

Bi-functionalized mesoporous organic-inorganic hybrid materials : synthesis, physico-chemical characterization and application for chromium removal

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Thèse

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Docteur de l'Université de Lorraine

Spécialité : Chimie et Electrochimie Analytiques

Par **Nataliya SHEVCHENKO ZAITSEVA**

Matériaux mésoporeux hybrides organo-minéraux bi-fonctionnalisés: synthèse, caractérisation physico-chimique et application à l'élimination du chrome

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ABBREVIATIONS

DPC– diphenylcarbazide;

-ED3A – ethylendiaminetriacetic acid groups immobilized at the surface of silica besed material;

FTIR – Fourier transform infrared spectroscopy;

ICP-AES –inductively-coupled plasma with detection by atomic emission spectroscopy;

TPD-MS – thermo-programmed desorption with mass spectroscopy detector;

XPS – X-ray photoelectron spectroscopy;

XFS – X-ray fluorescence spectroscopy;.

MCM-41 – silica based mesoporouse material with structuraly ordered hexogonal pores distributed pores ($d_{\oslash}$ =1.5-10 nm);

MCM-41-SH – thiol-functionalized mesoporous silica of MCM-41 type;

MCM-41-SH/SO_3H-X – a series of partually oxidized (by H_2O_2) thiol-functionalized mesoporous silica, where X=1-6 (6 corresponds to the sample most fully oxidized and 1 – to the sample which was not oxidized by H_2O_2);

MCM-41-SH/SO_3-2.X – a series of partually oxidized (by air oxygen) thiol-functionalized mesoporous silica, which were disposed on air during different peroid of time (from 1 day (X=1) to 2 months (X=3));

SBA-15 – structured mesoporous silica-based material with two-dimensional hexagonal pores ($d_{\oslash}$ = 5-9 nm);

–SH – mercaptopropyl groups immobilized at the surface of silica besed material;

SiO_2-ED3A – silica gel grafted with ethylendiaminetriacetic acid groups;

SiO_2-SH – silica gel grafted with mercaptopropyl groups;

SiO_2-SH/ED3A – silica gel simultaneously grafted with mercaptopropyl and ethylendiaminetriacetic acid groups;

–SO_3H – propylsulpfonic acid groups immobilized at the surface of silica based material;

– S-S – dipropyldisulfide groups immobilized at the surface of silica besed material.

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Introduction

Principalement utilisés dans l'industrie à des fins diverses, les composés du chrome sot classés comme des polluants environnementaux persistants. Le chrome entre dans la fabrication des alliages et de l'acier (jusqu'à 136 mille tonnes par an), des pigments et peintures, dans le tannage du cuir et les procédés d'électro-dépôt (jusqu'à 90 mille tonnes par an). L'apparition du chrome dans l'environnement est surtout imputable aux activités anthropiques. A titre d'exemple, la concentration de chrome relevés en Inde dans les effluents industriels est de 2-5 g L^{-1}, le déversement total de chrome atteignant donc jusqu'à une tonne par un.

Contrairement à la plupart des autres métaux, la toxicité du chrome dépend de son degré d'oxidation. Les composés du chrome(III), qui existent principalement sous la forme de particules chargées positivement en solution aqueuse, sont caractérisés par une labilité cinétique faible et sont ainsi moins enclin à l'adsorption biologique. En revanche, le chrome(VI), qui a un fort pouvoir oxydant, existe en solution sous forme d'anion. Etant isomorphe de sels minéraux importants, le chrome(VI) est cent fois plus toxique que le chrome(III), qui se traduit par une forte activité cancérogène. Les méthodes modernes de traitement des effluents contenant du chrome(VI) toxique sont principalement basées sur l'immobilisation des composés du chrome sous forme solide. Il s'agit notamment : 1) de l'électrodialyse ou electrocoagulation, et 2) de l'adsorption sélective sur du charbon actif, des résines fonctionnalisées ou des oxydes de minéraux, ou encore sur des biopolymères naturels. Ces méthodes sont souvent appliquées à l'élimination du chrome à partir de solutions concentrées (100 mg L^{-1}). Une percée significative dans le domaine des méthodes d'adsorption sélective de Cr(VI) concerne le recours à de matériaux polyfonctionnels présentant à la fois des propriétés de réduction et de fixation. A titre d'exemple, de tels matériaux sont des adsorbants composés de sulfures issus de la biomasse, des hydroxydes de fer et des sulfures métalliques, ou des adsorbants hybrides organo-minéraux.

A la surface de tels matériaux, Cr(VI) peut être réduit en Cr(III) qui peut être à

son tour spécifiquement fixé par un groupe fonctionnel ou co-précipicité sous forme d'oxyde. L'efficacité de tels matériaux polyfonctionnels dépend d'un ensemble de facteurs, tels que la faculté de réduction, l'affinité des groupements fonctionnels vis-à-vis des espèces Cr(III) et Cr(VI), ainsi que l'ingénierie de surface des matériaux. Ceci étant, les adsorbants de ce type peuvent présenter des inconvénients, dont les principaux sont des propriétés d'adsorption non reproductibles et caractérisés par de faibles cinétiques (particulièrement vrai pour la biomasse), des gammes de pH opérationnelles assez élevées (pH > 5, alors que la plupart des effluents contenant du chrome soient acides), de faibles quantitativités d'adsorption (< 80 %) et la formation d'énormes quantités de boues. La conception intelligente de matériaux polyfonctionnels pourrait permettre de contourner les principaux problèmes évoqués ci-dessus.

Dans le cadre de cette thèse, nous nous proposons d'examiner le comportement de deux silices bi-fonctionnalisées présentant une mésostructure (i.e., MCM-41) ou non (i.e., gel de silice, dénommé ici SiO_2), ainsi que leur réactivité vis-à-vis des espèces de chrome. Les groupements fonctionnels sélectionnés pour modifier les échantillons de silice afin d'atteindre ce but sont d'une part, le mercaptopropyle et l'acide propylsulfonique (MCM-SH,SO_3H), et d'autre part le mercaptopropyle et l'éthylènediaminetriacetate (SiO_2-SH/ED3A). La recherche a débuté avec des matériaux structurellement ordonnés, de type MCM-41, offrant une très grande aire spécifique tout en assurant un accès rapide et aisé vers les groupements fonctionnels. Sur la base d'une MCM-41 modifiée par des fonctions thiol oxydées à divers degrés, un ensemble d'échantillons d'adsorbants caractérisés par différents rapport de grupements greffés thiol/acide sulfonique (teneur constante en soufre = 1 mmol g^{-1}) ont été synthétisés. Une attention particulière a été portée à la caractérisation de la composition chimique de surface, pour laquelle on s'attend à une forte influence sur les propriétés de sorption. Une méthode simple, basée sur une seule technique instrumentale (titrage conductimétrique), a été appliquée pour la détermination simultanée des groupements thiol et sulfonique sur MCM-SH,SO_3H. Dans un second temps, les conditions expérimentales susceptibles de permettre un piégeage effectif de Cr(VI) sur MCM-

SH,SO_3H ont été définies, en étudiant notamment l'effet du pH, du rapport solide/solution, ou encore de la composition de l'adsorbant (i.e., rapport SH/SO_3H). Sur la base des données collectées, un mécanisme de réduction-sorption expliquant le processus d'immobilisation a été proposé. Dans une seconde approche, un autre type de silice bi-fonctionnelle (SiO_2-SH,ED3A) a été suggéré afin d'améliorer l'affinité (propriétés de sorption) du matériau vis-à-vis des espèces Cr(III) générées lors de la réduction de Cr(VI). Le gel de silice a été choisi comme matrice pour greffer des quantités contrôlées de groupements mercaptopropyls et éthylènediaminetriacetate à sa surface. La performance de tel adsorbants bi-fonctionnels a été évaluée au regard de paramètres expérimentaux variés susceptibles d'influencer le processus de sorption-réduction (pH, rappot solide/solution, concentration) afin de déterminer le mécanisme de séquestration et de le comparer avec les adsorbants précédents. Finalement, on montrera comment le second adsorbant présente également l'avantage de pouvoir être utilisé dans des conditions dynamiques (expériences en colonne).

Cette thèse a été structurée comme suit :

Le chapitre I traite des analyses bibliographiques ;

Le chapitre II liste les matériaux et réactifs utilisés pour la synthèse des silices bi-fonctionnalisée, ainsi que les méthodes mises en œuvre afin d'examiner leur propriétés physico-chimiques et les procédures appliquée pour l'étude des processus de sorption ;

Le chapitre III présente une méthode conductimétrique de détermination simultanée des groupements thiol et acide sulfonique sur MCM-SH,SO_3H, en discutant en parallèle les effets du rapport SH/SO_3H (fixé par oxidation partielle et contrôlée de silices thiolées avec des quantités variables de H_2O_2);

Le chapitre IV est dédié à l'étude de l'adsorption de Cr(III) sur silices thiolées (MCM-SH) et sulfonatées (MCM-SO_3H), ainsi que les processus de réduction-sorption de Cr(VI) sur MCM-SH et la discussion des mécanismes de fixation du chrome à la surface de MCM-SH,SO_3H bi-fonctionnel;

Le chapitre V est dévolu à l'évaluation des conditions optimales pour l'élimination

de Cr(VI) dans les eaux usées à l'aide d'adsorbants bi-fonctionnalisés SiO_2-SH/ED3A, et discute le mécanisme de fixation du chrome sur cet adsorbant via deux types d'interactions (électrostatiques avec -SO_3H, ou par formation de complexes avec – ED3A); La possibilité d'utiliser SiO_2-SH/ED3A pour l'analyse de Cr(VI) en phase solide par spectrométrie de fluorescence X est également démontrée.

Chapter I

1 Literature review

1.1 Aqueous chemistry of chromium

Chromium oxidation states are ranging from 0 to +VI. However in the environment it mainly occurs only in two oxidation states, Cr(III) and Cr(VI). Cr(IV) and Cr (V) are formed as intermediates during oxidation or reduction of Cr(III) and Cr(VI) respectively. The most stable oxidation state is Cr(III) and a considerable energy should be required to convert it into other state (see Fig.1.1). The negative standard potential (E_0) of Cr(III)/Cr(II) ion couple indicates that Cr(II) is readily oxidized to Cr(III), and Cr(II) is stable only in the absence of oxidants (anaerobic conditions). Cr(VI) in acidic medium shows a very high positive redox potential [1], which means that it is strongly oxidizing and unstable in the presence of electron donors.

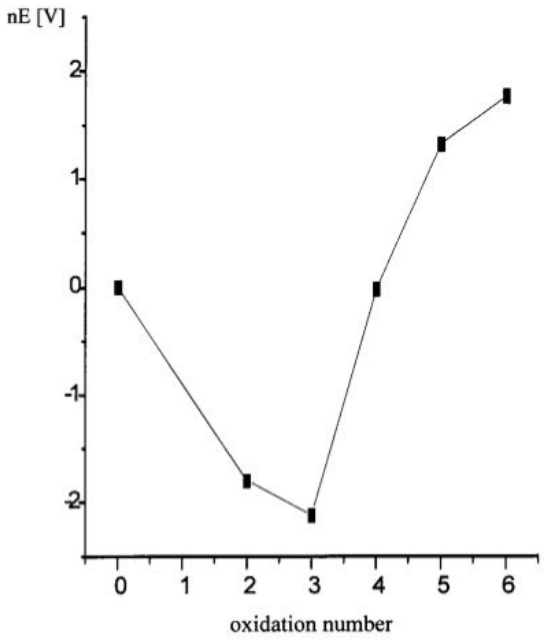


Fig. 1.1. The Frost diagram for chromium (Cr) species in acidic solution [2].

Considering the equilibria between Cr(III) and Cr(VI), the decisive role played by pH and redox potential must be emphasized. Formation of hydroxo complexes by Cr(III) and polynuclear species by both Cr(III) and Cr(VI), should also be taken into

account. To show the conditions of pH and potential under which each species is thermodynamically stable, a Pourbaix diagram is useful (see Fig. 1.2.). The approach, however, does not take into account kinetic constraints, and when Cr is introduced into, or exists in, the natural environment, its actual form may differ from that predicted by the diagram.

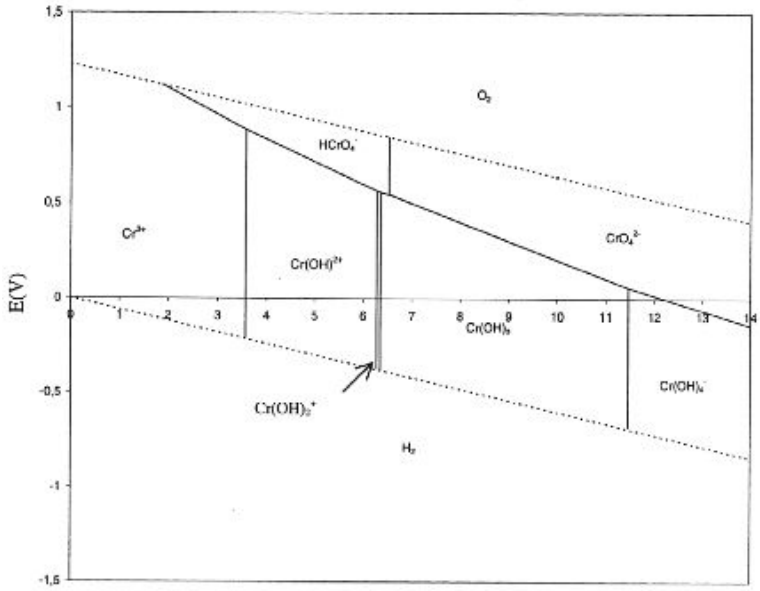


Fig. 1.2. A Pourbaix diagram for Cr species dominating in aireted aqueous solutions in the absence of any other complexing agents rather than OH^- and H_2O. Concentration of total chromium in solution is 10^{-4} M. [3]

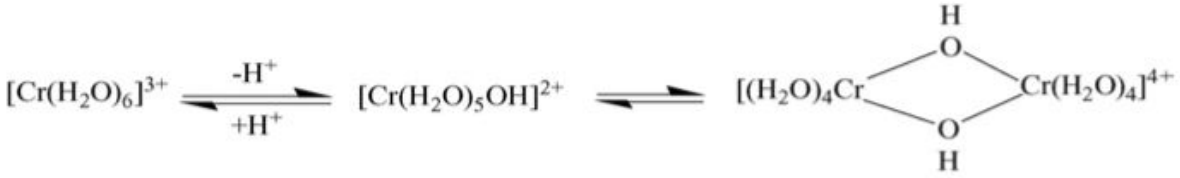
The content of aerated waters containing trivalent chromium changes in time as far as such solutions can be affected by hydrolysis, complexation, redox reactions and sorption. In the absence of complexing agents (except H_2O and OH^-), Cr(III) exists as a complex of hexaaquachromium(III) (relatively strong acid with pK ~ 4) and its hydrolysis products [4]:

$$Cr(H_2O)_6^{3+} + H_2O = Cr(OH)(H_2O)_5^{2+} + H_3O^+ \quad (1.1)$$

$$Cr(OH)(H_2O)_5^{2+} + H_2O = Cr(OH)_2(H_2O)^+ + H_3O^+ \quad (1.2)$$

$$Cr(OH)_2(H_2O)^{4+} + H_2O = Cr(OH)_3 + H_3O^+ \quad (1.3)$$

abbreviated as $Cr(OH)^{2+}$, $Cr(OH)_2^+$, $Cr(OH)_3$. They dominate consistently within pH 4-10. This range contains pH values that are characteristic for natural waters, and so the cited hydroxo complexes are the main forms of Cr(III) existence in the environment. Increasing of Cr(III) concentration (> 10^{-4} M) leads to formation of polynuclear hydroxo complexes ($Cr_2(OH)_2^{4+}$, $Cr_3(OH)_4^{5+}$, $Cr_4(OH)_6^{6+}$) [5]. The process of condensation through the formation of hydroxo-bridges is known as “olation” (eq. 1.4)



(1.4)

$Cr(OH)_3$ exhibits amphoteric properties, and so pH increasing leads to formation of soluble tetra-hydroxo complex $Cr(OH)_4^-$ (pK=15,4):

$$Cr(OH)_3 + H_2O = Cr(OH)_4^- + H_3O^+ \quad (1.5)$$

Distribution of Cr(III) ions in aqueous solution calculated for $5 \cdot 10^{-4}$ M solution for pH range from 2 to 12 is shown in Fig. 1.3.

