advanced Oxidation Processes; Electro-Fenton; Recycling; Bioassays

4.1 Introduction

The removal of hazardous polycyclic aromatic hydrocarbons (PAHs), which are strongly sorbed into soil, is a common concern. As an alternative to slow processes like biological treatments (enhanced natural attenuation…) or costly and soil denaturing processes like thermal treatments, soil washing (SW) and soil flushing (SF) appear to be reliable techniques (Colombano et al., 2010). Surfactants are traditionally employed to enhance such processes. These extracting agents have a hydrophilic head and a hydrophobic tail that allow solubilizing Hydrophobic Organic Compounds (HOCs) through micelles formation. The minimal concentration of surfactant at which the micelle formation occurs is called the Critical Micelle Concentration (CMC). Among the cationic, anionic, zwitterionic and non-ionic surfactants, the latter ones are the most efficient compounds, since their CMC and their sorption capacity into soil are much lower (Paria, 2008). Among these non-ionic surfactants, Tween 80 is typically used in SW/SF techniques. Widely used in other industrial applications (pharmaceutical formulations, analysis, …) (Del Valle, 2004), natural and semi-natural products like cyclodextrin (CD) have been proposed as another option in soil remediation field by several authors (Brusseau et al., 1994; Boving and Brusseau, 2000; Chatain et al., 2004; Viglianti et al., 2006; Petitgirard et al., 2009). These host/guest molecules have a toroidal shape with a hydrophilic external shape and a hydrophobic internal cavity whose dimensions vary according to the number of glucopyranose units (Szejtli, 1998). Among the CD, HPCD, which has seven glucopyranose units, is one of the most cost-efficient one to complex with HOCs from soil (Mousset et al. 2014). Compared to surfactant Tween 80, there is no foam formation, cyclodextrins hardly sorb to soil (Zeng et al., 2006) and are non-toxic (Rosas et al., 2011). Some properties of Tween 80 and HPCD are described in Table 4.1.

An effective combined treatment is required to treat SW and SF solutions that are usually heavily loaded. In order to reduce the cost of the process, this technique should also be able to degrade pollutants by saving and reusing the extracting agent in the meantime. Some treatments have been suggested in the presence of CDs. Heterogeneous photocatalysis process with TiO_2/UV has shown negative results since the CD is degraded leading consequently to inhibition of pollutant degradation (Petitgirard et al., 2009). An air stripping treatment with granular activated carbon has been suggested at field scale to treat tetrachloroethene (Tick et al., 2003). This method

works only with volatile organic compounds (VOCs). Another integrated treatment is a liquid-liquid extraction with natural colza oil allowing the regeneration of CDs by concentrating the PAHs in the organic phase with a small loss of carrier and fast kinetics of PAHs transfer (Petitgirard et al., 2009). However, an additional treatment is required to degrade the pollutant in colza oil solution. An electrochemical process was suggested to treat the exhausted washing solution in order to destroy the pollutant and to recycle Tween 80 (Gómez et al., 2010a) and HPCD (Gómez et al., 2010b). This technique consists of adding an electrolyte (NaCl or KBr) in solution and the Cl^- ions (or Br^-) allow generating Cl_2 (or Br_2) at the graphite anode. OH^- are formed at the graphite cathode and can then react with Cl_2 (or Br_2) to generate hypochlorite ion (ClO^-) (or BrO^-) that can oxidize organic pollutants (Cameselle et al. 2005). This process is different than an electrochemical advanced oxidation process (EAOP) since the latter one can produce hydroxyl radicals ($^{\bullet}OH$) that are stronger oxidizing agent. In Gomez et al. (2010a, 2010b) studies, the pollutant has been degraded only after 1 day and 3 days with HPCD and Tween 80, respectively. Another study suggests a SW process combined to activated carbon to remove pollutant from supernatant and recover the surfactant such as Tween 80 (Ahn et al., 2008). However activated carbon only permits the pollutant to be adsorbed but not to be degraded and then the carbon needs to be regenerated and the pollutant treated.

Besides, advanced oxidation processes (AOPs) that involve the i*n situ* generation of $^{\bullet}OH$ ($E°$ ($^{\bullet}OH/H_2O$) = 2.80 V/SHE), the second strongest oxidizing agent after fluorine, have been developed in the last two decades for wastewater treatments. These non-selective radicals have the ability to degrade any organic molecules present in the aqueous solution until total mineralization and especially the aromatic ones by an electrophilic addition to non-saturated bonds with kinetic constant values as high as 10^8 – 10^{10} M^{-1} s^{-1} (Cañizares et al., 2008; Brillas et al., 2009; Oturan et al., 2009; Panizza and Cerisola, 2009).

Well-known AOPs have been studied using Fenton's reagent (a mixture of H_2O_2 and Fe^{2+} ion; Eq. (4.1)) in the presence of CDs and organic pollutants have shown promising conclusions, since CDs can form a ternary complex with iron and the hydrophobic pollutant, which allows effective direct $^{\bullet}OH$ radical reaction towards contaminants (Lindsey et al., 2003; Zheng and Tarr, 2004, 2006; Hanna et al., 2005; Veignie et al., 2009).

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO^- + {}^{\bullet}OH \quad (4.1)$$

In this context, the electro-Fenton (EF) process, which consists of electrocatalytically assisted Fenton‘s reaction (Eq. 4.1), appears to be a promising way to treat SW solutions. Compared to classical chemical Fenton process, it permits to minimize the use of reagent since H_2O_2 is electrogenerated *in-situ* following the Eq. (4.2); and a catalytic amount of any soluble iron salt (Fe^{2+}, Fe^{3+}, or iron oxides) is sufficient to turn up the process, because ferrous iron is continuously electro-regenerated at the cathode (Oturan, 2000; Brillas et al., 2009; Sirés et al., 2010; Sirés and Brillas, 2012) following Eq. (4.3). Thanks to these enhancements, higher degradation rate and mineralization degree of organic pollutants and no sludge production are observed. Moreover, in contrast to classical EF process (which is optimal at pH 3), no pH adjustment would be necessary by taking into account the formation of the ternary complex (Sun and Pignatello, 1992, 1993; Lindsey et al., 2003) avoiding the precipitation of ferric iron at pH>3.

$$O_2 + 2\,H^+ + 2\,e^- \rightarrow H_2O_2 \quad (4.2)$$

$$Fe^{3+} + e^- \rightarrow Fe^{2+} \quad (4.3)$$

The continuous formation of the Fenton's reagent from Eqs. (4.2) and (4.3) allows continuous production of ${}^{\bullet}OH$, a very powerful oxidant, from Eq. (4.1). This radical is able to oxidize any organics present in the aqueous solution until total mineralization (Cañizares et al., 2008; Brillas et al., 2009; Oturan et al., 2009; Panizza and Cerisola, 2009).

In this study, Tween 80 and HPCD are chosen as representative cost-effective surfactant (Alcántara et al., 2008) and CD (Mousset et al., 2014), respectively. Phenanthrene (PHE), which is listed among the 16 hazardous PAHs by the environmental protection agency of United States (USEPA), was selected as model pollutant. PHE has three benzenic rings with a water-solubility about 1 mg L^{-1}. Its octanol-water partition coefficient (Log K_{ow}) is around 4.57 and its organic carbon water partition coefficient (K_{OC}) is around 4.18 L kg^{-1}, which makes it hydrophobic and strongly bounded to soil. PHE has low volatilization ability with a low vapor pressure (0.091 Pa at 20°C) (INERIS, 2010). According to the best of our knowledge, it is the first time that EF degradations of synthetic SW solutions heavily loaded with PHE and Tween 80 or HPCD were monitored and the environmental impact studied. Preliminary experiments

compare the toxicity, biodegradability and absolute rate constants of the reaction between $^{\bullet}OH$ and Tween 80 and HPCD. Then EF experiments on synthetic SW or SF solutions were performed to study the operating conditions for PHE degradation and the possibility to reuse HPCD or Tween 80. Much attention was focused on the effect of the catalyst (Fe^{2+}) during the degradation process. pH of initial solution was also set at near neutral value after studying the ternary complex model in which Fe^{2+} can play an important role. The impact of EF degradation on effluents toxicity and biodegradability was finally also assessed.

4.2 Materials and Methods

4.2.1 Chemicals

PHE (>99.5%), methanol (>99.9%, HPLC grade), sodium sulphate, 6-(P-toluidino)naphthalene-2-sulphonic acid sodium (TNS) and Tween 80 (polyoxyethylene (20) sorbitan monooleate) were purchased from Aldrich. Heptahydrated ferrous sulphate ($FeSO_4 \bullet 7H_2O$), sulphuric acid, 4-hydroxybenzoic acid and potassium dihydrogen phosphate (KH_2PO_4) were supplied by Acros at analytical grade. N-Allylthiourea (98%) was supplied by Alfa Aesar. HPCD was provided by Xi'an Taima Biological Engineering Company (China). Sodium phosphate dibasic (Na_2HPO_4), ammonium chloride (NH_4Cl), heptahydrated magnesium sulphate ($MgSO_4 \bullet 7H_2O$), dehydrated calcium chloride ($CaCl_2 \bullet 2H_2O$), D(+)-Glucose$\bullet H_2O$ were purchased from Merck at analytical grade. Analytical reagents like dipotassium phosphate (K_2HPO_4), hexahydrated ferric chloride ($FeCl_3 \bullet 6H_2O$) and NaOH were obtained from VWR. Potassium chloride (KCl) (>99.0%, Fluka) was also used. The carbon-felt electrode was a carbon Lorraine (France). Oxygen was supplied by compressed air system installed in the laboratory room. In all experiments, ultrapure water from a Millipore Simplicity 185 (resistivity > 18 MΩ cm) system was used.

4.2.2 Preparation of synthetic solutions

PHE was chosen as a PAH representative since no volatilization was observed compared to more water-soluble one such as naphthalene or fluorene in the presence of HPCD (10 g L^{-1}) or Tween 80 (data not shown). HPCD (10 g L^{-1} equivalent to 8 mM) or Tween 80 (0.75 g L^{-1} equivalent to 0.6 mM) was used to enhance the PHE solubilization and to mimic future soil extract solutions of washing or flushing

experiments. PHE was added in excess regarding the maximum solubilization ratio obtained with HPCD or Tween 80 agents. Thus, around 17 ± 0.2 mg L^{-1} of PHE concentration can be reached in both HPCD (10 g L^{-1}) and Tween 80 (0.75 g L^{-1}) solutions. In that way, it is assumed that all HPCD molecules or Tween 80 monomers were mobilized to complex or form micelles with PHE.

4.2.3 EF treatments

EF experiments were performed in a 0.40 L undivided, open and cylindrical glass electrochemical reactor at current controlled conditions (Fig. 4.1). The electrochemical cell was monitored by a power supply HAMEG 7042-5 (Germany). The working electrode (cathode) was a 150 cm^2 carbon-felt piece (Carbone-Lorraine, France), the counter electrode (anode) was a 5 cm height cylindrical (i.d. = 3 cm) platinum (Pt) grid, which was centered in the cell and surrounded by cathode covering the inner wall of the cell. An inert electrolyte (Na_2SO_4 at 150 mM) was added to the medium. Prior to each experiment containing HPCD, the solutions were saturated in O_2 (8.53 mg O_2 L^{-1} at 22°C) by supplying compressed air during 10 min at 0.25 L min^{-1}. Since too much foam was formed during bubbling system, the solutions containing Tween 80 were not bubbled with compressed air but the solutions were vigorously stirred as compensation in order to dissolved O_2 from ambient air. All the solutions were stirred continuously by magnetic stirrer. A heat exchanger system was provided to keep the solution at constant room temperature (22 °C ± 1) by using fresh water. The pH of initial solutions was set at the optimal value of 3.0 (± 0.1) by the addition of aqueous H_2SO_4 (1 M) solution, except in experiment at natural pH (around 6). In these experiments $FeSO_4 \bullet 7H_2O$ was also added at catalytic amounts as source of Fe^{2+} ion (catalyst). The pH changes were negligible during the electrolysis at pH 3.0 and it decreased slightly to 2.8 (± 0.1) at the end of experiments.

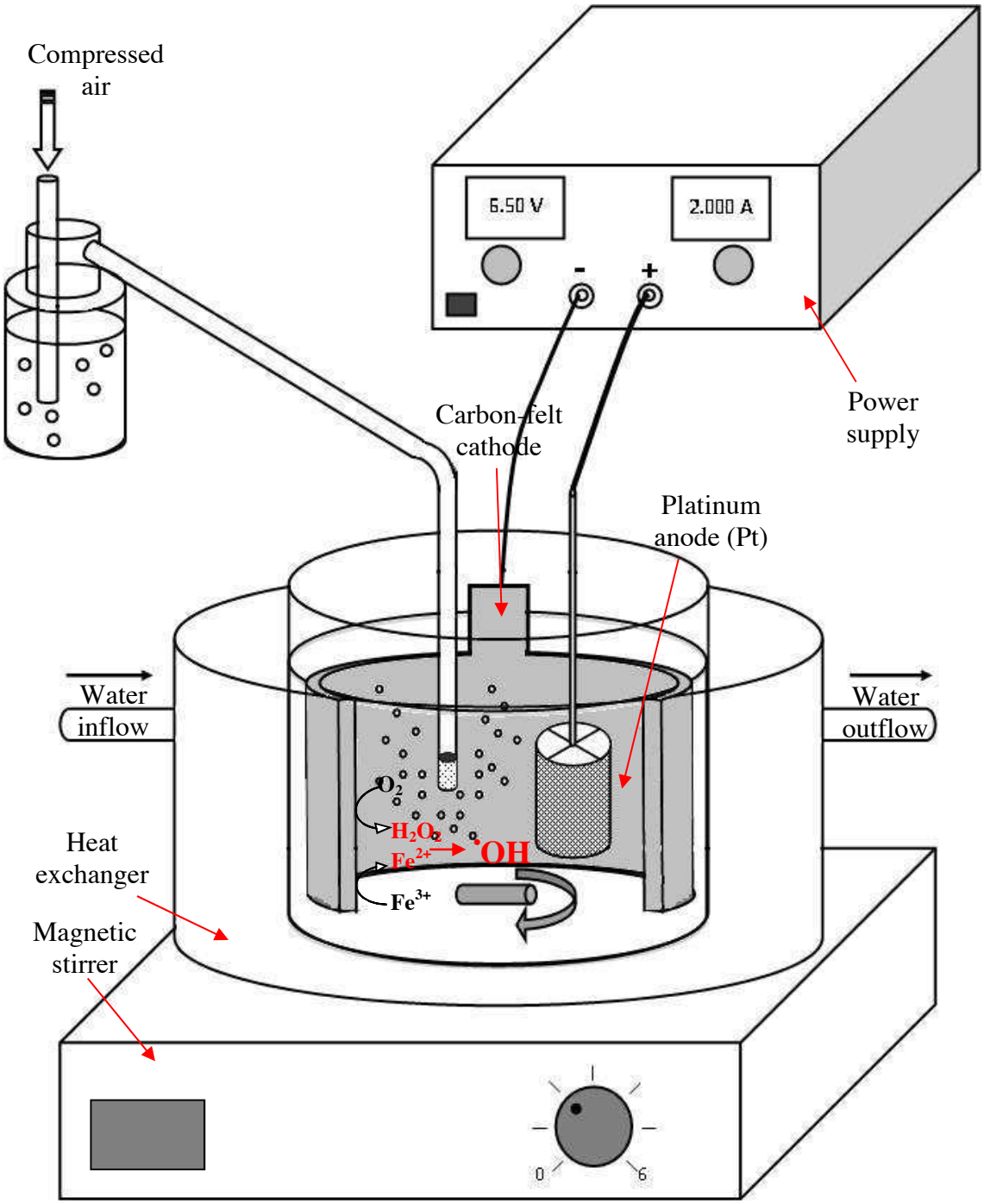

Fig. 4.1. *Schematic representation of EF process with Pt anode and carbon-felt cathode.*

4.2.4 Biodegradability assays

The biodegradability was given by the ratio between BOD_5 and COD. BOD_5 was determined by respirometric method (OECD 301F) with the OxiTop® control system (WTW). An aqueous solution containing a phosphate buffer solution (pH 7.2) and a saline solution was prepared according to Rodier et al. (2009). This solution was then saturated in oxygen. Bacteria extracted with KCl at 9 g L^{-1} (30 mL with 3 g of dried soil) and a IKA-MS1 mini-shaker (1800 rpm during 1 min) from uncontaminated soil were added just before adding the samples. All the samples were adjusted to circum-neutral pH. N-Allylthiourea (10 mg L^{-1}) was added to prevent nitrification during the 5 days of incubation. D(+)-Glucose•H_2O was used as a reference and a blank with Milli-Q water and the seed solution was prepared for each batch and taken into account for calculation. All the bottles containing the solutions were equipped with a rubber sleeve in which pure NaOH pellets were added to trap the CO_2 formed during biodegradation. The samples were incubated at 20°C (± 0.1) during 5 days in dark conditions. The BOD_5 measured in each blank, representing the Organic Matter (OM) extracted from soil and the endogenous respiration, was deduced from the BOD_5 of the samples. The BOD_5 of blanks were insignificant and caused no interferences. All the BOD_5 values were confirmed by measuring the difference of dissolved oxygen at the end and at the beginning of the experiment using the OxiTop® InoLab Oxi 730 (from WTW).

COD measurements were done by adding 2 mL of samples in COD cell test (Merck) and by heating at 148 °C during 2 h with a Spectroquant® TR 420 (Merck). COD analyses were accomplished by a photometric method requiring a Spectroquant® NOVA 60 (Merck) equipment. Since the H_2O_2 was produced *in situ* during EF experiment and the radicals formed during oxidative treatments had a limited lifetime, these oxidants caused no interferences during the BOD_5 or COD measurements.

4.2.5 Toxicity assays

Toxicity assays were performed by using Microtox® standard method (ISO 11348-3) with marine bacteria *Vibrio fischeri* from LUMIStock LCK-487 (Hach Lange). A Berthold Autolumat Plus LB 953 equipment was used. 22% of NaCl was added in each sample to ensure an osmotic protection for bacteria. Before each toxicity measurement, all the samples were adjusted with NaOH to circum-neutral pH and samples from EF

experiment were filtered with RC filters (0.2 μm) to remove iron precipitates (Dirany et al., 2011). In preliminary experiments, half-maximal effective concentration (EC_{50}), which was calculated by several dilutions, corresponded to the concentration that causes 50% inhibition of bioluminescence of bacteria. In each batch test, the inhibition percentage of a blank (sample without the compound studied) was also measured and used for percentage of inhibition calculation based on 15 min of exposure.

4.2.6 Analytical determinations

The HPCD concentration was determined by a fluorimetric technique based on enhancement of the fluorescence intensity of TNS, when they are complexed with the cyclodextrin (Hanna et al., 2005). This method allowed quantifying HPCD and slightly modified (hydroxylated) HPCD in the same time, since the non-polar HPCD cavity brought about a TNS fluorescence intensity enhancement until the CD cavity is cleaved by the degradation technique. A Kontron SFM 25 spectrofluorimeter was set out at 318 nm for excitation and 428 nm for emission. Each sample was diluted in TNS (3×10^{-6} M) with a dilution factor of 200. The fluorescence intensity of PHE was not significant in this range of wavelength and concentration (data not shown). Since TNS is photosensitive, TNS and the diluted samples were therefore stored in dark conditions. All the measurements were done at constant temperature (22 °C ± 1).

Tween 80 has been often determined by UV/VIS spectrophotometry around 235 nm (Ko et al., 1998a, 1998b; Zhu and Zhou, 2008). However, Tween 80 concentration is difficult to determine by this method during EF treatment, since some oxidation by-products absorb in the same range of wavelength. Thus, the Tween 80 concentration was measured by a new more specific method using fluorescence spectrometry (Kontron SFM 25 spectrofluorimeter) by quantifying the Tween 80-TNS micelles formed according to a previous study (Mousset et al., 2013).

In order to study the ternary complex formation (Fe^{2+}-HPCD-PHE) at pH 3 and at natural pH (around 6), all absorbance determinations were done with a Perkin Elmer Lambda 10 UV/VIS spectrometer. Blanks were prepared with ultrapure water and sodium sulphate (0.150 M) that was used as supporting electrolyte for EF treatment. The values of absorbance (A) were given in unit absorbance (UA).

The decay of PHE was followed by reversed phase (RP) liquid chromatography (HPLC) with an HPLC pump (model 426) from Alltech coupled with a diode array detector

UVD34OU from Dionex set to 249 nm. A RP C-18 end capped column (Purospher®, Merck) (5 µm, 25 cm x 4.6 mm (i.d.)) placed in an oven (TCC-100 from Dionex) and set at 40.0 °C was used. The mobile phase was a mixture of water/methanol (22:78 v/v) with a flow rate of 0.8 mL min^{-1} (isocratic mode). PHE exhibited a well-defined chromatographic pic at retention time of 6.9 min under these operating conditions. The injection volumes were 20 µL. To avoid difference of absorbance observed in the presence or absence of HPCD or surfactant during analysis (Wang and Brusseau, 1993), external standards are prepared in the presence of solubilizing agent.

The errors bars on each Figure are based on replicates that have been done for each experiment. When no bars are depicted, it means that the standard deviations were very low (< 2%).

4.3 Results and Discussion

4.3.1 Preliminary experiments

4.3.1.1 Determination of absolute rate constants for oxidation of HPCD and Tween 80 by hydroxyl radicals

Absolute rate constants of HPCD and Tween 80 degradation by $^{\bullet}OH$ during EF oxidation at pH 3 were determined by competition kinetics method. 4-hydroxybenzoic acid (HBA) was used as a well-known standard competitor whose absolute rate constant is 1.63 x 10^9 M^{-1} s^{-1} (Buxton et al., 1988). Having a very short life time, $^{\bullet}OH$ cannot be accumulated in the solution and thus a quasi-stationary state approximation can be made for its concentration (Dirany et al., 2010). This allows considering pseudo-first order reaction kinetics for oxidation of HPCD, Tween 80 and HBA by $^{\bullet}OH$. Therefore the straight lines obtained from kinetic analysis (Figs. 4.2a and 4.2b) allow determining the apparent rate constants (k_{app}) and then the absolute rate constant (k_{abs}) by the means of the Eq. (4.4) (Hanna et al., 2005):

$$k_{abs(S)} = k_{abs(HBA)} \times \frac{\ln(S_0 / S)}{\ln(HBA_0 / HBA)} = k_{abs(HBA)} \times \frac{k_{app(S)}}{k_{app(HBA)}} \qquad (4.4)$$

where S is the concentration of HPCD or Tween 80, S_0 and HBA_0 are the initial concentration of S and HBA, respectively.

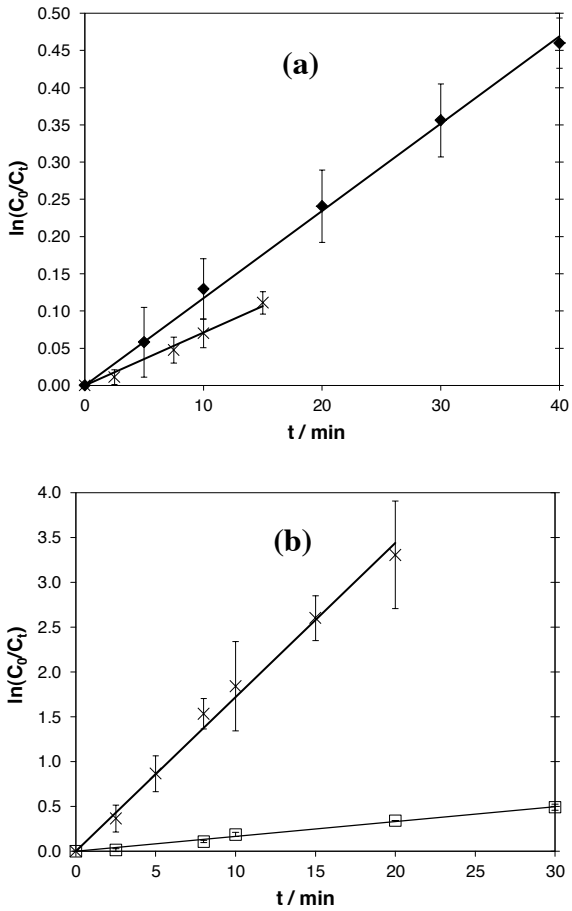

Fig. 4.2. *Absolute rate constants determined with competitive kinetic method using HBA (×) as standard competitor, HPCD (♦) (a) and Tween 80 (□) (b) as studied compounds during EF treatment; [HBA] = 0.25 mM, [HPCD] = 8 mM, [Tween 80] = 0.6 mM, [Fe^{2+}] = 0.2 mM, I = 1000 mA, [Na_2SO_4] = 0.150 M, V = 400 mL, pH 3 and Pt anode.*

The absolute rate constants values obtained in separated experiments for HPCD and Tween 80 were 2.6 x 10^9 and 1.6 x 10^8 M^{-1} s^{-1}, respectively (Table 4.1). The value obtained for HPCD is lower compared to the value reported by Hanna et al. (2005) (8.8 x 10^9 M^{-1} s^{-1}), probably because it is not exactly the same HPCD molecule with the same substitution degree. To the best of our knowledge, no values of absolute constant for Tween 80 degradation by $^{\bullet}OH$ are available in the literature. According to these rate constant values, HPCD reacts about sixteen times more quickly with $^{\bullet}OH$ than Tween 80.

4.3.1.2 Toxicity and biodegradability of HPCD and Tween 80 solutions

Considering the effective concentrations values at 50% inhibition (EC_{50}), HPCD is much less toxic (EC_{50} > 100 g L^{-1}) than Tween 80 surfactant (EC_{50} = 0.47 g L^{-1}) (Table

4.1), knowing that the percentage of inhibition is around 9% with HPCD at 100 g L^{-1}. Some studies also demonstrated that CDs present no toxicological effect or inhibition effect on soil microflora (Fava et al., 1998; Reid et al., 2000). According to this EC_{50} value, HPCD is clearly non-toxic and residual HPCD should cause no damage on soil microbial activity. However, residual Tween 80 begins to be too much toxic when the concentration in soil is higher than 0.5 g L^{-1}. Rosas et al. (2011) found that EC_{50} of Tween 80 (no data reported) is still higher than other nonionic surfactants like Triton X-100 (48 mg L^{-1}) or Brij 30 (0.5 mg L^{-1}). In some other studies Tween 80 was found less toxic to *Mycobacterium spp. KR2* than other surfactants following the rank: Tween 80 < Brij 35 < Brij 30 < linear alkane sulfonate (LAS) < tetradecyl trimethyl ammonium bromide (TDTMA) (Zhu and Zhou, 2008), meaning that Tween 80 is still useful in soil extraction experiments with surfactant.

According to BOD_5/COD ratios determined in this study (Table 4.1), it seems that Tween 80 (19%) has a low biodegradability and HPCD (0.04%) is non-biodegradable. At equivalent mass concentration, the BOD_5 value of Tween 80 (350 mg O_2/g Tween 80) is 875 times higher than that of HPCD (0.4 mg O_2/g HPCD). The biodegradability of glucose is about 87% in the same experimental conditions, which validates the protocol since glucose is known to be extremely biodegradable. Fava et al. (1998) found that HPCD is almost non-biodegradable in uncontaminated bioassays with standard biodegradability test (ISO 17556, 2001). However, it is biodegradable in real hydrocarbons contaminated soils, since the microflora of these soils is adapted to the xenobiotic compounds and especially the *Trichomonas* species seem to have strong degrading capacity toward the substituted CDs (Verstichel et al., 2004). Furthermore, CDs can be used as sole carbon and/or energy source by microorganisms from HOC contaminated soils (Fava et al., 1998, 2003; Bardi et al., 2000).

Table 4.1. Some properties of HPCD and Tween 80 as solubilizing agents.

Solubilizing agent	Formula	MW (g mol^{-1})	CMC (mg L^{-1})	EC_{50} (g L^{-1})[a]	Biodegradability[a]			k_{abs}[e] (M^{-1} s^{-1})
					BOD_5[d] (mg O_2 L^{-1})	COD_{tho}[d] (mg O_2 L^{-1})	BOD_5/COD_{exp} (%)	
Tween 80	$C_{64}H_{124}O_{26}$	1310	15.7[c]	0.47	35	200	19	(1.59 ± 1.53) x 10^8 (R^2 = 0.991)
HPCD[b]	$C_{48}H_{82}O_{37}$	1250	-	> 100	4	12,800	0.04	(2.60 ± 0.44) x 10^9 (R^2 = 0.998)

[a] calculated values

[b] considering a substitution degree of 0.3 (2 hydroxypropyl groups on HPCD external cavity)

[c] (Rosas et al., 2011).

[d] theoretical COD considering a concentration of HPCD and Tween 80 equal to 10 g L^{-1} and 0.1 g L^{-1}, respectively.

[e] calculated values; a 95% confidence interval was estimated in all cases by using the Student's t-distribution.

4.3.2 EF degradation of PHE

4.3.2.1 Optimum applied current intensity and catalyst concentration for PHE degradation

The effect of the current intensity and the Fe^{2+} concentration (as catalyst) on degradation kinetic of PHE were studied and shown in Fig. 4.3. Figure 4.3a illustrates an increasing kinetic of PHE degradation when the current intensity increases from 500 to 2000 mA.

Table 4.2 gives apparent rate constants values as function of applied current intensity assuming pseudo-first order kinetics model.

According to apparent rate constants values given in Table 4.2, the current intensity value of 2000 mA is the optimal value to degrade PHE in 100 min with a k_{app} of 0.046 min^{-1}. Application of higher current intensities would increase the extent of waste reactions, decreasing the process efficiency (Brillas et al., 2009). This optimal value is applied in all the following experiments and particularly experiments at different Fe^{2+} concentrations.

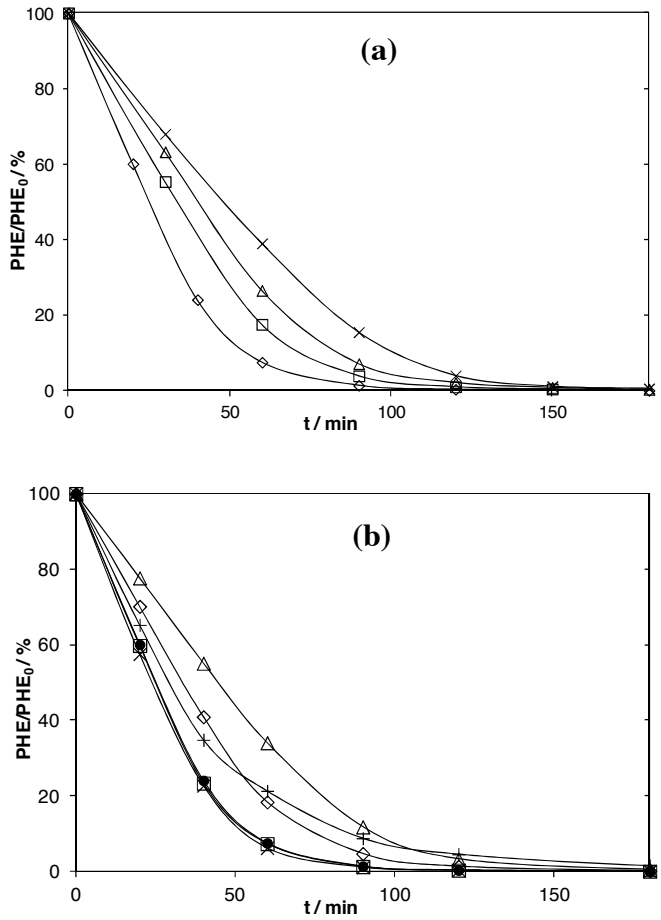

Fig. 4.3. *Effect of applied current intensity and Fe^{2+} concentration on EF degradation of 0.1 mM PHE. [HPCD] = 10 g L^{-1}, [Fe^{2+}] = 0.2 mM, [Na_2SO_4] = 0.150 M, V = 400 mL, pH 3 and Pt anode. (a) Current intensity (mA): 500 (×), 1000 (Δ), 1500 (□) and 2000 (◊). (b) Fe^{2+} concentration (mM): 0.05 (Δ), 0.1 (◊), 0.2 (●), 0.5 (□), 1 (x) and 10 (+).*

A large range of iron(II) concentration (from 0.05 mM to 10 mM) was also studied and results were shown in Fig. 4.3b. By still considering the degradation kinetic of PHE, an optimal catalyst (Fe^{2+}) concentration of 0.2 mM was found, thus confirming the results of numerous reports with EF (Brillas et al., 2009). At higher concentrations, the oxidant generation is progressively inhibited because of the greater extent of the following waste reaction (Brillas et al., 2009):

$$Fe^{2+} + {}^{\bullet}OH \rightarrow Fe^{3+} + HO^{-} \qquad (4.5)$$

Table 4.2. Apparent rate constants values (k_{app}) obtained for PHE degradation, assuming pseudo-first order kinetic model under different operating conditions of EF process.

	k_{app} (min^{-1})	R^2
EF – PHE+HPCD – 2 A – Different Fe^{2+} concentrations		
[Fe^{2+}] = 0.05 mM	0.027 ± 0.003	0.993
[Fe^{2+}] = 0.1 mM	0.034 ± 0.002	0.994
[Fe^{2+}] = 0.2 mM	0.046 ± 0.001	0.993
[Fe^{2+}] = 0.5 mM	0.046 ± 0.001	0.993
[Fe^{2+}] = 1 mM	0.047 ± 0.001	0.994
[Fe^{2+}] = 10 mM	0.026 ± 0.001	0.999
EF – PHE+HPCD – [Fe^{2+}] = 0.2 mM – Different current intensities		
I = 500 mA	0.028 ± 0.001	0.994
I = 1000 mA	0.031 ± 0.001	0.996
I = 1500 mA	0.035 ± 0.001	0.994
I = 2000 mA	0.043 ± 0.001	0.994
EF – PHE+Tween 80 – [Fe^{2+}] = 0.05 mM – I = 2A		
pH = 3	0.013 ± 0.001	0.999
EF – PHE+HPCD – [Fe^{2+}] = 0.05 mM – I = 2A		
Natural pH (around 6)	0.026 ± 0.001	0.998

4.3.2.2 Study of ternary complex formation with HPCD

One of the main objectives of this study is to carry out the possibility of a recirculation of the treated solution to reuse the washing solution for another SW process. Therefore, it is important to follow the decay of HPCD during EF treatment. To clarify the behavior of HPCD and catalyst Fe^{2+} during EF treatment, degradation of 0.1 mM PHE in presence of 10 g L^{-1} HPCD was conducted at pH 3 and 2000 mA, as function of Fe^{2+} (Fig. 4.4).

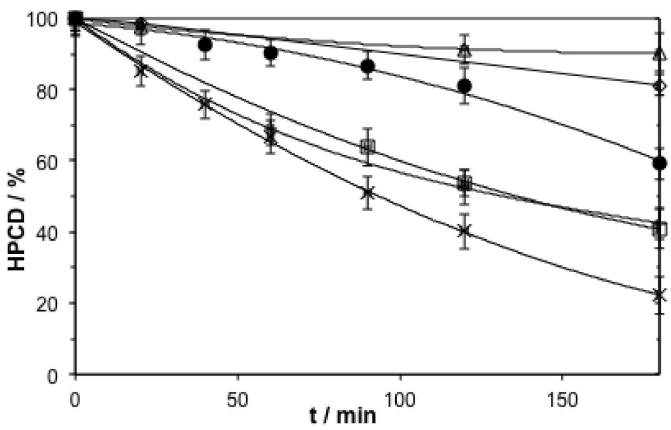

Fig. 4.4. *Effect of Fe^{2+} concentration: 0.05 mM (Δ), 0.1 mM (◊), 0.2 mM (●), 0.5 mM (□), 1 mM (×) and 10 mM (+) on EF degradation of HPCD (10 g L^{-1}) with the following operating conditions: $[PHE]_0$ = 0.1 mM, I = 2000 mA, $[Na_2SO_4]$ = 0.150 M, V = 400 mL, pH 3 and Pt anode.*

Figure 4.4 shows that the lower the Fe^{2+} concentration, the lower the kinetics of HPCD degradation. At $[Fe^{2+}]$ = 0.05 mM, only 10% of HPCD was degraded at the end of 180 min treatment. Thus, in EF treatment the optimal Fe^{2+} value is 0.05 mM regarding the possibility to preserve HPCD. This is the concentration selected for the next experiments. Two reasons can be evoked about the slow degradation of HPCD during the degradation of PHE. At low concentration there is a lack of Fe^{2+} to produce $^{\bullet}OH$ by reacting with H_2O_2 via Fenton's reaction, but that is not explaining why PHE is still degraded. A second reason can be explained by UV absorbance spectra of Fe^{2+}/HPCD/PHE mixtures performed at natural pH (around 6) and at pH 3 (Figs. 4.5a and 4.5b, respectively).