Cr(III) aqua-complexes are highly inert which means low rate of exchange of water molecules to other ligands. Half-time of such exchange can reach several days [6]. Except complexation with water molecules and hydronium ions, trivalent chromium mobility may also decrease due to binding with such macromolecular systems as humic acids [7].

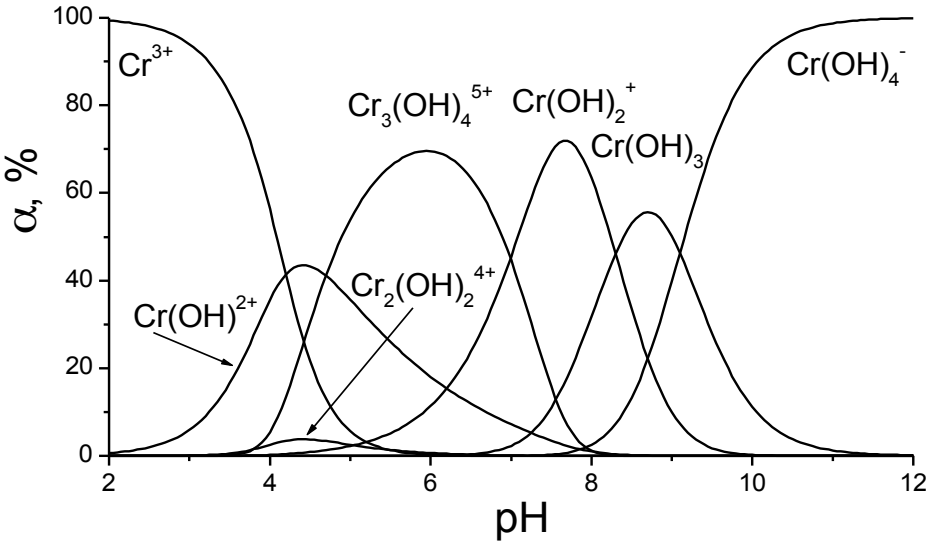


Fig. 1.3. Mole ratio of Cr(III) particles in aqueous solution with a total concentration of Cr(III) $5 \cdot 10^{-4}$ M (calculated with the help of ScQuery Vn. 5.34)

The main forms of Cr(VI) found in natural waters are $HCrO_4^-$ and CrO_4^{2-}. Under pH<1, strong acid H_2CrO_4 is formed [8, 9]. Distribution of these species according to pH is described by the following equations and constants [10] and is illustrated by Fig. 1.4. :

$$H_2CrO_4 = HCrO_4^- + H^+ \quad pK_{a,1} = 0.86 \tag{1.6}$$

$$HCrO_4^- = CrO_4^{2-} + H^+ \quad pK_{a,2} = 6.51 \tag{1.7}$$

Thus, tetrahedral yellow chromate ion CrO_4^{2-} is predominant above pH 6.5, H_2CrO_4 predominates only if the pH is below 0.9, while in the intermediate range, (1 < pH < 6) the dominant type is $HCrO_4^-$.

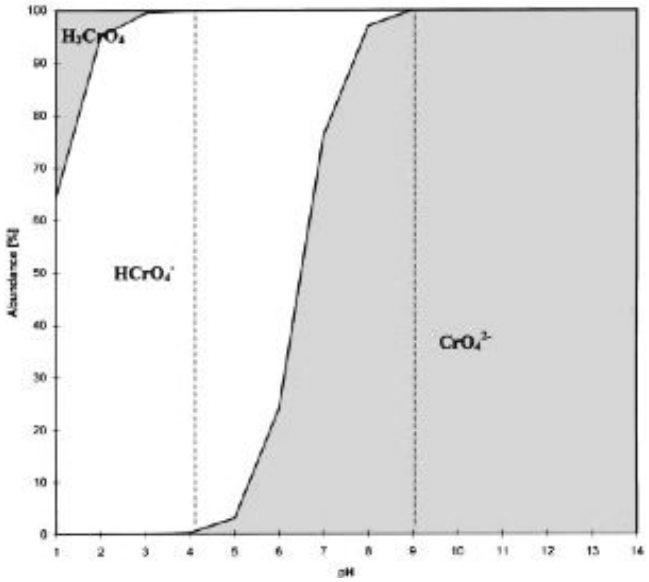


Fig. 1.4. Distribution of Cr(VI) species in water solutions versus pH ($C_{Cr(VI)} = 10^{-6}$ M)

In acidic media, in case when concentration of Cr(VI) is higher than 10 mM, chromate species dimerize to form orange red dichromate ion [10]:

$$2\ HCrO_4^- = Cr_2O_7^{2-} + H_2O \qquad pK = -1.54 \qquad (1.8)$$

Cr(VI) does not give rise to an extensive complex series of poly-acids and polyanions [11, 12] characteristics of somewhat less acidic oxides, such as those of V(V), Mo(VI) or W(VI). The reason for this is perhaps the greater extent of multiple bonding (Cr=O) for the smaller chromium. Polymerization beyond dichromate is apparently limited to formation of tri ($Cr_3O_{10}^{2-}$) and tetra ($Cr_4O_{13}^{2-}$) chromate [11].

Cr(VI) compounds are well soluble in water and therefore are highly mobile in the environment. They can be reduced to Cr(III) by electron donors present in water in the form of organic matter and/or reduced by inorganic particles.

As far as $HCrO_4^-$ reduction is accompanied by H^+ consumption (eq. 1.9), decrease in acidity decreases the formal potential (see, Fig.1.2). Basic solutions of chromates are less oxidizing; reduction of CrO_4^{2-} generates OH^- (eq. 1.10).

$$HCrO_4^- + 7H^+ + 3e^- = Cr^{3+} + 4H_2O \qquad E_0 = 1.47\ V \qquad (1.9)$$

$$CrO_4^{2-} + 4H_2O + 3e^- = Cr(OH)_3 + OH^- \qquad E_0 = -0.13\ V \qquad (1.10)$$

In natural waters the presence of Cr(III) and Cr(VI) and the ratio between these two forms depend on various processes, which include chemical and photochemical redox transformation, precipitation/dissolution and adsorption/ desorption reactions.

Under anoxic conditions, trivalent Cr should be the only form. In oxygenated aqueous solutions, Cr(III) is predicted by thermodynamic calculations as the stable species at pH≤6, whereas at pH≥7 the CrO_4^{2-} ions should predominate [13]. At intermediate pH values, the Cr(III)/Cr(VI) ratio is dependent on O_2 concentration. In oxygenated surface waters, not only pH and O_2 concentration but also the nature and concentration of reducers, oxidation mediators and complexing agents play an important role.

A high redox potential of Cr(VI)/Cr(III) metal-ion couple makes insignificant the chance of Cr(III) be oxidised by dissolved oxygen, and only the presence of manganese oxides (γ-MnO_2, β-MnO_2, α-MnO_2, δ-MnO_2) or H_2O_2 leads to its effective oxidation in ecological systems. [14]. Probability of transforming Cr(III) in Cr(VI) increases with pH increasing [15]. It becomes less effective for "aged" solution of Cr(III), where not labile precipitates of chromium hydroxides are formed [16]. Yet, if precipitetes had not been formed, manganese oxide can effectively oxidize Cr(III) (10^{-5} M) during 90 days ($3 < pH < 10$) [14]. Cr(III) complexes with organic ligands are also not so easily oxidized as their aqua/hydroxo analogues, which means that the trivalent state is better stabilized by ligands other than H_2O and/or OH^-.

Opposite to Cr(III) complexes, Cr(VI) species are only weakly sorbed to inorganic surfaces, being the most mobile form of Cr in the environment. Hydrogen peroxide, which reduces Cr(VI) to Cr(III) under acid conditions [17, 18], is one of the possible reductants in aqueous solutions. These also include Fe(II), sulfide, sulfite and a number of organic compounds [14].

The nature and behaviour of various Cr forms found in wastewater can be quite different from those present in natural waters because of altered physicochemical conditions of the effluents originating from various industrial sources. The presence and

concentration of Cr forms in discharged effluents depend mainly on the Cr compounds applied in the technological process, on pH and on organic and/or inorganic wastes coming from the material processing. Thus, hexavalent Cr will dominate in wastewater from the metallurgical industry, metal finishing industry (Cr hard plating), refractory industry and production or application of pigments (chromate colour pigments and corrosion inhibition pigments). Cr(III) will be found mainly in tannery, textile (printing, dying) and decorative plating industry wastewater. The presence of various inorganic and organic ligands, as well as the pH value in effluents, determines Cr forms by influencing their solubility, sorption and redox reactions. For example, although in tannery wastewater Cr(III) is the most expected Cr form, the redox reactions occurring in sludge can increase the concentration of the hexavalent form. Under slightly acidic or neutral pH conditions in this type of wastewater the poorly soluble $Cr(OH)_3$.aq should be the preferred form, but a high content of organic matter originated from hide material processing is effective in forming soluble organic Cr(III) complexes [19, 20].

1.2 Occurrence and biological effects of chromium

In Nature, chromium occurs quite extensively, mostly in its trivalent state in the form of minerals, mainly as chromite. Cr(III) can also be found in fruits, vegetables and meat. It is recognised as an essential trace element in human and animal diets and important in glucose metabolism. Most diets are considered to be deficient in chromium for which the recommended daily intake is 200 μg for adults [21].

Chromium can also occur as hexavalent chromium and persist in polyatomic anionic form as CrO_4^{2-} under strong oxidizing conditions. Natural chromates are rare. Cr(VI) and Cr(0) are mainly formed as a result of manufacturing processes.

Chromium at zero valency exists as metallic chromium and in many chromium-containing alloys, including stainless steels. In these cases, chromium on the surface is oxidized spontaneously to Cr(III) creating a passive film which prevents further oxidation and which is responsible for corrosion resistance.

Hexavalent chromium occurs predominantly in chemical manufacturing processes and to a much lesser extent in metallurgical processes such as ferrochromium and stainless steel production, stainless steel welding and in some high temperature furnace operations that use chromium-containing refractories.

Chemical manufacturing processes which cause formation of Cr(VI), namely are:

- The manufacture of chromate and dichromates through the roasting of chromite ore All other industrial chromium chemicals are in turn made from sodium dichromate or, to a much lesser extent, from sodium chromate.
- Chromium plating and surface treatment of metals. Conventional electrolytic processes for chromium plating use chromic acid to deposit chromium metal on surfaces of other metals.
- Leather tanning. Basic chromium sulphate, in which chromium is present in the trivalent state, has been used in leather tanning for nearly 150 years. Although historically hexavalent chromium salts were converted to chromium sulphate by tanners, this practice is now rare in most countries, where tanneries are supplied with chromium tanning agents which contain no detectable levels of hexavalent chromium.
- Spray painting. There is evidence of increased risk of lung cancer in workers engaged in the manufacture of zinc chromate and sparingly soluble chromate compounds which are classified as carcinogenic. These materials are used in anticorrosion primer paints applied to metal surfaces. Therefore, it is essential to minimise exposure by using local exhaust ventilation and personal protection equipment.
- Refractory industries. Although chromium-based refractories are generally considered to be inert, some hexavalent chromium compounds may be present during the manufacturing stages. Many chromium-containing refractories are used in processes where the conditions may lead to the formation of hexavalent chromium, particularly high temperature operations in atmospheres containing oxygen.
- Wood preservation industry. Chromium based wood preservatives are commonly used in the treatment of timber to extend its useful life. The chromium acts to fix the

other ingredients into the timber. It is anticipated that chromium-based ($Na_2Cr_2O_7$), arsenic-free preservatives continue to be used in the EU beyond this date.

- Manufacture of pigments and dyes. Sodium dichromate is used for pigments based on the chromate ion and on chromium (III) oxide. Lead, strontium, barium and zinc chromates are mainly used as colorants or anticorrosives in paints, plastics and fireworks. Chromium (III) oxide is synthesized by chemical reduction of sodium chromate or dichromate or thermal decomposition of chromic acid and is used as a green colorant in different applications. Wastewater may contain hexavalent chromium and must be treated prior to disposal.

The toxicity of trivalent and metallic forms of chromium by conventional exposure routes is low. Trivalent chromium is poorly absorbed by the body and does not easily cross cell membranes. Metallic and alloyed forms need to be ionized in order to cross any cell membrane.

The most significant occupational health effects are related to hexavalent chromium compounds. In aqueous solutions Cr(VI) exists as oxo-anions which are isomorphic to vitally important sulfates and phosphates [22]. The carcinogenic effect of hexavalent chromium is thought to relate to the ability of chromate ions to cross cell membranes, where subsequent chemical valence reduction is accompanied by genetic damage (see Fig.1.5.) The relationship between exposure and effect is complicated by the fact that extra-cellular body fluids can detoxify hexavalent chromium by reducing it to the trivalent state [23].

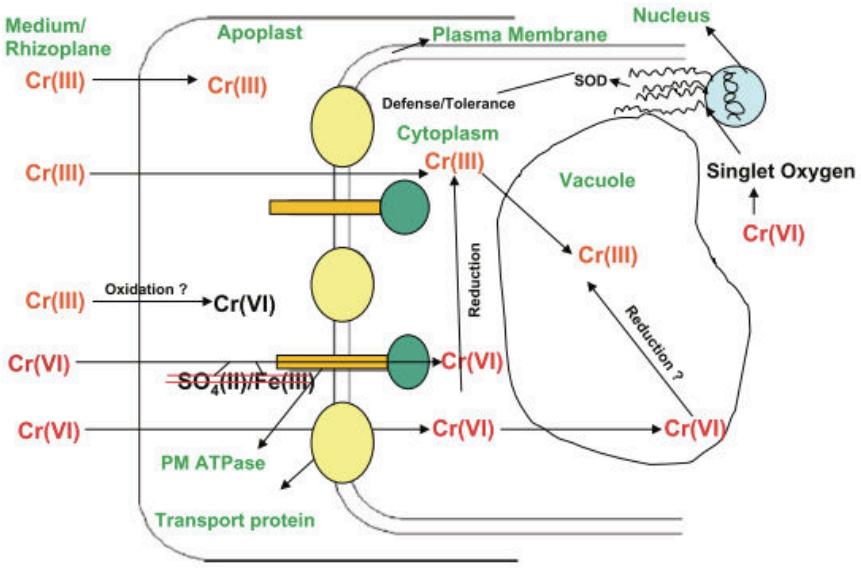


Fig. 1.5. Hypothetical model of chromium transport and toxicity in plant roots [24]

Exposure to such compounds may result in acute effects such as skin and nasal irritation, ulceration and nasal septum perforation and respiratory sensitisation. The most serious health effect is respiratory cancer. Epidemiological studies have confirmed that long-term exposure to high levels of hexavalent chromium as encountered historically in chromate chemicals and chromate pigments manufacture and electrolytic plating processes using chromic acid has led to a measurable excess incidence of respiratory cancer with a latency period in excess of 15 years [25, 26, 27, 28, 29]. Because of these health effects, all commercially available hexavalent chromium compounds are heavily regulated and in many areas are classified as occupational carcinogens. Table 1.1 shows the classification of carcinogenicity of chromium compounds established by international organization IARC [28].

Taking in account drastically different biochemical reactivity of Cr(III) and Cr(VI), the present-day regulations and quality guidelines call for accurate distinction between Cr(VI) and Cr(III) species. As shown at Table 1.2., maximum allowable concentrations (MAC) of hexavalent chromium in some countries can be 1000-times lower than concentration of total chromium.

Table 1.1

Evaluation of carcinogenicity of chromium compounds [30]

Chromium/Chromium Compounds	Degree of evidence for carcinogenicity	Overall evaluation*
Chromium (VI) compounds as encountered in the chromate, chromate pigment production and chromate plating industries: ($BaCrO_4$, $CaCrO_4$, $PbCrO_4$, $ZnCrO_4$, $SrCrO_4$, CrO_3, $Na_2Cr_2O_7$)	Sufficient	1
Chromium (III) compounds	Inadequate	3
Metallic chromium	Inadequate	3
Welding Fumes and gases	Limited	2

*Group 1: Carcinogenic to humans
Group 2: Probably carcinogenic to humans
Group 3: Not classifiable as to its carcinogenicity to humans

Table 1.2

Maximum allowable concentrations for waste waters, mg L^{-1} [30]

Total Cr	0,5	France, Ukraine, Germany (metallurgy, chemical industry), South Africa (waste waters)
	1	Germany (tanning)
	2	Japan (public water systems)
Cr(VI)	0,005	South Africa (ecosystems)
	0,05-0,1	France, Ukraine, Germany (metallurgy, chemical industry), South Africa (agricultural use)
	0,5	Germany (tanning), Japan (public water systems), USA

At the same time, concentrations of hexavalent chromium at the output of the regular galvanizing plant (see, Table 1.3) reach values thousand times higher than MAC.

Table 1.3

Concentration of the magor components in the effluent from galvanic plant [31]

Ingridient	Concentration, mg L^{-1}	Ingridinent	Concentration, mg L^{-1}
Cr(VI)	1000	Sn	10
Cu	30	Cl^-	500
Ni	50	SO_4^{2-}	1000
Zn	50	CN^-	30
Cd	15	NO_3^-	60
Pb	10	-	-

Considering afore cited toxicity of Cr(VI), technology used for purification of wastewaters ought to be that much effective to certify reduction of Cr(VI) concentrations from mg L^{-1} to μg L^{-1} levels.

1.3 Chromium removal techniques

Several well-documented reviews or monographs are available dealing with chromium removal from wastewaters [32, 33, 34, 35, 36, 37, 38, 39]. It came out that firstly proposed remediation schemes were directed to reduce the carcinogenic, soluble, and mobile Cr(VI) (i.e., in acidic medium, pH ~2) to the less toxic and less mobile Cr(III), which forms insoluble or sparingly soluble precipitates (i.e., in alkaline medium, above pH ~9-10). Such methods, however, are applicable only for concentrated industrial wastewater and have been considered as undesirable due to the use of expensive chemicals, poor removal efficiency for meeting regulatory standards, and the production of large amounts of chemical sludge [40]. This has thus generated a huge amount of works directed to investigate other approaches for chromium remediation. Nowadays existing technologies are mainly based on immobilization on solid supports, or separation and filtration processes, associated or not to reduction/precipitation. They include:

- membrane filtration (membrane separation [41], ultrafiltration [42, 43], reverse osmosis [44], dialysis/electrodialysis [45, 46] or electro-deionization [47, 48]) and other separation techniques (coagulation/electrocoagulation [49,50], reduction/ coagulation/ filtration [51], flotation [52]) or extraction processes (solvent extraction [53], chemical or electrochemical precipitation [54], electrokinetic extraction [54], sedimentation [55], coagulation-flocculation-sedimentation [56]);
- ion exchange (resins, mainly anion exchangers for Cr(VI) [57, 58, 59] but also cation exchangers for Cr(III) [60, 61], and ion exchange columns [62, 63, 64]);
- selective adsorption (on various, often low cost, adsorbents [34, 65, 66] such as activated carbon [34, 67], mineral oxides [68], functionalized resins [69, 70], sol-gel-derived functional materials [71, 72, 73] or natual (bio)polymers [38, 74]) and bio-adsorption (on various biological materials [75, 76, 77, 78]);
- and some other processes (photocatalytic reduction [79], phytoremediation, … [80]).

All these methods exhibit advantages and disadvantages and are most often applied to the removal of chromium from solutions containing relatively high initial chromium concentrations (i.e., > 100 mg L^{-1}). Adsorptive filtration and ion exchange are suitable for small-scale applications. Membrane technology is effective in removing both hexavalent and trivalent species of chromium, but can suffer from membrane fouling and high costs [39]. Adsorption, though likely to generate non-negligible amounts of sludge with associated disposal problems, merged recently among the most promising approaches for simple, efficient, and selective chromium removal [34, 35].

An interesting breakthrough in the field is the possibility to use adsorbents with both reductive and sorption properties in a single solid, giving rise to chromium immobilization according to a reduction-sorption process. In doing so, one part of the adsorbent has the propensity to reduce the most toxic Cr(VI) species while another part is likely to immobilize the so-generated Cr(III) moieties. Examples of materials reported to exhibit such reduction-sorption capabilities include mainly sludge and/or sulfur-containing biomass and other biosorbents [81, 82, 83, 84, 85, 86, 87], but also organic-inorganic hybrids [71] or inorganic iron metal or sulfides [88, 89]. Even if some

redox active centers (for Cr(VI) reduction) and/or complexing groups (for Cr(III) binding) can be identified [71, 81, 83, 86], the intrinsic complexity of these materials often made difficult the deep understanding of the main chemical parameters affecting the overall uptake process.

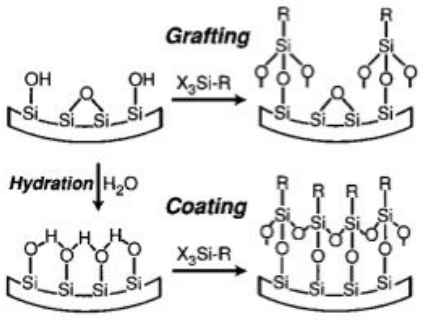
1.3.1 Functionalized adsorbents for chromium sequestration

Today there exists a variety of modified sorbents, creating for the concentration of heavy metals. They can be classified by matrix or modifier type. As a modifier can be used: organic reagents and their complex compounds, mineral acids (heteropolyacid) and their salts, natural compounds and some microorganisms [90]. As a matrix for adsorbents are used: synthetic and natural polymers, mineral carriers or inert materials, which can be grafted by modifying compounds.

Chemical modification of silica-based adsorbents can be divided into groups according to the method of their synthesis:

1. Covalent (chemical) bounding of functional groups at the surface of an adsorbent [91]:

- by grafting [92, 93], (scheme 1.1, a). Modification of an adsorbent matrix by attachment of functional molecules to the surface of the pores;

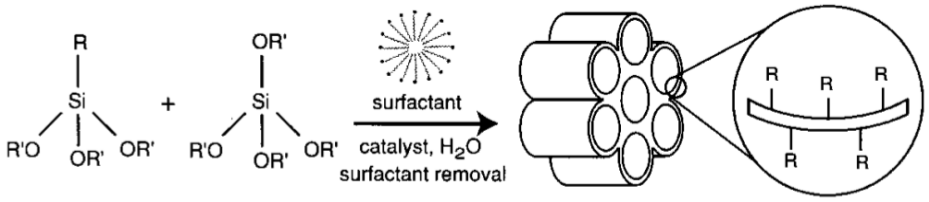


(1.1)

- by coating (scheme 1.1, b). In the grafting processes noted above, silylation reagents were typically added under dry conditions to avoid hydrolysis and condensation away from the pore walls. Under anhydrous conditions the hydrophilic portion of the silica surface is preserved during silylation and surface

groups are relatively isolated. However, by employing just enough water in the process to form a monolayer on the pore surface, more continuous coats of organosilanes may be obtained, leading to a high concentration of organics in the product. Excess water must be avoided, because it can lead to uncontrolled polymerization of the silylation reagents within the channels or external to the mesoporous adsorbent.

- by co-condensation principle [94], (polymerization, sol-gel technology), scheme 1.2. In this case, during the synthesis of material, modificator can be incorporated into the matrix of final material;



(1.2)

2. Non-covalent immobilisation [95] of functional groups at the surface by principle of:

- impregnation (soaking) of adsorbent matrix by solution of modificator;
- dispersion, electrostatic, dipol-dipole or hydrogen bonds interactions.

1.3.1.1 Ion-exchange

The exchange reaction of Cr(VI) with the ion exchangers are described by the following equations:

$$2R^{+}\text{-}OH^{-} + CrO_4^{2-} \leftrightarrow R^{+}_2\text{-}CrO_4^{2-} + 2OH^{-}$$
$$R^{+}_2\text{-}CrO_4^{2-} + CrO_4^{2-} + H^{+} \leftrightarrow R^{+}_2\text{-}Cr_2O_7^{2-} + OH^{-} \quad (1.11)$$

, where R is ion-exchanger matrix.

The NaOH solutions are applied for anion exchanger regeneration.

As mentioned earlier, the industrial wastewaters formed in chromium plating of surfaces of other metals also contain ions of other elements, besides chromium ions.

Therefore, the problem of separation of individual components and first of all the recovery of both chromium and other metals ions occupies an important position.

The performance of the chromate ion-exchange process has been reported to be greatly influenced by the properties of anion-exchange resins. Commercially available polymeric sorbents containing both weak and/or strong bases on the surface are used as anion-exchangers. Examples of strong anion-exchangers are Amberlite IRA 400 [96] and IRA-900 [97]. Weak anion exchengers are represented by such resins as Amberlite IR 67 RF and IRA-96 [98, 99]. Capacity of ion-exchengers depends on the type of their functional groups, the type of the matrix and concentration of functional groups. Comparison of these values are brought in line at Table 1.4.

Macroporous strongly basic anion exchanger — Lewatit MP-500A is characterized by high selectivity for Cr(VI) ions [100]. Its capacity depends on the concentration of Cr(VI) ion forms and the presence of other ions in the system. Best results are obtained when Cr(VI) is adsorbed from solutions of hydrochloric acid, at such pH values, where Cr(VI) is in the form $HCrO_4^-$. From the thermodynamic studies it may be concluded that the most effective removal of Cr(VI) ions from industrial wastewaters is obtained using OH^- forms of anion exchanger with the average pH values of the environment. Uncontrolled increase of acidity intensifies oxidizing character of Cr(VI) ions and as a result, faster degradation of the ion exchanger bed.

The strongly basic anion exchanger of gel structure and quaternary ammonium groups – Amberlite IRA- 400 in the chloride form was applied for removal of chromate ions from the solutions of various pH, various initial concentrations (1.030–15.449 mmol L^{-1}) [96]. It was found that the ratio of released chloride ions and sorbed chromate ions decreases with decreasing pH values of the solution and the effect of temperature is insignificant. This indicates that CrO_4^{2-} ions sorption proceeds first and then that of $HCrO_4^-$.

Clinoptilolite modified with HDTMA (hexadecyltrimethylammonium cation) proved to be a selective ion exchanger for Cr(VI) in a wide range of pH = 3–13 [101]. However natural zeolites treated with HDTMA are also effective sorbents for nonpolar organic, inorganic cations and inorganic anions (CrO_4^{2-}, SO_4^{2-}, SeO_4^{2-}).

Table 1.4

Comparison of the Adsorption Capacity of Several Amine or Quaternary Ammonium Based adsorbents

Sample	Functional groups	Sorption capacity, mg g^{-1}	references
Amberlite IRA 400	quaternary ammonium	60	102
Amberlite IRA 900		153	103
Amberlite IR 67 RF	imine	56	98
Amberlite IRA-96	amine	32	102
QAPAN fiber	amine, quaternary ammonium	248	111
APAN fiber	amine	35	104
APAN fiber	amine	133	105
4-VP grafted PET fiber	4-vinyl pyridine	72	106
PANI-jute fiber	amine and imine	63	107
RQA resin	amine, quaternary ammonium	48	108
RCl resin	N-methylimidazolium	132	109
VION AN-1	Pyridinium ion	130	110

A high distribution coefficient of Cr(VI) ions removal was found also applying anion exchange fibres with pyridine groups [110]. Investigations showed that basicity of the sorbent does not affect its selectivity for chromium ions. The capacity of the obtained resin with pyridine groups was estimated to be 130 mg g^{-1}. It was also found that the fibres containing pyridine groups of low basicity are resistant to oxidizing effect of Cr(VI) ions which stabilize their ion exchange capacity in sorption–desorption cycles. Transformation of pyridine groups into more basic forms decreases chemical stability of resin in Cr(VI) adsorption from solutions.

A novel fibrouse adsorbent functionalized with both amino and quaternary ammonium groups [111] can be repeatedly used for removal of aqueous Cr(VI). It is also stated that Cr(VI) is partially reduced to Cr(III) at its surface. The anion-exchanger

is characterized with a very fast adsorption kinetic (equilibrium achieved within 10 min) and an high adsorption capacity (248 mg g^{-1}) for Cr(VI). The range of working pH (from 2 to 8) is uniquely wide. But the presence of divalent (SO_4^{2-}) anions decreases sorption capacity.

Anion-exchange binding of Cr(VI) is used not only as a method of wastewater treatment, but also in analytical practice. Spectrophotometric detection of Cr(VI) at the surface of sol-gel film modified with pyrirdin groups is proposed [112]. After pre-concentration of Cr(VI), the film is treated by diphenylcarbezide, which provoke formation of coloured complex (Fig. 1.6.)

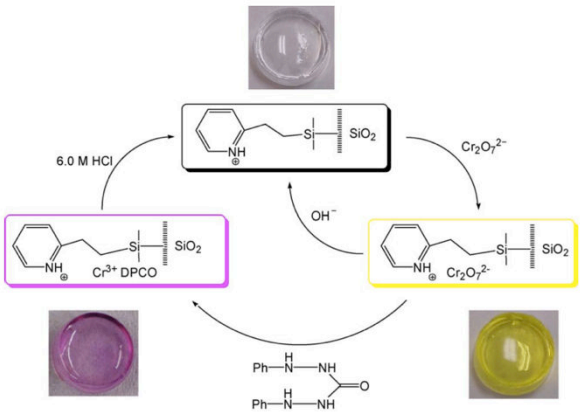


Fig. 1.6. Optical system of Cr(VI) detection on basis of films made from silica modified with pyridin groups

The system can be regenerated by 0.1 M solution of EDTA or 6 M solution of HCl. In both cases, effectiveness of the next cycle of Cr(VI) anion-exchange is reduced by 30%.

The influence of sulfate ions (H_2SO_4), which high concentrations are typically present in electroplating solutions, on adsorption of chromates was studied on the basis of AG-1X8 resin by Strelow et al. [113]. It was demonstrated that increasing of sulfuric acid concentration leads to decrease of the distribution coefficient of Cr(VI) and Cr(III), see. Table 1.5.

In several cases it has been also stated that application of anion-exchangers can lead to reduction of CrO_4^{2-} to Cr(III) at their surface [113, 114].

Table 1.5

Distribution coefficients of Cr(III) and Cr(VI) between AG-1X8 and solution of H_2SO_4 with different concentrations [113]

H_2SO_4, M	0,005	0,015	0,05	0,1	0,5	1,0	2,0
Cr(VI), ($n \cdot 10^{-3}$)	25	12	12	7,8	2,1	0,8	0,3
Cr(III)	5,1	3,4	2,1	0,7	<0,5	<0,5	<0,5

The principle of cation-exchange (scheme 1.12) is used to in order isolate chromium in its trivalent form:

$$nR\text{-}SO_3^-H^+ + M^{n+} \leftrightarrow nR\text{-}SO_3^-M^{n+} + nH^+ \qquad (1.12)$$

, where M^{n+} is either hexaaquachromium(III) or its hydrolysis products

For this purpose cation-exchangers with either strong sulphonic (Lewatit 100 S), iminodiacetic (Amberlite IRC 718 is) acid groups or weak carboxyl groups acid groups (Chelex-100, Amberlite IRC 76) are used [115, 116].