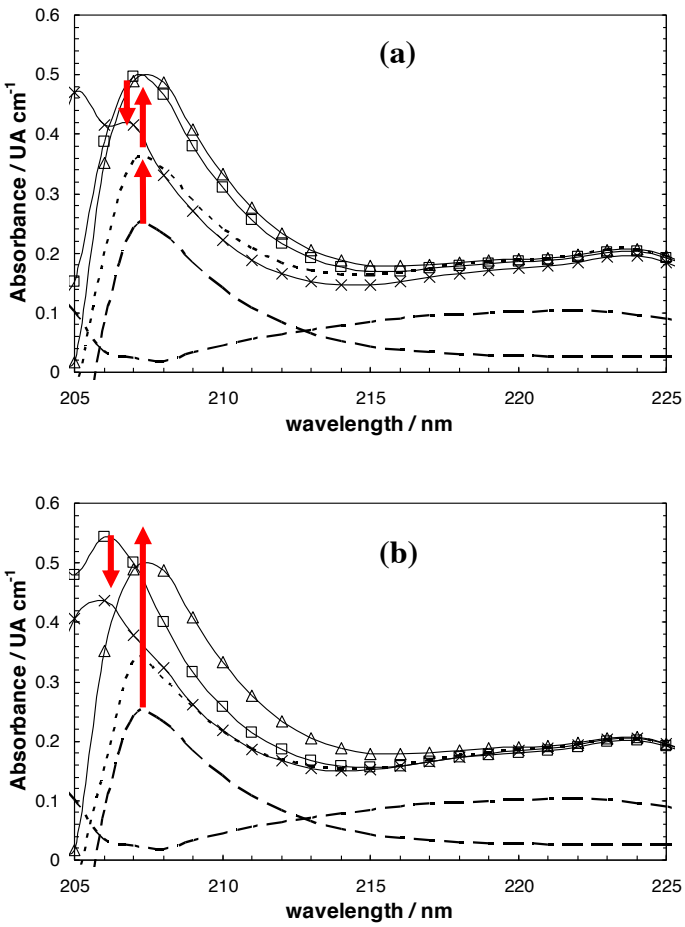

Fig. 4.5. *Study of the ternary complex formation between Fe^{2+}, HPCD and PHE, by performing UV absorbance spectra. (a) Measurements at natural pH (around 6) of the following mixture: HPCD (8 mM)/PHE (6 x 10^{-3} mM) and Fe^{2+} (0.05, 0.2, 1 mM)/HPCD/PHE; PHE (— - —), HPCD (— —), HPCD + PHE (- - -), PHE + HPCD + Fe^{2+} (0.05 mM) (Δ), PHE + HPCD + Fe^{2+} (0.2 mM) (□), PHE + HPCD + Fe^{2+} (1 mM) (×). (b) UV absorbance spectra at pH 3, with the same parameters as at pH 6.*

Both in Figs. 4.5a and 4.5b, hyperchromicity effects are observed at a wavelength of 207 nm between HPCD (8 mM; 10 g L^{-1}) alone and HPCD in the presence of PHE (6 x 10^{-3} mM; 1 mg L^{-1}) ($\Delta A \approx 0.10$ UA in both cases, where ΔA is the difference of absorbance values) and between HPCD with PHE and HPCD with PHE and Fe^{2+} whatever the Fe^{2+} concentration employed ($\Delta A \approx 0.10$-0.16 and 0.10-0.20 UA, respectively). These differences provide indirect evidence of the inclusion complex formation of HPCD with PHE (HPCD-PHE) and the ternary complex formation of HPCD-PHE and Fe^{2+} (Fe^{2+}-HPCD-PHE). It also can be concluded from Figs. 4a and 4b that the differences of absorbance are more pronounced at pH 3, meaning that the ternary complex is more stable at low pH. This result was expected, since Fe^{2+} converted to Fe^{3+} through reaction (4.1) begins to precipitate as $Fe(OH)_3$ for pH > 4 and the extent of removal of free iron ions from the solution increases with the increase of the solution pH. Spectra at pH 6 illustrate that the hyperchromicity effects are similar for initial Fe^{2+} concentrations of 0.05 and 0.2 mM, but it is lower for the concentration of 1 mM. This means that 0.05 and 0.2 mM Fe^{2+} concentrations have the same effect on the stability of the ternary complex and confirm the chosen value (0.05 mM) to run the following EF experiments. At pH 3, the hyperchromicity effect is more important and gives the following rank: 0.2 mM > 0.05 mM > 1 mM, meaning that 0.2 mM is the optimal concentration between these three values in term of complex stability.

These spectral data confirm the results obtained by Hanna et al. (2005) study in which the absorbance spectrum exhibited several changes including a shift and an increase in the 200-240 nm absorbance region upon addition of Fe^{2+} into a pentachlorophenol (PCP)-HPCD mixture. Lindsey et al. (2003) demonstrated the CD-iron complex formation by observing differences in absorbance spectra for beta-CD, carboxymethyl-beta-cyclodextrin (CMCD), Fe^{2+} and iron-CD mixtures. In addition, when injecting into a phenyl column TNT alone and a TNT ferrous ion mixture in a mobile phase containing 95% of a 5 mM MCD solution, it is observed a huge shift in retention times (t_R = 4.5 min instead of t_R = 13.8 min) (Yardin and Chiron, 2006). Others studies also demonstrated the ternary complex formation (Zheng and Tarr, 2004, 2006; Veignie et al., 2009). The evidence of ternary complex formation is also shown by the kinetics of EF degradation of PCP increased in the presence of HPCD compared to the kinetics of EF degradation of PCP alone (Hanna et al., 2005). The binding between Fe^{2+} and CDs depends on their functional group. For beta-CD and HPCD, iron is likely coordinated by

hydroxyl group on the rim of the CD, while for CMCD, oxygen in the carboxyl group is likely responsible for iron binding (Lindsey et al., 2003; Zheng and Tarr, 2006).

Based on the equilibrium (Eq. 4.6) suggested by Lindsey et al. (2003), the equilibrium constant (K) of the ternary complex can be written as following (Eq. 4.7) (Hoshino et al., 1981) and can be evaluated by varying Fe^{2+} concentration:

$$\text{HPCD:PHE} + Fe^{2+} \leftrightarrow Fe^{2+}\text{:HPCD:PHE} \quad (4.6)$$

$$\frac{A_\lambda - A_\lambda^0}{[Fe^{2+}]} \longleftrightarrow K(A_\lambda^\infty - A_\lambda) \quad (4.7)$$

where HPCD:PHE is the complex of PHE with HPCD, Fe^{2+}:HPCD:PHE is the ternary complex, A_λ, A_λ^0 and A_λ^∞ are the absorbance at the wavelength λ = (207 ± 1) nm at concentration of Fe^{2+} ($[Fe^{2+}]$) equal to 0.05 mM, in the absence of Fe^{2+} and at an infinite (optimal) concentration of Fe^{2+} (equal to 0.2 mM), respectively. The equilibrium constant was then calculated and found to be 56 mM^{-1} at pH 3. As expected, this constant value is very low and is in good agreement with the qualitative results of Zheng and Tarr (2006) given by NMR and fluorescence spectroscopy in the presence of Fe^{2+}, HPCD and 2-naphtol.

4.3.2.3 Comparison between HPCD/PHE and Tween 80/PHE degradation

Since the cost of extracting agent takes an important part in the overall cost of the SW followed by treatment with advanced oxidation process, it is worthwhile to find a process that degrades contaminant and recycles the solubilizing agent at the same time. Figure 4.6 compares EF experiments performed with PHE and HPCD, and PHE and Tween 80 after 4 h treatment.

PHE is completely degraded in the presence of HPCD with an apparent rate constant of 0.026 min^{-1} whereas in the presence of Tween 80 the apparent rate constant of PHE degradation (Table 4.2) is two times lower and the final degradation percentage reaches 95%. In the meantime, HPCD is slightly degraded (10%) whereas Tween 80 is much more degraded (50%). However, based on the absolute rate constants, the initial concentration of extracting agent and the operating parameters, it would be expected an opposite conclusion. The absolute rate constant of HPCD is 16 times higher than that of Tween 80, which would lead to a quicker degradation of HPCD. In addition, the initial Tween 80 concentration is more than 10 times lower than HPCD, which would allow

also a better degradation of PHE. Furthermore, oxygen is supplied by stirring vigorously during the Tween 80 experiment, which would slowdown the Tween 80 degradation if the O_2 supplied were not reaching the saturation level. The observed results can be explained by two different mechanisms according to two different ways to form complexes between CD-PHE and surfactant-PHE (Fig. 4.7).

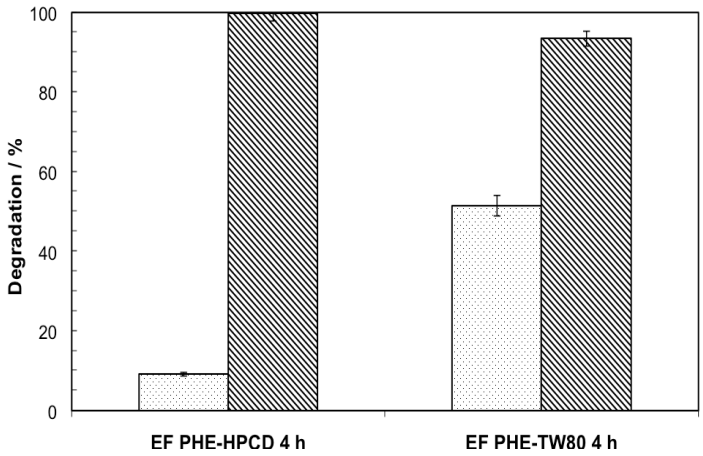

Fig. 4.6. *Comparison of EF degradation of PHE (0.1 mM) (▨) in the presence of HPCD (10 g L^{-1}) (▒) or Tween 80 (0.75 g L^{-1}) (▒) after 4 hours of treatment; I = 2000 mA, $[Fe^{2+}]$ = 0.05 mM, $[Na_2SO_4]$ = 0.150 M, V = 400 mL, pH 3 and Pt anode. Error bars represent standard deviations.*

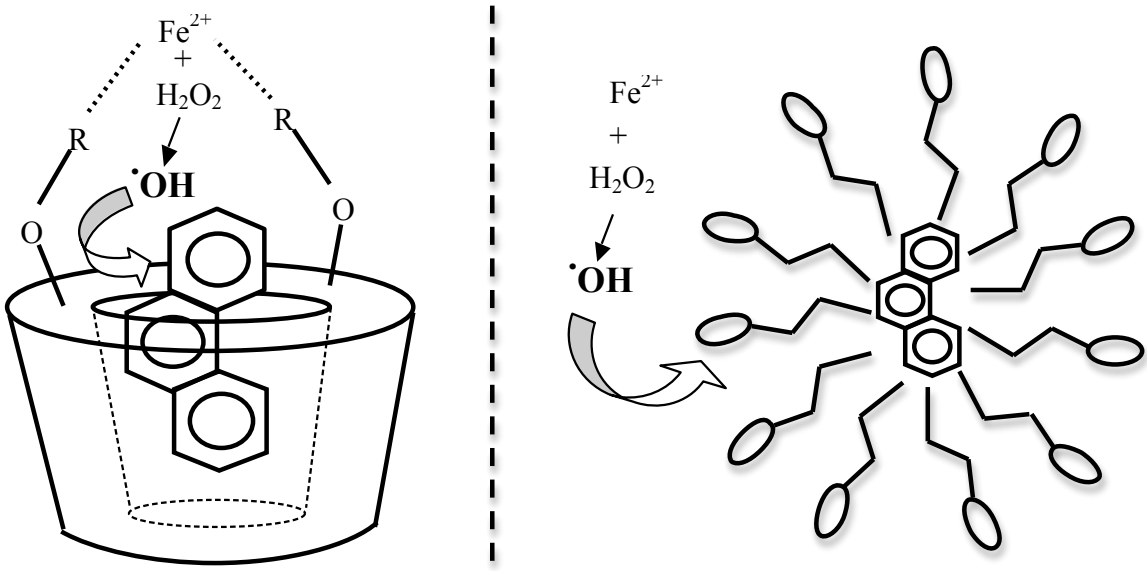

Fig. 4.7. *Schematic representation of two different ways for •OH oxidative degradation of HOC in the presence of cyclodextrin (a) or surfactant (b) in aqueous solution.*

In the case of HPCD, the HOC is trapped into the CDs cavity and the formation of the ternary complex (Fe^{2+}-HPCD-HOC) allows the hydroxyl radicals to directly degrade the contaminant (PHE) as already discussed above.

The following mechanism reactions with hydroxyl radical (Eqs. 4.8 and 4.9) should take place in the bulk at the beginning of PHE degradation:

$$Fe^{2+}\text{:HPCD:PHE} + {}^{\bullet}OH \rightarrow Fe^{2+}\text{:HPCD:PHE(OH)}^{\bullet} \quad (4.8)$$

$$Fe^{2+}\text{:HPCD:PHE(OH)}^{\bullet} + O_2 \rightarrow Fe^{2+}\text{:HPCD:PHE(OH)} + HO_2^{\bullet} \quad (4.9)$$

where HPCD:PHE and HPCD:Fe^{2+} are the complex formations of PHE with HPCD and Fe^{2+} with HPCD respectively, Fe^{2+}:HPCD:PHE, Fe^{2+}:HPCD:PHE(OH) and Fe^{2+}:HPCD:PHE(OH)$^{\bullet}$ are the ternary complex formation and PHE(OH), PHE(OH)$^{\bullet}$ are the hydroxylated PHE and hydroxylated PHE radical, respectively.

In contrast to HPCD, Tween 80 is a surfactant that forms micelles with the organic pollutant after reaching its CMC. $^{\bullet}OH$ has to degrade the micelle first before degrading the molecule that is trapped into the micelle core. As Tween 80 is not enough degraded, the pollutant is still not completely degraded as observed in Fig. 4.6.

The surfactant Tween 80 is difficult to be reused in these conditions since only 50% can be regenerated, whereas the percentage of regeneration is much better with HPCD (90%).

4.3.2.4 EF degradation of PHE in presence of HPCD at natural pH

By assuming the formation of a ternary complex, the waste reaction that consists of the formation of $Fe(OH)_3$ at pH higher than 4 could be avoided or limited. Figure 4.8 exemplifies an EF experiment carried out at natural pH (around 6) instead of the traditional optimal pH of 3.

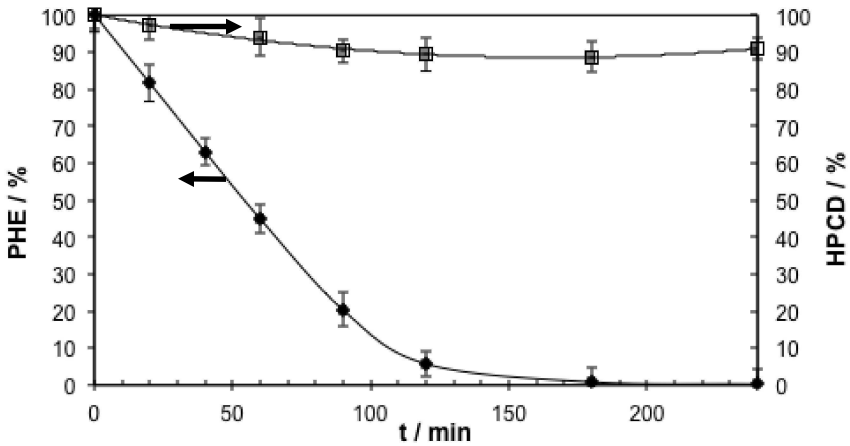

Fig. 4.8. *Study in natural pH conditions of EF degradation of PHE (0.1 mM) (♦) in the presence of HPCD (10 g L^{-1}) (□). I = 2000 mA, $[Fe^{2+}]$ = 0.05 mM, $[Na_2SO_4]$ = 0.150 M, V = 400 mL, pH 6 and Pt anode.*

By comparing the same experiment at pH 3, very similar results were obtained. It would firstly mean that no $Fe(OH)_3$ was formed during the experiment. Apparent rate constants of PHE (0.026 min^{-1}) are almost the same in both pHs (Table 4.2). Concerning the HPCD degradation similar behavior was given, i.e. only 10% is degraded after 4 h of treatment. It shows the existence of the ternary complex, even if the equilibrium constant (K) is low.

In these conditions, EF treatment can be achieved at natural pH without underperforming the degradation efficiency of the pollutant. This is an advantage since the SW effluents are usually at near neutral pH, due to the soil buffering capacity. In addition operating costs are diminished, since no sulfuric acid is required to adjust the pH to 3.

4.3.3 Environmental impacts of the treatment of SW solutions by EF process

Since one of the aims in this study is to reuse the treated solution for a further SW process, it seems important to know their environmental impact. Figure 4.9a outlines inhibition percentages of bacteria *Vibrio fischeri* in the presence of HPCD/PHE solution or Tween 80/PHE solution during EF treatment. Initial toxicity of Tween 80/PHE mixture (90% inhibition) is largely more important than initial HPCD/PHE mixture (45% inhibition), which corroborates the obtained EC_{50} values of Tween 80 and HPCD respectively (see sub-section 4.3.1.2). In both cases, the toxicity increases from the beginning to the end of PHE degradation (240 min), since the formed oxidation by-

products are more toxic than the initial ones, as reported by several authors (Oturan et al., 2008; Brillas et al., 2009; Dirany et al., 2012). Highly toxic intermediates, leading to 99% inhibition of luminescence of bacteria *Vibrio fischeri*, were formed from Tween 80 degradation just after the beginning of the treatment, while oxidation intermediates were formed only at the end of PHE degradation in the case of HPCD with almost no degradation of HPCD.

Biodegradability tests results are illustrated in Figs. 4.9b and 4.9c. Figure 4.9b depicts an initial BOD_5/COD ratio greatly higher in the presence of Tween 80 (0.07) than in the presence of HPCD (0.001), confirming the ratios determined with Tween 80 or HPCD alone. The biodegradability of HPCD/PHE solution becomes higher (0.1) after 2 h of treatment, whereas no enhancement is observed with Tween 80/PHE solution (still around 0.07). These enhancements are also highlighted in Fig. 4.9c. The biodegradability enhancement factor (E_{biodeg}) is proposed to be determined using the following equation:

$$E_{biodeg} = 100\times(1-R_i/R) \qquad (4.10)$$

where R and R_i are the BOD_5/COD ratio and BOD_5/COD initial ratio, respectively.

A great enhancement of BOD_5/COD ratio (95-98%) compared to the initial one ($(COD_{exp})_{init}$ = 11,150 ± 160 mg O_2 L^{-1}) was observed in HPCD experiment, even after 1 h of treatment. In contrast, the BOD_5/COD ratio of Tween 80/PHE solution was only enhanced by 8% compared to the initial one ($(COD_{exp})_{init}$ = 1,400 ± 20 mg O_2 L^{-1}), even after 4 h of treatment. These behaviors would make HPCD more useful in treatment of SW solutions by EF since the solution is more biodegradable and less toxic after 2 h of treatment (95% of PHE removed) compared to Tween 80/PHE solution.

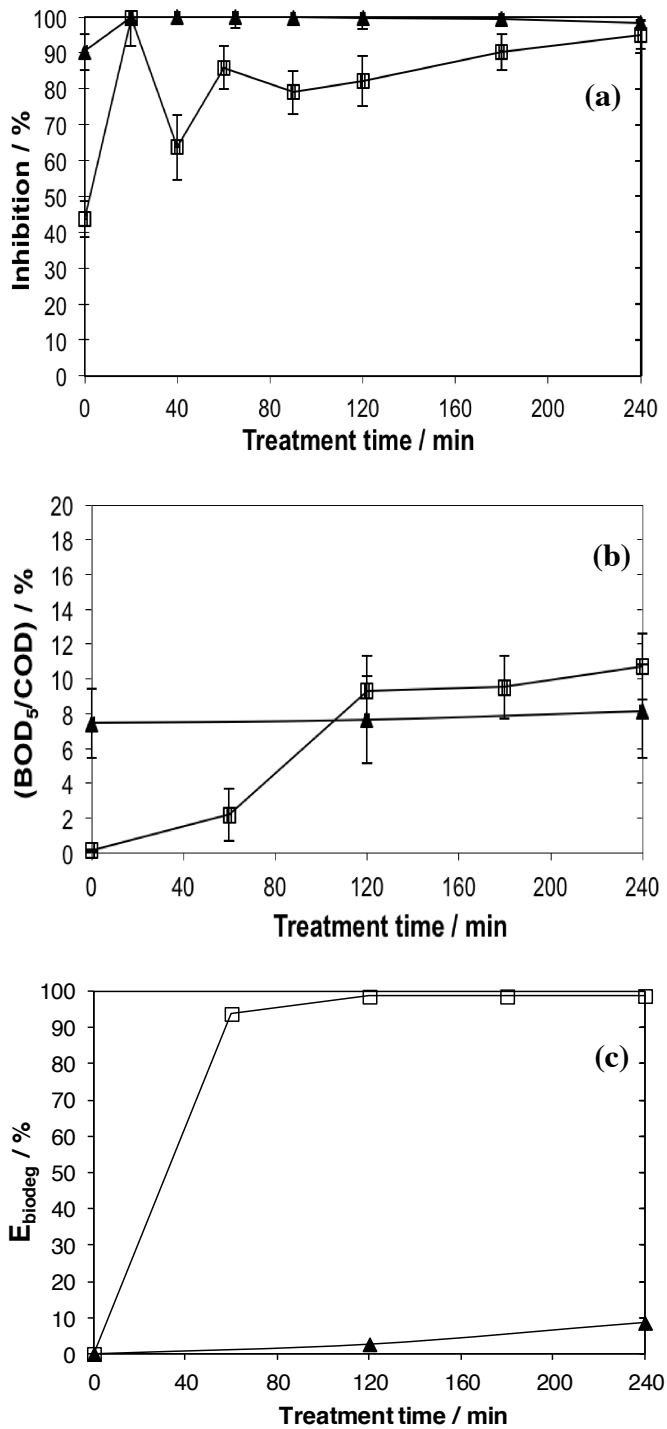

Fig. 4.9. *Toxicity evolution and biodegradability assessment (BOD_5/COD ratio) during EF degradation of PHE (0.1 mM) in the presence of HPCD (10 g L^{-1}) (□) or Tween 80 (0.75 mg L^{-1}) (▲). [Fe^{2+}] = 0.05 mM, I = 2000 mA, [Na_2SO_4] = 0.150 M, V = 400 mL, pH 3 and Pt anode. (a) Evolution of global solution toxicity during treatment. (b) Biodegradability assays. (c) Biodegradability enhancement (E_{biodeg}) from the initial BOD_5/COD ratio.*

4.4 Conclusions

Preliminary experiments showed: k_{abs} (HPCD) > k_{abs} (Tween 80), EC_{50} (HPCD) >> EC_{50} (Tween 80) and BOD_5/COD (HPCD) << BOD_5/COD (Tween 80). By considering an EF PHE degradation and a negligible HPCD degradation in the same time, the optimal operating parameters were determined as follow: $[Fe^{2+}]$ = 0.05 mM, I = 2000 mA and natural pH (around 6), since no much difference is observed compared to pH 3. Two different ways of pollutant degradation were suggested depending of the kind of solubilizing agent (HPCD or Tween 80). A ternary complex was formed between PHE, HPCD and Fe^{2+} (K = 56 mM^{-1}), which allows the $^{\bullet}OH$ to directly degrade the pollutant. In the case of Tween 80, the contaminant is trapped into the micelle core and $^{\bullet}OH$ needs to degrade the surfactant before reaching the targeted pollutants. These behaviors leaded to a faster degradation rate of PHE and a much slower degradation rate of HPCD compared to Tween 80/PHE solution. Though 10 times less concentration of Tween 80 was required to solubilize the same amount of PHE, EF treatment of Tween 80/PHE solution allowed regenerating only 50% of Tween 80, compared to 90% of HPCD in HPCD/PHE system. Furthermore, great biodegradability enhancements of initial HPCD/PHE solution were noticed. Even if the toxicity is still high (80% of inhibition) and the biodegradability was low (BOD_5/COD = 0.1) after 2 h of EF treatment, HPCD solutions showed better performance than Tween 80 solutions, regarding their environmental impact. Finally, HPCD is a great cost-effective agent, as it can be reused after combined SW-EF process without adjusting pH to 3 and by minimizing the environmental impact.

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CHAPTER 5

Influence of Anode Materials on Biodegradability and Toxicity

This chapter has been submitted for publication as:

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CHAPTER 5

Another aim of the present work is to study the possibility to combine EAOPs treatments (electro-Fenton (EF) or anodic oxidation (AO)) of bio-recalcitrant pollutants with a biological post-treatment. This combination allows minimizing the use of energy during the oxidation treatment. The influence of anode materials was assessed and bioassays were performed during EF or AO treatment of synthetic soil washing (SW) solutions.

The work in this chapter was partly presented in a summer school in Paris-Est (2012) and in DEEE'12 conference in Paris (2012):

E. Mousset, N. Oturan, M. A. Oturan, E. D. van Hullebusch, G. Guibaud, G. Esposito, Electro-Fenton and anodic oxidation treatments of phenanthrene in the presence of hydroxypropyl-beta-cyclodextrin: biodegradability and toxicity data. Summer school on contaminated soils: from characterization to remediation, Paris-Est (Champs-sur-Marne; France), June, 2012. (http://summer-school-soils.univ-paris-est.fr/).

E. Mousset, N. Oturan, E. D. van Hullebusch, G. Guibaud, G. Esposito, M. A. Oturan, Electro-Fenton treatment of soil washing solution of phenanthrene with cyclodextrin using different kind of anode materials: impacts on toxicity and biodegradability. 3rd international conference on Development, Energy, Environment, Economics (DEEE'12), Paris (France), December, 2012. (http://www.wseas.us/e-library/conferences/2012/Paris/DEEE/DEEE-14.pdf).

Influence of anode materials on toxicity and biodegradability of synthetic soil washing solutions containing phenanthrene and cyclodextrin during an anodic oxidation or electro-Fenton treatment

Abstract

Electrochemical advanced oxidation processes were applied to treatment of highly loaded synthetic soil washing solution were performed (initial Chemical Oxygen Demand (COD) = 11,150 ± 160 mg O_2 L^{-1} and initial Total Organic Carbon (TOC) = 4,500 ± 50 mg C L^{-1}). Phenanthrene (PHE) was chosen as a Polycyclic Aromatic Hydrocarbon (PAH) representative and hydroxypropyl-beta-cyclodextrin (HPCD) was applied as a solubilizing agent. Different anode materials such as platinum (Pt), Dimensionally Stable Anode (DSA; Ti/RuO_2/IrO_2) and Boron-Doped Diamond (BDD) thin film anodes were employed to carry out the treatment. Two electrochemical processes were compared: electro-Fenton (EF) and anodic oxidation (AO) with BDD as an anode. Toxicity (Microtox®) and biodegradability (BOD_5/COD), where BOD_5 is the biochemical oxygen demand after 5 days of incubation) of treated solutions during the treatment were assessed.

Pt anode was found to be the most efficient one in degradation of PHE, while BDD anode showed better ability to degrade HPCD and to mineralize the solution. This confirms the different ways to treat the effluent, which are related to the O_2 evolution overpotential at the electrode: degradation mechanism in the case of Pt and DSA, mineralization mechanism with BDD anode (AO-BDD) and paired electrocatalysis mechanism in the case of EF with BDD (EF-BDD). Toxicity and biodegradability assays corroborate these mechanisms. After a complete degradation of PHE and HPCD (including 60% of mineralization of HPCD) with EF-BDD and AO-BDD treatments, the toxicity starts to decrease and the biodegradability becames maximal (100%). In these conditions, the complete mineralization is achieved after 20 h of treatment. In the aim to study the possibility to combine EF or AO treatments to a biological post-treatment, six factors included energy consumptions values were compared after reaching a maximal biodegradability ratio, after reaching a biodegradability of 33% and after reaching complete mineralization. Performing an EF-BDD or AO-BDD treatment until reaching a BOD_5/COD ratio of 33% appears to be the best option, since EF and AO displayed most of the time a similar behaviour.

Keywords: Polycyclic Aromatic Hydrocarbons (PAHs); HPCD; Electro-Fenton; Anodes; BDD; Bioassays.

5.1 Introduction

Hydrophobic Organic Compounds (HOCs) like Polycyclic Aromatic Hydrocarbons (PAHs) are well-known to be hazardous contaminant and their potential environmental impact and human health risk is significant (Wang et al., 2013). Among the emerging techniques to treat them, Soil Washing (SW) and Soil Flushing (SF) appear to be cost-efficient techniques (Boving et al., 1999). Since PAHs tend to be strongly sorbed into soil, an amphiphilic extracting agent is needed. Cyclodextrins (CDs), known as host-guest molecules, have been suggested in the last decade as an alternative to the traditional surfactants (Landy et al., 2012; Mousset et al., 2014a). The CDs derivatives have a better water-solubility and higher solubilization efficiency. Among them, hydroxypropyl-beta-cyclodextrin (HPCD) is one of the most effective tested in SW experiment (Gómez et al., 2010).

As this process only transfers the pollutant from a solid matrix to an aqueous solution, a post-treatment of SW solution is required. However, these solutions represent a challenge to be treated since they are highly loaded and have most of the time a Chemical Oxygen Demand (COD) higher than 10,000 mg O_2 L^{-1}. Moreover, since these solutions contain many xenobiotic compounds, a biological treatment would not be efficient. Advanced Oxidation Processes (AOPs) (Glaze et al., 1987) have been developed as alternative technologies to biological and chemical conventional processes which are inefficient in case of persistent organic pollutants (POPs) like PAHs. AOP produce *in situ* hydroxyl radical ($^{\bullet}OH$), a highly oxidizing species (E° = 2.80 V/SHE, (Latimer, 1952)). These processes are especially efficient for aromatic molecules thanks to the electrophilic aromatic substitution of hydroxyl radical which then permits to open the ring. Among AOP, the Electro-Fenton (EF) process has shown promising results especially for industrial wastewaters treatments (Brillas et al., 2009). In this process, H_2O_2 is generated at the cathode with O_2 or air feeding (Eq. 5.1) while an iron catalyst (Fe^{2+}, Fe^{3+}, or iron oxides) is added to the effluent to produce $^{\bullet}OH$ at the bulk acidic solution via Fenton's reaction (Eq. 5.2):

$$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2 \quad (5.1)$$

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO^- + {}^{\bullet}OH \quad (5.2)$$

In contrast to the classical Fenton process, the Fenton's reagent (mixture of H_2O_2 and Fe^{2+}) is electrocatalytically *in situ* generated in the case of EF process (Oturan, 2000; Sirés et al., 2007), according to equations (Eqs. 5.1 and 5.3):

$$Fe^{3+} + e^- \rightarrow Fe^{2+} \quad (5.3)$$

EF is considered as a clean treatment without any production of sludge. Furthermore, no iron would be needed for the treatment of SW solution, since the iron could be directly extracted from soil (Mousset et al., 2013).

Another emerging electrochemical advanced oxidation processes (EAOP) is the Anodic Oxidation (AO). This process allows generating hydroxyl radical at the surface of high O_2-overvoltage anode (M), according to Eq. 5.4.

$$M + H_2O \rightarrow M(^{\bullet}OH) + H^+ + e^- \quad (5.4)$$

The Boron-Doped Diamond (BDD) electrode has an O_2-overvoltage of 2.3 V vs SHE, which is high enough to produce hydroxyl radical through Eq. 5.4 as intermediates of water oxidation to O_2. AO with BDD as an anode material has been studied in several studies (Ozcan et al., 2008; Sirés et al., 2008; Panizza and Cerisola, 2009; Oturan et al. 2012). One of the advantages of this process is that no reagents are added before or during the treatment.

Since chemical oxidation for complete mineralization is usually expensive, combination with biological treatment can reduce the operating costs (Sánchez-Pérez et al., 2013). Several studies evoke an AOP as pre-treatment combined to biological post-process (Oller et al., 2011). The most studied AOPs are Fenton (Lin et al., 2003; Wang et al., 2008; Rodrigues et al., 2009; Martins et al., 2010; Zimbron and Reardon, 2011), photo-Fenton and solar-photo-Fenton treatments (Lapertot et al., 2006; Farré et al., 2007; Malato et al., 2007; Elmolla and Chaudhuri, 2011; Serra et al., 2011; Vilar et al., 2011). According to our knowledge only two studies have reported the possibility to combine a biological post-process to an EF treatment (Mansour et al., 2011; Estrada et al., 2012;) and only one study to an AO treatment (Estrada et al., 2012). Estrada et al. (2012) have shown that EF is a better option to be combined with a biological post-treatment than other treatments like chemical flocculation and electro-coagulation. These two studies (Mansour et al., 2011; Estrada et al., 2012) are focused on synthetic solutions containing pharmaceutical compounds (cefalexin and sulfamethazine, respectively) at low initial COD values.

In the present paper, for the first time, we have carried out treatments of highly loaded synthetic SW solution by EF and AO processes by comparing the efficiency of different anode materials. The representative soil pollutant is PHE that is listed among the 16 hazardous PAHs by the Environmental Protection Agency of United States (USEPA). The solubilizing agent selected is HPCD. Platinum (Pt) and Dimensionally Stable Anode (DSA) ($Ti/RuO_2/IrO_2$) anodes that are known to be "active" electrodes (leading to chemisorption of $^{\bullet}OH$ on surface) are compared to BDD anode, which is a "non-active" electrode (leading to physisorption of $^{\bullet}OH$ on surface) (Panizza and Cerisola, 2009; Oturan et al., 2013). In a first part, the three anodes and the two processes (EF and AO) are compared by monitoring the PHE and HPCD decay and the mineralization rate at different current intensity. A second part of this study evokes the possibility of a biological post-treatment by following the biodegradability and the toxicity levels during the EF and AO treatments. In the last part, the different treatments with different anodes materials are compared by considering their respective energy consumptions.

5.2 Materials and Methods

Ultrapure water from a Millipore Simplicity 185 (resistivity > 18 MΩ cm) system was used in all experiments. All the replicates of experiments and analyses gave standard deviations below 6%.

5.2.1 Advanced Oxidation Processes

5.2.1.1 EF treatments

EF experiments were performed in a 0.40 L undivided, open and cylindrical glass electrochemical reactor at current controlled conditions. The electrochemical cell was monitored by a power supply HAMEG 7042-5. The working electrode (cathode) was a 150 cm^2 carbon-felt piece (Carbone-Lorraine). Each anode studied (Pt grid (5 cm height cylindrical and i.d. = 3 cm), DSA ($Ti/RuO_2/IrO_2$) plate (5 x 4 cm) and BDD plate (5 x 4 cm)) was centred in the cell and surrounded by cathode covering the inner wall of the cell. An inert electrolyte (Na_2SO_4 (Aldrich) at 0.150 M) was added to the medium and ensured a constant ionic strength (0.45 M). $FeSO_4 \bullet 7H_2O$ (Acros) was also added at 0.2 mM as source of Fe^{2+} ion (catalyst). This concentration was determined to be optimal in a former study (Mousset et al., 2014b). Prior to each experiment, the solutions were saturated in O_2 (8.53 mg O_2 L^{-1} at 22 °C) by supplying compressed air bubbling through

the solution starting 10 min before the beginning of the treatment, at a flow-rate of 0.25 L min^{-1}. Solutions were stirred continuously by a magnetic stirrer. A heat exchanger system was provided to keep the solution at constant room temperature (22 °C ± 1) by using fresh water. The pH of initial solutions was set at the optimal value of 3.0 (± 0.1) by the addition of H_2SO_4 (1 M) solution. The pH changes were negligible during the electrolysis at pH 3.0 and it decreases only to 2.8 at the end of experiments. PHE (>99.5%; Aldrich) was chosen as a PAH representative. HPCD (9 g L^{-1}) (from Xi'an Taima Biological Engineering Company, China) was employed to enhance the PHE solubilization and to mimic future soil extract solutions of washing or flushing experiment. A minimal concentration of cyclodextrin around 10 g L^{-1} is often required in SW batch experiment (Mousset et al., 2014a). Thus, around 16 mg L^{-1} (± 0.3 mg L^{-1}) equivalent to 0.09 mM of PHE was solubilized initially in each solution containing HPCD at 9 g L^{-1} equivalent to 7.2 mM.

5.2.1.2 AO treatments

AO were performed in the same conditions than EF without adding $FeSO_4 \bullet 7H_2O$ and without adjusting pH to 3.0 (± 0.1). The initial pH of the solution was equal to 6.0 (± 0.1). BDD thin film electrode (5 × 4 cm) was employed as anode. The same PHE (0.09 mM) with HPCD (9 g L^{-1}) solution was used.

5.2.2 Environmental parameters

5.2.2.1 Biodegradability tests

Respirometric methods (OECD 301F, ISO 9408) has the advantage of being a direct biological parameter of aerobic degradation in contrast to methods which measure dissolved organic carbon removal like *P. putida* bioassays or Zahn-Wellens tests (Reuschenbach et al., 2003; Ballesteros Martín et al., 2010). Thus, this techniques was operated to determine the BOD_5 using the OxiTop® IS 6 system (WTW).