Removal of Cr(III) from industrial wastewaters is accompanied by some difficulties particularly in the presence of sulphates. Literature data indicate existence of many Cr(III) complexes in the solution. Cr(III) complexes, in the amount from 10% to 32% were found which were not sorbed by sulphonic cation exchangers [117].

Besides, in acid solutions behavior of Cr(III) – cation-exchanger system becomes more complecated, due to formation of differently charged complexes. Their relative amount depends on the composition of the solutions and the conditions of their preparation. Thus purple aqueous solutions of Cr(III) salts are higly inert due to formation of aqua-complexes. Heating of such solutions in the presence of Cl^-, Br^-, I^-, NO_3^-, ClO_3^-, ClO_4^- anions cause formation of complex ions and change the colour from purple to green. Distribution coefficients of Cr(III) between cation-exchangers and acid solutions depends on acid concentrations, (see Table 1.6).

Table 1.6

Cr(III) distribution coefficients between cation-exchangers and acid solutions [118]

C, N	HCl	HNO_3	H_2SO_4
0,1	1130	5100	198
0,2	262	1620	176
0,5	73	418	126
1,0	27	112	55
2,0	8	27,8	18,7
3,0	5	19,2	0,9
4,0	3	10,9	0,2

For selective adsorption of Cr(III) from tanning baths a cation exchanger Amberlite IR-120 at the basis of polystyrenesulphone was described [119]. Sorption capacity of Amberlite IR-120 does not depend on pH in the range from 1 to 11 and is reported to be 35 mg g^{-1} However, studies of Cr(III) adsorption on Amberlite IR-120 in the protonated form showed that its capacity is significantly affected by increasing Na^+ concentration.

A well-known macroporous cation-exchanger that is widely used for treatment of industrial water from Cr(III) Purolite C-106 [120], contains carboxyl groups on the surface, and is capable to adsorb other metal cations. As far as a classical regeneration of cation-exchanger is not applicable in this case, which may be explained by the formation of strong bondings of Cr(III) with carboxylic groups, Purolite C-106 is regenerated in two steps. At the first stage an alkaline solution of H_2O_2 (pH = 12) is used to desorb chromium and aluminum in the form of chromates and aluminates, respectively. The second stage of purification use a classical method of regeneration from other metal cations (Fe (III), Cu (II), Zn (II), etc.).

Polymer resin based on macroporous Amberlite XAD-2, imprignated by solution of Cyanex 272 (bis (2,4,4-trymetylpentyl)phosphinic acid) [121] is used to adsorb Cr(III) from nitrate solutions with ionic strength 0.1 M. This imprignated adsorbent has high affinity to Cr(III) ions, which are adsorbed on the surface in the form of

$Cr(OH)(HL)_2(NO_3)_2$ or $Cr(OH)L_2$ (where HL is Cyanex 272). Elution of adsorbed metal ions from the resin can be carried out using 6 M of HCl. Desorption efficiency is 95%, but at the same time sorption capasity of imprignated adsorbent decreases. In order to use it again the matrix of Amberlite XAD-2 should be impregnated again.

Adsorption of Cr(III) by cation-exchanger is complicated by the formation of coordination bonds between the acidic groups (carboxylic and sulfonic acid groups) and the main complexes of Cr(III), which affects its quantitative removal. Particularly, it is seen from adsorption isotherm of Cr(III) on strongly acidic cation exchanger (sulfonic acid groups) [115] (see Figure 1.7) that in the concentration range 0.1 - 1 mmol L^{-1} binding of Cr(III) is not that much effective, as one would predict.

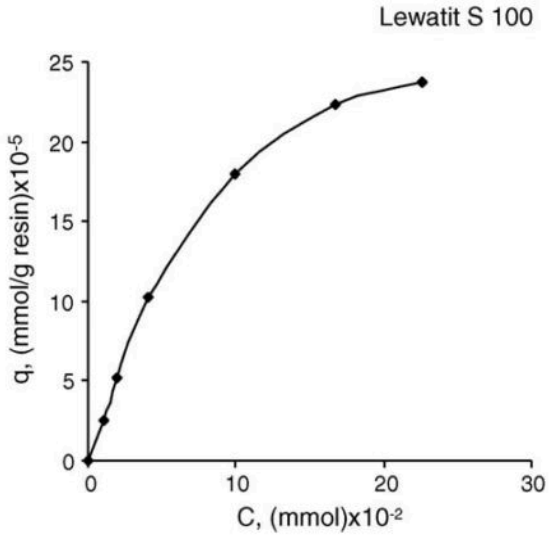


Fig. 1.7 Isotherm of Cr(III) sorption on Lewatit S 100. ($C_{original}$ (Cr(III)) = 0.1 – 1 mmol L^{-1}; $m_{adsorbent}$ = 0.5 g; $V_{solution}$ = 30 mL; pH =3.8, contact time: 150 min)

To sum up, ion-exchange must be an essential technique in case of purification of wastewaters with bulk Cr(VI) concentrations as mostly they are characterized with high adsorption capacity and recovery properties. However particular anion-exchangers can not selectively remove chromate ions from industrial wastewater with neutral and alkaline pH in the presence of other competing anions (sulphates, chlorides, nitrates, hydrocarbons). Recovery of Cr(III) by cation-exchange is generally characterized by lower sorption capacities (never exceed higher than 40 mg g-1, for comparison see Table 1.4) and worse recovery abilitites (due to possible formation of coordination

bondings between acid groups of cation-exchanger and Cr(III) aqua-complexes, even in case of such strong acid groups as sulfonic and phosphinic) in comparison with anion-exchange applied for Cr(VI) removal. Moreover sorption properties of cation-exchangers are strongly affected by increasing of ionic strength and so can not be recommended for effective chromium removal in its trivalent form after preliminary reduction of Cr(VI).

1.3.1.2 Chelating adsorbents

Alternative selective adsorption of chromium can be performed by chelating adsorbents. Since chromium is able to form complexes only in the trivalent state, Cr(VI) should be reduced before the contact with chelating adsorbent. The methods of chemical reduction were listed in Part 1.3. Despite this photocatalytic reduction on the improved organic-inorganic hybrid material ZnS(en)0.5 (Zn(II) sulfide modified with ethylenediamine (EN)) [122] and γ-ray irradiation in the presence of TiO_2, Al_2O_3 or SiO_2 [123] are used for Cr(VI) transformation.

Reduction of Cr(VI) before its adsorption was used by Sumida [124] for selective determination of both forms of chromium. This method is based on selective adsorption of Cr(III) on the surface of the polymer sorbent modified with iminodiacetic acid groups. To do this, two identical columns were used. A cap with reducing agent was placed between them. Cr(III) was adsorbed at the first column, while Cr(VI) was reduced in the cap and then adsorbed at the second column in the form of Cr(III). Elution was performed by 2 M solution of HNO_3.

To achieve selective binding and extraction of heavy metal ions, 4-Amino-3-hydroxy-2-(2-chlorobenzene)-azo-1-naphthalene sulfonic acid (AHCANSA) was used as a chelating agent [125]. AHCANSA groups were immobilized either physically (I) or covalently (II) at the surface of two silica samples. Concentrations of immobilized groups were 0.488 and 0.473 mmol g^{-1}, respectively. It was found that these adsorbents adsorb effectively such heavy metals as Cr(III), Ni (II), Cu (II), Zn (II), Cd (II), Pb (II). Sorption capacity of these metals for these adsorbents are in the range from 0.250 to

0.483 mmol g^{-1}. Both silica were found to be effective metal adsorbents (adsorpton yields were 95.2-98.1% and 92.5-97.1% respectively). Under optimal conditions, sorbents can remove trace amounts of metal ions (up to 1.0 and 2.00-2.50 μg mL^{-1}, respectively).

Chinolinol was immobilized on silica surface for the removal of trace amounts of metal ions such as Cr(III), Fe (III), Cu (II), Ni (II), Co (II), Mn (II), Zn (II) Cd (II), Pb (II) and Hg (II) in pH range 4-6. Sorption capacities of the metals are in the range 0.2-0.7 mmol g^{-1} [126]. Pre-concentration of Cr(III), Mn (II), Co (II), Ni (II), Cu (II), Zn (II), Pb (II) and Cd (II) from seawater was also reported with the help of silica gel modified groups 8-oxyhinolin [127]. Optimum pH range for separation of mixtures was 4.0-7.0 for Cu (II) and Cd (II), 4.5-7.0 for Pb (II), 3.0-6.0 for Cr(III) and Fe (III) 5.0-8.0 for Zn (II) and Co (II) and 6.0-8.0 for Ni (II). Sorption capacity of the adsorbent was in the range 92-448 μmol g^{-1}.

Adsorption of Cr(III) by silica gel modified with carbohydrazide groups was studied in the presence of metal ions such as Co (II), Ni (II), Cu (II), Zn (II), Hg (II), U (VI) [128]. Determination of sorption capacity of the material was performed by multi-element analysis of surface complexes formed by proton induced X-ray emission spectroscopy.

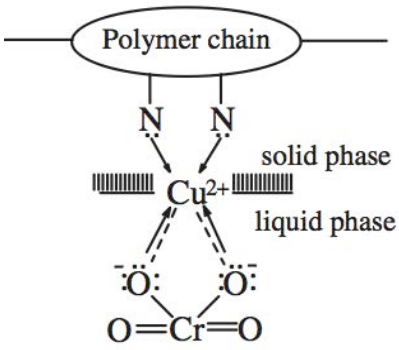


Fig. 1.8. Mechanism of chromate ion CrO_4^{2-} bonding.

Slightly different approach of using chelating adsorbents was proposed by Zha and all [129]. Covalently bounded charged metal complexes were used for chromates adsorption. This type of adsorbent (see, Fig.1.8) is a specific ion-exhanger on the basis of chelating adsorbent.

The polymer matrix built of crosslinked polystyrenedivinylbenzene was combined with the functional bis-picoliamine group containing nitrogen atom, which is a donor of electron pair for Levis acid-Cu(II) cation, in a covalent way. Copper ions are coordinated in such a way that complete neutralization of the positive charge does not

occur, which in turn, allows for the selective removal of chromate from solution with a neutral pH.

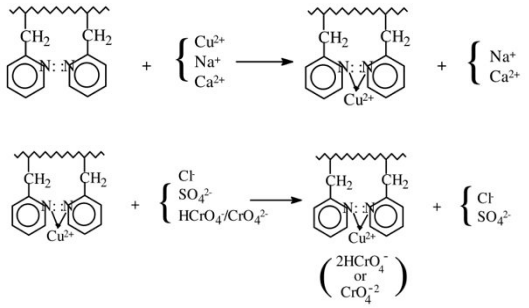


Fig. 1.9. Mechanism of simultaneous removal of heavy metal ions and chromates from a given medium.

In contaminated surface waters at pH lower than neutral, chromates can be accompanied by other heavy metal ions like Cu(II), Zn(II) and Ni(II). The above described chelating ion exchanger can be applied for simultaneous removal of both heavy metal ions and chromates(VI) from a given medium (Fig. 1.9).

Application of organic ligands capable of forming complex compounds with Cr(III) can be affected by other heavy methals ions, but the examples given in this section have demonstrated that the use of special experimental conditions (pH, chromatographic separation) can guarantee appropriate parameters of chromium adsorption. Quantitative sequestration of Cr(VI) on chelating adsorbents, after being reduced to Cr(III), can not be considered as qualitative approach to solving the problem. Cr(VI) reduction in solution requires special optimization in each and every case (qualitative and quantitative content of effluent must be considered) to avoid incomplete reduction. Moreover additional impurities like reducing agent and products of redox reaction are introduced into the treated wastewater.

1.3.1.3 Low cost (bio)sorbents from natural materials

Various natural and/or biological materials can relatively efficiently adsorb different metal ions: what in generalization is called bio-sorption [130]. A huge amount of work was devoted to sorption of Cr(VI) on such materials as sludge and/or sulfur-

containing biomass [85], inanimate bacteria [86], algae [83], fungi [81], bio-waste products [82, 84, 87] and iron sulfides [88, 89]. Over the past decade, more than 200 articles was published in various international journals concerning Cr(VI) biosorption. Most of the early studies suggest that Cr(VI) is removed from the aqueous phase by electrostatic interaction of chromates with positively charged groups of biomaterials. Recently it has been suspected that such interpretation was incorrect [131] as far as no attention was paid to chromium speciation in equilibrium solution, at the surface of bio-materials, and also, in many cases, contact time was insufficient to establish equilibrium [132]. It was reported that under a sufficient duration of contact of aqueous phase with biomaterial and in case of enough quantity of protons, Cr(VI) can be reduced to Cr(III) [133]. Therefore it is very important to check the effectiveness of Cr(VI) reduction after contact with biomaterials, namely to investigate both Cr(VI) and total chromium concentration in the equilibrium solution (a combination of spectrophotometric method with diphenylcarbazide and atomic-adsorption/atomic-emission spectroscopy) and check the oxidation state of chromium adsorbed at the surface of biomaterials (by X-ray absorption spectroscopy and X-ray photoelectron spectroscopy). Regardless of whether or not researchers have recognized and/or confirmed the occurrence of Cr(VI) reduction to Cr(III) by the biomaterial tested, most of them have accepted ‘adsorption-coupled reduction’ as the mechanism of Cr(VI) biosorption [134, 135, 136]. Park and co-workes has even outlined two types of possible interaction of Cr(VI) in the context of ‘adsorption-coupled reduction’ mechanisms (see Fig. 1.10) However, a number of researchers still believe that ‘anionic adsorption’ is the removal mechanism of Cr(VI) in their systems [137, 138].

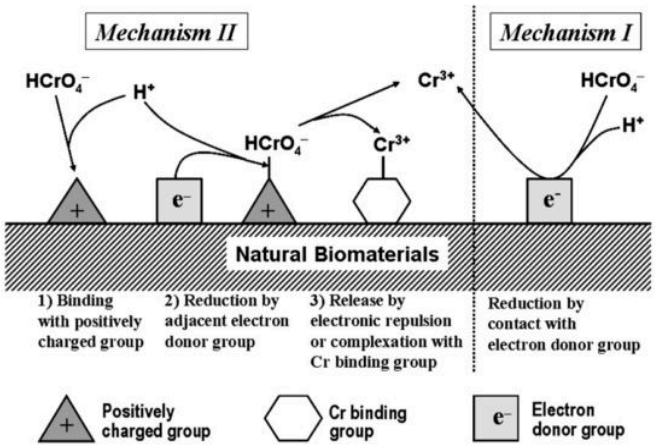


Fig. 1.10. Proposed mechanism of the Cr(VI) biosorption by natural biomaterials). Cr(VI) is removed from an aqueous system by natural biomaterials through both direct (I) and indirect (II) reduction mechanisms.

The latest review on bioadsorbent appearence [139] propose the existance of four models of Cr(VI) bio-sorption. They are as follows:

1. Anionic adsorption [137, 138, 140, 141]

Negatively charged chromium species (CrO_4^{2-}/$Cr_2O_7^{2-}$) bind through electrostatic attraction to positively charged functional groups on the surface of biosorbents. This mechanism is based on the observation that at low pH Cr(VI) adsorption increases and at high pH Cr(VI) adsorption decreases. At low pH functional groups of the biosorbent become protonated, and easily attract negatively charged chromium, but at high pH deprotonation occurs, functional groups become negatively charged repelling negatively charged chromium.