An aqueous solution containing a phosphate buffer solution and a saline solution was prepared by following Rodier et al. (2009) procedure. All the following products were used at analytical grade: potassium dihydrogen phosphate (KH_2PO_4) from Acros, sodium phosphate dibasic (Na_2HPO_4), ammonium chloride (NH_4Cl), heptahydrated magnesium sulfate ($MgSO_4 \bullet 7H_2O$) and dehydrated calcium chloride ($CaCl_2 \bullet 2H_2O$)

from Merck, dipotassium phosphate (K_2HPO_4) and hexahydrated ferric chloride ($FeCl_3$•$6H_2O$) from VWR. This solution was then saturated in oxygen (9.1 mg O_2 L^{-1} at 20 °C) overnight. Bacteria extracted with KCl (>99.0%, Fluka) at 9 g L^{-1} (30 mL with 3 g of dried soil) and a IKA-MS1 minishaker (1800 rpm during 1 min) from uncontaminated soil were added just before adding the samples. All the samples were adjusted to circum-neutral pH. All the bottles containing the solutions were equipped by a rubber sleeve in which pure NaOH pellets (VWR) are added to trap the CO_2 gas formed during biodegradation. The samples were incubated at 20°C (± 0.1) during 5 days in dark conditions. D(+)-Glucose•H_2O (Merck, analytical grade) was used as a reference. A blank, representing the endogenous respiration, prepared with milli-Q water and the seed solution was done for each batch and taken into account for calculation. The BOD_5 measured in each blank was insignificant compared to the BOD_5 of the samples and causes no interference. All the BOD_5 values were confirmed by measuring the difference of dissolved oxygen at the end and at the beginning of the experiment using the InoLab Oxi 730 (from WTW).

COD analyses were accomplished by a photometric method requiring a Spectroquant® NOVA 60 (Merck) equipment. The samples were diluted and prepared by adding 2 mL of each one in COD Cell test (15-300 mg O_2 L^{-1} range) (Merck) and by heating at 148°C during two hours with a Spectroquant® TR 420 (Merck). The tubes were let cool to room temperature before analysis.

Then the biodegradability was given by the ratio between BOD_5 and the COD (BOD_5/COD). Since the H_2O_2 was produced *in situ* during EF experiment and the radicals formed during EF or AO treatments have a limited life-time, these oxidants cause no interferences during the BOD_5 or COD measurements.

5.2.2.2 Toxicity assays

To assess the toxicity level, several tests with microorganisms, invertebrates, plants and fish have been developed. However, the most common one is the *Vibrio fischeri* bioluminescence inhibition assay (Ballesteros Martín et al., 2008). In the aim to get data comparable to other research papers, toxicity assays of the present study were performed by using Microtox® standard method (ISO 11348-3) with marine bacteria *Vibrio fischeri* from LUMIStock LCK-487 (Hach Lange). A BERTHOLD Autolumat Plus LB 953 equipment was used. 22% of NaCl was added in each sample to insure an

osmotic protection for bacteria. Before each toxicity measurement, all the samples were adjusted to circum-neutral pH (with NaOH) and samples from EF experiments were filtered with RC filter (0.2 μm) to remove iron precipitates (Dirany et al., 2011). In each batch test, the inhibition percentage of a blank (sample without the compound studied) was measured and used for percentage of inhibition calculation based on 15 min of exposure.

5.2.3 Analytical determinations

5.2.3.1 TOC analysis

TOC analyses were performed to quantify the mineralization degree during the different kind of treatments. The solution TOC values were determined by catalytic oxidation using a Shimadzu V_{CSH} TOC analyzer. All samples were acidified to a pH 2 with H_3PO_4 (25%) to remove inorganic carbon. The injection volumes were 50 µL. Calibrations were performed by using potassium hydrogen phthalate solutions (50 mg C L^{-1}) as standard. All measured TOC values were given with a coefficient of variance below to 2%.

Mineralization yields (r_{mine}) are considered to be equivalent to TOC removal and are calculated according to the following equation (5.5):

$$r_{\min e}(\%) = \frac{(\Delta TOC)_t}{TOC_0} \times 100 \qquad (5.5)$$

where $(\Delta TOC)_t$ is the difference between the TOC at time t with the initial TOC (TOC_0).

5.2.3.2 HPCD analysis

The HPCD concentration was determined by a fluorimetric technique based on enhancement of the fluorescence intensity of 6-(p-toluidino)naphthalene-2-sulfonic acid sodium (TNS) (Aldrich), when they are complexed with the cyclodextrin (Hanna et al., 2005). A Kontron SFM 25 spectrofluorimeter was set out at 318 nm for excitation and 428 nm for emission. Each sample was diluted in TNS (3 x 10^{-6} M) with a dilution factor of 200. All the measurements were done at constant temperature (22 °C ± 1). The fluorescence intensity of PHE was not significant in this range of wavelength and concentration (data not shown). Since TNS is photosensitive, TNS and the diluted

samples were kept in dark conditions. This method allows quantifying HPCD and slightly modified (hydroxylated) HPCD in the same time, since the non-polar HPCD cavity brings about a TNS fluorescence intensity enhancement until the CD cavity is cleaved by the degradation technique.

5.2.3.3 PHE analysis

The decay of PHE was followed by reversed phase liquid chromatography (HPLC) coupled with a diode array detector from Dionex set to 249 nm. A RP C-18 column (Purospher®, Merck) placed in an oven and set at 40.0 °C was used. The mobile phase was a mixture of water/methanol (Aldrich; HPLC grade) (22:78 v/v) with a flow rate of 0.8 mL min^{-1} (isocratic mode). PHE exhibited a well-defined chromatographic pic at retention time of 6.9 min under these operating conditions. The injection volumes were 20 µL. To avoid difference of absorbance observed in the presence or absence of HPCD during analysis (Wang and Brusseau, 1993), external standards were prepared in the presence of solubilizing agent.

5.2.4 Energy consumption calculation

The energy consumptions are calculated according to Brillas et al. (2009) (Eqs 5.6 and 5.7):

$$\text{Energy consumption (kWh m}^{-3}) = \frac{E_{cell} It}{V_S} \qquad (5.6)$$

$$\text{Energy consumption (kWh (kg TOC)}^{-1}) = \frac{E_{cell} It}{(\Delta TOC)_t V_S} \qquad (5.7)$$

where E_{cell} is the average cell voltage (V), I is the applied current (A), t is the electrolysis time (h), V_S is the solution volume (L) and $(\Delta TOC)_t$ is the TOC decay (g C L^{-1}).

5.3 Results and Discussion

5.3.1 Effect of applied current intensity

5.3.1.1 Comparison of oxidative treatments during PHE and HPCD degradations

Figure 5.1 depicts the effect of applied current intensity with different anode materials (Pt, DSA and BDD) and different kind of treatment (EF or AO) on PHE (0.09 mM) degradation in the presence of HPCD (9 g L^{-1}). The tested current intensities were 500 mA (3.3 mA cm^{-2}), 1000 mA (6.7 mA cm^{-2}) and 2000 mA (13.3 mA cm^{-2}).

Complete oxidation was not reached even after 240 min treatment with EF-DSA, EF-BDD and AO-BDD processes, while complete oxidation of PHE needed only 180, 150 and 90 min with Pt anode at 500, 1000 and 2000 mA, respectively, in a previous study (Mousset et al., 2014b). The apparent rate constants values (k_{app}) from Table 5.1, calculated assuming a pseudo-first order kinetic model, confirm that Pt anode exhibits significantly better degradation efficiency compared to EF-DSA, EF-BDD and AO-BDD treatments.

The kinetics of PHE oxidative degradation efficiency follows the rank: EF-Pt >> EF-DSA > EF-BDD ≈ AO-BDD, though it would be expected that EF-BDD and AO-BDD give the highest kinetic efficiency. In the case of EF-Pt, the kinetic of PHE degradation increases more rapidly (1.5 times) when the applied current increases, compared to AO-BDD. An optimal value is obtained with EF-BDD and EF-DSA at 500 mA and 1000 mA, respectively. Thus, the increase of current intensity, increases the extent of competitive reactions and limits or decreases the PHE degradation efficiency. Since oxidation by-products are formed from PHE and HPCD initially present in the solution, these compounds can compete with PHE molecules during the oxidative process.

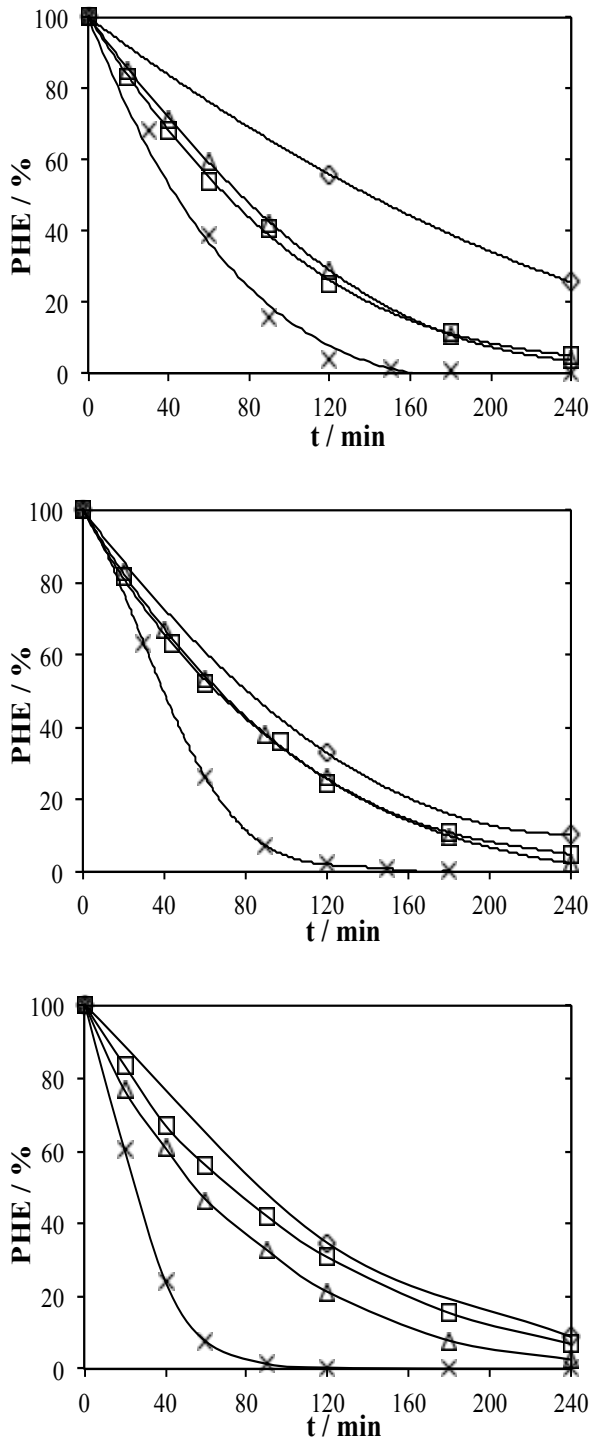

Fig. 5.1. *Effect of applied current intensity ((a) 500 mA, (b) 1000 mA and (c) 2000 mA) with different anode materials and different kind of treatments (EF-Pt (×), EF-DSA (Δ), EF-BDD (□) and AO-BDD (◊)) on PHE (0.09 mM) degradation in the presence of HPCD (9 g L^{-1}). EF-Pt curves from Mousset et al. (2014b).*

Table 5.1. Apparent rate constants values (k_{app}) obtained for PHE degradation (in the presence of HPCD) by EF or AO treatments, assuming pseudo-first order kinetic model.

	k_{app}(PHE) (min^{-1})	R^2
PHE + HPCD - 0.5 A		
*EF-Pt	0.0280 ± 0.0013	0.9937
EF-DSA	0.0130 ± 0.0005	0.9941
EF-BDD	0.0120 ± 0.0003	0.9953
AO-BDD	0.0060 ± 0.0002	0.9975
PHE + HPCD - 1 A		
*EF-Pt	0.0310 ± 0.0009	0.9956
EF-DSA	0.0150 ± 0.0008	0.9913
EF-BDD	0.0120 ± 0.0002	0.9978
AO-BDD	0.0100 ± 0.0003	0.9984
PHE + HPCD - 2 A		
*EF-Pt	0.0430 ± 0.0014	0.9940
EF-DSA	0.0140 ± 0.0004	0.9887
EF-BDD	0.0110 ± 0.0002	0.9969
AO-BDD	0.0110 ± 0.0004	0.9954

*values obtained from Mousset et al. (2014b)

It appears also important to focus not only on the pollutant degradation but also to the solubilizing agent decay. Figure 5.2 highlights the kinetics of HPCD degradation with the same solutions described previously.

The kinetics of degradation are slower than the PHE degradation, due to the tropoidal shape, the high Molar Weight (MW) (about 1250 g mol^{-1}) and the high initial concentration (9 g L^{-1} equivalent to 7.2 mM) of the HPCD molecules. According to the Table 5.2 giving apparent rate constants values of HPCD degradation (k_{app}(HPCD)), the difference between kinetics of PHE and HPCD degradation decreases by following treatment rank: EF-Pt > EF-DSA > EF-BDD > AO-BDD.

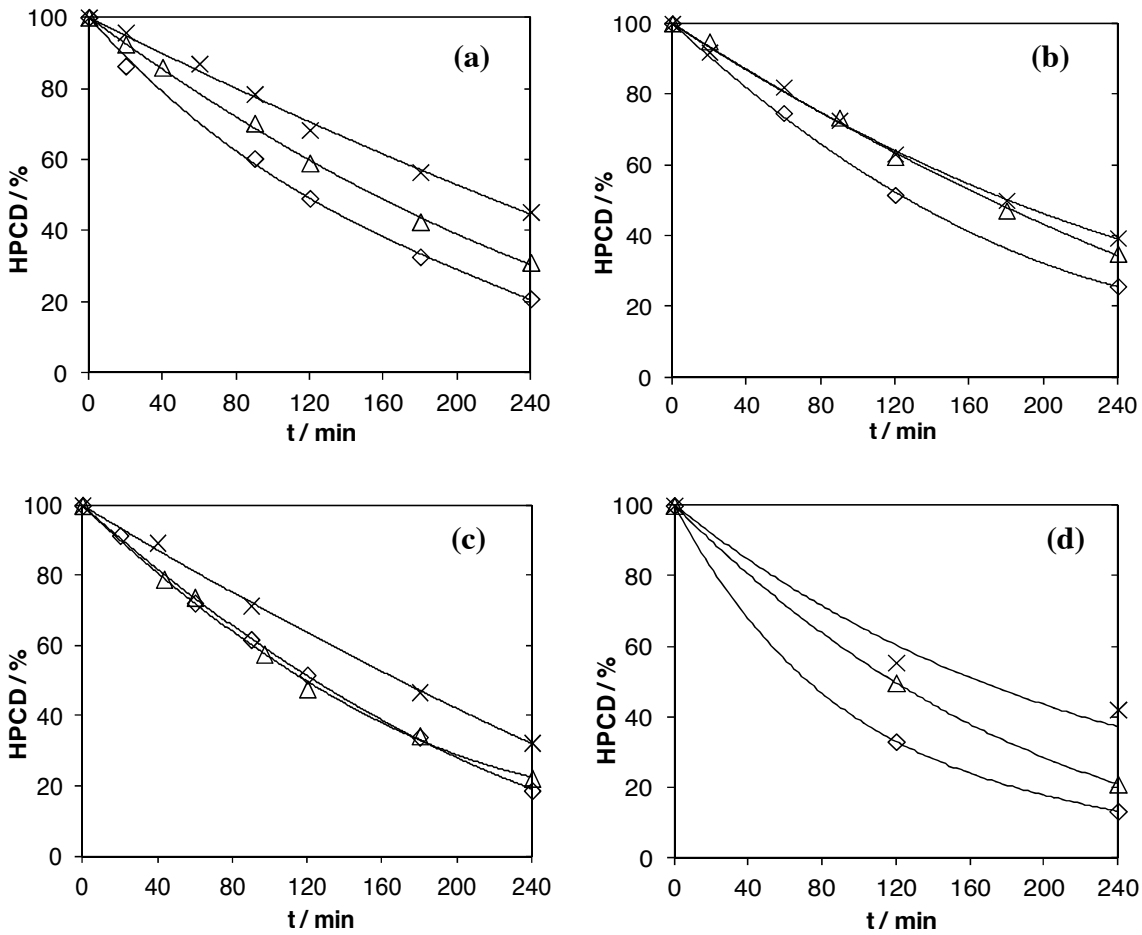

Fig. 5.2. *Effect of applied current intensity (500 mA (×), 1000 mA (Δ) and 2000 mA (◊)) with different anode materials and different kind of treatment (EF-Pt (a), EF-DSA (b), EF-BDD (c) and AO-BDD (d)) on HPCD (9 g L^{-1}) degradation in the presence of PHE (0.09 mM).*

These differences become very low with EF-BDD and AO-BDD treatments. The apparent rate constants of HPCD during EF-BDD and AO-BDD processes are higher than EF-Pt and EF-DSA treatments. At a constant current intensity, when k_{app}(PHE) values decrease, the k_{app}(HPCD) values increase. Thus, the k_{app}(HPCD) values are inversely correlated to the k_{app}(PHE) values, regarding the kind of applied treatment. This confirms the competitive degradation between the two compounds.

It is also denoted that the k_{app}(HPCD) values increase when the applied current intensity increases slightly in all kind of treatments.

Table 5.2. Apparent rate constants values (k_{app}) obtained for HPCD degradation (in the presence of PHE) by EF or AO treatments, assuming pseudo-first order kinetic model.

	k_{app}(HPCD) (min^{-1})	R^2	k_{app}(PHE) – k_{app}(HPCD) (min^{-1})
PHE + HPCD - 0.5 A			
EF-Pt	0.0026 ± 0.0001	0.9952	0.0250
EF-DSA	0.0034 ± 0.0002	0.9869	0.0100
EF-BDD	0.0041 ± 0.0001	0.9977	0.0080
AO-BDD	0.0042 ± 0.0001	0.9967	0.0020
PHE + HPCD - 1 A			
EF-Pt	0.0041 ± 0.0002	0.9927	0.0270
EF-DSA	0.0038 ± 0.0003	0.9797	0.0110
EF-BDD	0.0061 ± 0.0001	0.9978	0.0060
AO-BDD	0.0069 ± 0.0001	0.9991	0.003
PHE + HPCD - 2 A			
EF-Pt	0.0054 ± 0.0002	0.9938	0.0380
EF-DSA	0.0054 ± 0.0002	0.9955	0.0090
EF-BDD	0.0063 ± 0.0003	0.9881	0.0050
AO-BDD	0.0085 ± 0.0005	0.9993	0.0030

5.3.1.2 Comparison of oxidative treatments during mineralization

Figure 5.3 illustrates the comparison of TOC values after 4 h of different kind of treatment at different applied current intensity (500 mA, 1000 mA and 2000 mA).

Figure 5.3a shows that EF with Pt and DSA give approximately constant TOC decay rate, whatever the applied current intensity. However, treatments with BDD anodes lead to an increased mineralization rate. In all the applied current intensities, the kinetic of mineralization after 4 hours of treatment followed the sequence: EF-BDD > AO-BDD >> EF-DSA > EF-Pt. Treatments with BDD anodes demonstrated largely better mineralization efficiency, especially at higher current intensities.

The high mineralization power of BDD compared to Ti/RuO_2/IrO_2 and Pt anodes is already reported (Brillas et al., 2009; Oturan et al., 2012; Oturan et al., 2013; Panizza and Cerisola, 2009). Indeed, the higher O_2-overpotential (2.3 V/SHE) at the surface of BDD allows minimizing the extent of O_2 evolution. It leads to the generation of

heterogeneous BDD($^{\bullet}$OH) at the surface of BDD anode (Eq. 5.4). This allows the initial organic compound to be oxidized directly at the surface of the anode (in the diffusion layer). The organic by-product that is produced close to the surface of anode is then also oxidized and so on until the final mineralization step (organic oxidation into CO_2). Thus, the initial compound is quickly mineralized in this kind of mechanism. In the meantime, the initial compound present in bulk solution is slowly degraded, i.e. slowly oxidized into other organic by-products. It makes the PHE degradation slower (as shown in section 5.3.1.1.) but the HPCD (present at a much higher concentration) degradation and the mineralization quicker, compared to EF-Pt and EF-DSA.

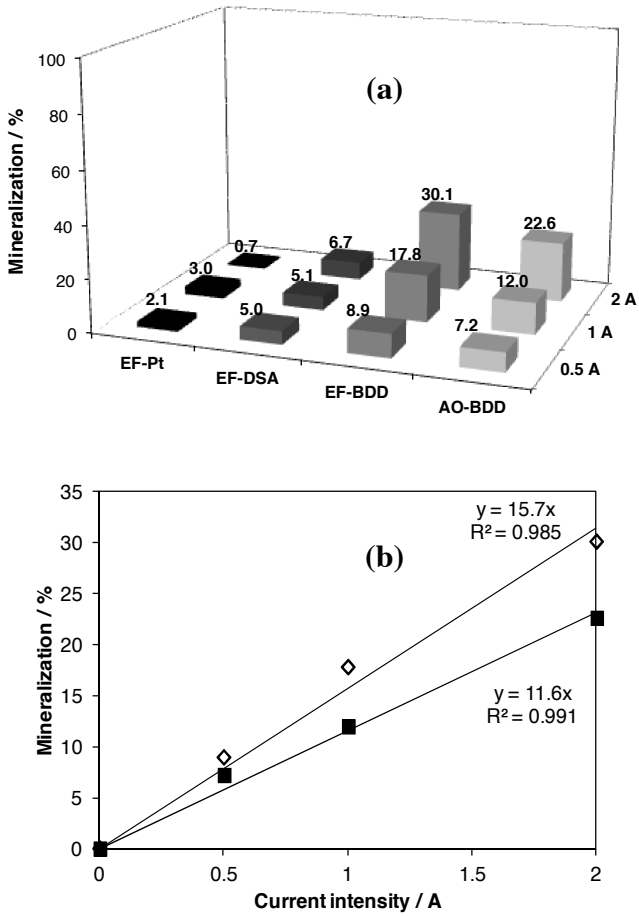

Fig. 5.3. *Effect of applied current intensity (500 mA, 1000 mA and 2000 mA) with different anode materials and different kind of treatment on the mineralization rate obtained after 4 h of EF or AO treatments of PHE (0.09 mM) with HPCD (9 g L^{-1}) solutions. (a) EF-Pt (■), EF-DSA (■), EF-BDD (■) and AO-BDD (■); (b) EF-BDD (◊) and AO-BDD (■).*

Moreover, during EF treatment with BDD anode, there are two sites of production for hydroxyl radicals, one at the surface of the anode and other one in the bulk solution from Fenton reaction. This is called the paired electrocatalysis process already evoked by other authors (Brillas et al., 2009). Both degradation and mineralization mechanisms take place at the same time, which could explain the better mineralization rates obtained with EF-BDD compared to AO-BDD. In the bulk solution the following reaction can occur (Brillas et al., 2009) leading to a greater extent of dehydrogenated and/or hydroxylated derivatives (Eqs. 5.8 to 5.10):

$$RH + {}^{\bullet}OH \rightarrow R^{\bullet} + H_2O \quad (5.8)$$

$$Fe^{3+} + R^{\bullet} \rightarrow R^{+} + Fe^{2+} \quad (5.9)$$

$$R^{+} + H_2O \rightarrow ROH + H^{+} \quad (5.10)$$

Figure 5.3b denotes a linear increase of mineralization yield (r_{mine}) when the current intensity (I) increases from 0 to 2000 mA with the use of BDD anode. The linear regressions give the following equations r_{mine} (%) = 15.7 × I (A) (R^2 = 0.985) and r_{mine} (%) = 11.6 × I (A) (R^2 = 0.991), in the case of EF-BDD and AO-BDD, respectively. EF-BDD leads to mineralization rates that are 1.35 times higher (in average) than with AO-BDD. Figure 5.3b also demonstrates that the optimal current intensity is widely higher (≥ 2000 mA) by considering the TOC removal compared to pollutant decay.

5.3.2 Bioassays

5.3.2.1 Enhancement of biodegradability

The aim of electrochemical treatments applied to wastewater treatment is to degrade and mineralize different kind of organic pollutants. However, sometimes it can consume too much energy, especially when the solutions are highly loaded. Thus, it is interesting to study the biodegradability in aerobic condition of treated effluent to combine the electrochemical treatment with a biological post-treatment. During EF and AO treatments at 1000 mA, the enhancement of biodegradability compared to the initial one is denoted in Fig. 5.4.

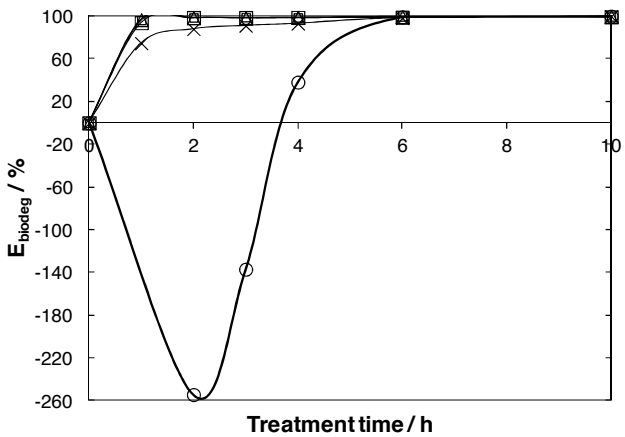

Fig. 5.4. *Biodegradability enhancement (E_{biodeg}) from the initial BOD_5/COD ratio during EF or AO degradation of PHE (0.09 mM) in the presence of HPCD (9 g L^{-1}) with different kind of anode materials: EF-Pt (□), EF-DSA (Δ), EF-BDD (×), AO-BDD (○), at constant current intensity (I = 1000 mA).*

The enhancement factor (E_{biodeg}) is determined according to the following equation (5.11) (Mousset et al., 2014b):

$$E_{bio\,deg} = 100\left(1 - \frac{R_i}{R}\right) \qquad (5.11)$$

where R and R_i are the BOD_5/COD ratio at time t and BOD_5/COD initial ratio, respectively.

The enhancement factors become very high (> 96%) after 1 h of EF-Pt and EF-DSA treatments, knowing that the initial biodegradability of the solution is very low (BOD_5/COD = 0.001). Different behaviors are observed during EF-BDD and AO-BDD treatments. The enhancement factors become higher than 98% only after 6 h of EF-BDD and AO-BDD treatments. In the case of EF-BDD, this factor increases until 6 h of treatment, whereas it largely decreases until -260% at 2 h and increases until 98% at 6 h with AO experiments. It means that the by-products at the beginning of the AO treatment are very poorly biodegradable compared to the others processes. It can be assumed that different amounts of by-products are released in the bulk solution depending on the degradation/mineralization kinetics. It depends on the kind of treatment (EF or AO) and the kind of anode materials (Pt, DSA or BDD) employed. The reason could be that only mineralization occurs during the AO-BDD process, while mineralization and degradation occur in EF-BDD process and only degradation

(conversion into other organic by-products) occurs during EF-Pt and EF-DSA processes. These considerations are confirmed in the previous sub-section 5.3.1.

5.3.2.2 Comparison of biodegradability during PHE and HPCD oxidative treatments

The biodegradability assays and mineralization rates during EF or AO treatments are described in Fig. 5.5 at a constant current intensity of 1000 mA.

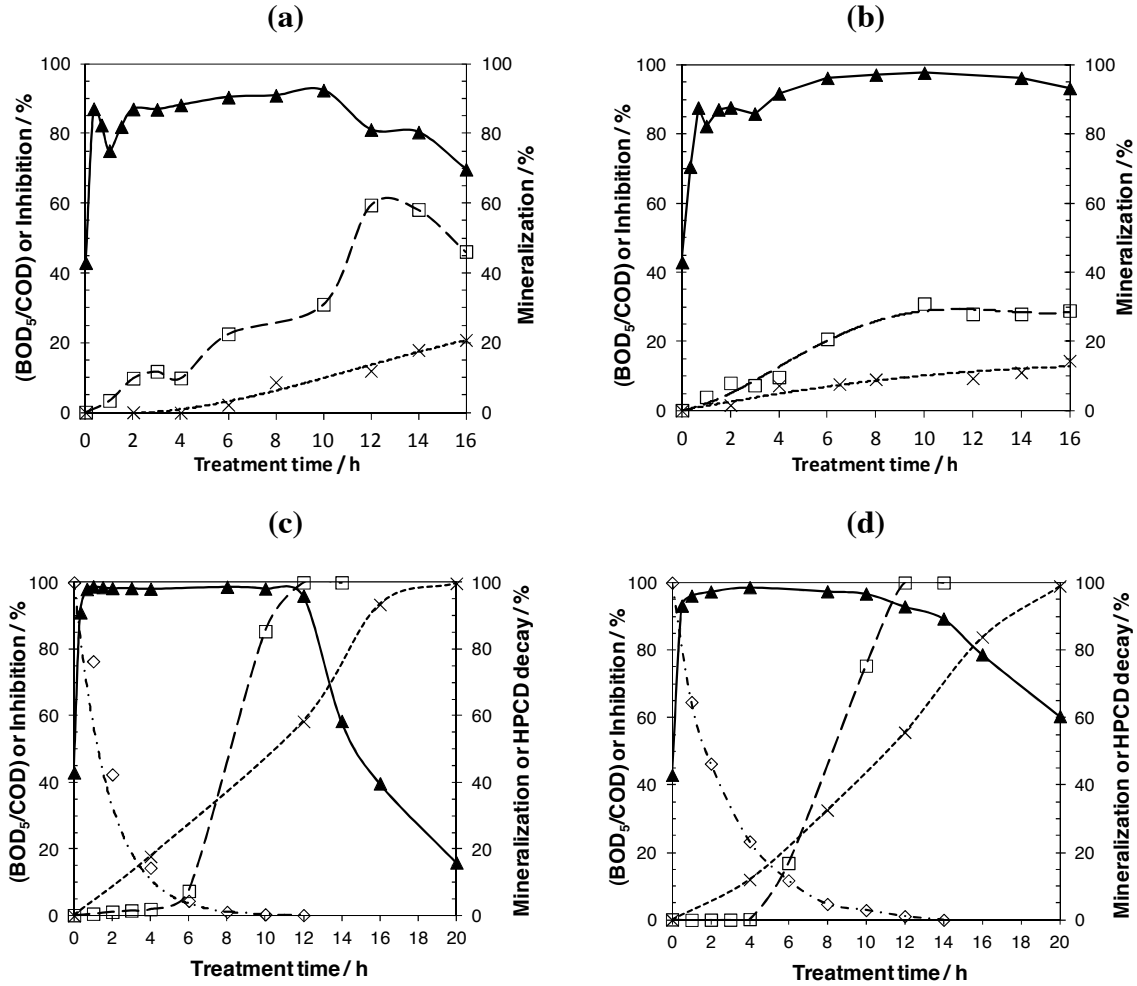

Fig. 5.5. *Biodegradability assessment (BOD_5/COD ratio) (— —□— —), toxicity evolution (— —▲— —), mineralization rate (- - -×- - -) and HPCD decay (— · —◊— · —) during EF or AO degradation of PHE (0.09 mM) in the presence of HPCD (9 g L^{-1}) with different kind of anode materials: EF-Pt (a), EF-DSA (b); EF-BDD (c), AO-BDD (d), at constant applied current intensity (I = 1000 mA).*

Mineralization data show that in each kind of treatment the mineralization increases with the treatment time. Mineralization rates during EF-BDD and AO-BDD increase largely quicker compare to EF-Pt and EF-DSA. The mineralization efficiency rank is the same as found for the study of the applied current intensity effect (EF-BDD > AO-

BDD >> EF-DSA > EF-Pt), which confirms the mineralization power of different treatments. It can be noted that the mineralization rates are negligible during the first hours of EF-Pt treatments, indicating that only degradation mechanism occurs during this process. That could also confirm the highest kinetic rate of PHE degradation obtained during EF-Pt process.

Biodegradability experiments highlight also different behaviors between the treatments, though an optimal ratio can be determined in each case. During the first 4 h of treatment, very low BOD_5/COD ratios are obtained during EF-BDD and AO-BDD treatments. It means that the by-products are too slowly biodegradable during this period of time. It can also be explained by the high toxicity of the solution during the first hours of treatment that is discussed in the following sub-section 5.3.2.3. However, the biodegradability increases very quickly between 6 h to 12 h of treatment, reaching a maximal ratio (BOD_5/COD = 100%). Regarding biodegradability experiments with DSA and Pt anodes, similar behaviors are noted between both processes until 10 h of treatment time. BOD_5/COD ratio increases until a plateau (10%) at 2 h of treatment. Then it increases from 4 h to 10 h of treatment reaching a ratio of 33%, indication that the treated solution becomes slightly biodegradable. This ratio is the optimal value obtained for EF-DSA treatment, whereas the optimal value in EF-Pt process is largely higher (60%) after 13 h of treatment. Biodegradabilities with EF-Pt and EF-DSA are higher than with EF-BDD and AO-BDD during the first 6 h of treatment, meaning that different degradation/mineralization kinetics are implicated during the oxidative treatments.

5.3.2.3 Comparison of toxicity during PHE and HPCD oxidative treatments

Evolution of toxicity effect of treated synthetic SW solution during EF and AO degradation of PHE in the presence of HPCD with Pt, DSA and BDD anodes is given in Figure 5.5.

It demonstrates that the solution toxicity became 40% higher than the initial toxicity during the first 10 h treatment (between 85-99% of inhibition), whatever the anodes employed. This is probably due to the formation of highly toxic oxidation by-products during electrolysis that are often observed in other publications (Brillas et al., 2009). A recent study denotes the fact that hydroxylated PAHs and particularly hydroxylated PHE have reprotoxic effect on carps (Fernandes and Porte, 2013), which can confirm

the quick increase of toxicity at the beginning of the treatment. However, the toxicity during the first 4 h of treatment (time to degrade PHE) is higher (99%) with BDD than with DSA and Pt (85-90%) anodes. That means that different oxidation/mineralization kinetics were involved according to the anode used, and the quicker formation of toxic intermediates observed with BDD anode can be explained by the mineralization process (see sub-section 5.3.1.2.) involved with this anode. Toxicity obtained with EF-DSA treatment is constant and is still high even after 16 h of treatment. During EF-Pt process, the toxicity starts to decrease after 10 h of treatment. However the mineralization rate is still low even after 16 h of treatment (20%) and the treatment is not accomplished yet at this time. In that way, it is possible that the toxicity restarts to increase after the 16 h of treatment. Regarding the treatments with BDD, the toxicity diminishes after 12 h of treatment. The quicker decrease with EF-BDD could be due to the paired electrocatalysis process (see sub-section 5.3.1.2.).

By comparing with biodegradability data, at the beginning of the treatment the toxicity is higher and BOD_5 is lower with EF-BDD and AO-BDD processes and the mineralization (inversely related to COD) is still too low. After 6 hours of treatment, the biodegradability of treated synthetic SW solution with BDD experiments increases very quickly. At this time the toxicity is still high and the BOD_5 is lower than with Pt and DSA, but the mineralization of organic compounds of treated synthetic soil solution increases very quickly in the meanwhile. The synthetic soil solutions treated with Pt anode are less toxic after 10 h of treatment and its biodegradability increases quickly, even if the mineralization is low (around 10-15%). After 13 h of treatment, the mineralization rate is still low (15-20%) and the BOD_5 decreases a little bit even if the toxicity decreases. Apparently, some less biodegradable by-products are formed. Regarding DSA experiments, the mineralization rate increases slowly and the toxicity is still higher after 10 h of treatment. Thus, toxicity results are in agreement with those obtained in section 5.3.1.

5.3.2.4 Comparison of EF-BDD and AO-BDD treatments until complete mineralization

Since Pt and DSA anodes give too low mineralization rates, only EF-BDD and AO-BDD are compared until complete mineralization.

Figure 5.5 shows the relation between toxicity, biodegradability, HPCD degradation and the mineralization rate during EF-BDD and AO-BDD treatments.

The same behavior is observed in both processes. HPCD is degraded by following a pseudo-first order kinetic model with apparent rate constant equal to 0.56 h^{-1} and 0.37 h^{-1} in the case of EF-BDD and AO-BDD, respectively. After reaching 60% of mineralization (at 12 h treatment with BDD anode), all the HPCD is degraded and the solution toxicity started to decrease until the complete mineralization (20 h) in both treatments. At this time of treatment (12 h), the biodegradability is maximal (100%).

The mineralization rate with AO-BDD (99.0%) is slightly lower than EF-BDD (99.7%) after 20 h of treatment and the final TOC values are 46.1 mg C L^{-1} and 13.2 mg C L^{-1}, respectively. Thus still few toxic compounds remain in the solution in the case of AO-BDD after 20 h of treatment.

It is also interesting to note that the biodegradability starts to increase only when the HPCD is almost degraded (5-10% in solution). Mansour et al. (2012) highlight also this behavior during EF of sulfamethazine solutions at initial COD of 88 mg O_2 L^{-1}.