2. Adsorption-coupled reduction [131, 142, 143]

Reduction followed by cationic adsorption was first proposed by Volesky for algae sargassum biomass [144]. This mechanism is popularized by Prabhakaran on the basis of experiments [145]. According to this mechanism Cr(VI) is totally reduced to Cr(III) by biomass in the presence of acid. Then part of Cr(III) is adsorbed to biomass. The amount of adsorption depends on the nature of the biomass.

3. Anionic and cationic adsorption [146, 147, 148]

According to this mechanism a part of hexavalent chromium is reduced to

trivalent chromium. The hexavalent chromium (anionic) and trivalent chromium (cationic) are adsorbed to biomass.

4. Reduction and anionic adsorption mechanism [149]

According to this mechanism a part of the hexavalent chromium is reduced to Cr(III) by biosorbent and mainly Cr(VI) is adsorbed to the biomass while Cr(III) remains in the solution.

It's interesting to consider the removal efficiency of different forms of chromium (Table 1.7) and total chromium (Table 1.8) on bio-adsorbents depending on pH.

Table 1.7

Efficiency of adsorption of different chromium species on low cost (bio)adsorbent at different pH [150**]**

Adsorbent	Adsorption yields, %			
	pH = 2		pH = 5	
	Cr(VI)	Cr(III)	Cr(VI)	Cr(III)
Wool	69,3	0,0	5,8	58,3
Olive pits	47,1	0,0	8,4	74,8
Sawdust	53,5	0,0	13,8	96,8
Pine needles	42,9	0,0	13,0	79,4
Almonds pits	23,5	0,0	2,3	60,0
Coal	23,6	-	2,4	99,4
Cactus	19,8	0,0	8,2	55,2

Efficiency of Cr(III) removal increases in more basic media, while the effectiveness of Cr(VI) reduction is restricted. The highest removal efficiency of total chromium is observed when spruce bark (85%) and pine cones (71.8%) are used at pH = 2.17, and coal (97%) is used at pH = 5. For other materials adsorption efficiency is very low (from 25 to 60%).

Several attempts were made to determine active redox centers [81, 83, 86] (responsible for Cr(VI) reduction) and binding groups (responsible for chromium

binding) present at the surface of bio-materials. Still chemical content of such complicate systems as biological materials is never fixed and may vary from sample to sample, depending on many factors (origin, method of preparation). Consequently, bio-adsorbents are charactarized with low reproducibility of their properties.

Table 1.8

Final solution pHs, removal efficiencies and sorption capacities of total Cr at equilibrium state on different types of low cost (bio)sorbents [77, 131]

Adsorbent	Removal efficiency of total Cr, %	Final solution pH	Sorption capacity, mg g^{-1}
Pine needle	38,0	2,21	21,5
Pine bark	85,0	2,17	-
Pine cone	71,8	2,17	-
Banana skin	25,5	2,37	-
Green tea waste	64,8	2,27	5,7
Oak leaf	48,7	2,29	-
Walnut shell	24,6	2,21	5,88
Rice straw	26,3	2,24	-
Peanut shell	41,0	2,19	-
Sawdust	19,9	2,24	53,5
Orange peel	49,9	2,27	-
Rice husk	25,2	2,21	45,6
Rhizopus	27,2	2,32	23,9
Ecklonia	77,2	2,5	-
Sargassum	64,1	2,46	32,6
Enteromorpha	15,8	2,37	-

As one can see from the Table 1.8 the sorption capacities of polifunctional (bio)sorbents are of the same order of magnitude as those reported for cation-

exchangers applied for Cr(III) removal. Moreover in case of (bio)sorbents the mechanism of chromium binding is not fully understood. For these reasons biosorption of Cr(VI) still is mainly confined to lab studies only. To understand the mechanizm a synthetic system reproducing the qualities of bio-adsorbents should be used. This would also help to obtain systems with better sorption capacity and specificity to target metal ion.

1.3.2 Application of silica for Cr(VI) removal via 'adsorption-coupled reduction' mechanism

The pioneer work which applies a silica-based materials for Cr(VI) sequestration by reduction-adsorption mechanism was a paper published by Deshpande et al. in 2005 [71]. They has introduced a bifunctional organic-inorganic hybrid material chemically modified with amino and/or thiol groups for one-step sequestration of Cr(VI). A comparative study of mono and bifunctionalized materials showed the advantages of those materials which were modified with both amino and thiol groups. In this work no attention was paid to control distribution of reductively-generated Cr(III) in solid and liquid phase. Chromium was considered to be adsorbed as Cr(III) on the basis of green color development by the treated adsorbent. Adsorption capacity of such bifunctionalized adsorbent was not calculated.

Another approach of reductive-precipitation mechanism of Cr(VI) removal with the silica application was described in 2007 [151] and maintained by the following range of works [152, 153, 154]. In the presence of silica gel, Cr(VI) was proposed to be reduced by a zero-valent metal (Fe(0), Zn(0)). Silica was suggested to catalyze reduction and assist further precipitation of freshly-generated Cr(III). This novel approach to combine strong inorganic reductant and advanced OH-bearing adsorbent has revealed several disadvantages: formation of huge amount of sludge, simultaneous contamination of waters by products of reduction (Zn(II), Fe(III), Cr(III)). However $Fe@SiO_2$ nanocomposite designed by [154] should be marked out as the most efficient among the material proposed for Cr(VI) sequestration. $Fe@SiO_2$ dose 0.15 g L^{-1} can help to remove 70 mg L^{-1} of Cr(VI) under pH 6, removal capacity of $Fe@SiO_2$ reaches

467 mg of Cr per g. In 2011 Guo et al. has published the data of reductive-adsorption capability of bacteria immobilized at sol-gel [153]. Unfortunately chromium adsorption parameters were not well examined. Moreover the proposed adsorbent is characterized with low kinetics of interaction. It takes days to reach complete reduction of Cr(VI).

In this work we propose to examine application of bifunctionalized silica based materials for selective Cr(VI) removal from acid solutions. By planning the chemical composition of the surface and the structure of bifunctionalized adsorbent, we will try to improve sorption properties and increase the efficiency of sequestration of chromium in its less toxic form. By analogy to [71], in this work we propose to consider silica based materials modified by thiolpropyl as a reductant group and either by propylsulfonic acid or ethylenediaminetriacetate as a binding group. We should now revise the literature concerned with interaction of previously mentioned ligands with Cr(III), Cr(VI) and other heavy metals.

1.4 Justification for functional group choice

1.4.1 Interaction of Cr(III) and Cr(VI) with thiols

Cr(III) belongs to hard acids [155], it forms inert complexs with coordination number 6 and octahedral configuration of ligands containing oxygen, nitrogen and sulfur as donor atoms. They include complexes with neutral groups (H_2O, NO, NH_3, NO_2, SO_2, S, P, CO, N_2H_4, NH_2OH, C_2H_5OH, C_6H_6 і т.д.) and ions (F^-, Cl^-, Br^-, I^-, CN^-, SCN^-, OH^-, NO_3^-, NO_2^-, SO_3^{2-}, SO_4^{2-}, CO_3^{2-}, $C_2O_4^{2-}$ etc.). The ability of ligands to form complexes decreases in the range: OH^-> $C_2O_4^{2-}$> SO_3^{2-}> CH_2COO^-> $HCOO^-$> SO_4^{2-}> Cl^-> NO_3^-. In aqueous solutions, because of the kinetic inertness of aqua-complexes, Cr(III) does not interact with sulfides [155] and thiols . Chromium(III) sulfide (Cr_2S_3), formed by $CrCl_3$ treatment with gaseous H_2S, is poorly soluble substance that decomposes very slowly in contact with water. This is the reason why there are any publication devoted to adsorption of Cr(III) by thiol-functionalized material from its aqueous solutions. Nevertheless thiol and sulfide-bearing materials are used for Cr(VI) reduction [156, 157]. Trofimchuk reports in his work [158] the possibility of using

thiol-disulfide modified silica for Cr(VI) adsorption. As a result Cr(III) and 2 disulfide groups are formed, with the possibility of chromium detection in the phase of the sorbent.

Among the articles dedicated to the mechanism of Cr(VI) interaction with thiol-bearing organic compounds it was found that Cr(VI) interacts stepwise with formation of thiochromates as intermediats (see, scheme 1.3) [159]. First Cr(VI) is reduced to Cr(IV), then thiel-radicals interact and form disulfid bonds [160]. In more recent works it is shown that sulfonic acids can also be formed. [161].

Great difference between standart redox-potentials of redox couple Cr(III)/Cr(VI) (E_o = 1.47 V) and S^{2-}/SO_4^{2-} (E_o = 0.303 V) or S^{2-}/S_2^{2-} (E_o = -0.524 V) means there exist the possibility of thiols to be transformed either in disulfide or sulphonate groups. Formation of Cr(III) in this case is proved by different X-ray spectroscopy methods [161, 162].

$$HOCrO_3^- + H^+ \rightleftharpoons (H_2O)CrO_3$$

$$RSH + (H_2O)CrO_3 \rightleftharpoons R{-}S(H)\cdots CrO_3(OH_2) \qquad (1.3)$$

It is known that thiolates - basic derivatives of sulfohidryl acids – can form stable complexes with many metal ions, especially with those that are classified as soft acids. Lots of works [163, 164, 165] are dedicated to examination of this kind of interaction at the thiol-modified surface. Thus Cu(II) and Cd(II) are adsorbed quantitatively in acid media [166]. Yanovskaya et al. [167] has used mercaptopropylsilica do adsorb Zn(II), Cd(II) and Pb(II). These cations are adsorbed quantitevely at pH = 6-9. At the same time Losev informs that [168] Cd(II) and Zn(II) are adsorbed at pH = 4-5 (see. Fig. 1.11), as well as other heavy metals. (Co(II), Ni(II)). Cu(II) and Bi(II), are those exceptions which intract with thiolpropylsilica at pH = 1. Neutral pH is good for efficient adsorption of Fe (II, III) [169].

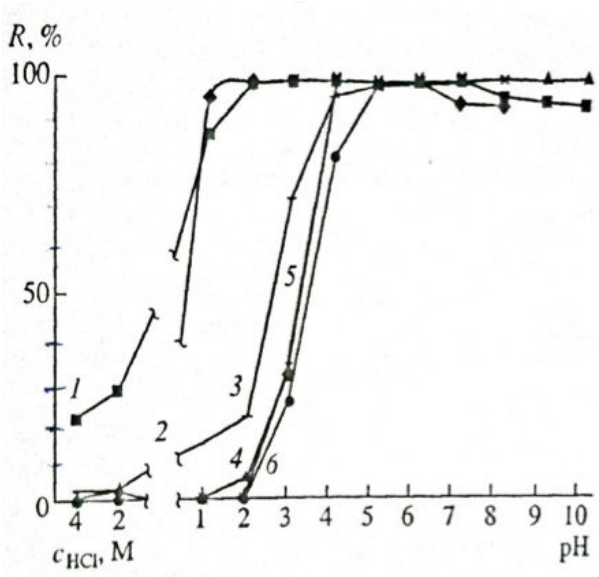


Fig. 1.11 Sorption efficiency of Cu(II) (1), Bi(II) (2), Cd(II) (3), Co(II) (4), Ni(II) (5), Zn(II) (6) by silica gel chemically modified with mercaptopropyl groups versus HCl concentration and pH (C_{Me} = 5 mg L^{-1} , V = 10 mL, m_c = 0,1 g, t = 5 min)

1.4.2 Interaction of Cr(III) and heavy metals with derivatives of ethylenediaminetetraacetate (EDTA)

Generally, interaction of a metal cation with the EDTA ligand can be written as follows:

$$M^{n+} + H_4Y \rightarrow MY^{(n-4)+} + 4H^+. \qquad (1.13)$$

EDTA can form complex with Cr(III) with coordination number 6 in 1:1 ratio. A high stability of these complexes (see Table 1.9) is explained by the presence of six functional groups as donor atoms in the molecule of EDTA (containing nitrogen and oxygen).

Trivalent chromium forms complexes with EDTA and its derivatives, but very slowly. In the literature one can find different information about the time of complex formation: 30 min [170, 171], 45 min [172] or 5 min [173]. The process can be accelerated by heat. Complex formation at ordinary temperatures can be speed up by adding a catalyst such as acetate and bicarbonate [174], as well as trace amounts of Cr

(II) [175]. Potassium dichromate in the presence of EDTA in weakly alkaline medium, is gradually reduced, the process is significantly accelerated when boiled in the presence of manganese salts [168]. As a result a purple compound is formed, which is likely to be the CrY^- complex. If a reduction agent (iodide) is present in solution, a violet complex is formed immediatly, most likely due to formation of anhydrous ion Cr^{3+} [176].

UV-spectra of this complex (Fig. 1.12) reveals two absorption peaks at pH 2 (396 and 538 nm) [177]. In basic medium (pH 11) the absorption peaks are shifted to 390 and 590 nm. This changes in color can easily be detected by eyes. A purple complex CrY^- in case of higher pH turns into darc blue complexes $Cr(OH)Y^{2-}$, $Cr(OH)_2Y^{3-}$. The CrY^- complex is very stable (see, Table 1.9) and characterized with constant values of light adsorption at pH = 1.5-4. The optimal light adsorption is observed in case of Cr to EDTA ratio 1:6. In such conditions spectrophotometric method anables to detect up to 6 mg of Cr(III) per liter [178].

Table 1.9

Stability constants of some EDTA complexes; t=20^{0}C; μ=0,1 in KNO_3 [179]

Cation	Complex	log K_{MY}^{2-}
Cu^{2+}	CuY^{2-}	18,8
Cd^{2+}	CdY^{2-}	16,46
Pb^{2+}	PbY^{2-}	18,04
Co^{2+}	CoY^{2-}	16,31
Ni^{2+}	NiY^{2-}	18,62
Zn^{2+}	ZnY^{2-}	16,5
Al^{3+}	AlY^-	16,13
Fe^{3+}	FeY^-	25,1
Cr^{3+}	CrY^-	23,4

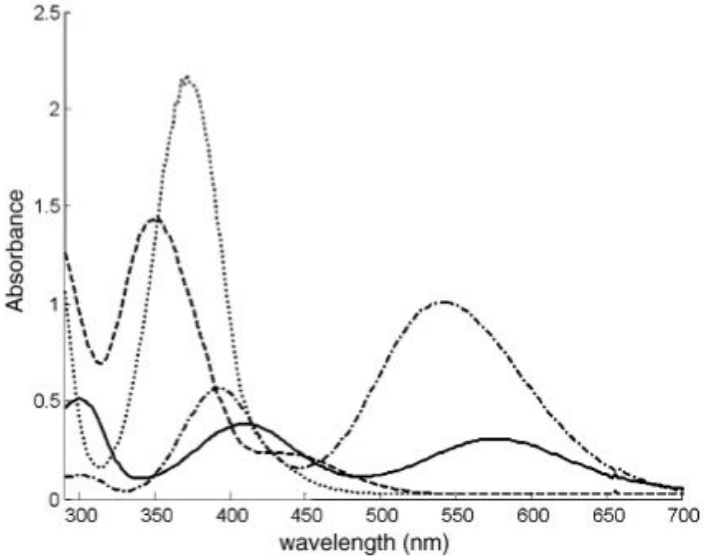


Fig. 1.12. UV-VIS spectra of chromium solutions: (———) Cr(III) 1000 mg L^{-1}; (·····) CrO_4^{2-} 25 mg L^{-1}; (– – –)$Cr_2O_7^{2-}$ 50 mg L^{-1}; (– · –) Cr(III)-EDTA 250 mg L^{-1}

Interaction of Cr(III) with ethylendiaminetriacetate (ED3A), which we propose to use as a binding ligand for selective reductive-adsorption of Cr(VI) by bifunctionalized adsorbent, presume formation of pentadentate complex. As far as ED3A includes three carboxyl groups one can suggest that the complex might be formed in much the same maner as complex of Cr(III) with diethylenetriamine pentaacetic acid (DTPA) shown on Fig. 1.13

The manuscript dedicated to studying of Cr(III)DTPA complex formation [180] mentions that in aqueous solutions there migh exist 5 main types of species shown on Fig. 1.13. In pH range from 4 to 7, together with the main CrY^{2-} form (where Y is DTPA), the monoprotonated CrHY species are present. At pH = 3 the complex is protonated with two protons. When pH is >7 the monohydrate complex predominates, the metal is coordinated with one water molecule (Fig. 1.14). Cr(III) complexes with DTPA (CrY^{2-}, $CrHY^{-}$, CrH_2Y, CrH_3Y^{+}) are characterized with the following constants: 22.05; 28.18; 31.03; 32.48. One could assume that the distribution diagram for similar processes but on the surface of silica gel will have a slightly different appearance, the curves would be shifted toward lower pH, as generally the strength of immobilized acid and so value of the protonation constants increases.

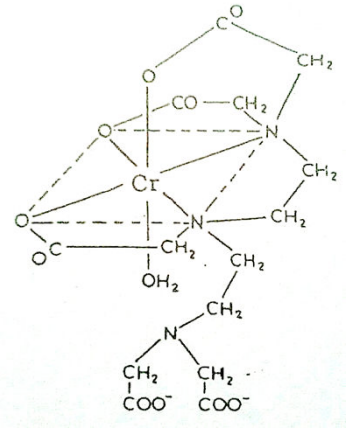


Fig. 1.13 The structure of Cr(III)DTPA complex

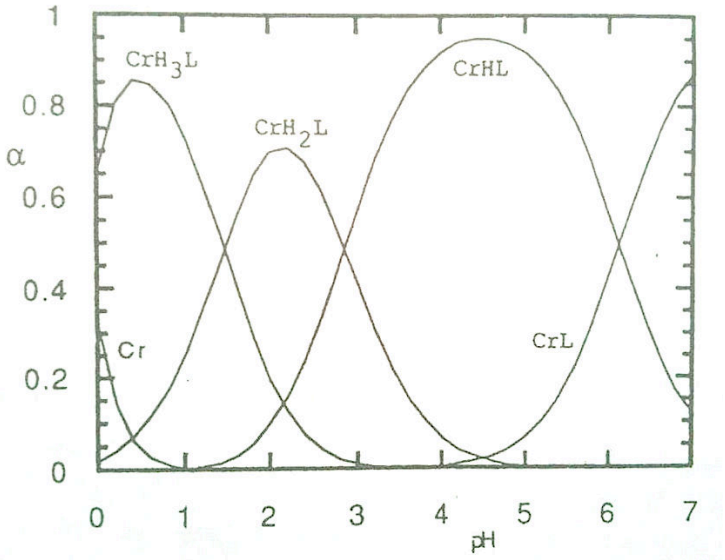


Fig. 1.14. Distribution of Cr(III)DTPA species in aqueous media depending on pH ($C_{Cr(III)} = C_{DTPA}$)

First attempts to immobilize covalently EDTA derivatives were made at the surfaces of different resins in the second part of the last century [181, 182]. Resins functionalized with iminodiacetic acid groups (IDA) became widely used for preconcentration of heavy metals. Different variations of these resins are known by their commercial names as Chelex-100, Dowex-100 etc. It proved impossibile to synthesize monofunctionalized polymer matrix containing analogues of EDTA as functional groups [183]. That's why chelating adsorbents which were used till 90s of the last century, were various IDA bearing resins.

Attempt to immobilize EDTA at the silica surface was made by optimizing the method of surface assembly [184]. First, surface silanization by 3-(2-aminoethyleneaminopropyl)-trimethoxysilane was conducted. The obtained silica functionalized with ethylendiamine groups was carboxymethylated by chloroacetic acid. Elemental analysis of so synthesized silica revealed that the surface layer contain the mixture of ethylendiamine, ethylendiamineacetic acid, ethylendiaminediacetic acid and ethylendiaminetriacetic acid.

Finally technology of synthesis of ED3A-containing silane was imroved and now it became commercialy available and so it is possible graft silica with ED3A groups in one stage. Despite the fact that this silane exists as 55-65% aqueous solution of sodium salt, it was stated that ED3A groups were covalently bounded [185, , 186, 187] at the silica surface.

Such chelating silica based adsorbent (SiO_2–ED3A) was used in column separation method [185, 184] for speciation of transition metals (Cu, Ni, Pb, Zn, Cd, Mn, Co) and for pre-concentraion of (Zn, Co, Cd, Pb, Cu, Ni) from sea water [188]. Dependence of adsorption efficiency of these metals versus pH was studied. Cu(II) and Ni(II) was effectively adsorbed at pH 1, quantitative extraction of Zn(II), Co(II), Cd(II), Pb(II) starts at pH 2 and reach maximum at pH 4-5. Effective adsorption of vanadium in the form of either V(V) or V(IV) at pH = 2.5-3 was reported.

1.5 Conclusions

Since concentrations of toxic Cr(VI) compounds at the outlet of enterprises and the established norms of maximum allowable concentrations differ thousand times, strict requirements are imposed for quality of water treatment for those chemical companies that use Cr(VI). The use of classical methods of watewater treatment (chemical reduction + precipitation) do not always guarantee that Cr(VI) concentration will decrease up to the required level and besides it leads to the formation of a large amount of sludge.

A literature review dedicated to the subject revealed that the modern methods of posttreatment of Cr (VI) containing solutions mostly use the principles of sorption. It allows to reduce efficiently the volume of industrial sludge and to stabilize toxic form of chromium. Conventional methods of chromium adsorption, which are based on ion-exchange and complexation, also have certain limitations in use. Analysis of the literature indicates that the removal of chromates by anion exchange ceases to be effective with increasing of ionic strength in solution, which is hard to avoid for galvanic solutions. On the other hand, adsorption of chromium which is based on

chelation, is applied for Cr(III) selective binding, which intend preliminary reduction of Cr(VI), and thus introduction of additional contaminating reagents into aqueous solutions.

A new principle of Cr (VI) adsorption based on combination of reduction and binding in the plane of single material (lately it was being used for explanation of sorption activity of low cost (bio)sorbents) can be exploit in predetermined designing of matreials with improved sorption characteristics. Planning composition and structure of analogouse synthetic materials can help to adjust optimal conditions, efficiency of sorption, and improve the reproducibility of polyfunctionalized materials. In this work mercaptopropyl groups are proposed to be immobilized at the surface of silica based material in order to reduce Cr(VI) in acid media. Two types of groups – sulfonic acid and ethylenediaminetriacetic acid – are selected so as that can bind reductively-genereted Cr(III).

Chapter II

2 Experimental

2.1 Objects of research

Organic-inorganic hybrid materials used in this work were characterized by different structure (organized or not) and were synthesized by two main routes:

1. *Surfactant templated sol-gel synthesis* was used to produce mono- and bifunctionalized silica of MCM-41 type, containing mercaptopropyl and/or propylsulfonic acid groups (MCM-SH, MCM-SH/SO_3H).

2. *Chemical modification of silica gel* was used to synthesize the non-ordered mono- and bifunctionalized silica samples: this was made by grafting amorphous silica gel with mercaptopropyl and/or ethylenediaminetriacetic acid groups (SiO_2-SH, SiO_2-ED3A, SiO_2-SH/ED3A)

Metal ions solutions. Equilibrium processes were studied from aqueous solutions of Cr(VI) and Cr(III) in the presence of functionalized silica based materials. Solutions of other metal ions (Cu(II), Pb(II), Co(II), Ni(II), Fe(III)) were used to evaluate their possible influence on chromium sorption.

2.2 Reagents and solutions

All reagents were analytical grade and solutions were prepared with high-purity water (18 MΩ cm^{-1}) from a Millipore Milli-Q water purification system.

Reagents

$K_2Cr_2O_7$, $Cr(NO_3)_3 \cdot 9H_2O$, $Cu(NO_3)_2 \cdot 10H_2O$, $Pb(NO_3)_2$, $Co(NO_3)_2 \cdot 6H_2O$, $Ni(NO_3)_2 \cdot 6H_2O$, $FeCl_3 \cdot 6H_2O$, $NaHSO_3$, NaCl, NaOH and diphenylcarbazide (DPC). Concentrated HCl (37%), HNO_3 (65%), H_2SO_4 (95-97%) and standart solutions of NaCl, NaOH and HNO_3.

Chemicals used to prepare the adsorbents were: (1) the silica support, a chromatographic grade silica Kieselgel 60 obtained from Merck (characterized by an average pore size of about 7 nm, and a surface hydroxyl content of 3.6 mmol OH g, an

average particle size of 125 ± 25 μm, a specific surface area of 425 ± 25 m^2 g^{-1}, (2) organosilanes, tetraethoxysilane (TEOS, >98%, Merck), mercaptopropyltrimethoxysilane (MPTMS, 95%, Lancaster) and N-[(3-trimethoxysilyl)-propyl]-ethylenediamine triacetate (ED3A, 50% (w/w) aqueous solution of sodium salt of ED3A-silane coupler, Petrarch Systems Inc.); (3) solvents, toluene (95%, Merck), ethanol, methanol (Merck) and (4) reagents cetyltrimethylammonium bromide (CTAB, Merck), ammonia (28%, Merck), hydrogen peroxide (35%, Merck)

Solutions

- Stock solution of Cr(III) was prepared by dissolving 0.7073 g of $K_2Cr_2O_7$ in 100 mL of 2M H_2SO_4 and adding 5 g of $NaHSO_3$ in small portions under vigorous stirring. The obtained medium was next boiled to complete Cr(VI) reduction into Cr(III) and to expel SO_2, and was then diluted to 1 L to get a final Cr(III) concentration of 0.250 g L^{-1}. Working solutions were prepared by dilution and pH was adjusted with nitric acid.

- Stock solutions of Cr(VI) were prepared by dissolving accurate weighed portions of a $K_2Cr_2O_7$ powder in deionized water, from which working solutions were prepared by dilution and pH adjustment using nitric acid.

- Other metal solutions were prepared by dissolving the appropriate analytical-grade reagents.

- Ag(I) solutions were obtained from its nitrate salt ($AgNO_3$). They were prepared by diluting a stock solution of 0.10 M (in 0.1 M HNO_3) in distilled water and stored in dark glass. Their concentrations were checked with conductimetric titration by using a certified standard solution of NaCl.

- DPC solution was prepared by dissolving 0,1 g of DPC in 50 mL of ethanol, by adding 20 mL of H_2SO_4 (1:9). The obtained solution was stored during 1 month at 3-5^oC.

2.3 Preparation of functionalized mesoporous silicas

2.3.1 Synthesis of thiol-functionalized mesoporous silicas

They were prepared by co-condensation of TEOS and MPTMS at room temperature in the presence of CTAB template, according to a published procedure [189, 190]. Briefly, 0.9 mole of a TEOS/MPTMS mixture (9:1 molar ratio) was added under stirring to a surfactant solution made of CTAB (0.3 mole), water (50 mole), ethanol (150 mole) and ammonia (10 mole). After precipitation, the medium was left stirring for 2 hours and the resulting solids were filtered, washed with ethanol, and dried under vacuum ($<10^{-2}$ bar) for 24 h. Template extraction was achieved in ethanol/HCl (1M) under reflux for 24 h. The whole synthetic procedure was applied under inert atmosphere (Ar) in order to avoid any oxidation of thiol groups. The resulting solid was ascribed as MCM-41-SH; it contained 0.9 mmol g^{-1} –SH groups and it was characterized by a well-defined hexagonal mesostructure (powder XRD d_{100} spacing of 33 Å), a specific surface area of 1598 m^2 g^{-1}, a total pore volume of 0.76 cm^3 g^{-1} and a pore diameter of 20 Å. Another sample was prepared without taking care about oxidation and used for comparison purposes (noted MCM-41-SH/SO_3H-1 as it contained some sulfonic acid moieties, see Chapter IV for explanation).

Another sample MCM-41-SH/SO_3H-2.0 was synthesized according to the aforementioned procedure of MCM-41-SH/SO_3H-1 synthesis without taking care about oxidation by air oxygen. It was divided into three parts and titrated after different time of storing on air. Conductimetric titration was performed on the samples being disposed on air during 1 day (MCM-41-SH/SO_3H-2.1), 2 weeks (MCM-41-SH/SO_3H-2.2) and 2 months (MCM-41-SH/SO_3H-2.3). Stractural parameters of functionalized materials are mentioned in Table 2.1.

2.3.2 Oxidation of thiol groups into sulfonic acid moieties

MCM-41-SH was partially oxidized by adapting a previously published procedure involving the use of H_2O_2 in a methanol-water mixture [191]. To get a fully oxidized material (MCM-41-SH/SO_3H-6), 0.7 g of MCM-41-SH was suspended in a

mixture of 10 mL of aqueous 35% H_2O_2 (3.5 g) and 35 mL of methanol. After 24 h stirring, the solid particles were filtered and washed with water and ethanol. The wet materials were re-suspended in 0.1 M H_2SO_4 and stirred for another 4 h period, filtered again, washed with water and ethanol, and dried under vacuum ($<10^{-2}$ bar) for 24 h. After oxidation, the material was always mesostructured, yet with a small lattice contraction (d_{100} at 30 Å), but its specific surface area fell down to 860 $m^2\ g^{-1}$ and the total pore volume to 0.42 $cm^3\ g^{-1}$ due to the bigger size of sulfonic acid groups and possible degradation of the long-range order in the material [191] (parameters of functionalized materials are listed in Table 2.1). Materials oxidized in different ways were obtained by adjusting varied amount of H_2O_2 in the oxidizing medium (i.e. 0, 0.19, 0.38, 1.15, 1.9 and 3.6 respectively). These materials are ascribed in the text as MCM-41-SH/SO_3H-X, where X corresponds to the number of the sample (from 1 to 6).

2.3.3 Pretreatment of silica-gel before functionalization

In order to remove possible trace metal impurities in silica, a pre-treatment was carried out as follows: 400 mL of concentrated acids H_2SO_4/HNO_3 (9:1) mixture was poured to 20 g of pure silica and stirred with mechanical agitator during one night. SiO_2 was then filtered, washed with distilled water (up to neutral pH) and dried at 100 °C. Purified silica was stored in a tightly closed vessel. Before silanization it was annealed in muffle furnace at 450 °C during 3 hours. To avoid absorption of water from the air, calcined silica was cooled in a vacuum desiccator under P_2O_5, before transferring it into reactor.

2.3.4 Silica gel with covalently attached mercaptopropyl groups

Thiol-functionalized silica samples (SiO_2-SH) were synthesized according to a grafting procedure described in the literature [192, 193]. Silica gel (5 g) was placed into a flask, which was then filled with toluene (60 mL) and left for blending for several minutes. Then a selected aliquot of MPTMS solution (2 mL) in toluene was added to the slurry to reach a final content of 1 mmol of organosilane for 1 g of silica gel. The grafting reaction was conducted at 100°C for 6 hours. The resulting precipitate was then

washed in Soxhlet's apparatus with toluene (1h) and then with methanol for 24h. The final material contained about 0.4 mmol of covalently immobilized thiol groups per gram of adsorbent (for more information about structural parameters see Table 2.1)

2.3.5 Silica gel with covalently attached mercaptopropyl and ethylenediaminetriacetate groups

Thiol- and ethylenediaminetriacetate-functionalized silica samples (SiO_2-SH/ED3A) have been prepared according to a similar procedure as that reported for getting ethylenediaminetriacetate-bonded silica gel (SiO_2-ED3A) [194]. Briefly, 5.0 g of SiO_2-SH was placed into 20 mL of water-methanol solution (1:1 in volume) and left blended for 30 minutes. Then 4.0 mL of ED3A-silane coupler solution was added to SiO_2-SH slurry and blended for 3 days at the room temperature. The adsorbent was filtered, washed with distilled water and dried at 100^{o}C under reduced pressure. It contained about 0.4 mmol of immobilized ED3A groups per gram of material, i.e., the same amount as SH groups (for other adsorbent parameters see Table 2.1). Such optimal conditions for functionalization of SiO_2-SH with ED3A groups have been defined after investigating the binding of the ED3A-silane coupler to pure silica gel (1 g mixed with 4 mL of a 1:1 water-methanol solution containing the ED3A-silane coupler at concentrations varying from 13 to 290 g L^{-1}).