5.3.3 Comparison of the different treatments efficiency and their relative energy consumption

Since an effluent with a BOD_5/COD ratio higher than 33% is considered as biodegradable in industrial wastewater treatment (Rodier et al., 2009), a biological post-treatment could be considered after reaching this threshold with EF process. Figure 5.6 illustrates radar diagrams comparing different ways to combine EF with or without a biological post-treatment. Table 5.3 gives values corresponding to Fig. 5.6.

The first option would be to do a biological treatment after reaching a maximal biodegradability ratio with EF treatment. The second one is to combine with a biological post-treatment after reaching the threshold value (33%). The last suggested solution would be to run EF treatment until the complete mineralization. The following parameters are taken into account: time of treatment, mineralization rate, biodegradability (%), toxicity (% of inhibition), energy consumption (kWh m^{-3}) (Eq. 5.6), and energy consumption per unit TOC mass removed (kWh (kg TOC)$^{-1}$) (Eq. 5.7).

At maximal biodegradability ratio, the treatments with BDD anode have better efficiency compared to EF-Pt and EF-DSA in terms of mineralization, biodegradability

and energy consumption per unit TOC mass removed. The energy consumption per volume with BDD anode is higher than Pt and DSA electrochemical treatments since the overpotential at BDD anode, which is a component of E_{cell} (Panizza and Cerisola, 2009), is higher than with Pt and DSA anodes as already discussed in sub-section 5.3.1.2.

At the threshold value that allows considering a biological post-treatment, EF-BDD and AO-BDD have shown better effectiveness by taking into account all the six parameters. Indeed, only 7 h (equivalent to 25% of mineralization) of BDD treatments is required to reach 33% of biodegradability against 10 h (equivalent to around 10% of mineralization) with Pt and DSA treatments. This leads to slightly better energy consumption per volume and largely better energy consumption per TOC. The toxicity is higher than 90% in all kinds of treatments. Even if EF-Pt gives similar values of energy consumption per volume as BDD treatments, the energy consumption per unit TOC mass removed and the mineralization remain still low.

Regarding the treatments until the complete mineralization, only processes with BDD are compared. EF-Pt and EF-DSA treatments demonstrated to have too slow mineralization rate to be running until the complete mineralization. EF-BDD and AO processes show similar efficiency with all the parameters, tough the toxicity is higher in the case of AO-BDD.

Treatments until complete mineralization are similar to treatments at maximal biodegradability ratio for processes with BDD in terms of energy consumption per TOC. In both case, energy consumption is between 2 and 3 times higher than for BDD treatments until 33% of biodegradability. Thus, by comparing the three different ways suggested with BDD treatments, the treatment until 33% of biodegradability appears to be a good compromise between energy consumption per volume and energy consumption per TOC. Besides, EF-BDD and AO-BDD have similar behavior in all cases. Whatever the way to treat the effluent, EF-DSA has the same behavior. EF-Pt and EF-DSA processes have shown less conclusive results than BDD treatments, whatever the way suggested.

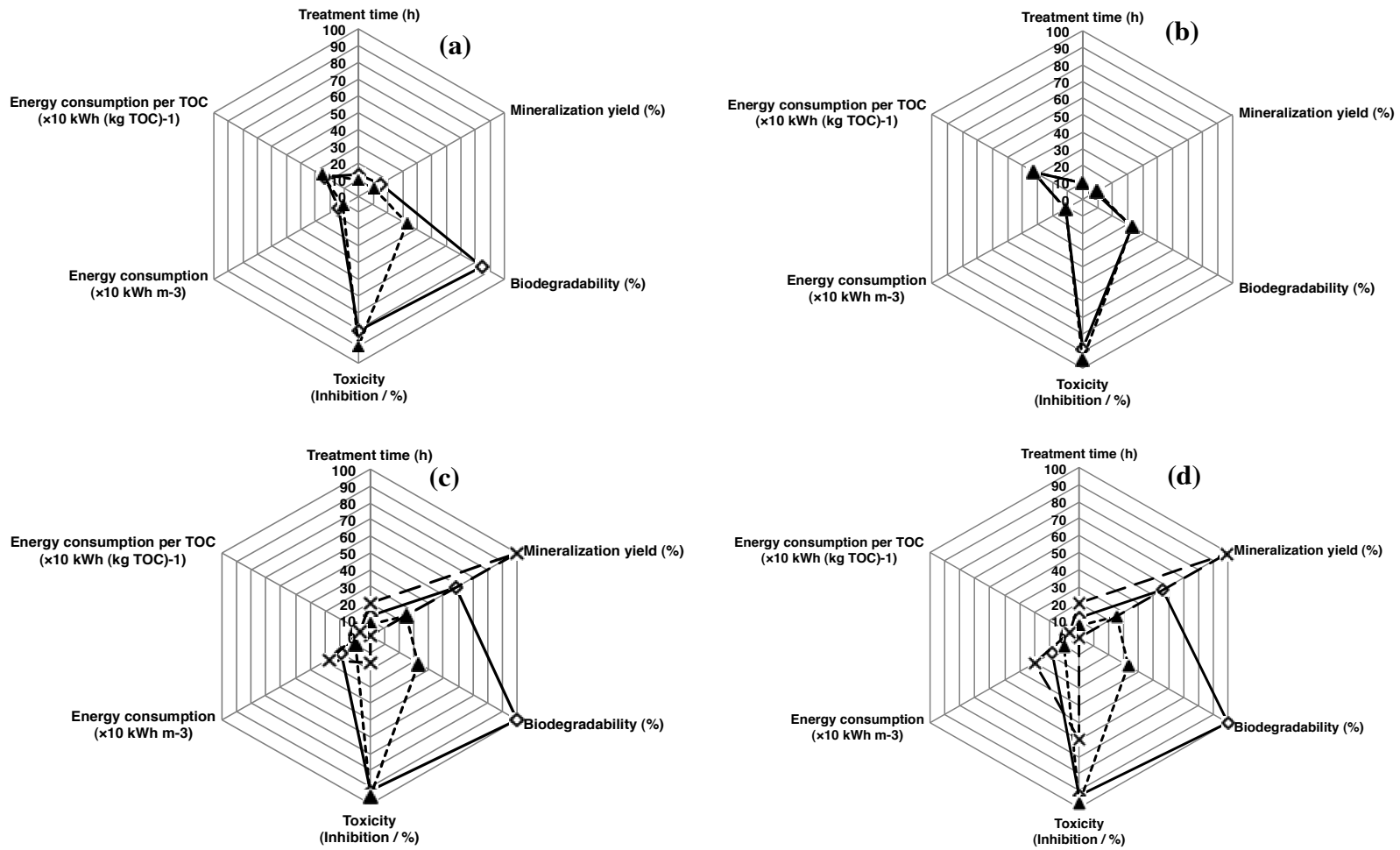

Fig. 5.6. *Comparison of different treatments efficiency such as EF-Pt (a), EF-DSA (b), EF-BDD (c) and AO-BDD (d) by considering six parameters: time of treatment, mineralization rate, biodegradability (%), toxicity (% of inhibition), energy consumption per volume (kWh m^{-3}), energy consumption per unit TOC mass (kWh (kg TOC)$^{-1}$). Three treatments conditions are suggested: maximal biodegradability ratio (——◊——), 33% of biodegradability (- - -▲- - -) and complete mineralization (— —×— —).*

Table 5.3. Synthesis table with data comparing EF processes with Pt, DSA or BDD anode materials and AO process with BDD anode. Six parameters are taken into account by considering three different approaches of treatment.

	Time of treatment (h)				**Mineralization yield (%)**				**Biodegradability (BOD_5/COD) (%)**				**Toxicity (Inhibition) (%)**				**Energy consumption per volume (kWh m^{-3})[(a)]**				**Energy consumption per TOC (kWh kg TOC^{-1})[(a)]**			
	EF -Pt	**EF-DSA**	**EF-BDD**	**AO-BDD**	**EF -Pt**	**EF-DSA**	**EF-BDD**	**AO-BDD**	**EF -Pt**	**EF-DSA**	**EF-BDD**	**AO-BDD**	**EF -Pt**	**EF-DSA**	**EF-BDD**	**AO-BDD**	**EF-Pt**	**EF-DSA**	**EF-BDD**	**AO-BDD**	**EF-Pt**	**EF-DSA**	**EF-BDD**	**AO-BDD**
Maximal biodegradability ratio	13	10	12	12	15	8	58	56	60	33	100	100	81	89	92	93	142	111	193	177	232	329	60	69
33% of biodegradability ratio	10	10	7	7	10	9	25	25	33	33	33	33	90	95	96	98	109	111	96	103	258	329	94	90
Complete mineralization	-	-	20	20	-	-	99.7	99.0	-	-	0	0	-	-	16	60	-	-	275	295	-	-	59	65

[(a)] only power supply for electrolysis was considered

Moreover, knowing that the cost of Pt material is much higher than BDD and DSA ones, it appears meaningful to consider BDD in a larger study scale as the best choice for an anode. Since iron is often present in soil, SW solution enhanced by an extracting agent like HPCD could have soluble iron. In that case, EF-BDD treatment would be suggested as the best option compared to EF-Pt and EF-DSA processes.

5.4 Conclusions

This study shows that anode materials play an important role in the oxidation of synthetic SW solutions containing PHE and HPCD in terms of compounds decay, mineralization, biodegradability, toxicity and energy consumption. Two different locations of hydroxyl radical generation are observed, one in the bulk solution (from Fenton reaction) and one at the surface of high O_2-overvoltage electrode (BDD). Thus, Pt and DSA electrodes favor the degradation mechanism while AO-BDD promotes mineralization and EF-BDD supports both ways. These results are confirmed by the time-course of PHE and HPCD decay and the biodegradability and toxicity assays. Competitive decay between PHE and HPCD are observed. EF-BDD and AO-BDD give largely better TOC decay than EF-Pt and EF-DSA. During BDD treatments, the mineralization increases linearly when the applied current efficiency increases from 0 to 2000 mA. It permits to note that EF-BDD is 1.35 times better than AO-BDD to mineralize solutions. At 1000 mA, the complete mineralization is achieved after 20 h of EF-BDD and AO-BDD treatments. In BDD treatments, when the degradation of initial compounds (PHE and HPCD) is achieved (at 60% of mineralization), the toxicity starts to decrease and the biodegradability reaches a maximum value (100%).

A minimum biodegradability ratio of 33% is taken into account to consider a biological post-treatment. Six parameters (the time of treatment, the mineralization rate, the biodegradability, the toxicity, the energy consumption per volume and the energy consumption per TOC) are taken into account to compare the electrochemical treatment until 33% of biodegradability, until maximal biodegradability ratio and until the complete mineralization. Considering a pre-treatment with EF-BDD or AO-BDD until reaching a biodegradability of 33% seems to be a good compromise. As the Pt electrode is more expensive than DSA and BDD ones the use of this anode at industrial scale is ruled out. These results give a promising methodology to perform further experiments with SW solution from a historically PAHs-contaminated soil.

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CHAPTER 6

Electro-Fenton Treatment of Real Soil Washing Solutions

This chapter will be submitted for publication as:

Mousset, E., Huguenot, D., van Hullebusch, E. D., Oturan, N., Guibaud, G., Esposito, G., Oturan, M. A., Soil washing by HPCD or Tween 80 combined to electro-Fenton to decontaminate historically PAHs-contaminated soil - a laboratory investigation study (to be submitted in *Journal of Hazardous Materials*).

CHAPTER 6

In this chapter are presented the results obtained with real soil washing (SW) solutions from a historically PAHs-contaminated soil. The data related to the recycling possibilities were presented in «AquaConSoil» conference:

- E. Mousset, D. Huguenot, E. D. van Hullebusch, N. Oturan, G. Guibaud, G. Esposito, M. A. Oturan, Soil washing combined to electro-Fenton treatments of PAHs contaminated soils in the presence of HPCD or Tween 80. 12th AquaConSoil conference, Barcelona (Spain), April, 2013. (http://www.aquaconsoil.org/AquaConSoil2013/Procs_Theme_D_files/ThS_D3_Poster.pdf).

Regarding the results about bioassays studies in real solutions, they were presented in «Conference in Environmental Science and Technology (CEST)» and in a summer school:

- E. Mousset, D. Huguenot, E. D. van Hullebusch, N. Oturan, G. Guibaud, G. Esposito, M. A. Oturan, A new integrated approach to remove PAHs from highly contaminated soil: soil washing combined to electro-Fenton process and possible post-biological treatment. 13th international conference in environmental science and technology (CEST2013), Athens (Greece), September, 2013.
- E. Mousset, D. Huguenot, E. D. van Hullebusch, N. Oturan, G. Guibaud, G. Esposito, M. A. Oturan, Electro-Fenton treatment of soil washing solutions of PAHs-contaminated soils with cyclodextrin or surfactant. Summer school on contaminated sediments: characterization and remediation, Delft (The Netherlands), June, 2013.

Soil washing by HPCD or Tween 80 combined to electro-Fenton to decontaminate historically PAHs-contaminated soil - a laboratory investigation study

Abstract

An innovative integrated process was suggested: soil washing (SW) of historically PAHs-contaminated soil combined to electro-Fenton (EF) treatment including study of recirculation loop and a possible biological post-treatment. Two extracting agents were compared: hydroxypropyl-beta-cyclodextrin (HPCD) (7.5 ± 0.2 g L^{-1} equivalent to 6 ± 0.2 mM) and non-ionic surfactant Tween 80 (7.5 ± 0.2 g L^{-1} equivalent to 5.7 ± 0.2 mM). Six PAHs were monitored: acenaphthene (ACE), phenanthrene (PHE), fluoranthene (FLA), pyrene (PYR), benzo(a)pyrene (BaP) and benzo(g,h,i)perylene (BghiP). Tween 80 has shown much better extraction efficiency (18 times) than HPCD. HPCD recovery during recycling studies was better than Tween 80, while the monitored pollutants were completely degraded. Even after EF treatment of SW solutions, Tween 80 can enhance soil respirometry whereas HPCD tends to inhibit it. EF treatment succeeded to completely mineralize HPCD and Tween 80 solutions having an initial Chemical Oxygen Demand (COD) equal to 10,050 ± 240 mg O_2 L^{-1} and 15,120 ± 410 mg O_2 L^{-1} after 20 h and 28 h, respectively. A biodegradability ratio (BOD_5/COD) of 33% can be reached after 7 h and 20 h with HPCD and Tween 80, respectively. This ratio allows considering a biological post-treatment. In terms of energy consumption per unit Total Organic Carbon (TOC) mass removed, whatever the treatment considered, HPCD solutions leads to 1.4-1.5 less energy consumption than Tween 80 solutions. However, considering the cost of extracting agents and the respective advantages of Tween 80 and HPCD, Tween 80 appear to be still the best option for this integrated process, despite the ecological aspect to use a semi-natural product (cyclodextrin derivatives).

Keywords: Historically contaminated soils; PAHs; Cyclodextrin; Surfactant; soil remediation; Advanced oxidation processes

6.1 Introduction

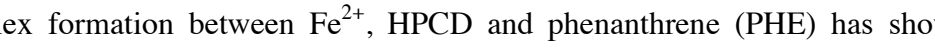
The remediation of polluted soils is a part of challenges of the coming years. In particular, soils contaminated by hydrophobic organic compounds (HOCs) such as hydrocarbons and Polycyclic Aromatic Hydrocarbons (PAHs) are a common concern since they are extremely difficult to remove because they are strongly bounded to soil and their potential toxicological impacts are significant (WHO, 2010). Moreover, PAHs are the third family compounds found in polluted and potentially polluted sites in France after hydrocarbons and lead (BASOL, 2013).

Their removal from contaminated soils and aquifers by traditional remediation approaches, such as pump and treat, turns out to be a slow process due to the low solubility of these compounds in water. As an alternative method, soil washing (SW) and soil flushing (SF) with extracting agents have emerged. Co-solvents and surfactants are the most conventional family of extracting agents being studied in SW/SF. Tween 80, a non-ionic surfactant, has demonstrated good performance as an enhancing agent, especially for its low adsorption into soil, its low Critical Micelle Concentration (CMC) and its high extraction efficiency (Gómez et al., 2010). However, in recent years, thanks to their physicochemical properties, cyclodextrins (CDs) such as the most cost-effective one, the hydroxypropyl-beta-cyclodextrin (HPCD) have been proposed as an alternative agent (Mousset et al., 2014a).

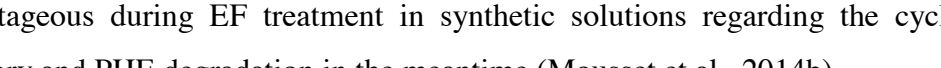
Since the enhanced SW or SF processes only permit to extract the pollutant but not to destroy it, a post-treatment is needed. Advanced oxidation processes (AOPs), which involve the *in-situ* generation of a very powerful oxidizing agent such as hydroxyl radical ($^{\bullet}OH$), have shown to be promising and environmentally friendly methods (Brillas et al., 2009; Panizza and Cerisola, 2009). One of them, namely electro-Fenton process (EF), is based on the electrochemically generated Fenton's reagent (a mixture of H_2O_2 and Fe^{2+} ion) to produce hydroxyl radical $^{\bullet}OH$ through the following reaction (in acidic medium) (Sirés and Brillas, 2012):

$$Fe^{2+} + H_2O_2 + H^+ \rightarrow Fe^{3+} + H_2O + {}^{\bullet}OH \qquad (6.1)$$

Compared to chemical Fenton process, the EF process allows minimizing the use of reagent since H_2O_2 is *in-situ* produced and a catalytic amount of soluble iron added initially to the solution is continuously electro-regenerated at the cathode trough the reactions 6.2 and 6.3 (Oturan, 2000; Sirés et al., 2007; Feng et al., 2013):



$$O_2 + 2\,H^+ + 2\,e^- \rightarrow H_2O_2 \quad (6.2)$$



$$Fe^{3+} + e^- \rightarrow Fe^{2+} \quad (6.3)$$

Thanks to these enhancements, higher degradation rate and mineralization degree of organic pollutants are obtained without any sludge production. Moreover, a ternary complex formation between Fe^{2+}, HPCD and phenanthrene (PHE) has shown to be advantageous during EF treatment in synthetic solutions regarding the cyclodextrin recovery and PHE degradation in the meantime (Mousset et al., 2014b).

Thus, in this study a new integrated approach is presented: SW combined to EF treatments of real PAHs-contaminated soils by comparing both Tween 80 and HPCD as extracting agents at the same mass concentration (7.5 ± 0.2 g L^{-1}), which is very similar to the molar concentration (equivalent to 6 ± 0.2 mM for HPCD solutions and equivalent to 5.7 ± 0.2 mM for Tween 80 solutions). Six PAHs were monitored according to their number of rings: acenaphthene (ACE) and phenanthrene (PHE) (3 rings), fluoranthene (FLA) and pyrene (PYR) (4 rings), benzo(a)pyrene (BaP) (5 rings), benzo(g,h,i)perylene (BghiP) (6 rings). All these PAHs are listed by the Environmental Protection Agency of the United States (USEPA) as hazardous pollutants. Three possible process set-ups are considered: a recirculation loop, a degradation followed by a possible biological post-treatment and a complete mineralization of SW solutions. The main experimental outputs monitored are: PAHs extraction efficiency, degradation rate by EF, extracting agent recovery, soil respirometry after SW, biodegradability ratio (BOD_5/COD) during EF process, mineralization rate and energy consumption during electrochemical treatment.

6.2 Materials and methods

6.2.1 Chemicals

Sodium sulfate, 2-(p-toluidino)naphthalene-6-sulfonic acid sodium (TNS), Tween 80 (polyoxyethylene (20) sorbitan monooleate) (Molar Weight (MW) = 1310 g mol^{-1}), acetonitrile, acetic acid, ACE, PHE, FLA, PYR and BaP were purchased from Aldrich. Hydroxypropyl-beta-cyclodextrin (HPCD) was provided by Xi'an Taima Biological Engineering Company (MW = 1250 g mol^{-1}). Ammonium acetate, hydroxylamine hydrochloride and BghiP were supplied by Acros. Analytical reagents like n-hexane, acetone, hydroxylammonium chloride and NaOH were provided by VWR. N-

Allylthiourea was provided by Alfa Aesar. Sodium phosphate dibasic (Na_2HPO_4), ammonium chloride (NH_4Cl), heptahydrated magnesium sulfate ($MgSO_4 \bullet 7H_2O$), dehydrated calcium chloride ($CaCl_2 \bullet 2H_2O$), potassium peroxodisulfate, phenanthroline 1,10 and iron standard solution were purchased from Merck. Potassium chloride (KCl) (>99.0%, Fluka) was also used. HNO_3 (70%) and fluorhydric acid (48%) from Fisher Scientific, HNO_3 (65%) from Fluka and chlorhydric acid (32%) from Riedel-de-Haën were employed. Mohr's salt was provided by Acros. All the reagents were of analytical grade. In all experiments, ultrapure water from a Millipore Simplicity 185 (resistivity > 18 MΩ cm) system was used.

6.2.2 Soil preparation and its characteristics

The polluted soil was sampled from a PAHs and hydrocarbons contaminated site. Before its utilization, the soil was sieved under 2 mm and homogenized by a sample divider (Retsch). The soil physicochemical characteristics obtained from an external certified laboratory (ALcontrol Laboratories) are described in Table 6.1.

Six PAHs were monitored: ACE, PHE, FLA, PYR, BaP, BghiP. Their physicochemical properties are described in Table 6.2. The total amount in soil of these PAHs was determined by Soxhlet extraction (Behr, Labor-Technik). Two grams of dried soil were mixed with 5 g of anhydrous sodium sulfate to prevent trace of humidity. A mixture of n-hexane/acetone (70 mL / 70 mL) was then added. Extractions were performed for 16 h (4-5 cycles per h) in triplicate. The calculated amount of PAHs were compared to the values obtained with the ALcontrol Laboratories data. The highest content measured was considered for each PAH. The final concentrations of selected pollutants are given in Table 6.1. The total concentration of the 16 PAHs listed by USEPA was 1,090 mg kg^{-1} Dry Weight (DW).

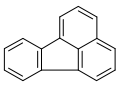
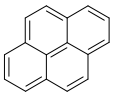
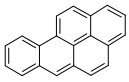
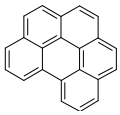
Total Petroleum Hydrocarbons (TPH) (C10-C40) contents were present at a level of 850 mg kg^{-1} DW. The other organic pollutants were not mentioned, as their concentrations are much below the regulations.

Table 6.1. Physicochemical soil characteristics.

Particle size distribution (%)	Clay (< 2 μm)	19.7
	Fine silt (2-20 μm)	23.3
	Coarse silt (20-50 μm)	7.5
	Fine sand (50-200 μm)	12.3
	Coarse sand (0.2-2 mm)	37.1
Organic Matter (OM) (%)		4.71
pH (H_2O)		8.3
CEC (soil pH) (meq kg^{-1})		203
Saturation of clay-humic complex with exchangeable cations (Ca^{2+}, Mg^{2+}, K^+, Na^+) (%)		100
Total Fe (mg kg^{-1} DW)[(a)]		9,550
Total hydrocarbons (C10-C40) (mg kg^{-1} DW)		850
Monitored PAHs (mg kg^{-1} DW)[(a)]	ACE	152
	PHE	308
	FLA	110
	PYR	80
	BaP	96
	BghiP	23
Total 16 PAHs (mg kg^{-1} DW)		1,090

(a) Values obtained by analysis in internal laboratory.

Table 6.2. Physicochemical properties of the monitored PAHs (ACE, PHE, FLA, PYR, BaP, BghiP).

PAHs structure	Molecular formula	MW (g mol^{-1})	Water solubility at 25°C (mg L^{-1})[(a)]	Log K_{ow}[(a)]	Log K_{oc}[(b)]	K_d (L kg^{-1})[(c)]	Henry constant (H) at 25°C (Pa m^3 mol^{-1}))[(b)]
ACE	$C_{12}H_{10}$	154.2	3.4×10^{0}	4.3	3.66	9.1×10^{1}	1.5×10^{1}
PHE	$C_{14}H_{10}$	178.2	1.3×10^{0}	4.4	4.15	2.8×10^{2}	4.0×10^{0}
 FLA	$C_{16}H_{10}$	202.3	2.6×10^{-1}	5.2	4.58	7.6×10^{2}	1.5×10^{0}
 PYR	$C_{16}H_{10}$	202.3	1.4×10^{-1}	5.3	4.58	7.6×10^{2}	1.1×10^{-3}
 BaP	$C_{20}H_{12}$	252.3	3.8×10^{-3}	6.0	6.74	1.1×10^{5}	5.0×10^{-2}
 BghiP	$C_{22}H_{12}$	276.3	3.0×10^{-4}	7.0	6.20	3.2×10^{4}	1.4×10^{-2}

[(a)] Manoli and Samara (1999)

[(b)] Martens and Frankenberger (1995)

[(c)] Calculated according to the following equation: $K_d = f_{oc}*K_{oc}$ with f_{oc} the carbon organic fraction of soil; $f_{oc} = 0.02$ for soil-water interaction (INERIS, 2005)

6.2.3 SW experiments

SW experiments were performed in a 500 mL glass bottle at a soil/liquid ratio equal to 10% (40 g / 400 mL). Solutions of Tween 80 (7.5 ± 0.2 g L^{-1}) or HPCD (7.5 ± 0.2 g L^{-1}) were used and the mixtures were rotated in a Rotoshake RS12 (Gerhardt, Germany) at 10 rpm for 24 h. Then the particles settled for 12 h and the supernatants were filtered with a 0.7 μm glass microfiber filter. SW experiments with ultrapure water were also performed in same conditions as blanks. The supernatants were then used for PAHs, TOC, HPCD, Tween 80, pH, conductivity and Fe measurements and EF treatments. The soil was used for respirometry assays and recycling studies.

Successive SW by using fresh solution (Tween 80 or HPCD at 7.5 ± 0.2 g L^{-1}) were performed by reusing each time the same soil and the same soil/liquid ratio (40 g / 400 mL).

6.2.4 Soil respirometry assays

Soil respirometry tests were performed after successive SW cycles. Thirty grams of sludge mixture from SW experiments washed with ultrapure water or HPCD or Tween 80 solutions were placed in container from Oxitop® Control OC 110 system (WTW). A volume of 25 mL of NaOH (1 M) was added in a beaker placed above the sludge mixture in order to trap the CO_2 formed during microorganims respiration. The samples were then incubated for 5 days at 20°C. The standard deviations from respirometric assays were always less than 0.20 mg O_2 L^{-1} and 0.12 mg O_2 L^{-1} in the case of Tween 80 and HPCD mixtures, respectively, which leads to low errors percentages (< ± 6%). In order to be repeatable and comparable, each sample was performed with similar humidity rate. These humidity tests were performed in an oven at 105 °C for 48 h. The average humidity rates obtained for ultrapure water, HPCD and Tween 80 tests were 46.0 ± 4.6%, 48.0 ± 4.5% and 43.7 ± 3.7%, respectively.

6.2.5 EF treatment

EF experiments of SW solutions were performed at room temperature (22 ± 1°C), in a 0.40 L undivided glass electrochemical reactor at current controlled conditions. The cathode was a 150 cm^2 carbon-felt piece (from Carbone-Lorraine, France). Regarding the recirculation study, a Platinum (Pt) grid (5 cm height cylindrical (i.d. = 3 cm)) anode

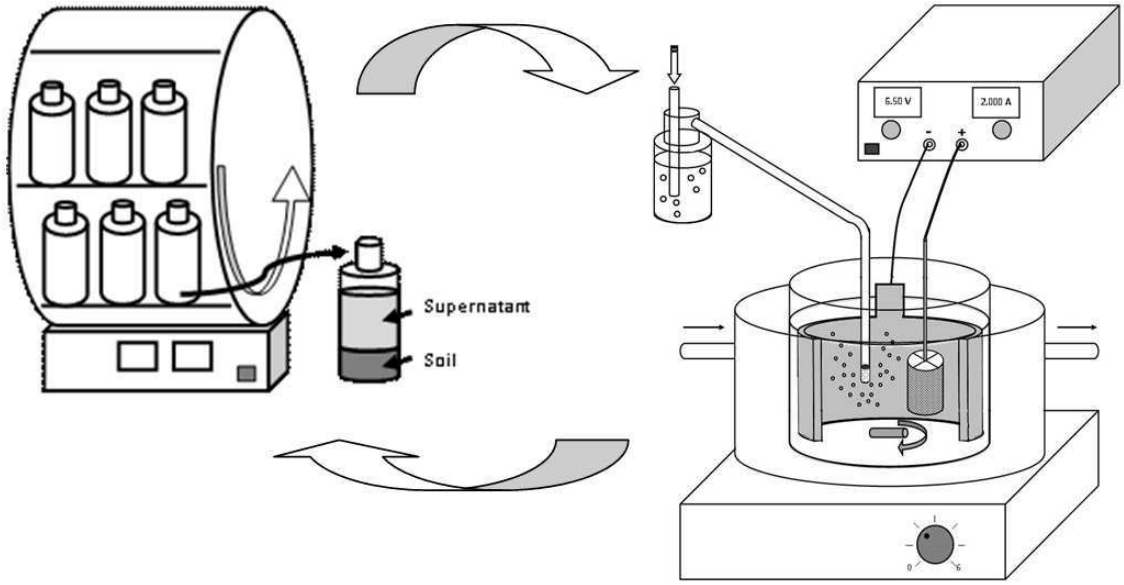
was employed. When studying the possibility of a biological post-treatment, Boron-Doped Diamond (BDD) plate anode was used, since this electrode was determined to be the best option (compared to Pt and Dimensionally Stable Anode (DSA; $Ti/IrO_2/RuO_2$) anodes) in a previous study (Mousset et al., 2014b). Each anode was centred in the cell and surrounded by cathode covering the inner wall of the cell. The electrochemical cell was monitored by a power supply HAMEG 7042-5 and applied current was set to 2000 mA and 1000 mA for recycling and biodegradability studies, respectively. An inert electrolyte (Na_2SO_4 at 0.150 M) is added to the medium since the conductivity of solutions was too much low (see 6.2.8.3 sub-section). Prior to each experiment, the solutions containing HPCD were saturated in O_2 by supplying compressed air (10 min at 0.25 L min^{-1}). Since too much foam is formed during bubbling system, the solutions containing Tween 80 were not saturated with O_2. However, solutions were stirred continuously and vigorously by a magnetic stirrer to compensate O_2 depletion, as mentioned in a previous study (Mousset et al., 2014b). A heat exchanger system is provided to keep the solution at constant room temperature by using fresh water. The pH of initial solution was not adjusted to pH 3 as usual. No iron was added since it was assumed that iron was already present in SW solutions. The results about initial iron content in solutions are presented in sub-section 6.3.1.2.

The schematic representation of the integrated process (SW + EF treatment) is shown in Fig. 6.1. Figure 6.1a represents the study of recirculation loop (Pt anode, I = 2000 mA) and Fig. 6.1b represents the study of a possible biological post-treatment (BDD anode, I = 1000 mA).

6.2.6 Recirculation procedure

Two successive SW experiments by reusing each time the solution treated by EF were performed. Each time the same soil and the same soil/liquid ratio (40 g / 400 mL) were used. Soil respirometry assays were also performed by applying the same procedure than the one described in sub-section 2.4. The degradation of monitored PAHs and extracting agents was carried out.

(a)



(b)

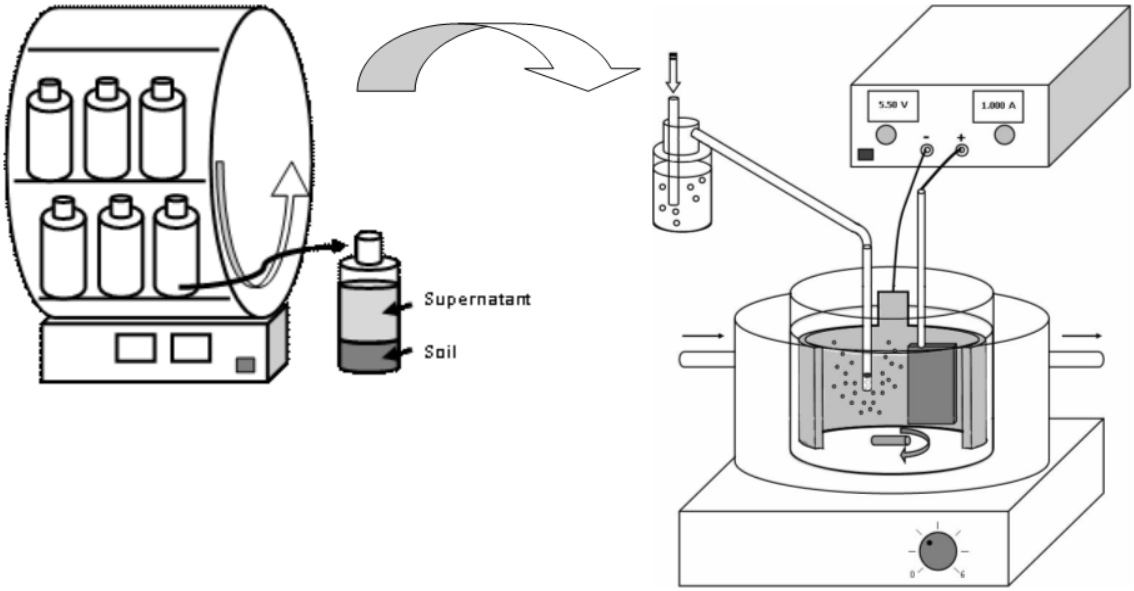


Fig. 6.1. *Schematic representation of the process: SW combined to EF process. (a) Recirculation loop studies (Pt anode, I = 2000 mA), (b) Possibility of biological post-treatment studies (BDD anode, I = 1000 mA).*

6.2.7 Biodegradability assays

The biodegradability was given by the ratio between BOD_5 and the COD. BOD_5 was determined by respirometric method (OECD 301F, ISO 9408) by manometric measurement with the OxiTop® IS 6 system (WTW). The system measured the

difference of pressure due to the consumption of oxygen by aerobic microorganisms (Eq. 6.4):

$$BOD = \frac{M(O_2)}{RT_m}\left(\frac{V_{tot} - V_{sample}}{V_{sample}} + \alpha\frac{T_m}{T_0}\right)\Delta p(O_2) \qquad (6.4)$$

where $M(O_2)$ is the MW of O_2 (32000 mg mol^{-1}), R is the gas constant (83.144 L mbar $(mol\ K)^{-1}$), T_0 is the reference temperature (273.15 K), T_m is the measuring temperature, V_{tot} is the bottle volume (nominal volume in mL), V_{sample} is the sample volume in mL, α is the Bunsen absorption coefficient (0.03103), $\Delta p(O_2)$ is the difference of the oxygen partial pressure (mbar).

The CO_2 released in the meantime by microorganisms was trapped in a rubber sleeve in which NaOH pellets were added. An inoculum is added in each sample solution just before starting the experiment. It consists of bacteria extracted with KCl at 9 g L^{-1} (30 mL with 3 g of dried soil) and an IKA-MS1 minishaker (1800 rpm during 1 min) from uncontaminated soil were added just before adding the samples. In order to promote the bacterial growth, nutrients were added. It consists of an aqueous solution containing a phosphate buffer solution (pH 7.2) and a saline solution prepared according to Rodier et al. (2009) (Mousset et al., 2012). This solution was then saturated in oxygen. All the samples were adjusted to circum-neutral pH. N-Allylthiourea (10 mg L^{-1}) was added to prevent nitrification. The samples were then incubated at 20°C (± 0.1) during 5 days in dark conditions. In order to consider the Organic Matter (OM) extracted from soil and the endogenous respiration, the BOD_5 measured in each blank was deduced from the BOD_5 of the samples. The BOD_5 of blanks were insignificant and caused no interferences.

COD measurements were achieved by a photometric method requiring a Spectroquant® NOVA 60 (Merck) equipment. Two millimeters of diluted samples were added in each COD cell test (Merck). The tests were then heated at 148°C for 2 h with a Spectroquant® TR 420 (Merck).

Since the H_2O_2 was produced *in situ* during EF experiment and the radicals formed during EF treatments have a limited life-time, these oxidants cause no interferences during the BOD_5 or COD measurements.

6.2.8 Analysis determination

6.2.8.1 PAHs quantification

The PAHs quantification in solution was followed by reversed phase with a high performance liquid chromatography (HPLC) ELITE LaChrom® coupled with an UV-absorbance (L-2400) and a fluorescence (L-2480) detectors (Merck Hitachi). The UV detection was set at 254 nm. The fluorescence detection was performed at the following excitation/emission wavelengths: 275/350 nm for ACE and PHE, 270/440 nm for FLA and PYR and 290/430 nm for BaP and BghiP. A C-18 end capped column (Purospher®) (5 µm, 25 cm × 4.6 mm (i.d.)) placed in an oven set at 40°C was used. For ACE, PHE, FLA and PYR analysis, the mobile phase was a mixture of water/acetonitrile (35:65 v/v) and the flow rate was set at 1.0 mL min^{-1} (isocratic mode) with a pump (L-2130, Merck Hitachi). For BaP and BghiP analysis, the mobile phase was a mixture of water/acetonitrile (15:85 v/v) and the flow rate was set at 1.0 mL min^{-1} (isocratic mode).