Table 2.1

Parmeters of functionalized materials

Sample	C(-**SO_3H**), mmole g^{-1}	C(-**SH**), mmole g^{-1}	C(-**ED3A**), mmole g^{-1}	BET surface area, m^2 g^{-1}	Mesopore volume, cm^3 g^{-1}	Pore diameter, Å
MCM-SH/SO_3H-1 … MCM-SH/SO_3H-6	0.035 … 0.606	0.898 … 0.327	-	≥860	≥0,42	≥20
MCM-SH	-	0.931	-	1598	0,76	20
SiO_2-SH/ED3A	-	0,382	0,401	346	-	5
SiO_2-SH	-	0,392	-	448	-	6
SiO_2-ED3A	-	-	0,181	364	-	5

2.4 Instrumentation

2.4.1 Solution analysis

Solution-phase analysis of total chromium was performed by inductively-coupled plasma with detection by atomic emission spectroscopy (ICP-AES, Plasma 2000, Perkin-Elmer). Distinction between Cr(VI) and Cr(III) species was made using the conventional diphenylcarbazide (DPC)-UV/Vis spectrometric method [195]. Other metal ions were analyzed by atomic absorption spectrometry (AAS) using a flame atomization "Saturn" apparatus and a propane-butane-air flame.

2.4.2 Characterization of materials

Composition of the adsorbents was determined by elemental analysis (CHONS) using a Thermofinnigan FlashEA 1112 analyzer.

The amount of thiol and sulfonic acid groups in MCM-41-SH/SO_3H-X materials was also determined by conductimetric titration, as performed in the Arrhenius cell. Conductivities of suspensions were measured by means of AC Conductivity Bridge R-5058 at operational frequency of 1000 Hz at room temperature. For acid-base conductimetric titration, solutions of 0.011-0.024 M NaOH were used to titrate residual and bulk concentrations of sulphonic acid groups respectively. A batch of each sample (~0.15 g) was previously soaked in 25 mL of deionised water. Titration of equilibrated suspension was performed in in 24h. For back conductimetric titration 0.1M NaCl solution was used to titrate excess of silver ions. The sample (~0.15 g) was equilibrated with a mixture of 10 mL of 0.04 M $AgNO_3$ and 20 mL of deionised water. The suspension was kept without light access during 12 h. It was then filtrated and an aliquot of equilibrated solution was titrated in the Arrenius cell. pH of silver nitrate mixture was checked before and after the contact with samples. It was always stated to be 4-5. Solid desiccation under pressure (over P_2O_5) preceded all of the titration experiments.

FTIR spectra were measured from self-supporting transparent tablets on a "Nexus-470" spectrometer, manufactured by "Termo-Nicolet" in nitrogen, at 120°C.

X-ray photoelectron (XPS) spectra were obtained using an electron energy analyzer (VSW, MCD 5000) and an unmonochromatized Mg Kα (1253.6 eV) source of photons. Powders were pressed at room temperature onto the adhesive side of a copper adhesive electrical tape. The binding energies were corrected on the basis of the standard value of C_{1S} from contaminants at 284.6 eV. Narrow scanned spectra were used to obtain the chemical state information for sulfur and chromium.

Thermogravimetric studies were performed on Q-1500 D derivatograph of Paulic-Paulic-Erdey system (Hungary) at atmospheric pressure, with open platinum crucibles and Al_2O_3 as standard for comparison. Heating rate was 10 °C·min^{-1} in the range between 20 and 800°C.

X-ray fluorescence (XRF) spectra were taken with the help of "ElvaX-Light" spectrometer, with an energy dispersion detector sensitive to radiation with 2-45 eV. Time of accumulation for each sample was 300 seconds. The tablets for XRF spectra were made by pressing sorbent with the filler (poly(vinyl alcohol)) in correlation 1:1 (0.05 g : 0.05 g) using a mold with 10 mm diameter.

Diffuse reflectance spectra (DRS) were recorded on a "Specord M-40" spectrometer in the wavelength region 12000-40000 cm^{-1}. Measuring precision of position of the absorption maximum is ± 40 cm^{-1}.

2.5 Equilibration procedures

2.5.1 Static mode

Batch equilibrations were performed at room temperature, under magnetic stirring. Solid and liquid phases were separated by filtration and analyzed with spectroscopic methods described in section 2.4.1. Equilibrated solutions of Cr(VI) were analyzed for the content of either Cr(VI) or Cr (III).

2.5.1.1 Sorption of Cr(III) and Cr(VI) versus pH

Studying sorption/reduction efficiency of Cr(III) and/or Cr(VI) versus pH was performed in suspensions containing selected amounts of adsorbents and constant volumes (see Table 2.2) in the pH range 1-7.

Table 2.2

Conditions applied in experiments which study effect of pH on Cr uptake

Cr species	Sorbent	m, g	V, mL	t, hours
Cr (III)	MCM-41-SH/SO_3H-6	0,02	25	24
		0,15		
	MCM-41-SH/SO_3H-1	0,02		
	MCM-41-SH			
	SiO_2-ED3A	0,05		
Cr (VI)	MCM-41-SH/SO_3H-1	0,01	20	
		0,15		
	SiO_2-SH/ED3A	0,05	25	

2.5.1.2 Sorption of Cr(III) and Cr(VI) versus solid-to-solution ratio

Effect of solid-to-solution ratio on sorption of Cr(III) and Cr(VI) was studied in suspensions with constant concentrations of Cr species, constant volumes and selected amount of adsorbents (see Table 2.3).

Table 2.3

Conditions applied in experiments which study effect of solid-to-solution ratio on Cr uptake

Cr species	Sorbent	m, g	V, mL	C, mole·L^{-1}	pH	t, hours
Cr (III)	MCM-41-SH/SO_3H-6	0,01-0,35	50	$5\cdot10^{-5}$-10^{-4}	2,2	24
Cr (VI)	MCM-41-SH	0,01-0,20				
	MCM-41-SH/SO_3H-2	0,03-0,2				
	MCM-41-SH/SO_3H-3	0,03-0,2				
	MCM-41-SH/SO_3H-5	0,05-0,2				
	SiO_2-SH/ED3A	0,01-0,3			3	

2.5.1.3 Sorption of Cr(III) and Cr(VI) versus time of interaction

These experiments were conducted in suspensions with constant amount of sorbents, concentration of Cr species and pH (which corresponded to optimal sorption conditions). For more details see Table 2.4

Table 2.4

Conditions applied in experiments which study kinetics of Cr(III) and Cr(VI) interaction with sorbents

Cr species	Sorbent	m, g	C, mole L^{-1}	pH	t, hours
Cr (III)	SiO_2-ED3A	0,1	$1{,}92 \cdot 10^{-4}$	5	72
Cr (VI)	SiO_2-SH/ED3A	0,05	$1{,}00 \cdot 10^{-4}$	2,5	24

2.5.1.4 Sorption of Cr(III) and Cr(VI) versus concentration of chromium species in solution

Adsorption isotherms were studied in conditions of optimal pH, constant volumes and amount of sorbents. Detailed information is listed in Table 2.5

Table 2.5

Conditions applied in experiments which study effect chromium concentration on sorption

Cr species	Sorbent	V, mL	m, g	C, mole L^{-1}	pH	t, hours
Cr (III)	MCM-41-SH/SO_3H-6	25	0,02	10^{-5}-$1{,}7 \cdot 10^{-3}$	2	24
Cr (VI)	SiO_2-SH		0,125	$4 \cdot 10^{-5}$-$4 \cdot 10^{-3}$	2,5	
	SiO_2-SH/ED3A			$2 \cdot 10^{-6}$-$2 \cdot 10^{-2}$		

2.5.1.5 Sorption of Cr(VI) on SiO_2-SH/ED3A versus ionic strength

Equilibrations were performed for 24 hours in 25 mL solution with constant SiO_2-SH/ED3A amount (0.05 g) and Cr(VI) concentration (10^{-3} mole L^{-1}) and pH = 2.5. Ionic strength was adjusted with NaCl (from 0.01 to 1M).

2.5.1.6 Sorption of Cr(VI) on SiO_2-SH/ED3A influenced by different concentrations of other metal ions

Interference studies were performed during 24 hours by adding metal ions (Fe(III), Cu(II), Ni(II)), at concentrations ranging from 0.004 to 0.48 mmol L^{-1} in the suspensions made of 0.05 g of adsorbent in 25 mL of solution containing 0.23 mmol L^{-1} of Cr(VI).

2.5.2 Dynamic mode

For all tests performed in dynamic mode, the same column (d⦸ = 7mm) was filled with 0,1 g of sorbent (SiO_2-SH/ED3A). Before placing SiO_2-SH/ED3A into the column it was soaked in distilled water during 12 hours. After the column was packed with sorbent, it was stored under the layer of distilled water. Before use, the column was washed with a solution of distilled water with a working pH = 2.5. pH of Cr(VI) solutions were adjusted to 2.5.

1.1.1.1 Sorption of Cr(VI) versus solution flow rate

Solution (25 mL) containing 0.2 mmol L^{-1} of Cr(VI) were passed through the column with different speed rates: 0.1; 0.2; 0.5; 0.7; 1.0 mL min^{-1}. 2 mL aliquots collected at the output of the column were adjusted to 25 mL and concentration of total chromium and Cr(VI) was detected in each of the sample using ICP-AES and (DPC)-UV/VIS spectrometric method respectively.

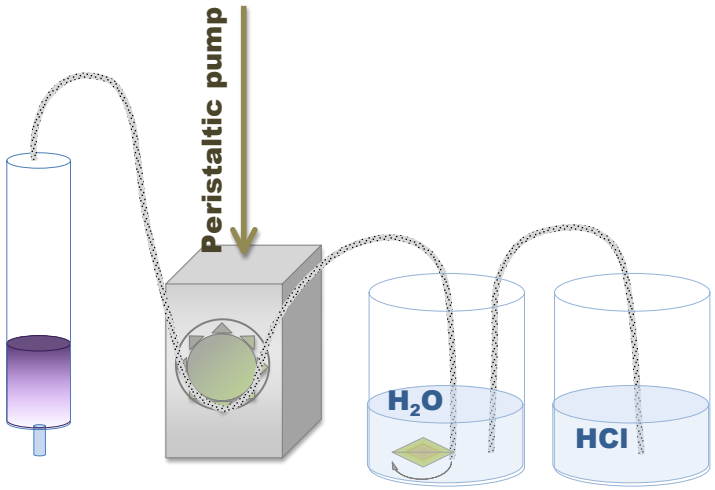
2.5.2.1 Studying of the breakthrough volume for the column filled with SiO_2-SH/ED3A

The experiments have been performed at two Cr(VI) concentrations (2 mM and 4 mM), at pH 2.5. 25 mL of such solutions were passed through the column (parameters mentioned in section 2.5.2) at three different flow rates (0.1 mL min^{-1} 0.4 mL min^{-1}, and 1.0 mL min^{-1}). Aliquots at the output of the column (2 mL) were diluted up to 25

mL and were analyzed by ICP-AES method.

2.5.2.2 Desorption of metals from the column filed with SiO_2-SH/ED3A

A series of metals Cu(II), Pb(II), Co(II), Ni(II), Fe(III) and Cr(VI)were pre-adsorbed on SiO_2-SH/ED3A from their water solution with C=80 µmole L^{-1}. Desorption was accomplished by passing hydrochloric acid with variable concentration through the column filled with SiO_2-SH/ED3A in a salt form (Na^+). In order to achieve constant changings in concentration of hydrochloric acid a system of "communicating vessels" was built (see Scheme 2.1).



(2.1)

Two 25 mL cylinders were interconnected with a teflon tube. The liquids in both cylinders were always at the same level. If the liquid was drawn off from one cylinder (speed rate 1 mL min^{-1}), then the liquid from another cylinder went via the tube into the first cylinder and the level of liquid in both cylinders was balanced again. Thus the solution of hydrochloric acid (0.1 M) from the second cylinder was gradually added to the first cylinder filled with distilled water where magnetic stirrer was constantly mixing the liquid. In the process of liquid moving from one cylinder to another, concentration of hydrochloric acid in the first cylinder was increasing in monotonic way. Such a solution with a gradient concentration of hydrochloric acid was passed through the column filled with SiO_2-SH/ED3A to check the changings of pH in each aliquot at the output of the column (2 mL). Than the heavy metals were pre-

concentrated in the same conditions as Cr(VI) and diluted by the previously mentioned technique. Each aliquot was deleted to 25 mL and analyzed by spectroscopic method.

2.5.2.3 Intensity of Kα line of Cr (XRF spectroscopy) versus the content of chromium in matrix of the sorbent

Solutions (25 mL) with different concentrations of Cr(VI) were passed through the column with the flow rate 1 mL min^{-1}. Solutions at the output of the column were analyzed by (DPC)-UV/VIS spectrometric method. The solid samples were dried on air and the tablets for Cr(VI) solid phase XRF detection were prepared.

2.5.2.4 The influence of Cr(VI) solution volume on chromium sorption at column filed with SiO_2-SH/ED3A

Different volumes of solution (from 0.01 to 1 L) with constant values of pH = 2.5 and constant amount of Cr(VI) (10^{-5} mole) were passed through the column at the flow rate 1 mL min^{-1}. After passing through the column solution was analyzed by ICP-AES method. The solids were taken out from the column and dried on air. The tablets were prepared for XRF analysis by the technique mentioned in section 2.4.2.

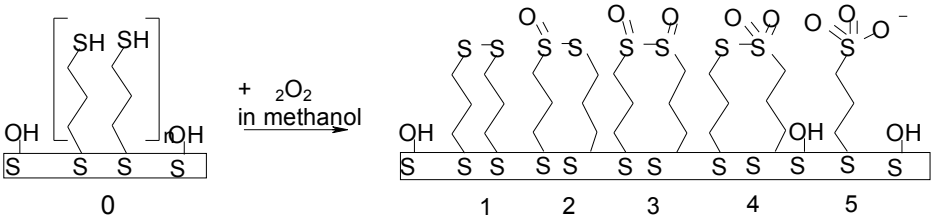
Chapter III

Ce chapitre est dédié à la détermination quantitative, par titrages conductimétriques, des groupements thiol et acide sulfonique présents à la surface de silices mésoporeuses organiquement modifiées (MCM-SH,SO_3H) constituées de différents rapports thiol/acide sulfonique. Dans cet objectif, un ensemble d'échantillons de type MCM-41 contenant 1 mmol g^{-1} de groupements mercaptopropyle (MCM-SH) a été oxydé à l'aide de quantités sélectionnées de peroxyde d'hydrogène afin de produire des matériaux présentant différents rapports SH/SO_3H. Le titrage conductimétrique a été proposé comme technique susceptible de distinguer les teneurs respectives des groupements thiol et acide sulfonique présents simultanément à la surface du matériau. Cette méthode permet d'estimer quantitativement la présence d'acide sulfonique à des teneurs inférieures à 1% en masse. Les concentrations en acides forts (SO_3H), elles aussi calculées d'après les courbes de titrage conductimétrique, se sont révélées être directement proportionnelles à la quantité d'oxydant ajouté. Les données calculées sur base des titrages conductimétriques ont été confirmées par des analyses XPS, démontrant une bonne corrélation des résultats obtenus par ces deux techniques. A partir de ces données, et conformément à la littérature, la transformation incomplète des groupements thiol en acide sulfonique (65%), même en utilisant un excès molaire d'un oxydant d'un facteur 100, a été confirmée. La spectrométrie de masse avec thermo-désorption programmée (TPD-MS) a également été utilisée pour compléter l'étude. Il a été démontré que l'oxidation de MCM-SH par le peroxyde d'hydrogène en concentrations croissantes ne conduit pas à la formation de quantités notables de groupements disulfures. La formation de groupements poly-sulfonates stables a été suggérée comme une des raisons possibles de l'oxydation incomplète des groupements thiol à la surface du matériau.