6.2.8.2 TOC analysis

The TOC values were determined by thermal catalytic oxidation using a Shimadzu V_{CSH} TOC analyzer. The temperature was set at 680°C (± 1°C) and Pt was used as catalyst. Calibrations were performed by using the potassium hydrogen phthalate solutions (50 mgC L^{-1}) as standard. All samples were acidified to a pH value of 2 with H_3PO_4 (25%) to remove inorganic carbon contents. The samples were then analyzed by non-purgeable organic carbon method. The injection volumes were 50 µL. All samples values are given with a coefficient of variance below to 2%.

6.2.8.3 pH and conductivity of solutions

The pH of solutions was measured with a CyberScan pH 1500 pH-meter from Eutech Instruments. Before each use, the pH-meter was calibrated with standard buffer solutions at 6.87 and 4.1. All the samples and buffer solutions were at room temperature (22 ± 1°C) before each measurement. The standard deviations of replicates were always less than 0.15. These values were too low to be readable on graphs.

Conductivity measurements were done with a MeterLab CDM 210 from Radiometer analytical SA. The conductivity values were adjusted according to the temperature of solutions.

6.2.8.4 HPCD and Tween 80 quantifications

The HPCD and Tween 80 concentrations were determined by a fluorimetric technique based on enhancement of the fluorescence intensity of TNS, when they are complexed with the cyclodextrin (Hanna et al., 2005) and Tween 80 (Mousset et al., 2013). This method allows quantifying HPCD and slightly modified HPCD (hydroxylated) in the same time, since the non-polar HPCD cavity brings about a TNS fluorescence intensity enhancement until the CD cavity is cleaved by the degradation technique. A Kontron SFM 25 spectrofluorimeter was set out at 318 nm for excitation and 428 nm for emission for both HPCD and Tween 80 quantification. Each sample is diluted in TNS at 3×10^{-6} M and 5×10^{-5} M for HPCD and Tween 80, respectively. The fluorescence intensity of Soil Organic Matter (SOM) and organic pollutant are not significant in this range of concentration (Mousset et al., 2013). Since TNS is photosensitive, TNS and the diluted samples were therefore stored in dark conditions.

6.2.8.5 Iron quantification in soil and solutions

- Total dissolved iron concentration

Total dissolved iron was measured by molecular absorption spectrometry with phenanthroline 1,10, according to Rodier et al. (2009). 50 mL of samples were acidified at pH 1 (HCl) and 5 mL of potassium peroxodisulfate (40 g L^{-1}) is added. The samples were then boiled during 40 min and let cool down at room temperature. Ammonium acetate was added in order to have a solution at pH around 4.5. Then 2 mL of phenanthroline 1,10 (0.5 %) was added and kept in dark conditions during 15 min. The absorbance measurements were performed with a spectrophotometer UV-VIS Lambda 10 at 510 nm. A blank without iron was prepared by following the same protocol and was deduced from the absorbance value of the samples. An external calibration curve was done with Mohr's salt (1 mM).

- Sequential extraction for iron fractionation

A three-stage sequential extraction speeding up with focused ultrasound method was employed (Pérez-Cid et al., 1998) to study iron fractionation (Mossop and Davidson, 2003) in the contaminated soil by combining both protocols. The applied operating conditions are described in Table 6.3. The amount of soil used was 0.25 g DW. Each

soil after SW with Tween 80, HPCD and ultrapure water were studied. These three kinds of soil were previously dried at 105°C during 48 h before sequential extraction. The ultrasound system was a Bandelin UW70 probe with a Bandelin Sonopuls GM70 equipment providing a sonication power of 20 W.

Table 6.3. Operating conditions used for ultrasound accelerated sequential extraction methods.

Stage	Reagents			Ultrasound time (min)
	Compound	Concentration	Volume	
Stage #1: acid soluble fraction (e.g. carbonates)	CH_3COOH	0.11 M	10 mL	7 min
Stage #2: reducible fraction (e.g. Fe-Mn oxides)	$NH_2OH.HCl$ (pH 1.5)	0.5 M	10 mL	7 min
Stage #3: oxidisable fraction (e.g. OM)	H_2O_2 + CH_3COONH_4 (pH 2)	30% w/v + 1 M	5 mL + 12.5 mL	2 min + 6 min

The solution pH in stage #2 and stage #3 were adjusted with HNO_3 (70%). Between each stage the samples were centrifuged (3000 g) during 15 min at 20°C with Jouan-KR22i equipment. The supernatant were then filtered (0.45 µm) and diluted in volumetric flask with the respective reagents used for the concerned stage. These liquid samples were kept for further atomic absorbance spectrometric (AAS) measurements. The soil samples were then rinsed with ultrapure water by centrifuging (3000g, 15min, 20 °C) a second time.

The total concentration of iron in soil was performed with a 0.25 g of dried contaminated soil. The mineralization was done in a Mutliwave 3000 (Anton Paar) at 1400 W during 30 min with a mixture of HNO_3 (65%), HCl (32%) and HF (48%) with the respective following ratio: 5 mL / 2 mL / 1 mL. The F^- ions were then complexed with boric acid (0.7 M) with a ratio of 6 mL of H_3BO_3 per mL of HF. These samples were then mineralized at 1400 W during 20 min. The samples were then diluted in 50 mL volumetric flask and filtered (0.2 µm) before their quantification by AAS. The total iron content in soil was reported in Table 6.1.

The AAS analyses of iron were performed with a Varian SpectrAA 220 with Flame provided by air/acetylene gas and a hollow cathode SpectrAA lamp as a radiation source for iron element. An external calibration was done with standard solutions of iron. Each sample was then analyzed in triplicate with a standard deviation less than 5%.

6.2.9 Energy consumption calculation

The energy consumptions are calculated according to Brillas et al. (2009) (Eq 6.5):

$$\text{Energy consumption (kWh (kg TOC)}^{-1}) = \frac{E_{cell} I t}{(\Delta TOC)_t V_S} \qquad (6.5)$$

where E_{cell} is the average cell voltage (V), I is the applied current (A), t is the electrolysis time (h), V_S is the solution volume (L) and $(\Delta TOC)_t$ is the TOC decay (g C L^{-1}).

6.3 Results and discussion

6.3.1 Effect of successive SW cycles

6.3.1.1 Extraction efficiency: Tween 80 versus HPCD

Concentrations of PAHs extracted with HPCD (7.5 g L^{-1}) and Tween 80 (7.5 g L^{-1}) are described in Table 6.4.

Table 6.4. Amount of PAHs extracted after four successive SW experiments.

PAHs	Initial PAHs amount in soil (mg kg^{-1} DW)	Successive SW with HPCD (7.5 ± 0.2 g L^{-1}) [PAHs] extracted (mg kg^{-1} DW) with fresh solution				Successive SW with Tween 80 (7.5 ± 0.2 g L^{-1}) [PAHs] extracted (mg kg^{-1} DW) with fresh solution			
		SW # 1	SW # 2	SW # 3	SW # 4	SW # 1	SW # 2	SW # 3	SW # 4
ACE	152	6.0 ± 1.9	0.02 ± 0.01	0.24 ± 0.15	0.39 ± 0.12	66.2 ± 4.4	38.1 ± 0.9	22.4 ± 1.3	8.9 ± 0.9
PHE	308	0.5 ± 0.4	0.20 ± 0.02	0.22 ± 0.01	2.07 ± 0.52	141.9 ± 6.3	100.9 ± 1.6	52.8 ± 5.6	15.8 ± 1.4
FLA	110	8.6 ± 0.2	0.65 ± 0.6	0.39 ± 0.33	0.67 ± 0.13	54.2 ± 2.8	32.0 ± 0.7	18.1 ± 1.9	0.7 ± 0.1
PYR	80	3.9 ± 0.1	0.66 ± 0.4	1.35 ± 0.40	0.03 ± 0.003	34.3 ± 0.8	17.8 ± 4.2	14.5 ± 0.4	6.3 ± 0.4
BaP	96	1.0 ± 0.01	1.08 ± 0.01	0.19 ± 0.16	0.08 ± 0.01	30.3 ± 1.2	14.1 ± 6.1	11.8 ± 0.46	5.7 ± 0.4
BghiP	23	0.3 ± 0.03	1.30 ± 0.02	0.18 ± 0.01	0.13 ± 0.02	6.9 ± 0.2	5.3 ± 0.2	3.2 ± 0.17	0.02 ± 0.001

As expected the amount of extracted PAHs are higher with both extracting agents compared to water alone in accordance with the water-solubility of each PAH (Table 6.2). Moreover, it is obvious that the successive SW processes allow extracting more amounts of PAHs with the use of Tween 80 compared to HPCD extractions. It can also be noticed that each successive cycle allows extracting lower amount of PAHs than the previous ones, especially when initial amounts is sufficiently high like with Tween 80 solutions, and may need a higher number of extraction.

Extraction efficiency obtained from successive SW processes by adding each time a fresh solution of HPCD (7.5 ± 0.2 g L^{-1}) or Tween 80 (7.5 ± 0.2 g L^{-1}) are given in Fig. 6.2. The percentages are given as a function of the initial concentration of pollutants in initial contaminated soil.

It is observed higher amounts of extracted pollutants with PAHs having lower soil-water partition coefficient (K_d) (with 2-, 3- and 4-rings) according to Table 6.1, especially with Tween 80 solutions. Extraction efficiencies with Tween 80 are particularly high in the case of PHE and FLA extraction, respectively 101.1% and 95.5%. Furthermore, after four successive cycles with fresh SW solutions, the averages of total extraction efficiency of the 6 PAHs are about 85 ± 6.0% and 4.5 ± 1.4% in the case of Tween 80 and HPCD, respectively. Thus, in average Tween 80 allowed extracting 18 times higher amount of PAHs than HPCD. This difference was expected since this ratio was around 13.3 in synthetic solutions (Mousset et al., 2014b), by considering that the solubilization efficiency is proportional to the concentration of the surfactant above the CMC.

Moreover, by comparing the colors of solutions (Fig. 6.3) after one SW experiments with ultrapure water, HPCD and Tween 80, it can be seen that the solutions are browner according to the following rank: Tween 80 >> HPCD ≥ ultrapure water. This could confirm the higher solubilization power of the surfactant towards organic molecules, especially those from SOM.

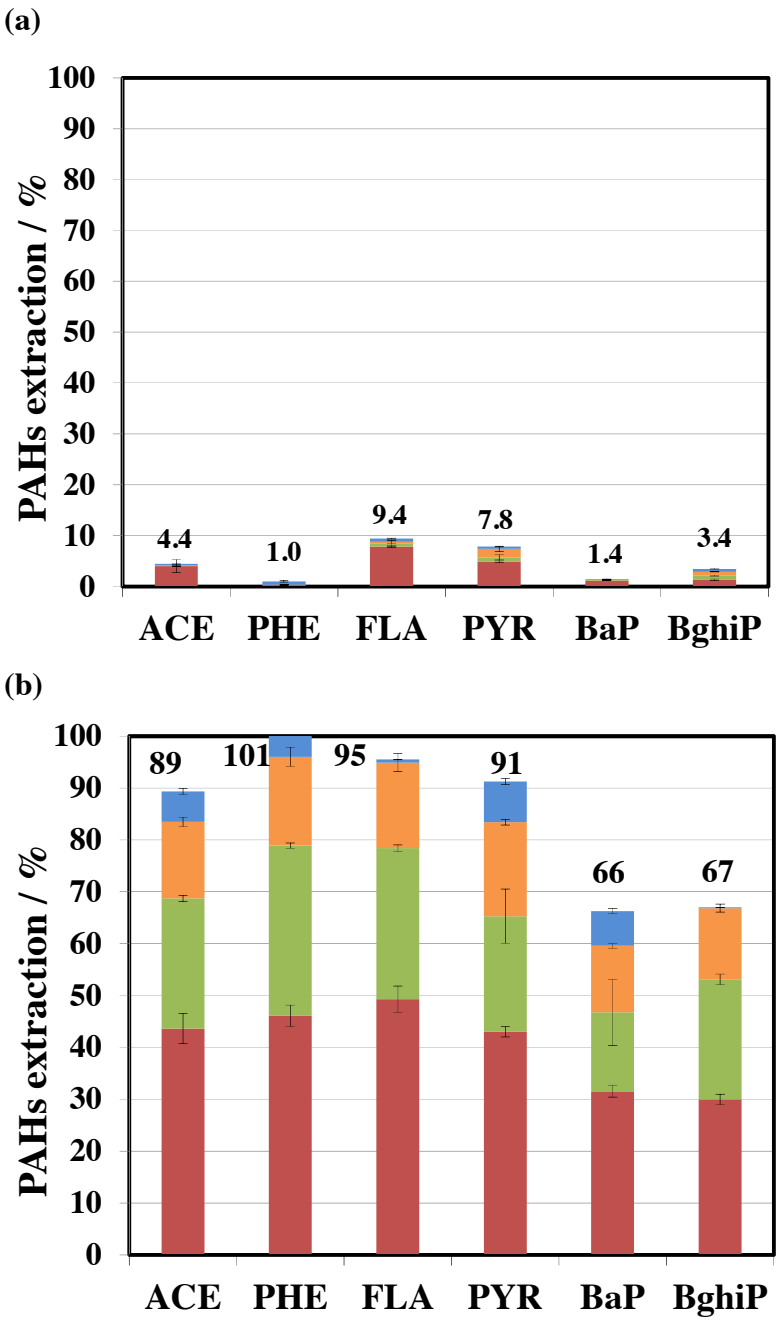


Fig. 6.2. *PAHs extraction efficiency after successive SW cycles with different solutions: HPCD (7.5 ± 0.2 g L^{-1}) (a), Tween 80 (7.5 ± 0.2 g L^{-1}) (b). One SW step (■), two successive SW steps (■), three successive SW steps (■) and four successive SW steps (■).*

a) (b) (c)

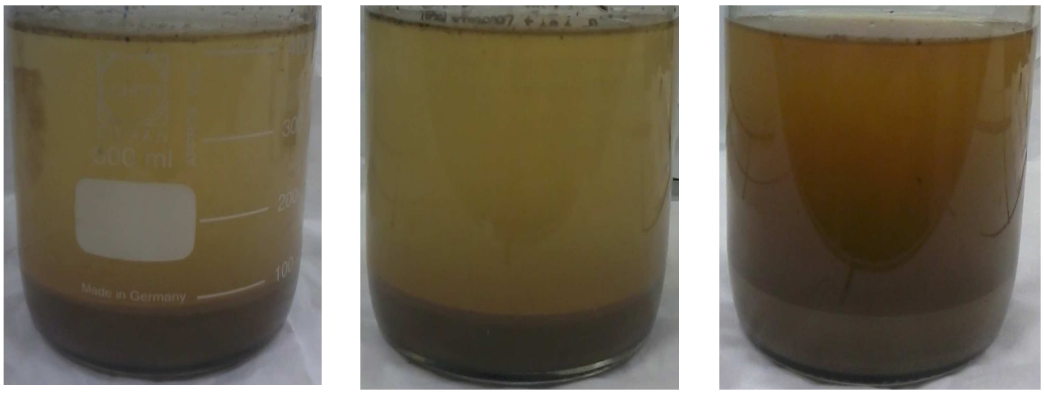


Fig. 6.3. *SW experiments with different solutions: ultrapure water (a), HPCD (7.5 ± 0.2 g L^{-1}) (b) and Tween 80 (7.5 ± 0.2 g L^{-1}) (c), with the following operating parameters: 10 rpm during 24 h, 40 g soil / 400 mL solution, pH (solution) = 8, 12h of sedimentation.*

6.3.1.2 Impact of extracting agents on the conductivity of SW solutions

Conductivity of SW solutions prepared with ultrapure water, HPCD and Tween 80 were 0.34, 0.36 and 0.37 mS cm^{-1}, respectively. In all the case, the conductivity was low and similar, meaning that HPCD and Tween 80 had no more impact on ions solubilization compared to water alone. Regarding the low conductivity values, external salts solution (Na_2SO_4 (0.15 M) in that case) need to be added as an electrolyte, in the aim to apply these solutions to an EF process, leading to a final conductivity of 18.0 mS cm^{-1}.

6.3.1.3 Impact of extracting agents on the mobilization of iron

The total dissolved iron concentrations were 0.020 ± 0.013 mM and 0.060 ± 0.013 mM for SW solutions with HPCD and Tween 80, respectively. It corresponds to an average of 0.011 ± 0.007 mg kg^{-1} DW and 0.033 ± 0.007 mg kg^{-1} DW of extracted iron from soil with HPCD and Tween 80, respectively. These values are very low compared to the initial iron content in soil that is around 9,550 mg kg^{-1} DW. However, both amounts are sufficient to perform an EF treatment, especially when studying the recirculation possibilities. Indeed, a concentration of 0.05 mM of iron(II) was found to be optimal in order to degrade PHE in particular and to save maximum solubilizing agent (HPCD) in a former study (Mousset et al., 2014b).

It can also be noticed that Tween 80 allows a relatively higher extraction of iron than HPCD. One of the hypotheses could be iron fractionation in soil. In that way sequential extraction of iron in soils coming from three kinds of SW experiments according to the

extracting agent used (HPCD, Tween 80 and ultrapure water) were performed. These results are presented in Fig. 6.4. In acid soluble fraction the following rank in terms of concentrations of iron in soil, was observed: Tween 80 > HPCD > ultrapure water. Regarding the reducible fraction the following rank is obtained: ultrapure water > HPCD > Tween 80, and about the oxidizable fraction: ultrapure water > Tween 80 ≈ HPCD. This trend could be explained by the higher solubilization capacity of Tween 80 towards SOM. Indeed, the iron oxides (reducible fraction) that can be present in SOM (Gu et al., 1996) are mobilized by Tween 80 and can then be considered as soluble iron when first stage of sequential extraction is performed. This could also confirm the slightly higher amount of iron in SW solution with Tween 80.

Besides, the average of total iron concentration in soil after SW with Tween 80, HPCD and ultrapure water are 766, 776 and 850 mg kg^{-1} DW, respectively. The very low difference between Tween 80 and HPCD solutions confirms the low difference of extracted iron in both solutions.

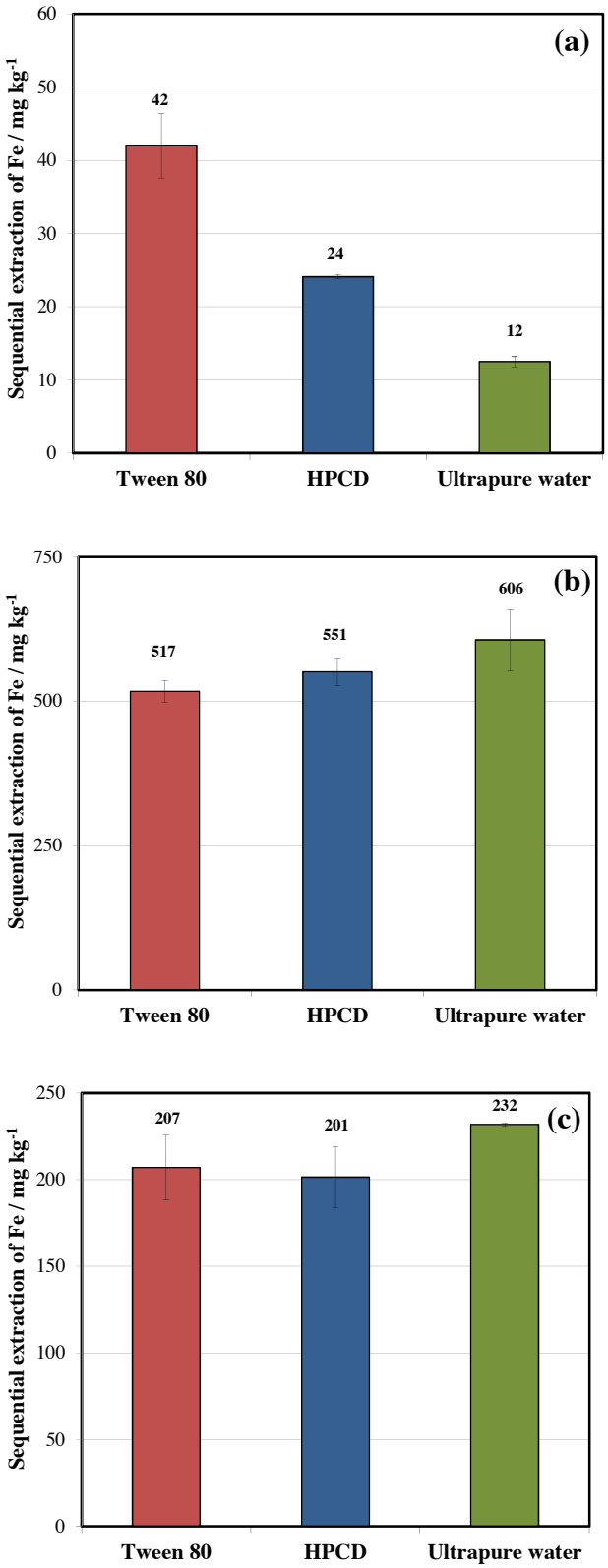


Fig. 6.4. *Sequential extraction of iron in soil after SW with different solutions: Tween 80 (7.5 ± 0.2 g L^{-1}), HPCD (7.5 ± 0.2 g L^{-1}) and ultrapure water. (a) 1st stage: acid soluble fraction, (b) 2nd stage: reducible fraction, (c) 3rd stage: oxidizable fraction.*

6.3.1.4 Impact of fresh SW solutions on soil respirometry

When a recirculation loop is considered, it is important to study the impact of SW solution on soil microbial activity. In that way, soil respirometry assays after successive SW cycles with Tween 80, HPCD or ultrapure water were performed. The results are depicted in Fig. 6.5.

By assuming a linear regression between the soil respirometry value as a function of time, the respirometry ratio obtained between the slopes of Tween 80 experiments and ultrapure water experiments are 1.8, 1.6 and 4.1 after 1, 2 and 3 SW cycles, respectively. The respirometry ratio obtained between HPCD and ultrapure water experiments are 0.9, 0.3 and 0.7 after 1, 2 and 3 SW cycles, respectively. It can be noticed that the soil respirometry decreases when the number of successive washing increases. It is also highlighted an enhancement of soil respirometry in presence of Tween 80 after three successive washing, compared to ultrapure water or HPCD experiments. In contrast, HPCD inhibits the soil microbial activity compared to water alone.

Two reasons can be mentioned to explain this behavior. The first one is that Tween 80 is known to greatly enhance the organic pollutant extraction compared to HPCD, which leads to lower contaminants content level in soil and therefore a better soil respirometry. Another reason would be the presence of Tween 80 or HPCD in soil after SW process, though their concentration should be low regarding their low sorption coefficient values to soil (Mousset et al., 2014a). Consequently, Tween 80 could be a substrate that can induce respiration, due to its linear structure compared to the toroidal shape of cyclodextrin. In recent studies, it has been demonstrated that Tween 80 can enhance bioremediation (Zhang and Zhu, 2012) and phytoremediation (Gao et al., 2007).

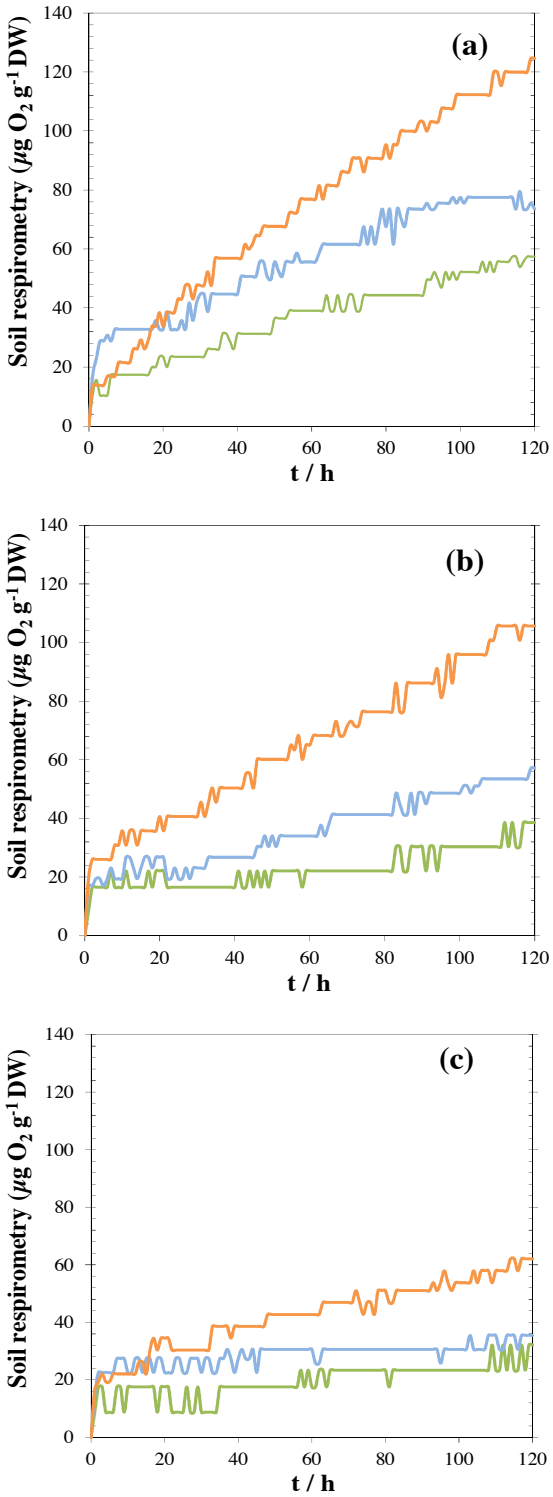


Fig. 6.5. *Soil respirometry after successive washings with different solutions: Tween 80 (7.5 ± 0.2 g L^{-1}) (— —), HPCD (7.5 ± 0.2 g L^{-1}) (— —), ultrapure water (— —). (a) 1 SW step, (b) 2 successive SW steps, (c) 3 successive SW steps. Error bars were not reported on the graph in order to be readable.*

6.3.2 Recycling possibilities after EF treatments

After SW process, EF treatments were performed in order to degrade organic pollutants and to reuse the solution for another SW step.

6.3.2.1 Degradation efficiency of SW solutions

The initial PAHs concentrations in SW solution with HPCD were 0.8, 0.1, 0.7, 0.3, 0.1 and 0.2 mg L^{-1} for ACE, PHE, FLA, PYR, BaP, BghiP, respectively. Regarding the Tween 80 SW solutions, the PAHs concentrations were 9.3, 12.3, 5.4, 3.1, 0.5 and 0.5 mg L^{-1} for ACE, PHE, FLA, PYR, BaP, BghiP, respectively. It has been demonstrated that the monitored PAHs were completely degraded after 4 h of treatment in the presence of HPCD and 8 h in the presence of Tween 80. Apparent kinetic constant (k_{app}) values of PAHs oxidation during EF treatment (assuming a pseudo-first order kinetic model) are displayed in Table 6.5. As expected the degradation rates decrease with the increasing number of PAH rings. The slower degradation rate observed in the case of Tween 80 solutions can be mainly explained by the higher amount of extracted SOM and organic pollutants such as PAHs. Indeed, after the first SW, the initial COD value with Tween 80 solutions was around 15,120 ± 410 mg O_2 L^{-1} compared to 10,050 ± 240 mg O_2 L^{-1} with HPCD solutions. This represents around 1.5 times higher initial load than with HPCD solution.

Table 6.5. Apparent kinetic constant (k_{app}) values of PAHs from SW solutions degraded after EF treatment (I = 2 A, Pt anode), assuming pseudo-first order kinetic model.

EF treatment of SW solutions with HPCD				**EF treatment of SW solutions with Tween 80**			
PAHs	**k_{app} (h^{-1})**	**R^2**	**$t_{1/2}$ (min)**	**PAHs**	**k_{app} (h^{-1})**	**R^2**	**$t_{1/2}$ (min)**
ACE	2.607	0.995	16	**ACE**	0.721	0.993	58
PHE	1.770	0.997	24	**PHE**	0.448	0.995	93
FLA	1.161	0.987	36	**FLA**	0.409	0.992	102
PYR	1.081	0.988	38	**PYR**	0.402	0.993	103
BaP	1.058	0.997	39	**BaP**	0.232	0.998	179
BghiP	0.826	0.985	50	**BghiP**	0.196	0.993	211

The difference in initial COD can be firstly explain by the higher theoretical COD of Tween 80 (2 g O_2 (g Tween 80)$^{-1}$) compared to HPCD (1.3 g O_2 (g HPCD)$^{-1}$). The presence of SOM and organic pollutants that is higher with Tween 80 solutions than HPCD solutions can also explain the difference of COD. Due to the non-selective properties of hydroxyl radicals, it leads to higher competitive reactions between the organic molecules, in the case of Tween 80 solutions.

6.3.2.2 Efficiency of extracting agents recovery

After the complete degradation of monitored PAHs, the extracting agents concentrations and the respective TOC of solutions are quantified and reported in Fig. 6.6.

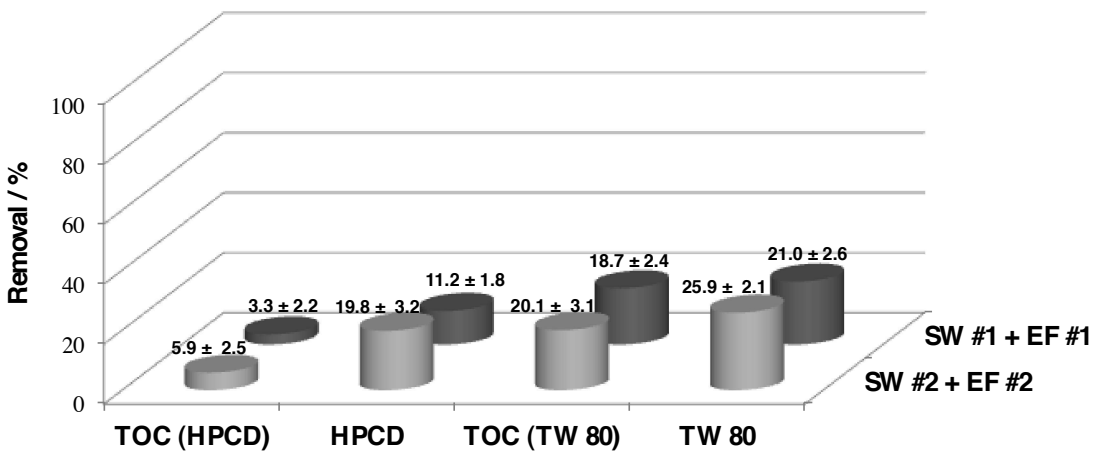


Fig. 6.6. *TOC and extracting agents decay after 4 h and 8 h of EF treatment (I = 2 A, Pt anode) with HPCD and Tween 80 SW solutions, respectively: after one recirculation (■) and after two recirculations (□).*

While the monitored PAHs were completely degraded after the first cycle, about 11% of HPCD was degraded compared to 21% of Tween 80. In the meantime, about 3.5% and 19% of TOC were removed, respectively. After the second cycle, about 20% of HPCD is degraded compared to 26% of Tween 80 while about 94% and 80% of TOC was removed, respectively. The fact that the solutions were less loaded during the second cycle, could explain why Tween 80 and HCPD are degraded more quickly than for the first cycle.

6.3.2.3 Extraction efficiency

Regarding the results in sub-section 6.3.2.2, extracting agents can be saved enough to consider a recirculation loop. Still it is important to know the extraction efficiency of PAHs with the treated SW solutions. PAHs extraction efficiencies during SW experiments before and after an EF treatment are listed in Table 6.6.

The second SW step after EF allowed the extraction of 1.4 ± 0.4% of PAHs (in average) with HPCD solutions compared to 0.4 ± 0.1% after a second cycle with a fresh HPCD solutions. Tough this difference is low, it means that the oxidation by-products could slightly enhance the extraction of organic pollutants. Moreover, another reason is the fact that the hydroxylated cyclodextrin by-products are still able to extract organic pollutants since the hydrophobic internal shape could stay intact in a while.

Regarding Tween 80 SW solutions, 7.5 ± 2.5% of PAHs (in average) were extracted with oxidized solutions against 24.5 ± 2.5% with fresh solutions. The reason could be that the concentration of Tween 80 after oxidation of solution is 21% lower than in fresh solution as mentioned in sub-section 6.3.2.2. However, Tween 80 allows extracting more PAHs than HPCD, e.g. 5.3 times higher on the second SW and 10.5 times higher by combining first and second SW processes.

Table 6.6. Extraction efficiency of PAHs extracted during SW experiments before and after an EF treatment.

PAHs	HPCD			Tween 80		
	SW # 1 with fresh solution	SW # 2 after EF treatment of SW # 1 solution		SW # 1 with fresh solution	SW # 2 after EF treatment of SW # 1 solution	
	Extraction efficiency (%)	[PAHs] extracted (mg kg^{-1} DW)	Extraction efficiency (%)	Extraction efficiency (%)	[PAHs] extracted (mg kg^{-1} DW)	Extraction efficiency (%)
ACE	4.0 ± 1.2	0.5 ± 0.1	0.4 ± 0.1	43.6 ± 2.9	14.8 ± 1.1	9.7 ± 1.0
PHE	0.2 ± 0.1	8.0 ± 1.4	2.6 ± 0.3	46.1 ± 2.0	10.0 ± 0.8	3.2 ± 0.4
FLA	7.8 ± 0.2	1.1 ± 0.2	1.0 ± 0.2	49.3 ± 2.5	1.1 ± 0.1	1.0 ± 0.1
PYR	4.9 ± 0.1	0.4 ± 0.1	0.4 ± 0.1	43.0 ± 1.0	2.1 ± 0.2	2.6 ± 0.2
BaP	1.1 ± 0.2	1.2 ± 0.2	1.3 ± 0.2	31.6 ± 1.1	16.1 ± 1.2	16.8 ± 1.5
BghiP	1.3 ± 0.1	0.6 ± 0.1	2.6 ± 0.3	30.0 ± 1.5	2.7 ± 0.2	11.5 ± 1.7

6.3.2.4 Evolution of pH during oxidative treatment

pH evolutions during EF treatments of SW solutions are depicted in Fig. 6.7. The initial pH of HPCD and Tween 80 SW solutions was around 8.0 ± 0.1 in both cases and similar to the pH value of soil measured with water (pH = 8.3) (Table 6.1). After the first SW cycle, the pH is decreasing quickly until a plateau around pH 3.4 and 2.8 is reached after 1h of EF treatment with both solutions. The decrease of pH is due to the formation of carboxylic acids that can be quickly formed, especially from the break of aromatic rings that are numerous in PAHs-polluted solutions. Moreover, the carboxylic acids of the organic OM – much more present in Tween 80 solutions - can also participate in the acidification of solutions. Furthermore, these pH values are better for EF treatment since it is very closed to the optimal pH value of 3.

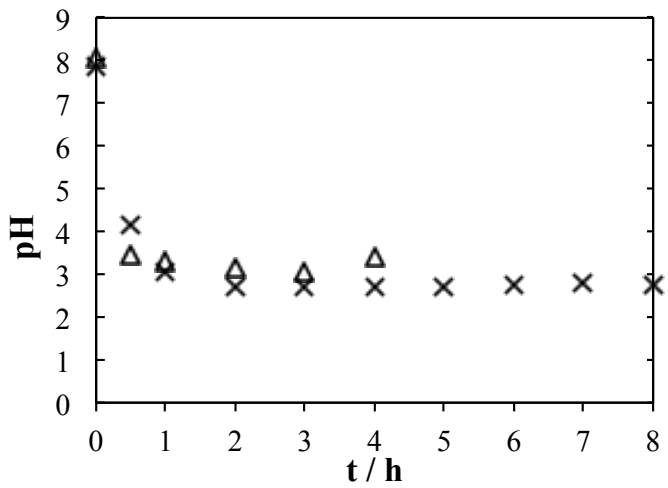


Fig. 6.7. *pH evolution during EF treatment (I = 2 A, Pt anode) of solutions after one SW containing HPCD (Δ) or Tween 80 (×) extracting agents.*

After a second SW with treated solutions, the initial pH of SW solutions was still around 8 in both cases. It means that the soil buffering capacity is stronger than the one of treated solutions. This strong soil buffering capacity can be explained by the presence of clay minerals and OM. Moreover, since this clay-humic complex is saturated in exchangeable cations (Ca^{2+}, K^{+}, Mg^{2+}, Na^{+}) (Table 6.1) all protons from the SW solutions can be adsorbed on the complex by ionic exchange with these cations, giving back the natural soil pH (Sposito, 2008). Moreover, after the second EF treatment the pH values are 3 and 2.5 with HPCD and Tween 80 solutions, respectively. In both cases the pH has slightly decreased, since the concentration of carboxylic acids increases with

the time of EF treatment (Özcan et al., 2013). Particularly, oxalic acid (pKa_1 = 1.25) is widely known to be one of the most last frequent carboxylic acid formed during the oxidation pathway of organic compounds (Oturan et al., 2008; Pimentel et al., 2008).

6.3.2.5 Impact of treated SW solutions on soil respirometry

Since oxidation by-products are present in SW solutions treated by EF, the impact on soil respirometry has to be assessed for SW cycles studies. The results of soil respirometry tests after a second SW experiment with SW solutions treated by EF are illustrated in Fig. 6.8.

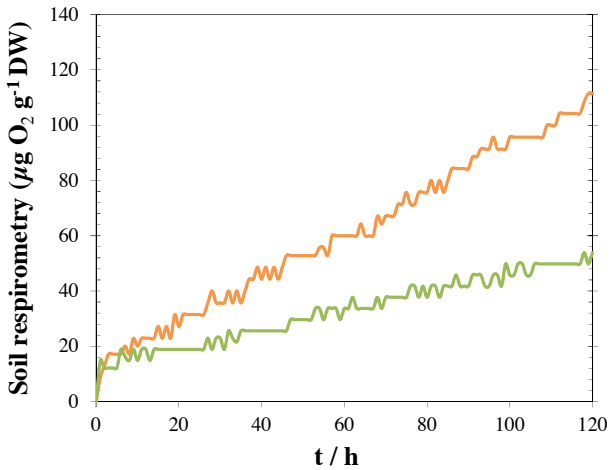


Fig. 6.8. *Soil respirometry after a second SW with SW solutions treated by EF (I = 2 A, Pt anode) with two kind of extracting agents: Tween 80 (— —) or HPCD (— —). Error bars were not reported on the graph in order to be readable.*

The respirometry ratio obtained between the slopes of Tween 80 or HPCD experiments and ultrapure water experiments after 2 cycles are 2.0 and 0.9, respectively. Thus, the soil respirometry is better with HPCD and Tween 80 treated solutions compared to second cycle with fresh ones. Moreover, the respirometry values are similar than the first SW process (sub-section 6.3.1.4), meaning that the oxidation of SW solutions does not affect the soil microbial activity. One reason would be that the by-products are usually more water-soluble - thanks to the hydroxylation - than the original one. It means that these by-products would have few interactions with soil. Furthermore, still Tween 80 show an enhancement of soil respirometry compared to an inhibition with HPCD solutions, compared to the first ultrapure water washing cycle.

6.3.3 Study of possible biological post-treatment

6.3.3.1 Mineralization rates

As shown in Fig. 6.9, the complete mineralization was reached after 20 h of EF treatment with HPCD solution compared to 28 h with Tween 80, leading to a mineralization rate 1.4 times slower with surfactant solutions. The fact that Tween 80 solutions are around 1.5 times more loaded (in terms of initial COD of solutions) than HPCD solutions would explain this difference already observed during degradation studies (sub-section 3.2.2). It could be also explained by the fact that less mass transport of contaminants towards electrode is occuring with Tween 80 solutions since no bubbling is applied. Moreover, the same behavior between Tween 80 and HPCD is observed in synthetic solution (Mousset et al., 2014b).

6.3.3.2 Biodegradability assays

The biodegradability assays data are also reported in Fig. 6.9. In both kinds of solutions, the biodegradability increases with treatment time, but it is quicker with HPCD solution. It could be explain by the presence of more organic pollutants in Tween 80 SW solutions. This would partly confirm the respirometry results (sub-section 6.3.1.4) that show an enhancement of soil microbial activity since more pollutants are extracted with Tween 80 solutions compared to HPCD solutions.

During the first 4 h the biodegradability is still very low (< 1%) in both case, since the first by-products, like the hydroxylated PAHs are known to be toxic (Fernandes and Porte, 2013) and the COD is sill too high to have a better biodegradability ratio. Considering that a minimal BOD_5/COD ratio of 33% is required to suggest a biological post-treatment of industrial effluents (Rodier et al., 2009), the EF treatment time would be 7 h (equivalent to 33% of mineralization) and 20 h (equivalent to 85% of mineralization) for HPCD and Tween 80 solutions respectively. This ratio is obtained when 94% of HPCD is removed compared to 88% of Tween 80 (data not shown).

6.3.3.3 Evolution of pH during mineralization

Again, the pH values are decreasing during the oxidation. A pH value of 3 is quickly reached during the first hour of treatment, corresponding to carboxylic acids formation. For example the pH values are 3.2 and 3.0 after 7 h and 20 h of EF treatment with

HPCD and Tween 80 SW solutions, respectively. It means that if a biological post-treatment is considered, an alkaline reagent such as lime should be added right after the electrochemical treatment to adjust at circum-neutral pH.

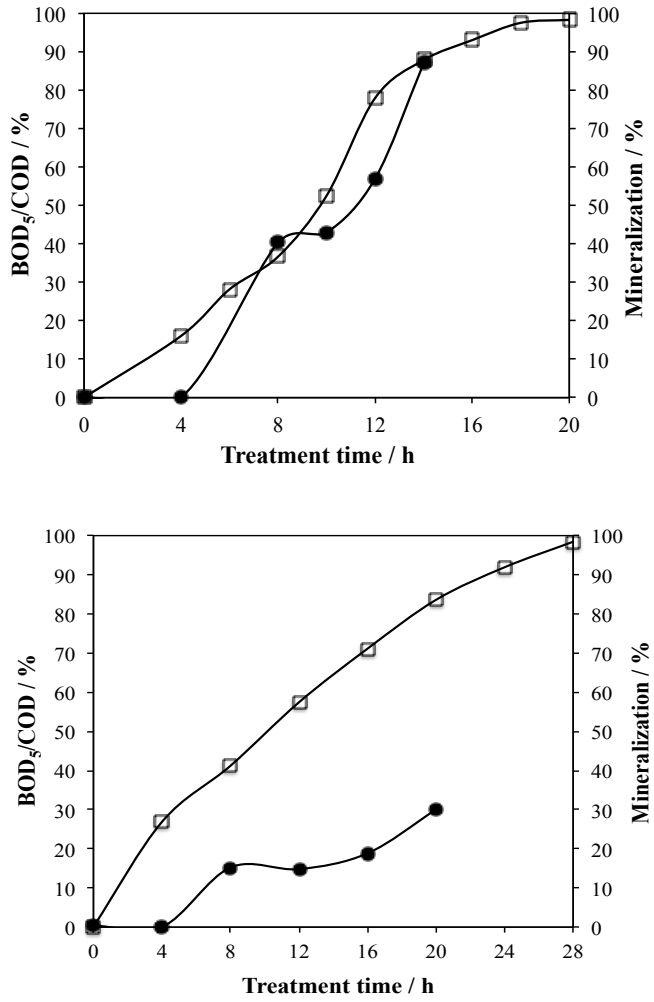


Fig. 6.9. *Evolution of biodegradability (BOD_5/COD) (●) and mineralization rates (□) during a SW treatment by EF (I = 1 A, BDD anode) with two kind of extracting agents: HPCD (a) or Tween 80 (b).*

6.3.4 Energy consumption: HPCD vs Tween 80 solutions

Table 6.7 describes the energy consumption calculations during EF treatments of HPCD and Tween 80 solutions during recycling and biological post-treatment possibilities. Experiments about recycling studies need more energy to be achieved since the electrochemical conditions (I = 2 A, Pt anode) were chosen in order to degrade the pollutants by minimizing the extracting agents oxidation (less TOC removal). With HPCD solutions the energy consumption is slightly fewer to reach the complete mineralization of the solutions considering a biological post-treatment, in contrast to Tween 80 solutions.

In all the cases, the energy consumption is less important with HPCD solutions. For example, in the case of a possible biological post-treatment, to work with Tween 80 needed about 1.4 times more energy consuming compared to HPCD solutions. However, considering that Tween 80 allows extracting much more organic pollutants than HPCD (sub-sections 6.3.1.1 and 6.3.2.3), much more SW cycles would be required and EF treatment would be finally much longer and more energy consuming with HPCD agents.

Table 6.7. Energy consumption (per unit TOC mass removed) calculations during EF treatments of HPCD and Tween 80 solutions during recycling studies and biological post-treatment possibilities.

	HPCD solutions				**Tween 80 solutions**			
	Recycling studies		**Biological post-treatment possibilities**		**Recycling studies**		**Biological post-treatment possibilities**	
	1 cycle	**2 cycles**	**At 33% of biodegradability**	**Complete mineralization**	**1 cycle**	**2 cycles**	**At 33% of biodegradability**	**Complete mineralization**
Treatment time (h)	4	8	7	20	8	16	20	28
Mineralization rate (%)	4	6	33	> 98%	19	21	85	> 98%
Energy consumption (kWh (kg TOC)$^{-1}$)[(a)]	350	760	82	77	690	1,115	113	127

[(a)]Only power supply for electrolysis is considered.

6.4 Conclusions

It was shown in this study that Tween 80 solutions were able to extract about 85 ± 6.0% of monitored PAHs compared to 4.5 ± 1.4% with HPCD after 4 successive SW cycles with fresh solutions. Tween 80 was in average 18 times more efficient for the extraction than HPCD by using the same initial mass concentration (7.5 ± 0.2 g L^{-1}), with very similar molar concentrations.

When considering a recirculation loop with EF treatment, extraction efficiencies were still higher with Tween 80 solutions. The kinetic of degradation of PAHs were twice quicker with HPCD solutions, but the initial COD of Tween 80 solutions were 1.5 times more loaded. It leads to more energy consumption (1.5 times) with Tween 80 solutions after 2 cycles. Though Tween 80 was more degraded than HPCD, it was still possible to save HPCD and Tween 80, while the monitored PAHs were completely degraded. According to the soil respirometry assays, Tween 80 could enhance soil respirometry on the contrary to HPCD, even after a recirculation loop with EF treatment.

The EF process performed to treat these highly loaded solutions succeeded to completely mineralize the HPCD and Tween 80 solutions after 20 h and 28 h, respectively. By considering a biodegradability ratio of 33%, which is the threshold value prior to consider a biological treatment, this value was reached after 7 h of treatment with HPCD solution compared to 20 h in the case of Tween 80 solution. This represents energy consumption per unit TOC mass removed 1.4 times higher than with HPCD solution. In both solutions the pH is decreasing until a pH value around 3 (± 0.5) during the EF treatment. This can improve the efficiency of EF treatment, since these values are close to the optimal pH value for EF process. However, an alkaline reagent such as lime is needed to be added before considering a biological post-treatment.

Finally, regarding the cost of chemicals (around 17 times less), extraction efficiency and the impact on soil respirometry, Tween 80 still appears to be a better extracting agent than HPCD, even if the EF treatment requires more time and is more energy consuming.

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CHAPTER 7

General Overview and Future Perspectives

CHAPTER 7

7.1 General overview

The main goal of this work was to study an innovative integrated process by combining soil washing (SW) techniques with an electro-Fenton (EF) or anodic oxidation (AO) treatments. Two approaches were considered. The first one is to study the recycling possibilities between SW and EAOPs (main parameters: extracting agent recovery, PAHs degradation, extraction efficiency after oxidation of SW solutions, toxicity of solutions, impact on soil respirometry, energy consumption). The second approach was to study the possibility of combining these EAOPs with a biological post-treatment in order to minimize energy consumption (main parameters: mineralization rate, PAHs oxidation, extracting agent decay, biodegradability and toxicity of oxidized SW solutions, pH of oxidized solution, energy consumption). The use of a cyclodextrin (*i.e.* HPCD) as extracting agent in SW experiments was compared with a traditional surfactant (*i.e.* Tween 80). Phenanthrene (PHE), as a model of PAHs pollutant, was monitored for degradation in synthetic solutions. Experiments with SW solutions from historically PAHs-contaminated soils were also performed and 6 PAHs extractions and degradation yields were monitored (acenaphthene (ACE), PHE, fluoranthene (FLA), pyrene (PYR), benzo(a)pyrene (BaP) and benzo(g,h,i)perylene (BghiP)). The four following related studies are presented in this work:

- A new analytical method to quantify Tween 80,
- Study of SW recycling possibility,
- Role of anode materials on toxicity and biodegradability during EAOPs treatments,
- EF treatment of real SW solutions.

7.2 Preliminary study: need of a new Tween 80 quantification method

As a preliminary study, an alternative analytical method was found to be useful to quantify Tween 80 (Chapter 3). The main results are listed below:

- A linear relation was obtained between the fluorescence of Tween 80-TNS micelles and the concentration of Tween 80 (F = 3.1123 (± 0.12) × [Tween 80] + 7.1849 (± 2.33)),
- Fluorescence analysis had a low detection (LD) and quantification (LQ) limit (0.13 µM and 0.39 µM, respectively) compared to UV-absorbance (LD = 3.18 µM, LQ = 9.64 µM) or TOC (LD = 0.27 µM, LQ = 0.85 µM) analysis,
- Low interference with hydrophobic organic pollutants such as PAHs, with oxidation by-products (< 3.5%) as well as with Soil Organic Matter (SOM) (< 4.0%) due to the high sensitivity of this method was observed.

The new Tween 80 analytical method allowed quantifying Tween 80 solutions in more complex matrix (presence of Organic Matter (OM), organic pollutants, oxidation by-products) than former methods that were developed (especially TOC and UV-absorbance). This fluorescence technique was useful for SW solutions recycling possibility studies (Chapter 4) and for Tween 80 quantification in real SW solutions presented in Chapter 6.

7.3 Solubilization/extraction efficiency with HPCD versus Tween 80

7.3.1 PAHs extraction efficiency: advantage of Tween 80

In synthetic solutions, the solubilization of PHE was about 13 times higher with Tween 80 than with HPCD (Chapter 4), by considering that the micellar solubilization ratio was proportional to the concentration of the surfactant above the Critical Micelle Concentration (CMC) (Paria, 2008).

Comparatively, with a historically PAHs-contaminated soil, PHE extraction yield was much better with Tween 80 (230 times better) than with HPCD (Chapter 6). However, after one SW cycle, the extraction efficiency of the 6 PAHs monitored was around 13 times (in average) higher with Tween 80 compared to HPCD. Moreover, after four successive SW cycles, the averages of total extraction efficiency of the 6 PAHs were about 85% and 4.5% in the case of Tween 80 and HPCD, respectively. Thus, in average Tween 80 allowed achieving a PAHs extracting efficiency 18 times higher than HPCD.

7.3.2 Comparison with regulations for inert wastes disposal

When the average extraction efficiency after four SW cycles with Tween 80 and HPCD were applied on the total 16 PAHs, it could be calculated that around 160 mg and 1,050 mg per kg of soil of PAHs were still remaining, respectively. Regarding the regulations about soil disposal in landfill for inert wastes in France, still 110 mg kg^{-1} DW and 1,000 mg kg^{-1} DW of PAHs (around 10% and 92% of the total amount) needed to be extracted with Tween 80 and HPCD respectively, compared to the threshold value of 50 mg kg^{-1} DW. Few other SW cycles with Tween 80 were requested to reach this value while HPCD appears not to be appropriated to reach this threshold.

7.3.3 Mobilization of total dissolved iron needed for EF treatment

After one SW cycle Tween 80 solutions allowed extracting slightly more iron (0.060 ± 0.013 mM) than HPCD solutions (0.020 ± 0.013 mM). Knowing the ability of HPCD to form ternary complex with iron(II) and the organic pollutant (Chapter 4), and the ability of Tween 80 to form micelles only with organic molecules, it would be expected opposite results. However, a study of iron fractionation in soil (Chapter 6) has shown that the iron oxides present in SOM can be mobilized by Tween 80 SW experiments.

Besides, the amount of total dissolved iron was high enough to perform an EF treatment, particularly for recycling studies where a concentration of 0.05 mM of iron(II) was found to be optimal (Chapter 4).

7.3.4 Low level of extracted ionic species leading to low conductivity

The conductivity of SW solutions were low (0.35 ± 0.1 mS cm^{-1}) whatever the extracting agents use (Tween 80 or HPCD), even with ultrapure water (Chapter 6). This can show that Tween 80 or HPCD had no impact on solubilizing ionic species, which was expected since these species are polar whereas the solubilizing agents are able to solubilize only apolar molecules. Moreover, this conductivity was not sufficient for electrolysis experiments. An electrolyte was therefore added in SW solutions.

7.3.5 Enhancement of Tween 80 fresh SW solutions on soil respirometry

An enhancement of respirometry ratio from 1.6 until 4.1 with Tween 80 fresh SW solutions on soil respirometry was observed (Chapter 6), compared to ultrapure water

washing when the number of SW cycles increases. In contrast, HPCD solutions tend to inhibit the soil microbial activity with respirometry ratio from 0.3 until 0.9 (Chapter 6). The first reason was that fewer pollutants are remaining in soil washed with Tween 80 solutions than with HPCD solutions. The second reason would be that the linear structure of Tween 80 could be more adapted for biodegradation compared to the toroidal shape of HPCD. Moreover, the initial biodegradability of Tween 80 measured in solution (19%) was much higher than HPCD (0.04%), which would confirm this behavior (Chapter 3).

7.4 Recycling possibilities: a need to save extracting agent

7.4.1 Complete pollutants oxidation by EF in specific operating conditions

Optimal parameters with EF oxidation of HPCD/PHE solutions were determined in order to save most of HPCD molecular structure and to degrade PHE in the meantime. These parameters were: Platinum (Pt) anode, 2000 mA, $[Fe^{2+}]$ = 0.05 mM (Chapter 4). These conditions were used for EF treatments of real SW solutions (Chapter 6).

Moreover, a stronger competitive decay between oxidation of PHE and HPCD are observed with Boron-Doped Diamond (BDD) anode (Chapter 5), which means that the use of BDD anode for recirculation studies compared to Pt anode is less advantageous.

7.4.2 Extracting agent recovery: advantage of HPCD

Two different mechanisms of PHE oxidation by hydroxyl radicals were suggested according to the solubilizing agents (*i.e.* HPCD or Tween 80) employed (Chapter 4). There is the formation of Fe^{2+}-HPCD-PHE complex that allows $^{\bullet}OH$ to directly degrade the contaminant. Comparatively, the configuration of micelles between Tween 80 and PHE makes difficult the access of $^{\bullet}OH$ to the pollutant. More Tween 80 need to be degraded before the $^{\bullet}OH$ reach the contaminant. It results to 50% of Tween 80 that can be reused versus 90% in the case of HPCD.

In real SW solutions Tween 80 was also more degraded than HPCD, *i.e.* 25-30% compared to 10-20% respectively, but it can also be attributed to the longer EF treatment time since the initial load of pollution was significantly higher in the former case (Chapter 6).

7.4.3 PAHs extraction efficiency: Tween 80 keeps its advantage

The second SW cycle after EF treament still allowed extracting more PAHs with Tween 80 solutions than HPCD, compared to the use of fresh agents (Chapter 6). However, the average extraction efficiency of the 6 PAHs monitored was lower with Tween 80 by reusing the treated SW solution compared to a fresh one.

7.4.4 Impact on soil respirometry: Tween 80 keeps its advantage

When studying the recirculation between SW process and an EF process it is important to assess the impact of oxidation by-products on soil respirometry. Tween 80 solutions still showed an enhancement of soil respirometry, while HPCD solutions still inhibited it (Chapter 6). However, in both cases the soil respirometry was better with a second SW treated solutions than a fresh one, meaning that the oxidation of SW solutions and their low pH values do not affect the general soil microbial activity.

7.5 Minimizing energy consumption during EF treatment with a possible biological post-treatment

7.5.1 High mineralization efficiency with BDD anode

It has been shown that anode material was an essential factor when studying the biological post-treatment (Chapter 5). Three different mechanisms to oxidize the pollutant were observed according to the anode employed such as Pt, Dimensionally Stable Anode (DSA) or BDD) and the kind of treatment (EF or AO): degradation mechanism with EF-Pt and EF-DSA, mineralization mechanisms with AO-BDD, both mechanisms with EF-BDD (Chapter 5). BDD anode was determined to have much better performance in terms of mineralization efficiency compared to Pt or DSA anodes in synthetic solutions (Chapter 5) and real SW solutions (Chapter 6). During BDD treatments, EF-BDD was 1.35 times better than AO-BDD to mineralize synthetic solutions, thanks to the paired-electrocatalysis process (Chapter 5). BDD anode was therefore employed for a possible biological post-treatment study with real SW solutions (Chapter 6).

7.5.2 Impact of dissolved SOM and initial organic load on oxidation efficiency

The impact of SOM on EF treatment could be seen by the difference of initial Chemical Oxygen Demand (COD) between HPCD and Tween 80 SW solutions, since more SOM were present in Tween 80 solutions (Chapter 6). SOM would compete with targeted organic pollutants and make the electrochemical treatment longer. Indeed, in experiments with real solutions, the complete mineralization was reached after 20 h with HPCD solution compared to 28 h with Tween 80, leading to a mineralization rate 1.4 times slower with surfactant solutions. Knowing that Tween 80 solutions were around 1.5 times more loaded (in terms of COD), it would explain this difference also observed during recycling studies with real SW solutions. The difference in initial COD could be firstly explain by the higher theoretical COD of Tween 80 (2 g O_2 (g Tween 80)$^{-1}$) compared to HPCD (1.3 g O_2 (g HPCD)$^{-1}$). The presence of SOM and organic pollutants that were higher with Tween 80 solutions than HPCD solutions could also explain the difference of COD. The competitive oxidation between OM and organic pollutant by hydroxyl radicals was already known (Westerhoff et al., 1999), especially in Fenton treatment (Shiavello, 1987; Lindsey and Tarr, 2000a; Lindsey and Tarr, 2000b).

7.5.3 A toxicity decrease of HPCD solutions related to HPCD degradation

The toxicity (measured by Microtox® method as function of inhibition of *Vibrio fischeri* marine bacteria) was increasing during the oxidation of PHE in the presence HPCD in synthetic solutions (Chapter 5). However, as soon as both compounds (PHE and HPCD) were completely degraded, the toxicity started to decrease corresponding to a mineralization rate around 55-60%.

7.5.4 A biodegradability ratio higher than 33%: possibility of biological post-treatment

An optimum biodegradability value (determined by BOD_5/COD ratio) was measured in each kind of treatment with Pt, DSA and BDD anodes and succeeds to reach 100% in case of BDD treatments with HPCD/PHE solutions (Chapter 5). BDD anode was therefore employed for biodegradability studies. A great enhancement of biodegradability was observed with HPCD and Tween 80 SW solutions compared to their initial biodegradability that were around 0.1% with HPCD and around 0.4% with

Tween 80 in both synthetic and real SW solutions (Chapters 5 and 6; Mousset et al., 2013). It was interesting to note that the biodegradability started to increase only when the HPCD was almost completely degraded (90-95% of HPCD removal) in synthetic solutions (Chapter 5).

In all studies, a biological post-treatment was considered possible for each treatment at BOD_5/COD ratio higher than 33%. In HPCD synthetic solutions, the biodegradability of 33% was reached after 7 h equivalent to 25% of mineralization (Chapter 5). Comparatively, the biodegradability ratio of 33% in Tween 80 (9 g L^{-1})/PHE (17 mg L^{-1}) mixture was reached after 12 h corresponding to 45% TOC removal (Mousset et al., 2013). In real SW solutions, a ratio of 33% could be reached after 7 h (equivalent to 33% of mineralization) and 20 h of EF treatment for HPCD and Tween 80 solutions, respectively (Chapter 6). This ratio was obtained when 94% of HPCD was removed compared to 88% of Tween 80 (equivalent to 85% TOC removal). The biodegradability was similar in synthetic and real HPCD SW solutions, since the initial amount of extracted organic pollutants and SOM were low in real solutions. Regarding Tween 80 solutions, the difference between synthetic and real SW solutions was much higher, because the initial amount of organic molecules was much higher in real solutions. Furthermore, the lower biodegradability ratio of Tween 80 solutions compared to HPCD solutions could be explained by the presence of more organic pollutants that are extracted from soil. This could also partly explain the results of soil respirometry experiments (sub-section 7.3.5). Indeed, Tween 80 solutions appear enhancing the soil microbial activity since less pollutants are present in soil compared to experiments with HPCD solutions (Chapter 6).

7.5.5 A decrease of oxidized SW solutions pH: need of a neutralization step

The pH values were decreasing during the oxidation of SW solutions whatever the anode use and the extracting agents employed (Chapter 6). A pH value around 3 was quickly reached during the first hour of treatment, corresponding to carboxylic acids formations. This value was optimal for EF treatment. However, it means that if a biological post-treatment is considered, an alkaline reagent like lime should be added after the electrochemical treatment to adjust the treated SW solution at circum-neutral pH.

7.6 A short cost-benefit study: comparison between HPCD and Tween 80

7.6.1 Data comparisons between HPCD and Tween 80 experiments

It appears interesting to compare the kind of extracting agent employed for SW experiments. Table 7.1 summarizes the main data obtained during the thesis work and compares the two solubilizing agents (HPCD and Tween 80) that have been employed during the integrated process (Chapters 3 to 6; Mousset et al., 2013).

Table 7.1. Comparisons between HPCD and Tween 80 during integrated process of synthetic and real SW solutions.

Criteria	HPCD	Tween 80
General information about the agents		
$COD_{theorical}$ (mg O_2 (mg products)$^{-1}$)	1.3	2
Initial biodegradability ratio of agents (%)	0.04	19
EC_{50} (g L^{-1})	> 100	0.47
Absolute rate constant of agents oxidation by $^{\bullet}OH$ (M^{-1} s^{-1})	2.60×10^{9}	1.59×10^{8}
Cost of agents (€kg^{-1})	**70**	**4**
Extraction efficiencies		
Synthetic solutions		
Agent concentration (g L^{-1})	10	0.75
Solubilization of PHE (mg L^{-1})	17	17
Real SW solutions (10 rpm, 24 h, 40 g of soil / 400 mL of solution)		
Initial agent concentration (g L^{-1})	7.5	7.5
Conductivity (mS cm^{-1})	0.34	0.36
Total dissolved iron concentration (mM)	0.02	0.06
Average of monitored PAHs extraction efficiency after 4 cycles (%)	**4.5**	**85**
Soil respirometry after 1, 2 and 3 SW cycles	**< H_2O**	**> H_2O**
Recycling possibilities study		
Synthetic solutions (I = 2000 mA, [Fe^{2+}] = 0.05 mM, [PHE] = 0.1 mM, Pt anode)		
Agent concentration (g L^{-1})	10	0.75
Treatment time to degrade pollutant (h)	4	4
% of PHE degraded	99	95
% of saved agents	**90**	**50**
% of mineralization rate	6	85
Energy consumption during EF treatment (kWh (kg TOC)$^{-1}$)[(a)]	**500**	**370**

Real SW solutions (I = 2000 mA, Pt anode)		
Initial agent concentration (g L^{-1})	7.5	7.5
Initial COD (mg O_2 L^{-1})	10,050	15,120
Total dissolved iron concentration (mM)	0.02	0.06
Treatment time to degrade monitored pollutants (h)	4	8
% of monitored PAHs degraded	> 99%	> 99%
% of saved agents after 1 cycle	**90**	**79**
% of mineralization rate	4	19
Energy consumption during EF treatment (kWh (kg TOC)$^{-1}$)[(a)] after 1 cycle	**350**	**690**
Soil respirometry after 2nd SW of oxidized solutions	**< H_2O**	**> H_2O**
Possibility of biological post-treatment study		
Synthetic solutions (I = 1000 mA, [Fe^{2+}] = 0.2 mM, [PHE] = 0.09 mM, BDD anode)		
Initial agent concentration (g L^{-1})	9	9
Initial COD (mg O_2 L^{-1})	11,150	17,400
Total treatment time (h)	20	28
Energy consumption after complete EF mineralization (kWh (kg TOC)$^{-1}$)[(a)]	**59**	**95**
Time to reach 33% biodegradability ratio (h)	7	12
COD (mg O_2 L^{-1})	7,400	7,975
% of agents removed	90	64
% of mineralization rate	25	36
Energy consumption during EF treatment (kWh (kg TOC)$^{-1}$)[(a)]	**94**	**116**
Real SW solutions (I = 1000 mA, BDD anode)		
Initial agent concentration (g L^{-1})	7.5	7.5
Initial COD (mg O_2 L^{-1})	10,050	15,120
Total dissolved iron concentration (mM)	0.02	0.06
Total treatment time (h)	20	28
Energy consumption after complete EF mineralization (kWh (kg TOC)$^{-1}$)[(a)]	**77**	**127**
Time to reach 33% biodegradability ratio (h)	7	20
COD (mg O_2 L^{-1})	6,500	2,900
% of agents removed	94	88
% of mineralization rate	33	85
Energy consumption during EF treatment (kWh (kg TOC)$^{-1}$)[(a)]	**82**	**113**

[(a)]Only power supply for electrolysis is considered

The main important values regarding the costs of extracting agent, their respective PAHs extraction efficiency, the extracting agent recovery, the impact on soil respirometry, the energy consumptions are highlighted in bold. The difference of costs of respective extracting agents can be particularly mentioned, since Tween 80 is around 18 times less expensive than HPCD.

7.6.2 Energy consumption during EF treatment in recycling studies

In synthetic solutions, Tween 80 was 1.35 times less energy consuming than HPCD (Chapter 3). One reason could be that Tween 80 was quicker and more degraded than HPCD. Indeed HPCD was able to form a ternary complex between Fe^{2+}-HPCD-PHE leading to the direct degradation of PHE and hardly degradation of HPCD (Chapter 3).

In contrast, Tween 80 was 2 times more energy consuming than HPCD in real SW solutions (Chapter 6). The main reason would be that the initial amount of pollutant dissolved in Tween 80 solution was much higher than in HPCD solution. It leads to a 2 times longer EF treatment time (Chapter 6) and a TOC removal in HPCD and Tween 80 solutions similar since the mineralization efficiency were very low with Pt anode compared to BDD anode (Chapter 5).

7.6.3 Energy consumption during EF treatment in possible biological post-treatment studies

Since their mineralization rates were quicker and higher, EF and AO with BDD anode gave better performance than EF-Pt and EF-DSA in terms of energy consumption per unit TOC mass removed, especially if a biological post-treatment was considered after reaching 33% of biodegradability (Chapter 5). This could also explain why the energy consumptions were much lower in biological post-treatment study compared to recycling studies that were performed with Pt anode.

HPCD SW treatments required less energy consumption per unit TOC mass removed when the EF treatment was performed until the complete mineralization compared to the study of a possible biological post-treatment, especially in synthetic solutions (Chapters 5 and 6). Tween 80 SW solutions required less energy consumptions per unit TOC mass removed when the electrochemical process was accomplished until complete mineralization only in synthetic solutions. In that way, considering a biological post-treatment would be less useful.

EF treatment of Tween 80 SW solutions lead to energy consumptions (in kWh (kg TOC)$^{-1}$) about 1.2 times and 1.4 times higher than that of HPCD solution with synthetic and real solutions, respectively (Chapter 6; Mousset et al., 2013). However, considering that Tween 80 allows extracting much more organic pollutants than HPCD (Chapter 4 and 6), if the energy consumption was related to the amount of pollutants degraded an opposite behavior would be observed. Moreover, in order to reach the same extraction efficiency, much more SW cycles would be required and EF treatment would be finally much longer and more energy consuming with HPCD agents. For example, it is considered that 10 SW cycles are required with HPCD against 1 SW cycle with Tween 80 in order to reach the same residual organic pollutant concentration. Then before considering a biological post-treatment, 820 kWh (kg TOC)$^{-1}$ would be required with HPCD solutions against 113 kWh (kg TOC)$^{-1}$ in the case of Tween 80 solutions during an EF treatment, by assuming a linear relation between the initial load and the electrochemical treatment time.

7.6.4 Conclusions: choosing between HPCD and Tween 80 extracting agents

Finally, quicker biodegradation of synthetic and real SW solutions with HPCD led to lower energy consumptions when considering a biological post-treatment. However, Tween 80 solutions had the great advantage to have much better organic pollutants extraction efficiency, to cost around 17 times less and to enhance the soil respirometry. In that way, Tween 80 could be still considered as a better option.

7.7 Outgoing Research/Perspectives

Still experiments have to be performed to overcome the scientific and engineering challenge. A development at larger scale will also be required. These aspects are highlighted in the present section.

7.7.1 Scientific challenge

7.7.1.1 Potential impact of electrolyte and salinity on biological post-treatment

Since conducting medium (electrolyte) is needed for electrochemical treatment, the salinity of solutions should be monitored because it could inhibit the biological treatment at too high concentration level. Moreover, other inorganic ions (NH_4^+, NO_3^-,

Cl^-, SO_4^{2-},…) can be formed during the mineralization of solution during electrolysis, depending on the heteroatoms (N, Cl, S,…) present in the initial organic pollutants.

7.7.1.2 Dealing with mixed contaminated soils

If a soil is contaminated by organic and inorganic pollutants, the SW solutions could also contain heavy metals at too high concentration to be supported by the biological treatment. In that case, a preliminary step would be to use a separation technique (for example, a spiral separator) to remove heavy metals from the SW solution.

7.7.1.3 Impact of SOM and initial load of extracting agents

Further studies would be needed to understand better the impact of Dissolved Organic Matter (DOM), especially humic substances, during an EF process.

Moreover, EF of soil slurry containing surfactant or cyclodextrin and soil particle smaller to 2 mm could be also studied. There will be many competitors (like SOM) with targeted pollutants but the process should be still experimented. Moreover, a recent study has shown that modified Fenton treatment was able to regenerate activated carbon saturated by organic pollutants (Chiu et al., 2013). The latter work demonstrated that the pollutant could be oxidized even in the presence of a large quantity of other organic compounds.

Futhermore, since the initial organic load of the extracting agent is predominant in the total organic load of SW solutions, it could be interesting to add a preliminary separation step before the electrochemical treatment. This step could adsorb through activated carbon the organic pollutant in order to recover the extracting agent as already suggested by Ahn et al (2008). Then activated carbon could be regenerated by an EF treatment. In that way the initial load would be much lower and maybe less energy consuming. The activated carbon having an adapted shape (like a plate sufficiently porous or granular placed in a metallic cage) and could be also used as an electrode in the electrochemical treatment, since activated carbon can be conductor (Wang et al., 2010).

7.7.1.4 Combining operating parameters for recycling and possible biological post-treatment studies

It would be interesting to combine the recirculation loop system to a final biological post-treatment. In the latter part BDD was determined to be a promising option compared to Pt anode in recirculating studies. Moreover, 2000 mA was the optimal current intensity in recirculating treatment but this current is too high if BDD anode is used. Indeed, the surface of BDD electrode is altered too quickly at this extent of current intensity. Furthermore, the optimal ferrous iron concentration for mineralization experiments is 0.2 mM against 0.05 mM when recirculation loop is considered in synthetic solutions (Chapter 4). In addition, when a biodegradability ratio of 33% is reached in synthetic and real solutions only 10% and 6% of HPCD molecules remain in solutions compared to 33% and 12% of Tween 80 molecules, respectively (Chapters 5 and 6 ; Mousset et al., 2013). This means that the extracting agents concentrations are very low compared to the initial one and would be much less efficient when considering a recirculation loop in these operating conditions.

In the aim to combine both processes, optimal parameters have to be the same. Further experiments need to be accomplished in the same conditions to find the best options.

7.7.2 Technical/Engineering challenge: design and control of electrochemical treatment

- *Study in continuous flow mode*

From an engineering point of view, another step is to verify first the EAOPs alone and then the combination of EF (or AO) and biological treatments with a continuous flow mode. Plug-flow Reactor (PFR) and Continuously Stirred Tank Reactor (CSTR) would need to be compared by varying some operational parameters such as Hydraulic Retention Time (HRT), removal efficiency, and organic loading rate in the system.

- *Control of temperature*

The temperature will need to be also monitored, since it can increase during the electrochemical treatments, especially when the applied current intensity is high.

- *Management of foaming*

If surfactants are employed, foaming needs to be managed, especially during aeration for EF. If no oxygen were supplied in case of the use of surfactants, then supplementary studies would need to be performed like O_2 transfer from gas into solution.

7.7.3 Choice of the biological post-treatment

The choice of the biological post-treatment will be also important. Firstly, the choice between an aerobic or anaerobic treatment of organic pollution will have to be done. The anaerobic process has the advantage to produce biogas that can be converted into energy but hydraulic retention times are longer than in aerobic condition. The aerobic treatments have the disadvantage to be oxygen consuming and to produce much more biological sludge compared to anaerobic treatments.

Secondly, the feeding mode will have to be determined. The sequential biological reactor (SBR) has some advantages, since it is a modular and flexible technique. By controlling the sludge retention time, a process intensification can be achieved (Doyle et al. 2001). The SBR consists of four successive steps. The first one is to feed the biological reactor. The second step is to let the microorganism react with organic pollution in order to degrade it. Thirdly, the particles are let settled. Finally, the treated water is sweep out.

Moreover, the biological process could be adapted to other kind of pollution like nitrogenous, sulphurous or phosphorous pollution, depending on the kind of atoms that are present on the pollutant molecule (N, S, P). For example, by alternating the aerobic/anoxic conditions in a SBR, it is possible to remove NH_4^+, NO_3^- and organic pollution in a single reactor.

7.7.4 Modeling of the integrated process

The modeling is also an important step in order to understand better the oxidation pathway of compounds in a mechanistic study. It is also interesting to foresee the EF experiments when initial operating parameters are known (initial concentration of compounds, iron concentration, O_2 concentration, applied current intensity, electrode surface, volume of solution, pH of solution, electrolyte concentration,…). In that way, one could predict the time needed to degrade the organic compounds until its complete

mineralization. It could be predicted the time when the effluent is biodegradable in order to consider the biological post-treatment and then the combined processes could be also predicted.

It has to be known that a modeling study was performed during this thesis work about a simple aromatic compound (i.e. phenol) oxidation by EF. A complete oxidation pathway is suggested and the by-products evolutions are modeled until the complete mineralization. This study represents a preliminary step before carrying out a more complex solution with more complex compounds like PAHs. By modeling the influence of operational paramaters on the by-products evolution, it would also help to monitor the biological post-treatment. This work will be submitted soon after the PhD defense.

7.7.5 Development at pilot scale and industrial scale

In the future, the final goal will be to develop the process at industrial scale. An intermediary step would be at a pilot scale. The performance of electrodes would need to be studied at this scale (optimal surface per volume of solution, the life duration of electrode, distance between electrode…). Moreover, the stirring is also important for the mass transfer of compounds towards electrodes. The dead zone should be avoided by choosing the right reactor design.

A suggested representation of an experimental setup for SW pilot tests is given in Fig. 7.1.

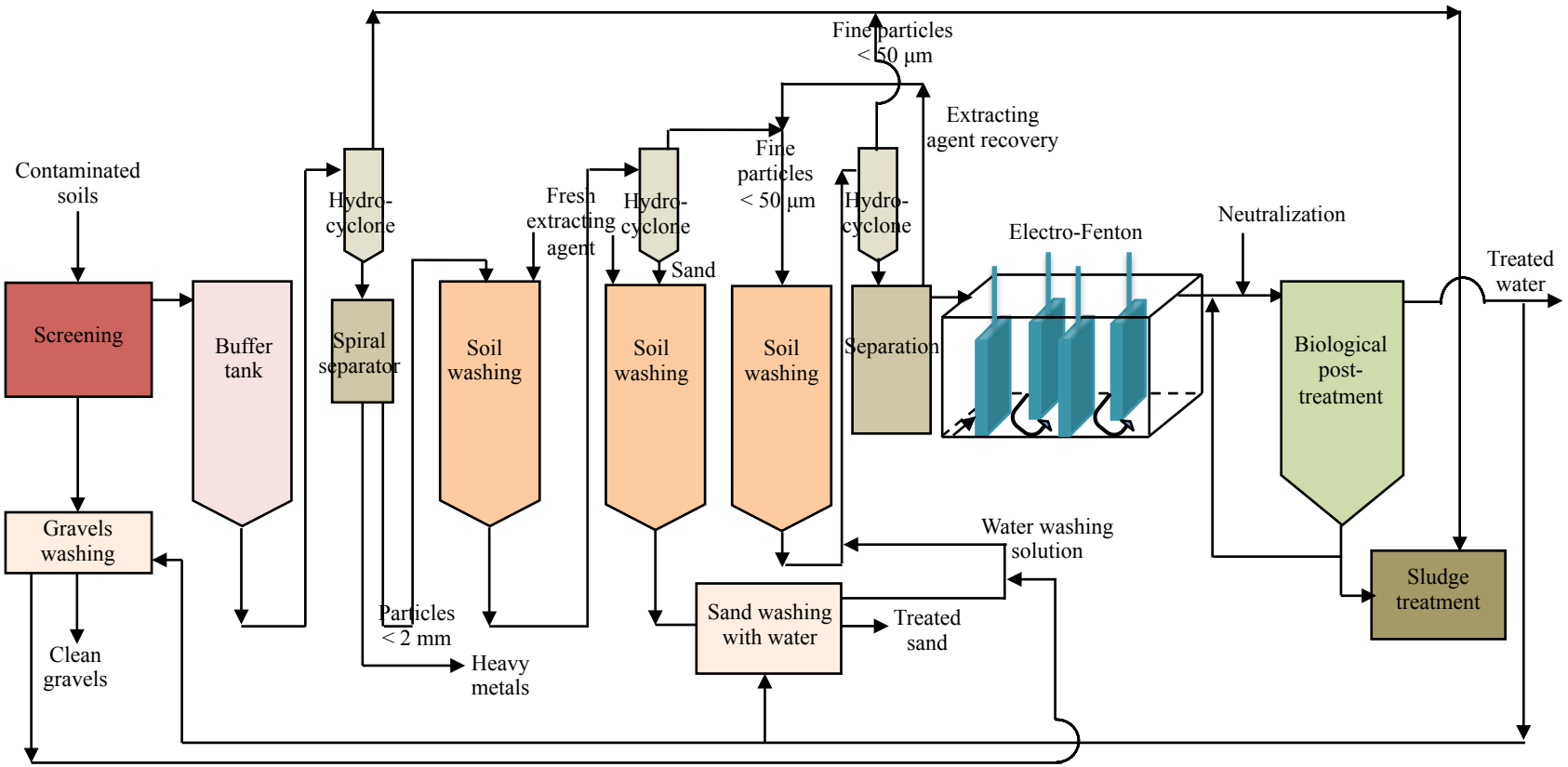

Fig. 7.1. *Suggested schematic representation of an experimental setup for SW pilot tests.*

Firstly the contaminated soil is screened and sieved and the gravels are just washed with clean water, since the pollutants are mainly concentrated in fine particles. Then the hydrocyclone allows separating the particles lower than 2 mm (polluted fraction) from the rest of the soil that is directly sent to a sludge treatment. Then heavy metals are separated with a spiral separator from the soil and a first SW is performed. A second SW is done for only sand particles. This sand is therefore washed with clean water and ready to be reused as clean sand. The fine particles (< 50 µm) that are separated from the sand by a second hydrocyclone are therefore washed in a third SW step. These fine particles are then separated by a third hydrocyclone from the rest of washing solution and send to a sludge treatment. The SW solutions are therefore sent to a separation technique like adsorption onto activated carbon. The extracting agent can be recovered and reused in the SW step of fine particles. The activated carbon containing the pollutants can be then regenerated by EF treatment (or AO treatment, depending on the presence or not of dissolved iron in the solution). The oxidized solution can be then sent to a biological post-treatment in order to achieve the treatment. The final treated effluent can be partly reused to clean gravels and sand. The rest of solution can be sent to a wastewater treatment plant or in natural water, according to the effluent characteristics and the regulations. A treatment for sludge from the biological step is also considered. The water employed to clean gravels and sand is then treated by the electrochemical treatment.

7.7.6 Development for other kinds of pollutants and matrix

- *Development for other family of pollutants*

The integrated process could be enlarged to other kind of organic pollutant that could be present in soil like some pesticides, dioxins, PCB…According to the kind of extracting agent employed, the possibility to extract a mixed pollution (organic and metals) from contaminated soil could be considered. The metals that are becoming scarce could be further recovered and reused.

- *Development for other kinds of matrix*

The combination of EAOPs treatments with a biological post-treatment could be also extended to the removal of other compounds (pharmaceuticals, dyes,…) that are present in industrial effluents. This process could also be used for the treatment of landfill

leachates, reverse osmosis concentrates, dredging sludges, as some of them were already performed at laboratory scale by modified Fenton treatments (Zhang et al., 2006; Zhou et al., 2012).

This combined process can also be employed for SF techniques. Indeed, during this thesis work, some column experiments have been performed with a historically Total Petroleum Hydrocarbons (TPH)-contaminated soil by using Tween 80. The SF solutions were then treated by EF and the effluent biodegradability was assessed. This work performed in close collaboration will be also submitted soon after the PhD.

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APPENDICES

APPENDIX 1: Valorization of the PhD research work

Papers:

- **Mousset, E.**, Oturan, N., van Hullebusch, E. D., Guibaud, G., Esposito, G., Oturan, M. A., (2013) A new micelle-based method to quantify the Tween 80 surfactant for soil remediation, *Agronomy for Sustainable Development*, 33(4), 839-846. doi:10.1007/s13593-013-0140-2.
- **Mousset, E.**, Oturan, N., van Hullebusch, E. D., Guibaud, G., Esposito, G., Oturan, M. A., (2014) Influence of solubilizing agents (cyclodextrin or surfactant) on phenanthrene degradation by electro-Fenton process – study of soil washing recycling possibilities and environmental impact. *Water Research*, *48*, 306-316. http://dx.doi.org/10.1016/j.watres.2013.09.044.
- **Mousset, E.**, Oturan, M. A., van Hullebusch, E. D., Guibaud, G., Esposito, G., (2014) Soil washing/flushing treatments of organic pollutants enhanced by cyclodextrins and integrated treatments: state of the art, *Critical Reviews in Environmental Science & Technology* (in press), doi:10.1080/10643389.2012.741307. (http://www.tandfonline.com/doi/abs/10.1080/10643389.2012.741307#.Ujp8VLy0x7g)
- Oturan, M. A., **Mousset, E.**, van Hullebusch, E. D., Oturan, N., (2014) Method for determining the concentration of non-ionic surfactants in an aqueous solution by excitation-emission fluorescence sepctroscopy based on the enhancement of the fluorescence of 6-p-toluidino-2-naphthalenesulfonic acid. European patent number: 13305580.6 – 1554, Applicant: Université Paris-Est Marne-la-Vallée.
- **Mousset, E.**, Oturan, N., van Hullebusch, E. D., Guibaud, G., Esposito, G., Oturan, M. A., Influence of anode materials on toxicity and biodegradability of synthetic soil washing solutions containing phenanthrene and cyclodextrin during an anodic oxidation or electro-Fenton treatment. *Applied Catalysis B: Environmental* (submitted).
- **Mousset, E.**, Huguenot, D., van Hullebusch, E. D., Oturan, N., Guibaud, G., Esposito, G., Oturan, M. A., Soil washing by HPCD or Tween 80 combined to electro-Fenton to decontaminate historically PAHs-contaminated soil - a

laboratory investigation study (to be submitted in *Journal of Hazardous Materials*).

Preface:

- van Hullebusch E. D., Huguenot, D., Esposito, G., **Mousset, E.,** (2013) Preface. *Reviews in Environmental Science and Bio/Technologies*, 12(4), 333. (http://link.springer.com/article/10.1007%2Fs11157-013-9324-0).

Conferences:

- **E. Mousset**, D. Huguenot, E. D. van Hullebusch, N. Oturan, G. Guibaud, G. Esposito, M. A. Oturan, A new integrated approach to remove PAHs from highly contaminated soil: soil washing with cyclodextrin or surfactant combined to an electro-Fenton process. Abstract of the INTERSOL conference, Lille (France), March 2014. *(Oral)*
- **E. Mousset**, D. Huguenot, E. D. van Hullebusch, N. Oturan, G. Guibaud, G. Esposito, M. A. Oturan, A new integrated approach to remove PAHs from highly contaminated soil: soil washing combined to electro-Fenton process and possible post-biological treatment. 13th international conference in environmental science and technology (CEST 2013), Athens (Greece), September, 2013. *(Oral)*
- **E. Mousset**, N. Oturan, E. D. van Hullebusch, G. Guibaud, G. Esposito, M. A. Oturan, Role of anode materials and initial COD on toxicity and biodegradability of synthetic soil washing solution containing Tween 80 and phenanthrene during electro-Fenton treatment. 16ème Journées d'électrochimie (JE), Paris (France), July, 2013. *(Oral)*
- **E. Mousset**, D. Huguenot, E. D. van Hullebusch, N. Oturan, G. Guibaud, G. Esposito, M. A. Oturan, Soil washing combined to electro-Fenton treatments of PAHs contaminated soils in the presence of HPCD or Tween 80®. 12th AquaConSoil conference, Barcelona (Spain), April, 2013. *(Poster)*

  (http://www.aquaconsoil.org/AquaConSoil2013/Procs_Theme_D_files/ThS_D3_Poster.pdf).
- **E. Mousset**, N. Oturan, E. D. van Hullebusch, G. Guibaud, G. Esposito, M. A. Oturan, Electro-Fenton treatment of soil washing solution of phenanthrene with

cyclodextrin using different kind of anode materials: impacts on toxicity and biodegradability. 3rd international conference on Development, Energy, Environment, Economics (DEEE'12), Paris (France), December, 2012. *(Oral)* (http://www.wseas.us/e-library/conferences/2012/Paris/DEEE/DEEE-14.pdf).

Summer school presentations:

- **E. Mousset**, D. Huguenot, E. D. van Hullebusch, N. Oturan, G. Guibaud, G. Esposito, M. A. Oturan, Electro-Fenton treatment of soil washing solutions of PAHs-contaminated soils with cyclodextrin or surfactant. Summer school on contaminated sediments: characterization and remediation, Delft (The Netherlands), June, 2013. *(Oral)*
- **E. Mousset**, N. Oturan, M. A. Oturan, E. D. van Hullebusch, G. Guibaud, G. Esposito, Electro-Fenton and anodic oxidation treatments of phenanthrene in the presence of hydroxypropyl-beta-cyclodextrin: biodegradability and toxicity data. Summer school on contaminated soils: from characterization to remediation, Paris-Est (Champs-sur-Marne; France), June, 2012. (http://summer-school-soils.univ-paris-est.fr/). *(Oral)*
- **E. Mousset**, E. D. van Hullebusch, M. A. Oturan, J. Mouton, J-M. Riom, G. Guibaud, G. Esposito, Cyclodextrins enhanced remediation of soil polluted by hydrophobic organic pollutants and electro-Fenton treatment. Summer school: biological and thermal treatment of municipal solid waste, Naples (Italy), May, 2011. (http://www.iat.unina.it/summerschool/home.html). *(Oral)*

Seminars:

- **E. Mousset**, N. Oturan, D. Huguenot, E. D. van Hullebusch, G. Guibaud, G. Esposito, M. A. Oturan, Electro-Fenton treatment of soil washing solutions of PAHscontaminated soils with cyclodextrin or surfactant, PhD day, Naples (Italy), April, 2013. *(oral)*
- **E. Mousset**, E. D. van Hullebusch, G. Guibaud, G. Esposito, M. A. Oturan, Integrated processes for removal of organic pollutants : soil washing and advanced oxidation processes coupled to biological processes, PhD day, Paris-Est (France), February, 2011. *(oral)*

Projects:

- Co-organization of the summer school on "contaminated soil: from characterization to remediation", Paris-Est (Champs-sur-Marne; France), June, 2012. (http://summer-school-soils.univ-paris-est.fr/).
- Collaboration to a funding project (accepted in 2012) from île-de-France region, entitled "Combinaison des procédés d'oxydation avancée et biologique pour le traitement des solutions de lavage de sols contenant des polluants organiques". (http://www.r2ds-ile-de-france.com/spip.php?article919).
- Collaboration to a project on *in situ* soil flushing of hydrocarbons-contaminated soils in partnership with a company (2012).
- Guest editor and reviewer in « Reviews in Environmental Science and Bio/Technology » journal regarding the special issue on contaminated soils (2012-2013).
- Involvement in the transnational workshop « CityChlor » in order to propose a new integrated approach to tackle the threats caused by contamination with chlorinated solvents in urban areas (Paris, November 2010).

APPENDIX 2: Synthetic tables of Chapter 2

APPENDIX 2.1. Enhanced solubilization of HOCs with CDs.

Pollutant	CDs (Conc.)[1]	Time of shaking	Ratio of complex	Apparent stability constant (K_s or K_{CW})	Max enhancement factor E (Max apparent solubilization)	Ref.
				PAHs		
NAP	β-CD (0-0.9 mM) (0-0.1%)	-	1:1	-	1.55-fold	(Wang and Brusseau, 1995a)
NAP	γ-CD (0-3 mM) (0-0.4%)	-	1:1	-	1.25-fold	(Wang and Brusseau, 1995a)
NAP	HPCD (0-50 g L^{-1}) (0-5%)	72 h	1:1	611 L mol^{-1}	20-fold	(Badr et al., 2004)
NAP	β-CD (0-1.7 mM) (0-0.2%)	72 h	1:1	471 L mol^{-1}	1.7-fold	(Badr et al., 2004)
NAP	HPCD (0-70 g L^{-1}) (0-7%)	48 h	1:1	522 L kg^{-1}	37-fold	(Wang and Brusseau, 1993)
ACE	β-CD (0-0.6 mM) (0-0.07%)	-	1:1	-	1.2-fold	(Wang and Brusseau, 1995a)
ACE	γ-CD (0-0.8 mM) (0-0.1%)	-	1:1	-	1.65-fold	(Wang and Brusseau, 1995a)
FLE	β-CD (0-6 g L^{-1}) (0-0.6%)	-	1:1	0.865	5.8-fold	(Shixiang et al., 1998)
FLE	CMCD (0-50 g L^{-1}) (0-5%)	-	1:1	0.544	28-fold	(Shixiang et al., 1998)
PHE	β-CD (0-12 g L^{-1}) (0-1.2%)	24 h	1:1	0.78904	10-fold	(Wang et al., 2010)
PHE	CMCD (0-30 g L^{-1}) (0-3%)	24 h	1:1	0.74429	22-fold	(Wang et al., 2010)
PHE	GCD (0-30 g L^{-1}) (0-3%)	24 h	1:1	0.96355	30-fold	(Wang et al., 2010)
PHE	HPCD (0-100 g L^{-1}) (0-10%)	72 h	1:1	-	124-fold (161.3 mg L^{-1})	(Wang et al., 1998)
PHE	β-CD (0-9 mM) (0-1%)	-	1:1	-	12-fold	(Wang and Brusseau, 1995a)

PHE	γ-CD (0-4 mM) (0-0.52%)	-	1:1	-	2.2-fold	(Wang and Brusseau, 1995a)
PHE	HPCD (0-50 g L^{-1}) (0-5%)	72 h	1:1	2749 L mol^{-1}	90-fold	(Badr et al., 2004)
PHE	β-CD (0-1.7 mM) (0-0.2%)	72 h	1:1	1226 L mol^{-1}	3-fold	(Badr et al., 2004)
PHE	Mod-β-CD_{12} (0-4 mM)	48 h	1:1	-	13-fold (0.06 mM)	(Sales et al., 2011)
PHE	Mod-β-CD_{12}(2.4) (0-4 mM)	48 h	1:1	-	4.3-fold (0.02 mM)	(Sales et al., 2011)
PHE	β-CD (0-10 g L^{-1}) (0-1%)	-	1:1	1.005	11-fold	(Shixiang et al., 1998)
PHE	CMCD (0-50 g L^{-1}) (0-5%)	-	1:1	0.698	35-fold	(Shixiang et al., 1998)
PHE	HPCD (1, 10%)	24 h		-	(79.7 mg L^{-1})	(Wu et al., 2010)
ANT	β-CD (0-9 mM) (0-1%)	-	1:1	-	18-fold	(Wang and Brusseau, 1995a)
ANT	γ-CD (0-4 mM) (0-0.52%)	-	1:1	-	1.1-fold	(Wang and Brusseau, 1995a)
ANT	β-CD (0-12 g L^{-1}) (0-1.2%)	-	1:1	1.733	21-fold	(Yang et al., 2010)
ANT	EDCD (0-12 g L^{-1}) (0-1.2%)	-	1:1	2.735	33-fold	(Yang et al., 2010)
ANT	GluCD (0-12 g L^{-1}) (0-1.2%)	-	1:1	4.602	56-fold	(Yang et al., 2010)
ANT	HPCD (0-70 g L^{-1}) (0-7%)	48 h	1:1	2 936 L kg^{-1}	205-fold	(Wang and Brusseau, 1993)
FLA	β-CD (0-9 mM) (0-1%)	-	1:1	-	5-fold	(Wang and Brusseau, 1995a)
FLA	γ-CD (0-4 mM) (0-0.52%)	-	1:1	-	4.1-fold	(Wang and Brusseau, 1995a)
PYR	β-CD (0-0.6 mM) (0-0.07%)	-	1:1	-	2.5-fold	(Wang and Brusseau, 1995a)
PYR	γ-CD (0-4 mM) (0-0.52%)	-	1:1	-	9-fold	(Wang and Brusseau, 1995a)
PYR	HPCD (1, 10%)	24 h	-	-	(7.4 mg L^{-1})	(Wu et al., 2010)
BaP	β-CD (0-0.01 M) (0-1.1%)	-	1:1	2,808 L mol^{-1}	38-fold	(Veignie et al., 2009)
BaP	HPCD (0-0.01 M)	-	1:1	3,989 L mol^{-1}	53-fold	(Veignie et al., 2009)
BaP	RAMEB (0-0.01 M)	-	1:1	5,344 L mol^{-1}	72-fold	(Veignie et al., 2009)

BaP	HPCD (1, 10%)	24 h	-	-	(4.6 mg L^{-1})	(Wu et al., 2010)
			Pesticides, derivatives and by-products			
NFL	α-CD (0-100 mM) (0-9.7%)	1 week	1:1	50.7 M^{-1}	4.5-fold (0.45 mM)	(Villaverde et al., 2005b)
NFL	γ-CD (0-100 mM) (0-13%)	1 week	1:1	37.0 M^{-1}	3.8-fold (0.38 mM)	(Villaverde et al., 2005b)
NFL	-CD (0-12 mM) (0-1.4%)	1 week	1:1	360 M^{-1}	5.5-fold (0.55 mM)	(Villaverde et al., 2005a)
NFL	RAMEB (0-100 mM)	1 week	1:1	558.5 M^{-1}	55-fold (5.5 mM)	(Villaverde et al., 2007)
NFL	HPCD (0-100 mM)	1 week	1:1	389.5 M^{-1}	35-fold (3.5 mM)	(Villaverde et al., 2007)
MF	β-CD (0-9 mM) (0-1%)	24 h	1:1	2.38	23-fold	(Guo et al., 2010)
Butachlor	β-CD (0-12 mM) (0-1.4%)	72 h	1:1	443 M^{-1}	6.3-fold (0.22 mM)	(Bian et al., 2009)
m-parathion	HPCD (0-120 g L^{-1}) (0-12%)	24 h	1:1	-	91-fold	(Zeng et al., 2006)
DDT	HPCD (0-70 g L^{-1}) (0-7%)	48 h	1:1	11,170 L kg^{-1}	767-fold	(Wang and Brusseau, 1993)
HCB	MCD (0-100 g L^{-1}) (0-10%)	72 h	1:1	0.006	(0.5 mg L^{-1})	(Wan et al., 2009)
CB	HPCD (0-70 g L^{-1}) (0-7%)	48 h	1:1	83 L kg^{-1}	7.5-fold	(Wang and Brusseau, 1993)
			Chlorinated solvents			
PCP	β-CD (0-18 g L^{-1}) (0-1.8%)	72 h	1:1	309 M^{-1} (pH 3) 258 M^{-1} (pH 7)	3.5-fold (pH 3) 3.2-fold (pH 7)	(Hanna et al., 2004a)
PCP	HPCD (0-80 g L^{-1}) (0-8%)	72 h	1:1	703 M^{-1} (pH 3) 153 M^{-1} (pH 7)	40-fold (pH 3) 10-fold (pH 7)	(Hanna et al., 2004a)
PCP	MCD (0-80 g L^{-1}) (0-8%)	72 h	1:1	803 M^{-1} (pH 3) 373 M^{-1} (pH 7)	46-fold (pH 3) 23-fold (pH 7)	(Hanna et al., 2004a)
PCP	CMCD (0-80 g L^{-1}) (0-8%)	72 h	1:1	789 M^{-1} (pH 3) 367 M^{-1} (pH 7)	45-fold (pH 3) 22-fold (pH 7)	(Hanna et al., 2004a)
TCP	β-CD (0-6.5 g L^{-1}) (0-14 g L^{-1})	48 h	1:1	103 L kg^{-1} (pH 3) 9 L kg^{-1} (pH 8.8)	1.7-fold (pH 3) 1.12-fold (pH 8.8)	(Hanna, 2003)
TCP	HPCD (0-75 g L^{-1}) (0-7.5%)	48 h	1:1	255 L kg^{-1} (pH 3) 15 L kg^{-1} (pH 8.8)	20-fold (pH 3) 2.2-fold (pH 8.8)	(Hanna, 2003)

TCP	MCD (0-70 g L^{-1}) (0-7%)	48 h	1:1	280 L kg^{-1} (pH 3) 33 L kg^{-1} (pH 8.8)	21-fold (pH 3) 3.25-fold (pH 8.8)	(Hanna, 2003)
TCE	HPCD (10%)	24 h	-	-	5.5-fold (5,962 mg L^{-1})	(Boving et al., 1999)
TCE	MCD (10%)	24 h	-	-	6.6 (10,298 mg L^{-1})	(Boving et al., 1999)
TCE	HP-α-CD (0.5-5%)	5 h	1:1	0.136 mM^{-1}	-	(Yang et al., 2010)
TCE	HPCD (0.5-5%)	5 h	1:1	0.119 mM^{-1}	-	(Yang et al., 2010)
TCE	HP-γ-CD (0.5-5%)	5 h	1:1	0.032 mM^{-1}	-	(Yang et al., 2010)
TCE	MCD (0.5-5%)	5 h	1:1	0.136 mM^{-1}	-	(Yang et al., 2010)
TCE	HPCD (0-70 g L^{-1})	48 h	1:1	51 L kg^{-1}	4.5-fold	(Wang and Brusseau, 1993)
TeCE	HPCD (10%)	24 h	-	-	15.5-fold (2,962 mg L^{-1})	(Boving et al., 1999)
TeCE	MCD (10%)	24 h	-	-	29.1-fold (7,138 mg L^{-1})	(Boving et al., 1999)
TeCE	CMCD (0-100 g L^{-1}) (0-10%)	1 week	1:1	71.4 L kg^{-1}	8.6-fold (2150 mg L^{-1})	(Skold et al., 2008)
TeCE	HP-α-CD (0.5-5%)	5 h	1:1	0.030 mM^{-1}	-	(Yang et al., 2010)
TeCE	HPCD (0.5-5%)	5 h	1:1	0.279 mM^{-1}	-	(Yang et al., 2010)
TeCE	HP-γ-CD (0.5-5%)	5 h	1:1	0.056 mM^{-1}	-	(Yang et al., 2010)
TeCE	MCD (0.5-5%)	5 h	1:1	0.299 mM^{-1}	-	(Yang et al., 2010)
				NACs		
TNT	HPCD (0-4%)	48 h	1:1	14.5 μM^{-1}	-	(Sheremata and Hawari, 2000)
TNT	DMCD (0-4%)	48 h	1:1	55.8 μM^{-1}	-	(Sheremata and Hawari, 2000)
4-ADNT	HPCD (0-4%)	48 h	1:1	254.1 μM^{-1}	-	(Sheremata and Hawari, 2000)
4-ADNT	DMCD (0-4%)	48 h	1:1	443.1 μM^{-1}	-	(Sheremata and Hawari, 2000)
2,4-DANT	HPCD (0-4%)	48 h	1:1	123.3 μM^{-1}	-	(Sheremata and Hawari, 2000)
2,4-DANT	DMCD (0-4%)	48 h	1:1	78.9 μM^{-1}	-	(Sheremata and Hawari, 2000)
2-NB	β-CD (0-8 g L^{-1}) (0-0.8%)	48 h	1:1	-	4.2-fold (59.9 mg L^{-1})	(Cai et al., 2006)
2-NB	HPCD (0-8 g L^{-1}) (0-0.8%)	48 h	1:1	-	2.8-fold (40.4 mg L^{-1})	(Cai et al., 2006)
2-NB	CMCD (0-8 g L^{-1}) (0-0.8%)	48 h	1:1	-	5.6-fold (80.0 mg L^{-1})	(Cai et al., 2006)
NBZ	β-CD (0-5 mM) (0-0.57%)	24 h	1:1	-	1.3-fold (12.8 mM)	(Chen et al., 2006)

BTEX and derivatives						
TOL	HPCD (0-10%)	72 h	1:1	0.59	8-fold	(Carroll and Brusseau, 2009)
EB	HPCD (0-10%)	72 h	1:1	1.21	20-fold	(Carroll and Brusseau, 2009)
BB	HPCD (0-10%)	72 h	1:1	9.09	121-fold	(Carroll and Brusseau, 2009)
Phenolic compounds						
4-NP	HP-α-CD (0-65 mM)	24 h	1:4	-	(195 mM)	(Kawasaki et al., 2001)
4-NP	HPCD (SD = 0.6) (0-55 mM)	24 h	1:3	-	(155 mM)	(Kawasaki et al., 2001)
4-NP	HPCD (SD = 0.8) (0-55 mM)	24 h	1:4.3	-	(215 mM)	(Kawasaki et al., 2001)
4-NP	HPCD (SD = 1.0) (0-55 mM)	24 h	1:1.7	-	(85 mM)	(Kawasaki et al., 2001)
4-NP	HP-γ-CD (0-55 mM)	24 h	1:2	-	(98 mM)	(Kawasaki et al., 2001)

APPENDIX 2.2. SW with CDs.

Contaminants		Washing agents		Soil's characteristics						Kind of soil and type of contamina-tion	S/L ratio (pulp density)	Contact time	Percentages of removal	Ref.
Pollutants	**Conc.**	**Kind of washing agents**	**Conc.** [(2)]	**Sand (%)**	**Silt (%)**	**Clay (%)**	**OM (%)**[(1)]	**CEC (meq/100g)**	**pH**					
PHE	157 mg kg^{-1}	GCD	5-40 g L^{-1} (0.5-4%)		nd		3.14	nd	6.80	1 Spiked soil	0.5 g : 25 mL (2%)	24 h	78.8% (40 g L^{-1} of GCD)	(Wang et al., 2010)
PHE	456 mg kg^{-1}	HPCD	1-40 g L^{-1} (0.1-4%)	43	40	17	15.04	6.02	4.78	1 Spiked soil	2.5 g : 50 mL (5%)	24 h	70% (with 4% of HPCD)	(Gomez et al., 2010)
		MCD	1-40 g L^{-1} (0.1-4%)										70% (with 4% of MCD)	
PHE	kaolin soil: 500 mg kg^{-1} soil A: 193 mg kg^{-1} soil D: 260 mg kg^{-1}	HPCD	10-100 g L^{-1} (1-10%)	84 50.1-87.7 (gravel: 1.4-15.4) 4	nd nd nd	16 10.9-34.5 96	19.17 4.7-6.4 ~ 0	nd nd nd	7.05 6.9 4.9	MGP soil A MGP soil D 1 spiked kaolin soil	5 g : 25 mL (20%)	24 h	Kaolin soil: 44%; soil A: 96%; soil D: 22.9% (10% of HPCD)	(Maturi and Reddy, 2008))
		β-CD	0.5-10 g L^{-1} (0.05-1%)										Kaolin soil: 10%; soil A: 10.8%; soil D: 2% (1% of β-CD)	
		Tween 80	5-50 g L^{-1} (0.5-5%)										Kaolin soil: 52%; soil A: 100%; soil D: 48.3% (5% of Tween 80)	
		I-CA-720	5-50 g L^{-1} (0.5-5%)										Kaolin soil: 33.6%; soil A: 100%; soil D: 72.6% (5% of I-CA-720)	

		EDTA	0.01-0.2 M (0.3-5.8%)										Kaolin soil: 0.4%; soil A: 2.5%; soil D: 4.2% (0.01 M of EDTA)	
		DTPA	0.01-0.2 M (0.4-7.9%)										Kaolin soil: 0.55%; soil A: 0.7%; soil D: 4.6% (0.05 M of DTPA)	
		THF	50-200 g L^{-1} (5-20%)										Kaolin soil: 8.0%; soil A: 10%; soil D: 3% (5% of THF)	
		n-But	50-200 g L^{-1} (5-20%)										Kaolin soil: 46.2%; soil A: 100%; soil D: 18.4% (20% of n-But)	
PHE (Total PAHs)	260 mg kg^{-1} (1493 mg kg^{-1})	HPCD	10-100 g L^{-1} (1-10%)	50.1-87.7 (gravel: 1.4-15.4)	nd	10.9-34.5	2.69-3.75	nd	6.9	1 natural contaminated soil	5 g : 25 mL (20%)	24 h	22.5% (10% HPCD)	(Khodadoust et al., 2005)
		-CD	0.5-10 g L^{-1} (0.05-1%)										1% (1% β-CD)	
		I-CA-720	5-50 g L^{-1} (0.5-5.0%)										75% (5.0% I-CA-720)	
		Tween 80	5-50 g L^{-1} (0.5-5.0%)										53% (1% Tween 80)	
		EDTA	2.92-58.4 g L^{-1} (0.01 to 0.2 M)										2.5% (0.01M EDTA)	
		DTPA	3.93-78.6 g L^{-1} (0.01 to 0.2 M)										3.25% (0.2M DTPA)	
		THF	5-20%										3% (20% THF)	
		n-But	5-20%										18.5% (20% n-But)	
NAP PHE	NAP: 35 and 55 mg kg^{-1} (s1 & s2)	HPCD	5 g L^{-1} (0.5%)	39.8 40.9	42.5 42.0	17.7 17.1	2.0 5.0	0.86 1.10	7.4 6.9	Soil s1 Soil s2 (2 spiked soils)	5 g : 15 mL (33.3%)	48 h	Soil s1: 80% (NAP), 64% (PHE) 68% (NAP), 29% (PHE) (in mixture: NAP+PHE) Soil s2: 69% (NAP), 42% (PHE) 56% (NAP), 18% (PHE) (in mixture: NAP+PHE)	(Badr et al., 2004)

		β-CD	5 g L^{-1} (0.5%)										Soil s1: 68% (NAP), 53% (PHE) 60% (NAP), 25% (PHE) (in mixture: NAP+PHE) Soil s2: 58% (NAP), 34% (PHE) 48% (NAP), 16% (PHE) (in mixture: NAP+PHE)	
FLE FLA	100 mg kg^{-1} 100 mg kg^{-1}	HPCD	70 mM	40.7 9.20 13.4 34.7	22.5 51.6 61.9 46.9	36.8 39.2 24.7 18.4	1.72 1.63 2.47 1.19	nd nd nd nd	4.56 4.74 6.02 7.35	Soil 1 Soil 2 Soil 3 Soil 4 [4 spiked soils (aged of contamination 1, 4 and 16 weeks)]	3 g : 15 mL (20%)	120 h	FLE (after 1 week): 96.9%, 96.9%, 96.5%, 96.3% (soils 1 to 4 respectively), FLE (after 16 week): 90.3%, 87.1%, 86.2%, 89.5% (soils 1 to 4 respectively), FLA (after 1 week): 77.5-94.8% for soils 1-4, FLA (after 16 week): 66.3-75.7% for soils 1-4	(Gao et al., 2009)
PYR	1.07, 9.72, 88.4, 152 and 429 mg kg^{-1}	HPCD	50 mM	50.5	37	12.5	2.1	7.76	5.95	1 Spiked soil (aged of contamination: 0, 69, 150 and 222 days)	2 g : 25 mL (8%)	20 h	PYR (1.07 mg kg^{-1}): 39.64%, 35.31%, 23.65%, 13.50% PYR (9.72 mg kg^{-1}): 53.08%, 51.03%, 40.20%, 32.87% PYR (88.4 mg kg^{-1}): 68.16%, 63.68%, 57.19%, 51.25% PYR (152 mg kg^{-1}): 70.95%, 67.71%, 60.62%, 56.54% PYR (429 mg kg^{-1}): 51.49%, 47.15%, 45.41%, 39.35% (express with the increase of aged-contaminated soil)	(Khan et al., 2011)
PHE PYR	123 mg kg^{-1} 141 mg kg^{-1}	MCD	0-50 g L^{-1} (0-5%) (0-0.038 M)		nd		2.2	nd	7.6	1 Spiked soil	0.5 g : 5 mL (10%)	20 h	PHE: 100% Pyrene: 60% (50 g L^{-1} MCD)	(Petitgirard et al., 2009)
FLE PHE PYR	-100 and 1.4 mg kg^{-1}, -500 and 9.7 mg kg^{-1},	HPCD	60 mM	88 83	12 17	0 0	nd nd	nd nd	nd nd	UEA soil TW soil (1 spiked soil and 1 natural	3 g : 30 mL (10%)	20 h	UEA soil: FLU 88%, PHE 85%, PYR 71% TW soil: FLU 49%, PHE 42%, PYR 41%	(Latawiec and Reid, 2009)

	-250 and 10.1 mg kg^{-1}, in UEA soil and TW soil respectively	Brij 700	5.25 mM							contaminated soil)	3 g : 30 mL (10%)	16 h	UEA soil: FLU 60%, PHE 38%, PYR 51% TW soil: FLU 34%, PHE 26%, PYR nd%	
		BuOH	Pure solution (100%)								3 g : 4.5 mL (66.7%)	120 s	UEA soil: FLU 63%, PHE 62%, PYR 64% TW soil: FLU 65%, PHE 64%, PYR 65%	
ANT PHE PYR	72 mg kg^{-1}, 102 mg kg^{-1}, 99 mg kg^{-1}	MCD	10 g L^{-1} (1%)	7.3	79.1	13.6	16,7	nd	6.05	1 Spiked soil	0.5 g : 5 mL (10%)	24 h	PHE: 13% ANT: 10% PYR: 1%	(Navarro et al., 2007))
		γ-CD	10 g L^{-1} (1%)										PHE: 2% ANT: 1% PYR: 0.5%	
		Tween 80	10 g L^{-1} (1%)										PHE: 38% ANT: 26% PYR: 23%	
		DNA	10 g L^{-1} (1%)										PHE: 28% ANT: 8% PYR: 40%	
PYR BAP	300 mg kg^{-1}, 300 mg kg^{-1}	HPCD	50 mM			High sand, low OM High OM, high clay Moderate OM and clay				Boyndie soil, Cruden Bay soil Insch soil (3 Spiked soils)	1.2 g : 20 mL (6%)	20 h	PYR (120 days aged-soil): 20 %, 9% and 9% BAP (185 days aged-soil): 1%, 0.8% and 0.8% (Boyndie soil, cruden bay soil and Insch soil respectively)	(Hua et al., 2007)
-MGP soil : Total PAHs -s1 & s2 : PHE PYR BAP	MGP: 1000 mg kg^{-1} Spiked: 200 mg kg^{-1} (s1) and 400 mg kg^{-1} (s2) of each PAH	HPCD	100 g L^{-1} (10%)	54.8 41.8	36 47	9.2 11.2	19.82 2.18	nd nd	7.16 7.65	1 MGP soil 2 spiked soils	2 g : 20 mL (10%)	16 h	PHE: 50% and 65% PYR: 23% and 25% BAP: 30% and 25% (s1 and s2 spiked soils respectively)	(Gong et al., 2010)
		TX-100	100 g L^{-1} (10%)										PAHs: 3% (MGP soil) PHE: 60% and 70% PYR: 60% and 65% BAP: 45% and 44% (s1 and s2 spiked soils respectively)	

			PAHs: 22% (MGP soil)
Tween 80	100 g L^{-1} (10%)		PHE: 72% and 70% PYR: 74% and 65% BAP: 63% and 44% (s1 and s2 spiked soils respectively) PAHs: 31% (MGP soil)
S-FAME	Pure solution (100%)	5 g : 5 mL (10%)	PHE: 86% and 82% PYR: 92% and 86% BAP: 77% and 68% (s1 and s2 spiked soils respectively) PAHs: 46% (MGP soil)
M-biodiesel	Pure solution (100%)		PHE: 78% and 63% PYR: 86% and 63% BAP: 57% and 40% (s1 and s2 spiked soils respectively) PAHs: 35% (MGP soil)
Soybean oil	Pure solution (100%)		PHE: 90% and 75% PYR: 90% and 78% BAP: 75% and 59% (s1 and s2 spiked soils respectively) PAHs: 17% (MGP soil)
MeOH	Pure solution (100%)		PHE: 81% and 78% PYR: 80% and 77% BAP: 75% and 70% (s1 and s2 spiked soils respectively) PAHs: 28% (MGP soil)

Total PAHs (MGP A, B & C) PHE (s1 & s2) PYR (s1 & s2) BaP (s1 & s2)	MGP A: 996.9 mg kg^{-1} MGP B: 229.6 mg kg^{-1} MGP C: 52.8 mg kg^{-1} s1 and s2: 192 and 386 mg kg^{-1} 175 and 369 mg kg^{-1} 168 and 361 mg kg^{-1}	HPCD	10 and 100 g L^{-1} (1 and 10%)	54.8 41.8	36 47	9.2 11.2	19.82 2.18	nd nd	7.16 7.65	3 MGP soils (A, B &C) 2 spiked soils (s1 & s2)	5 g : 50 mL (10%)	16 h	s1 and s2 (HPCD 10%): PHE (50% and 62%), PYR (28% and 27%), BAP (30% and 25%) MGP A: 62%, MGP B: 9%, MGP C: 7% (for total PAHs with HPCD 10%)	(Wu et al., 2010)
		Tween 80	10 and 100 g L^{-1} (1 and 10%)										s1 and s2 (Tween 80 10%): PHE (70% and 70%), PYR (72% and 69%), BAP (62% and 62%) MGP A: 90%, MGP B: 32%, MGP C: 30% (for total PAHs with Tween 80 10%)	
		Biodiesel	Pure solution (100%)								5 g : 5 mL (100%)		s1 and s2: PHE (90% and 88%), PYR (92% and 83%), BAP (80% and 78%) MGP A: 100%, MGP B: 88%, MGP C: 80% (for total PAHs)	
NAP	1.74 1.33 1.71 0.55 0.98 1.06 (mg kg^{-1})	HPCD	50 mM	56.9 38.1 41.3 58.0 42.8 46.6	29.5 42.4 36.2 31.5 29.7 31.9	13.6 19.5 22.5 10.5 27.5 21.5	9.4 9.6 10.2 10.2 11.7 12.6	nd nd nd nd nd nd	6.5 7.4 7.2 6.4 7.1 7.5	Soil 1 Soil 2 Soil 3 Soil 4 Soil 5 Soil 6 (6 MGP soils)	1.5 g : 20 mL (7.5%)	24 h	80.4%, 84.9%, 88.8%, 76.3%, 55.1%, 75.4% (For soil 1 to 6 respectively)	(Papadopoulos et al., 2007)
PHE	3.64 3.59 6.09 2.55 2.43 4.22 (mg kg^{-1})												80.2%, 81.0%, 83.2%, 66.2%, 43.2%, 78.1% (For soil 1 to 6 respectively)	

PYR	4.15 3.65 5.90 2.03 18.13 3.44 (mg kg^{-1})	16.1%, 34.2%, 17.9%, 25.1%, 18.1%, 29.0% (For soil 1 to 6 respectively)
BaP	3.86 3.80 4.68 2.88 1.29 3.38 (mg kg^{-1})	15.0%, 12.1%, 5.5%, 10.0%, 12.4%, 12.1% (For soil 1 to 6 respectively)
Total PAHs	44.02 42.70 53.21 27.24 34.83 43.99 (mg kg^{-1})	28.5%, 28.6%, 26.8%, 25.7%, 19.6%, 29.1% (For soil 1 to 6 respectively)

NFL	4, 12 and 20 mg L^{-1}	β-CD	0.11-11.35 g L^{-1} (0.01, 0.5, 2.0, 5.0, 7.0, 10.0 M and 1:1 molar ratio of -CD in relation to NFL adsorbed)	16.4 92.8 56.7 2.7 61.1 87.6	61.2 4.4 23.8 31.5 29.0 4.0	22.6 2.5 19.5 65.9 9.8 8.4	1.90 0.51 1.38 1.76 5.34 0.79	17.2 3.5 5.8 39.0 20.1 4.8	7.6 6.5 5.7 8.0 4.8 8.0	Soil 1 Soil 2 Soil 3 Soil 4 Soil 5 Soil 6 (6 spiked soils)	10 g : 20 mL (50%)	24 h	-Constant NFL concentration (20 mg L^{-1}): 100% for soil 2 and soil 6 (with all the β-CD concentration); 100% for soil 3 (except 71.7% for 0.0268 mM of β-CD) and soil 5 (except 95.6% for 0.0192 mM of β-CD); soil 1 (25.4%, 28.8%, 32.4%, 35.9%, 45.8%, 49.9%, 61.6% with an increase concentration of -CD); soil 4 (32.9%, 38.6%, 44.5%, 51.5%, 77.1%, 92.9%, 97.6% with an increase concentration of β-CD). -Constant β-CD concentration (0.01 mM): soil 1 (25.5%, 49.1%, 61.6%), soil 2 (100%, 100%, 100%), soil 3 (83.9%, 95.0%, 100.0%), soil 4 (92.8%, 98.2%, 97.6%), soil 5 (100%, 100%, 100%), soil 6 (89.0%, 100%, 100%) with an increase concentration of NFL.	(Villaverde et al., 2005a)
NFL	4, 12 and 20 mg L^{-1}	α-CD γ-CD	9.73 g L^{-1} (0.97%) (0.01 M) 12.97 g L^{-1} (1.3%) (0.01 M)	16.4 87.6	61.0 4.0	22.6 8.4	1.90 0.79	17.2 4.8	7.6 8.0	AL soil CR soil (2 spiked soils)	10 g : 20 mL (50%)	24 h	AL soil: 20.5%, 39.5%, 55.5% and CR soil: 100%, 100%, 100% (for 4, 12 and 20 mg L^{-1} of NFL) AL soil: 3.0%, 25.6%, 33.7% and CR soil: 100%, 100%, 100% (for 4, 12 and 20 mg L^{-1} of NFL)	(Villaverde et al., 2005b)

NFL	4, 12 and 20 mg L^{-1}	β-CD	11.35 g L^{-1} (1.1%) (0.01 M)	16.4 92.8 56.7 2.7 61.1 87.6	61.2 4.4 23.8 31.5 29.0 4.0	22.6 2.5 19.5 65.9 9.8 8.4	1.90 0.51 1.38 1.76 5.34 0.79	17.2 3.5 5.8 39.0 20.1 4.8	7.6 6.5 5.7 8.0 4.8 8.0	Soil 1 Soil 2 Soil 3 Soil 4 Soil 5 Soil 6 (6 spiked soils)	10 g : 20 mL (50%)	24 h	-Soil 1: 13.7%, 18.3%, 5.64% -Soil 2: 100%, 71.4%, 77% -Soil 3: 48.8%, 34.8%, 69.6% -Soil 4: 62.4%, 33.8%, 37.5% -Soil 5: 100%, 80%, 79% -Soil 6: 100%, 87.9%, 87.5% (values with increasing NFL concentration)	(Villaverde et al., 2006)
NFL	20 mg L^{-1}	β-CD	11.35 g L^{-1} (1.1%) (0.01 M)	56.7 16.7 49.8 2.7	23.8 58.6 34.5 31.5	19.5 24.7 15.7 65.9	1.38 1.41 1.40 1.76	nd nd nd nd	5.7 6.0 5.5 8.0	Soil 1 Soil 2 Soil 3 Soil 4 [4 spiked soils (aged of contamination 1, 15 and 30 days)]	5 g : 10 mL (50%)	24 h	100% for the 4 soils with 1 and 15 days of contamination 64.87%, 89.39%, 100.00%, 57.02%, respectively for soils 1, 2, 3 and 4 with 30 days of contamination	(Villaverde, 2007)
MF	1 mg L^{-1} ($3.35x10^{-3}$ mM)	β-CD Tween 80	8.0 g L^{-1} (0.8%) (0-7.1 mM) 9.3 g L^{-1} (0.93%) (0-7.1 mM)	nd nd nd nd	nd nd nd nd	62 30.8 43.6 19.8	1.52 2.16 1.85 2.59	11.60 14.70 17.70 24.55	5.03 7.61 7.82 5.78	Soil A Soil B Soil C Soil D (4 spiked soils)	0.5 g : 20 mL (2.5%)	48 h	98.5%, 98.5%, 89.5%, 89.5% respectively for Soil A, B, C, D (β-CD 4.82 g L^{-1} (4.25 mM)) 89.5%, 86.5%, 86.5%, 83.6% respectively for Soil A, B, C, D (Tween 80 5.57 g L^{-1} (4.25 mM))	(Guo et al., 2010)
Lindane	70 ppm (real soil) 135 ppm (model soil)	α-CD β-CD γ-CD	0.23 g L^{-1} (0.023%) ($2.4x10^{-1}$ mM) 0.27 g L^{-1} (0.027%) ($2.4x10^{-1}$ mM) 0.31 g L^{-1} (0.031%) ($2.4x10^{-1}$	97.97 99.5	0.017 0.003	2.01 0.06	1.31 0	1.5 5.5	7.88 11.14	1 real soil 1model soil (2 spiked soil)	50 g : 50 mL (100%)	0-5500 min	5% (real soil) 2.8% (model soil) 4.8% (real soil) 2.7% (model soil) 8.6% (real soil) 4.8% (model soil)	(Bartolo et al., 2008)

			mM)											
PCP	160 mg kg^{-1} (introduce for sorption preliminary experiment)	β-CD	1.13-5.67 g L^{-1} (0.11-0.57%) (1, 2 and 5 mM)	39.8	42.5	17.7	2.0	0.86	7.4	1 Spiked soil	10 g : 30 mL (33.3%)	48 h	47% (1 mM β-CD) 58% (2 mM β-CD) 70% (5 mM β-CD)	(Hanna et al., 2004b)
PCP	300 mg kg^{-1}	HPCD	5 mM	54.4	23	22.6	6.5	23.5	8.3	1 Spiked soil	- (33.3%)	5 days	Improved by 3.5 fold compared to water washing solution	(Hanna et al., 2005)
TeCP	100 mg kg^{-1}	CMCD	5-50 mM	54.4	23	22.6	6.5	23.5	8.0	1 Spiked soil	10 g : 30 mL (33.3%)	48 h	78% (40 mM CMCD)	(Chatain et al., 2004)
HCB	55 mg kg^{-1}	β-CD	10 g L^{-1} (1%)	35.8	25.4	38.8	~ 0	1.85	4.7	1 Spiked soil	1 g : 20 mL (5%)	72 h	8.5%	(Yuan et al., 2006)
		Tween 80	10 g L^{-1} (1%)										37.7%	
HCB	10.3 mg kg^{-1} 9.4 mg kg^{-1}	MCD	0-100 g L^{-1} (0-10%)		nd nd (kaolin soil)		7.1 0.5	nd nd	5.5 5.8	1 natural contaminated soil, 1 spiked soil	0.5 g : 5 mL (10%)	72 h	Natural soil: 18% (100 g L^{-1} of MCD) Kaolin soil: 2% (100 g L^{-1} of MCD)	(Wan et al., 2009)
		MCD + EtOH	0-100 g L^{-1} + 10%										Natural soil: 20% (100 g L^{-1} of MCD)	
		MCD + EtOH	0-100 g L^{-1} + 30%										Natural soil: 42% (100 g L^{-1} of MCD) Kaolin soil: 70% (100 g L^{-1} of MCD)	
		MCD + EtOH	0-100 g L^{-1} + 50%										Natural soil: 75% (100 g L^{-1} of MCD) Kaolin soil: 100% (100 g L^{-1} of MCD)	

TNT 4-ADNT 2,4-DANT	70 and 340 mg kg^{-1} 20 and 50 mg kg^{-1} 25 and 28 mg kg^{-1} (Topsoil and Illite soil respectively)	HPCD	10 g L^{-1} (1%)	83 0	12 0	4 100	8.4 ~ 0	14.6 9.0	5.6 8.2	Topsoil Illite soil (2 spiked soils)	2 g : 15 mL (Topsoil ; 13.3%), 1 g : 15 mL (Illite soil ; 6.7%)	22 h	Topsoil: 45% of TNT (70 mg kg^{-1}), 48% of 4-ADNT (20 mg kg^{-1}), 4% of 2,4-DANT (25 mg kg^{-1}) Illite soil: 7% of TNT (340 mg kg^{-1}), 40% of 4-ADNT (50 mg kg^{-1}), 43% of 2,4-DANT (28 mg kg^{-1})	(Sheremata and Hawari, 2000)
		DMCD	10 g L^{-1} (1%)										Topsoil: 88% of TNT (70 mg kg^{-1}), 58% of 4-ADNT (20 mg kg^{-1}), 10% of 2,4-DANT (25 mg kg^{-1}) Illite soil: 18% of TNT (340 mg kg^{-1}), 49% of 4-ADNT (50 mg kg^{-1}), 48% of 2,4-DANT (28 mgkg^{-1})	
TNT	200 mg kg^{-1}	MCD	5 mM	54.4	23	22.6	6.5	23.5	8.3	1 Spiked soil (aged of 2 months)	-	5 days	-	(Yardin and Chiron, 2006)
2,4-DNT	480 mg kg^{-1}	HPCD	10-50 g L^{-1} (1, 2 and 5%)	4 20	18 44	78 36	~ 0 2.8	1-1.6 13-18	4.9 8.2	1 kaolin soil 1 glacial till soil (2 spiked soils)	1 g : 5 mL (20%)	24 h	-kaolin soil: 75.0% and 81.2% with 1% and 5% HPCD respectively, -glacial soil: 11.5%, 17.5% and 18.0% with 1, 2 and 5% HPCD respectively	(Khodadoust et al., 2006)
RDX	1 000 mg L^{-1}	HPCD	1%			-				1 Spiked soil	2 g : 10 mL (20%)	4 h	45.4%	(Hawari et al., 1996)
		HPCD	0.1, 1, 2.5, 5, 10%										45.4, 49.4, 82.8, 87.3% (with an increase HPCD concentration)	
		MCD	1%										28.3%	
		SDS	1%										21.7%	
PCB	92.4 mg kg^{-1}	HPCD	100 g L^{-1} (10%)	52	33	16	12.5	9.5	7.5	1 natural contaminated soil	3 g : 20 mL (15%)	10 min of sonication	41% (after 3 successive extracttion with same initial charge) 42% (after 3 successive extraction with fresh reagent)	(Ehsan et al., 2007)

		RAMEB (SD: 12.6)	100 g L^{-1} (0-10%)								76% (after 3 successive extracttion with same initial charge) 78% (after 3 successive extraction with fresh reagent)	
PCDDs PCDFs	-	α-CD	20 g L^{-1} (0-2%)	heavy-metal contaminated site				1 Spiked soil	10 g : 50 mL (20%)	1, 5, 8 and 28 days	45% (in 28 days, total PCDDDs/PCDFs)	(Cathum et al., 2007)
		β-CD	20 g L^{-1} (0-2%)								50% (in 28 days, total PCDDDs/PCDFs)	
		HP-α-CD	20 g L^{-1} (0-2%)								73% (in 28 days, total PCDDDs/PCDFs)	
		HPCD	20 g L^{-1} (0-2%)								96% (in 28 days, total PCDDDs/PCDFs)	
		HP-γ-CD	20 g L^{-1} (0-2%)								80% (in 28 days, total PCDDDs/PCDFs)	
p-cresol	400 mg L^{-1}	HPCD	0.005-20 g L^{-1} (0-2%)	Loamy sand soil	4.9	12.8	7.8	1 Spiked soil	1 g : 1 mL to 1 g : 5 mL (20-100%)	0 to 96 h	42% (in 96 h, at 10 g L^{-1})	(Rosas et al., 2011)
		Tween 80	0.005-20 g L^{-1} (0-2%)								58% (in 96 h, at 10 g L^{-1})	
		Brij 30	0.005-20 g L^{-1} (0-2%)								55% (in 96 h, at 10 g L^{-1})	
		TX-100	0.005-20 g L^{-1} (0-2%)								45% (in 96 h, at 10 g L^{-1})	

APPENDIX 2.3. CDs' sorption onto soil.

Washing agents		Soil's characteristics									Kind of model			
Kind of washing agents	**Conc.(2)**	**Sand (%)**	**Silt (%)**	**Clay (%)**	**OM (%) (1)**	**CEC (meq/100g)**	**pH**	**Kind of soil and type of contamination**	**Solid/liquid ratio (pulp density)**	**Contact time**	**Model**	**Constant**	**Percentages of washing agent adsorption**	**Ref.**
GCD	2, 4, 8 and 10 g L^{-1}		nd		3.14	nd	6.80	1 Spiked soil	0.5 g : 25 mL (2%)	24 h	nd		3.5%, 2.0%, 3.1%, 2.8% (For increasing CD concentration respectively)	(Wang et al., 2010)
β-CD	2, 4, 8 and 10 g L^{-1}												6.9%, 6.3%, 6.6%, 5.9% (For increasing CD concentration respectively)	
HPCD	5 g L^{-1}	39.8 40.9	42.5 42.0	17.7 17.1	2.0 5.0	0.86 1.10	7.4 6.9	Soil s1 Soil s2 (2 spiked soils)	5 g : 15 mL (33.3%)	72 h	linear sorption isotherm	nd	4% and 10.8% (in soils s1 and s2 respectively)	(Badr et al., 2004)
β-CD	5 g L^{-1}											nd	13.6% and 24% (in soils s1 and s2 respectively)	
MCD	13.1-65.5 g L^{-1} (0.01-0.05 M)		nd		2.2	nd	7.6	1 Spiked soil	1 g : 30 mL (3.3%)	24 h	nd		< 2%	(Petitgirard et al., 2009)
β-CD	0.057-0.40 g L^{-1} (5.10^{-5}, 1.10^{-4}, $2.5.10^{-4}$, $3.5.10^{-4}$ M)	16.4 92.8 87.6	61.2 4.4 4.0	22.6 2.5 8.4	1.90 0.51 0.79	17.2 3.5 4.8	7.6 6.5 8.0	Soil 1 Soil 2 Soil 6 (3 spiked soils)	10 g : 20 mL (50%)	24 h	Freundlich isotherm	1.42 (soil 1) 0.19 (soil 2) 0.19 (soil 6) (in terms of K_d values)	-Soil 1: 30.1%, 20.8%, 20.7%, 20.7%, -Soil 2: 100%, 100%, 86.4%, 60.0%, -Soil 6: 100%, 100%, 95.6%, 48.3%, (values with increasing β-CD concentration)	(Villaverde et al., 2006)

β-CD	0.057-0.40 g L^{-1} (5.10^{-5}, 1.10^{-4}, $2.5.10^{-4}$, 5.10^{-4}, $7.5.10^{-4}$, 1.10^{-3} M)	56.7 16.7 49.8	23.8 58.6 34.5	19.5 24.7 15.7	1.38 1.41 1.40	nd nd nd	5.7 6.0 5.5	Soil 1 Soil 2 Soil 3 (3 spiked soils)	5 g : 10 mL (50%)	24 h	nd		-Soil 1: 14.99%, 21.51%, 18.72%, 17.15%, 13.46%, 10.01%, -Soil 2: 53.06%, 36.47%, 27.19%, 19.28%, 16.59%, 14.72%, -Soil 3: 0% for each soil, (values with increasing β-CD concentration)	(Villaverde, 2007)
β-CD	0-5.2 g L^{-1} (0-4.6 mM)	nd nd nd nd	nd nd nd nd	62 30.8 43.6 19.8	1.52 2.16 1.85 2.59	11.60 14.70 17.70 24.55	5.03 7.61 7.82 5.78	Soil A Soil B Soil C Soil D (4 spiked soils)	0.5 g : 20 mL (2.5%)	48 h	linear sorption isotherm	9.92 (A) 9.21 (B) 9.67 (C) 7.53 (D) (in terms of Kd values)	53.3 mmol/kg, 51.1 mmol/kg, 46.6 mmol/kg, 37.7 mmol/kg respectively for Soil A, B, C, D (β-CD 5.2 g L^{-1} (4.6 mM))	(Guo et al., 2010)
Tween 80	0-7 g L^{-1} (0-5.3 mM)										Langmuir isotherm	28.26 (A) 15.12 (B) 15.48 (C) 13.41 (D) in terms of q_{max} (mmol kg^{-1})	23 mmol/kg, 16.5 mmol/kg, 17.5 mmol/kg, 15.5 mmol/kg respectively for Soil A, B, C, D (Tween 80 7.0 g L^{-1} (5.3 mM))	
CMCD	-	54.4	23	22.6	6.5	23.5	8.0	1 Spiked soil	-	-	nd		4%	(Chatain et al., 2004)
HPCD	0.1-5 g L^{-1}	nd			2.47	6.55	4.58	Soil from a vegetable plantation (1 Spiked soil)	-	24 h	Langmuir isotherm	0,021 (qmax in mg g^{-1})	1% (maximum of adsorption: 0.021 mg g^{-1})	(Zeng et al., 2006)
Brij 35	< and > CMC								-		Langmuir isotherm	5.13 (q_{max} in mg g^{-1})	99% (conc<CMC) (maximum of adsorption: 5.1 mg g^{-1})	
Tween 80	< and > CMC								-		Langmuir isotherm	14.2 (q_{max} in mg g^{-1})	99% (conc<CMC) (maximum of adsorption: 14.2 mg g^{-1})	

HPCD	0-10 mM	nd			nd	nd	nd	1 kaolinite spike soil	5 g : 25 mL	48 h	nd	negligible	(Ko et al., 1999)
HPCD	10 g L^{-1} (1% w/w)	83 0	12 0	4 100	8.4 ~ 0	14.6 9.0	5.6 8.2	Topsoil Illite soil (2 spiked soils)	2 g : 15 mL (Topsoil), 1 g : 15 mL (Illite soil)	22 h	nd	Topsoil: negligible Illite soil: negligible	(Sheremata and Hawari, 2000)
DMCD	10 g L^{-1} (1% w/w)											Topsoil: 2.2% Illite soil: 9.9%	

APPENDIX 2.4. SF with CDs.

Contaminant		Kind of flushing agent (conc.)[2]	Soil's characteristics						Kind of soil and type of contamination	Column caracteristics	Mass of soil (g)	PV (nb of PV) (total vol)	Flow rate (kind of flow) (applied time)	Percentages of removal	Ref.
Pollutant	**Conc.**		**Sand (%)**	**Silt (%)**	**Clay (%)**	**OM (%) [1]**	**CEC (meq/100g)**	**pH**							
NAP	-	CMCD (2 and 5 g L^{-1}) (0.2 and 0.5%)	75.2	17.4	7.4	4.9	nd	7.2	1 Spiked soil	2.54 cm i.d., 4 cm length (polycarbonate)	-	8.1 mL (160) (1.6 L)	0.08 mL min^{-1} (-) (14 d)	70% (2 or 5 g L^{-1} CMCD)	(Jiradecha et al., 2006)
NAP	9.3 mg kg^{-1}	HPCD (10%)	fine-to-coarse sand interbedded with gravel and clay stringers						1 natural contaminated soil	-3m x 5m area and between 8 m and 8.5 m of depth -5.1cm i.d. for injection and extraction wells	-	8175 L (8) (65,400 L)	4.54 L (or mM) min^{-1} (horizontal) (10 d)	77%	(McCray and Brusseau, 1998)
PHE	456 mg kg^{-1}	HPCD (0.1-4%)	43	40	17	15.04	6.02	4.78	1 Spiked soil	3.2 cm i.d., 10 cm length	112	-	0.25 mL min^{-1} (up flow) (6 d)	70% (HPCD 1%)	(Gomez et al., 2010)
PHE	1.8 7.1 93.0 (mg kg^{-1})	CMCD (10 g L^{-1}) (1%) CMCD (5 g L^{-1}) (0.5%) + HPCD (5 g L^{-1}) (0.5%)	98.0 88.5 77.7	1.0 4.3 18.1	1.0 10.2 4.2	0.09 0.14 2.42	1.1 6.3 nd	8.3 7.5 7.9	-Borden soil (1) -Hayhook soil (fresh and aged (38 days)) (2) -Surface soil (3) (3 spiked soils)	2.1 cm i.d., 7.0 cm length (precision-bore stainless steel), 2.8 cm i.d., 10 cm length (plexiglass column for soil 3)	-	- (12 (s (1)), 42 (s (2))) - (42 (aged and fresh s(2)), 100 (s (3)))	30 cm h^{-1}	100% (soil (1), 95% (soil (2)) 98% (fresh soil (2)), 96% and 99% (fresh and aged soil (2)), 75% (soil (3))	(Brusseau et al., 1997b)
PHE ANT (total of PAHs)	200 mg kg^{-1}, 71 mg kg^{-1} (655 mg kg^{-1})	HPCD (10-100 g L^{-1}) (1% 10%) MCD (10-100 g L^{-1}) (1-10%)	94.4	3.7	1.9	2.7	nd	8.15	1 natural contaminated soil	2.6 cm i.d., 40 cm length (glass)	50	100 mL (1)	1 mL min^{-1} (up flow)	23% (PHE) 33% (ANT) (100 g L^{-1} of HPCD) 31% (PHE) 43%(ANT) (100 g L^{-1} of MCD)	(Viglianti et al., 2006)

		β-CD (20 to 90 mmol kg^{-1}) HPCD (10 g L^{-1}) (1%)										100 mL (1-5) (100-500 mL)		3% (PHE) 1% (ANT) (90 mmol kg^{-1} of β-CD) - 3.7% of PHE and 10% of ANT (1 PV, 10 g L^{-1} of HPCD) - 11% of PHE and 22.5% of ANT (5 PV, 10 g L^{-1} of HPCD)	
PYR	0.16 mg L^{-1}	HPCD (10 g L^{-1}) (1%)	98	1	1	0,50	nd	nd	1 Spiked soil	2.1 cm i.d., 7.0 cm length (precision-bore stainless steel) and plexiglass column	-	- (1)	1.6 mL min^{-1}	99%	(Brusseau et al., 1994)
PHE	123 mg kg^{-1}	MCD (0.01 to 0.03 M)	Sandy soil			2.2	nd	7.6	1 Spiked soil	2.2 cm i.d., 15 cm length (glass)	20	- - (200 mL in a continous flow)	1 mm min^{-1} (up flow)	75% (2600 min)	(Petitgirard et al., 2009)
PYR	141 mg kg^{-1}													27.5% (2600 min)	
NFL	3.96 kg ai/ha	β-CD (0.01 M) (1.1%)	16.4 92.8 87.6	61.0 4.4 4.0	22.6 2.5 8.4	1.9 0.51 0.8	17.2 3.5 4.8	7.6 6.5 8.0	soil 1 soil 2 soil 6 (3 spiked soils)	3.0 cm i.d., 30 cm length (metacrylate)	197 (s1) 300 (s2) 246 (s6)	-41.0 mL (7 ; 287 mL) (s1) -88.0 mL (20 ; 1760 mL) (s2) -57.45 mL (13 ; 747 mL) (s6)	25 mL/day with water until no detection of NFL in the leachate (down flow)	38.42% (s1) 59.55% (s2) 59.13% (s6)	(Villaverde et al., 2006)

NFL	3.96 kg ai/ha	β-CD (0.01 M) (1.1%)	56.7 16.7 49.8	23.8 58.6 34.5	19.5 24.7 15.7	1.38 1.41 1.40	nd	5.7 6.0 5.5	soil 1 soil 2 soil 3 (3 spiked soils)	3.0 cm i.d., 18 cm length (metacrylate)	125 (s1) 100 (s2) 120 (s3)	32.40 mL (19 ; 616 mL) (s1) 53.33 mL (19 ; 1013 mL) (s2) 32.80 mL (24 ; 787 mL) (s3)	10 mL/day with water and then 1 time 10 mL with β-CD (down flow)	- 40.20%, 18.67%, 43.28% (s1, s2, s3 respectively; with β-CD only) - 80.88%, 18.73%, 88.59% (s1, s2, s3 respectively; with water and then β-CD)	(Villa verde, 2007)
Lindane	70 ppm (real soil) 135 ppm (model soil)	α-CD ($2.4x10^{-1}$ mM) (0.023%) β-CD ($2.4x10^{-1}$ mM) (0.023%) γ-CD ($2.4x10^{-1}$ mM) (0.031%)	97.97 99.5	0.017 0.003	2.01 0.06	1.31 0	1.5 5.5	7.88 11.14	1 real soil 1model soil (2 spiked soils)	-	50	- 1, 5 and 10 (50-500 mL)	-	4% (Real soil) 2.8% (Model soil) (10 PV) 4% (Real soil) 2.7% (Model soil) (10 PV) 4.8% (Real soil) 4.8% (Model soil) (10 PV)	(Barto lo et al., 2008)
m-parathion	200 mg L^{-1}	HPCD (0.1-5 g L^{-1}) (0.01-0.5%)		nd		2.47	6.55	4.58	Soil from a vegetable plantation (1 Spiked soil)	4.0 cm i.d., 15 cm length (glass)	80	- - (300 mL)	1 mL min^{-1}	-	(Zeng et al., 2006)
		Brij 35 (0.1-1 G L^{-1}) (0.01-0.1%)												-	
		Tween 80 (0.1-1 G L^{-1}) (0.01-0.1%)												-	
2,4-D	500 mg L^{-1}	β-CD (0.01 M) (1.1%)	17	58	25	1.41	12.36	6.0	1 Spiked soil	5 cm i.d., 15 cm length (PVC)	150	80 mL (12.5) (1 L)	1 mL min^{-1} (down flow)	100%	(Moril lo et al., 2001)

1,2-DCB	164.0 mg kg^{-1}	HPCD (10%)	fine-to-coarse sand interbedded with gravel and clay stringers						1 natural contaminated soil	-3m x 5m area and between 8 m and 8.5 m of depth -5.1cm i.d. for injection and extraction wells	-	8175 L (8) (65,400 L)	4.54 L min^{-1} (horizontal) (10 d)	78%	(McCray and Brusseau, 1998)
TCE	14 mg kg^{-1}													93%	
TCE	2.65 g	HPCD (5%)	98	1	1	0.50	nd	nd	1 Spiked soil	2.5 cm i.d., 5.0 cm length (borosilicate glass)	-	10 mL (144)	0.48 mL min^{-1} (horizontal)	91.9%	(Boving and Brusseau, 2000)
	2.44 g	MCD (5%)										10 mL (77)		93.2%	
	2.83 g	SDS (5%)										10 mL (60)		94.1%	
	2.62 g	DOWFAX 8390 (5%)										10 mL (83)		92.7%	
	2.56 g	DOM (5%)										10 mL (85)		93.8%	
	2.39 g	EtOH (50%)										10 mL (40)		95.0%	
TCE	0.197 to 4.31 mg kg^{-1}	HPCD (20%)	Fine-grained silts and clays						1 natural contaminated soi	Well with a depth of 55.15 m (stainless steel)	-	- - (3977 L)	7.6 L min^{-1} (vertical)	Enhancement factor of 3 compared to water flush	(Blanford et al., 2001)
TeCE	68.6 L	HPCD (15%)	medium to fine sands with interbedded gravels, silts, and clay lenses						1 Spiked soil	-3 m i.d., 4.6 m length (steel) -5.1 cm i.d. for injection and extraction wells (PVC)	-	- - (12,000 L)	1-2 L min^{-1} (up flow) (54 d)	48%	(Tick et al., 2003)
TCE TeCE	1.63 g 2.56 g	HPCD (5%)	98	1	1	0.50	nd	nd	1 Spiked soil	2.5 cm i.d., 5.0 cm length (borosilicate glass)	-	10 mL (83 (TCE) and 241 (TeCE))	0.69 mL min^{-1} (horizontal)	94.4% (TCE) 92.8% (TeCE)	(Boving et al., 1999)

TeCE	1.78 g	HPCD (5%)										10 mL (181 (TeCE))	0.69 mL min^{-1} (vertical)	90.4% TeCE)	
TCE TeCE	1.8 g 2.18 g	HPCD (10%)										10 mL (64 (TCE) and 130 (TeCE))	0.69 mL min^{-1} (horizontal)	91.1% (TCE) 93.2% (TeCE)	
TCE TeCE	2.44 2.36	MCD (5%)										10 mL (85 (TCE) and 95 (TeCE))	0.69 mL min^{-1} (horizontal)	93.0% (TCE) 92.0% (TeCE)	
TCE TeCE	2.70 1.96	MCD (10%)										10 mL (71 (TCE) and 53 (TeCE))	0.69 mL min^{-1} (horizontal)	89.8% (TCE) 90.5% (TeCE)	
2,4-DNT		CMCD (1 and 5 g L^{-1}) (0.1-0.5%)	75.2	17.4	7.4	4.9	nd	7.2	1 Spiked soil	2.54 cm i.d., 4 cm length (polycarbonate)	-	8.1 mL (150) (1.6 L)	0.08 mL min^{-1} (14 d)	72% (2 or 5 g L^{-1} CMCD)	(Jiradecha et al., 2006)
CV	0.6 mg	HPCD (SD=0.8) (4 mM)		Sand		nd	nd	5.5	1 Spiked soil	1.2 cm i.d., 6.0 cm length (polyethylene)	9	3 mL (15) (45 mL)	0.12, 0.29, 0.47 and 1.5 mL min^{-1} (down flow)	88% with 0.12, 0.29 and 0.47 mL min^{-1} and 75% with 1.5 mL min^{-1}	(De Lisi et al., 2007)
		HPCD (SD=0.43) (4 mM)											1.5 mL min^{-1} (down flow)	65%	
		β-CD (4 mM)												30%	
		HP-α-CD (SD=0.6) (4 mM)												2%	
		HP-γ-CD (SD=0.6) (4 mM)												7%	
		MCD (SD=1.8) (4 mM)												80%	
TOL	33.3 mg kg^{-1}	HPCD (10%)	fine-to-coarse sand interbedded with gravel and clay stringers						1 natural contaminated soil	-3m x 5m area and between 8 m and 8.5	-	8175 L (8)	4.54 L min^{-1} (horizontal)	80%	(McCray and

EB	4.0 mg kg^{-1}	m of depth -5.1cm i.d. for injection and extraction wells	(65,400 L)	(10 d)	77%	Brussseau, 1998)
o-XYL	20.3 mg kg^{-1}				70%	
m,p-XYL	6.6 mg kg^{-1}				70%	
1,2,4-TMB	8.9 mg kg^{-1}				39%	
DEC	73.1 mg kg^{-1}				3%	
UNDEC	300 mg kg^{-1}				18%	