3 Speciation analysis of bifunctionalized mesoporous silica containing both thiol and sulfonic acid moieties (MCM-41-SH/SO_3H)

3.1 Study of MCM-41-SH/SO_3H-X by conductimetric titration

Mesoporous silicas functionalized with thiol groups (the obvious case was mentioned in Chapter III – surfactant templated MCM-41-SH), which are generally used to remove heavy metals [164, 196], often serve as precursors for preparation of alkylsulfonic acid functionalized silica [197, 198] (MCM-41-SH/SO_3H-X in Chapter II and III, where X corresponds to the number of the sample (from 1 to 6)). Extensive use of both thiol-functionalized materials and their oxidized derivatives was the reason of a vigorous interest in study the composition of their immobilized layer. It was shown that oxidation of immobilized propylthiol species with H_2O_2 leads to generation of a poly-functional layer [199, 200] that consists of both unreacted propylthiol groups and S-containing groups with different oxidation state [201] (demonstrated on scheme (3.1)). With the help of C^{13} CP/MAS NMR [201], RAMAN, IR and XPS methods [202] it was demonstrated that functional layer of such materials as MCM-41-SH/SO_3H-X mainly consist of propylthiol (type 0, scheme 3.1) and propylsulfonate (type 5, scheme 3.1) fragments.



(3.1)

On the other hand, it was demonstrated that the surface layer of MCM-41-SH could also be poly-functional. For instance during sol-gel synthesis of MCM-41-SH in alkaline aqueous solution, atmospheric oxygen can cause oxidation of surface alkylthiol-groups to disulfide moieties (type 1, scheme 3.1) [203].

Most commonly, the contents of immobilized thiol or sulfonic acid groups are

calculated from the results of elemental analysis of the adsorbent [189, 204]. However, the method cannot selectively determine S-containing groups with different degree of oxidation. Selective determination of thiol groups was suggested to perform by the methods, which use the principle of chemical interaction with immobilized thiol groups, namely: iodometric titration [169], titration with Ellman's reactive [205], measurements of the adsorbents capacity towards mercury [189] or silver [206], esterification of thiol groups with Rhodamine B [207]. Selective determination of sulfonic acid moieties is generally conducted by acid-base titration [208, 209] but it doesn't help to reveal residual alkylthiol groups, presented in the immobilized layer. Any spectroscopic method proposes to characterize quantitatively the composition of polyfunctionalized layer of neither MCM-41-SH nor MCM-41-SH/SO_3H-X. Particularly XPS is very useful to determine polyfunctional nature of immobilized layer, but cannot provide quantitative characteristics for thiol and sulphonic acid contents [189] similar to solid state NMR [204]. Both approaches are mostly used as comparative indicators. One may suggest that any combination of the listed methods cannot be applied for an accurate analysis of a thiol-functionalized surface layer containing admixture of sulfonic acid groups and vice versa, as no reliable method of speciation based on the single technique of detection was proposed.

Two sets of silica (MCM-41-SH/SO_3H-X and MCM-41-SH/SO_3H-2.X) with immobilized propylthiol groups were synthesized from corresponding silane by self-assemble co-condensation under procedure (but without taking care about oxidation), leading to formation of MCM-41 type matrix. The sets differ in concentration of propylthiol groups: the first one (MCM-41-SH/SO_3H-X) has 1 mmol g^{-1} of the functional group while the second one (MCM-41-SH/SO_3H-2.X) has only 0.5 mmol g^{-1}. Experimental samples (MCM-41-SH/SO_3H-X) were obtained from MCM-41-SH/SO_3H-1 by its oxidation with hydrogen peroxide in the conditions preserving the total loading of functional groups (X differ from 1 to 6, where 6 corresponds to the sample most fully oxidized and 1 – to the sample which was not oxidized by H_2O_2). To obtain samples having different degree of oxidation of the immobilized layer, concentrations of H_2O_2 was varied while time of treatment remained permanent.

Oxidation of immobilized propylthiols with H_2O_2 leads to polyfunctional layer of the adsorbent that may also include unreacted propylthiol groups. Taking into account this fact and essential distinction in protolytic behavior of thiols and sulfonic acid groups, we assumed that conductimetric acid-base titration can be used for determination of alkylsulfonic fragments on MCM-41-SH/SO_3H-X surface. Conductimetric titration can also be used for quantitative determination of propylthiol groups on the same adsorbent, but with another approach. It is known that immobilized SH groups can strongly bound silver ions from solution [210]. This adsorption process can easily be monitored by back-conductimetric titration of silver excess in solution with NaCl [211]. None of immobilized fragments on MCM-41-SH/SO_3H-X except –SH is able to bound silver in acid condition, so the proposed approach can be used for selective determination of –SH residuals on MCM-41-SH/SO_3H-X.

The features of a direct acid-base titration were first studied for the material (SiO_2-SO_3H) characterized with monofunctionalized layer of sulfonic acid groups [212] to be safe from overlapping of deprotonation of thiol-groups. Similarly to neutralization of strong acid in solution, the curve of conductimetric titration of SiO_2-SO_3H in aqueous suspension is V-shaped (see curve 1, Fig. 3.1).

At the same time the conductivity of aqueous suspension of unmodified structurally ordered silica based material of SBA type (see curve 2, Fig. 3.1) in selected range increases in linear proportion to quantity of added base. Similarly to silanol groups, immobilized propylthiol groups shall not affect to smooth increase of suspension conductivity [162]. Indeed, acid-base titration of MCM-41-SH demonstrates no inflexion on conductimetric curve, similar to titration of SBA (see later discussions). This observation is typical for neutralization of weak acid with $pK_a \geq 6$ in solution and was also expected for immobilized mercaptopropyl groups. So the concentration of bonded –SO_3H groups was determined from the position of V-type minimum on the titration curve as 0.28 mmol g^{-1}. This number is in good agreement with the concentration calculated for the same material discussed in [212]. Sharp V-type minimum on the curve of acid-base titration of SiO_2-SO_3H and weak interference with other immobilized groups as well as with silica matrix suggest that conductimetry is

applicable for quantitative determination of acidic group loading on MCM-41-SH/SO_3H-X. The approach was verified using the samples obtained from the same initial MCM-41-SH/SO_3H-1 (synthesized on air) but treated with H_2O_2 at various extent. Similar to SiO_2-SO_3H, all MCM-41-SH/SO_3H-X samples demonstrate V-type shape titration curves (Fig. 3.2) indicating the presence of propylsulfonic acid on the surface. Similarly to SiO_2-SO_3H we assign position of V-type minimum on MCM-41-SH/SO_3H-X titration curves to concentration of immobilized acid.

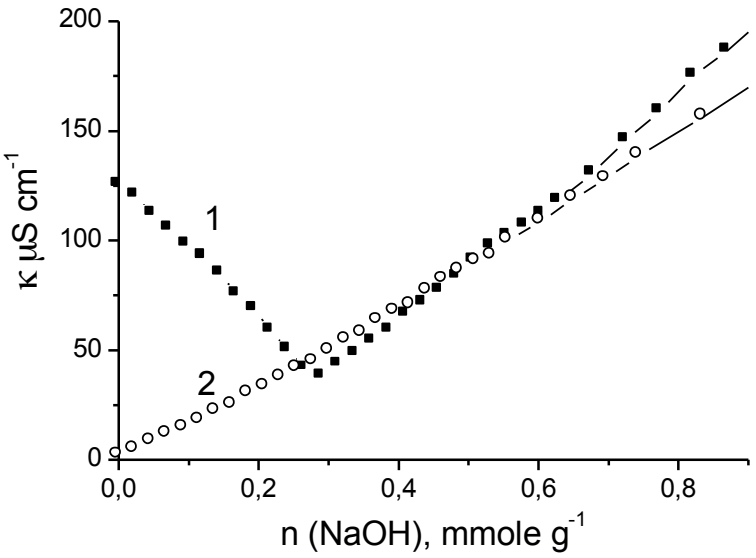


Fig. 3.1. Curves of conductimetric titration of SiO_2 with covalently attached groups of ethylsulfonic acid (1) and unmodified structurally ordered silica based material (SBA type) (2)

The results presented on Fig. 3.3 indicate that concentration of immobilized acidic groups for different MCM-41-SH/SO_3H-X samples, which were determined form the position of the curve minimum, depends on concentration of the applied oxidizing agent. Particularly it is linear in the range of H_2O_2 concentrations from 0.2 to 2.5 mmol L^{-1}. So, from the titration results it can be suggested that the transformation degree of immobilized thiol groups to sulfonic acid moieties grows proportionally to the increase of hydrogen peroxide concentration in the reaction mixture. The curve of conductimetric titration of MCM-41-SH/SO_3H-1 (a sample that was not treated with

H_2O_2, but was stored on air) also exhibits a small V-shaped minimum, which corresponds to 30 μmol g^{-1} of $–SO_3H$ (Fig. 3.3, solid square). The origin of sulfonic acid groups presented at the MCM-41-SH surface is concerned with spontaneous oxidation on air and will be discussed hereafter.

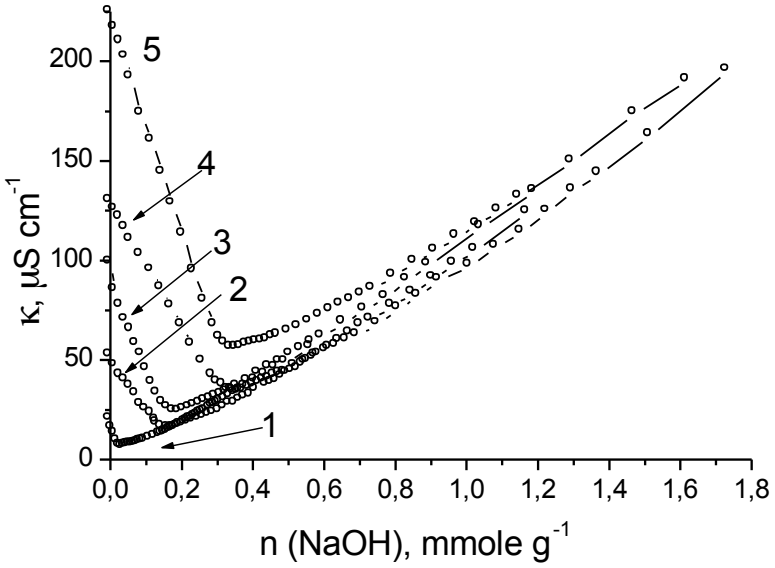


Fig. 3.2. Curves of direct conductimetric titration of differently oxidized samples: MCM-41-SH/SO_3H-X, where (*1*) X = 1, (*2*) X = 2, (*3*) X = 3, (*4*) X = 4, (*5*) X = 1

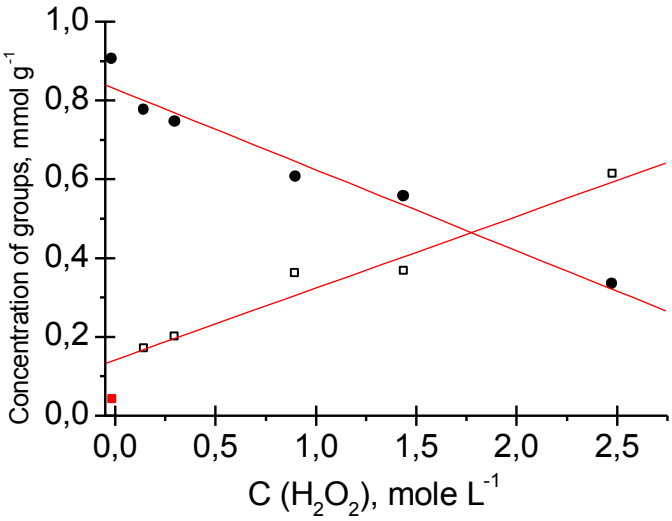


Fig. 3.3. Variation of thiol (solid circles) and sulfonic acid concentrations (hollow circles) with quantity of oxidizing agent used during the synthesis

Back-conductimetric titration of the Ag^+ excess with NaCl was performed to quantify immobilized propylthiol groups on MCM-41-SH/SO_3H-X samples. The general reaction that takes place at the surface site under Ag^+ treatment can be presented by next equation:

$$\overline{SiO_2-(CH_2)_3-SH} + Ag^+ \Rightarrow \overline{SiO_2-(CH_2)_3-SAg} + H^+ \qquad (3.1)$$

In order to minimize the influence of silica surface silanol groups and immobilized alkyl-sulfonic groups, reaction was performed in acidic medium [213]. It was stated that in the proposed conditions a nonspecific bounding of silver ions didn't exceed the value of detection error.

The results of –SH group determination on different samples of MCM-41-SH/SO_3H-X by conductimetric titration, are presented on Fig. 3.3. It can be seen that the concentration of immobilized propylthiol linearly decreases with increasing of H_2O_2 concentration in the range 0.2 - 2.5 mmol L^{-1}.

Nevertheless, correlation between concentration of H_2O_2 in solution and transformation of –SH to -SO_3H is limited. Complete transformation of –SH to -SO_3H is newer reached neither in this research nor in other known sources [191, 214]. Indeed, from Table 3.1, where the compositions of immobilized layer for different samples of MCM-41-SH/SO_3H-X are summarized, it can be seen that for selected conditions maximum degree of transformation (ω_H+) from –SH to –SO_3H groups is 65%. The results obtained from conductimetric titration of MCM-41-SH/SO_3H-X agreed with the data received from elemental analysis of MCM-41-SH/SO_3H-X samples (see Table 3.1). Indeed, for all MCM-41-SH/SO_3H-X samples overall concentration of –SH and –SO_3H groups (ΣC_L), determined from conductimetric titration is about equal to the concentration of immobilized groups determined from elemental analysis on sulfur. In this regard, all MCM-41-SH/SO_3H-X samples, synthesized by hydrogen peroxide oxidation are polyfunctional and contain at least two types of immobilized groups: propylthiol and sulfonic acid.

Table 3.1

Concentrations of different sulfur groups in MCM-41-SH/SO_3H-X series

Sample	$C(H_2O_2)$, mmol L^{-1}	C(-SO_3H), mmol g^{-1}	C(-SH), mmol g^{-1}	ΣC_L, mmol g^{-1}	ΣC_L[c], mmol g^{-1}	ω_H+, %
MCM-41-SH	0	0	0.931	0.931	1.06	0
MCM-41-SH/SO_3H-1	0[a]	0.035	0.898	0.933		4
MCM-41-SH/SO_3H-2	0.16	0.164	0.769[b]	-		18
MCM-41-SH/SO_3H-3	0.31	0.194	0.739[b]	-		21
MCM-41-SH/SO_3H-4	0.91	0.354	0.599	0.953		37
MCM-41-SH/SO_3H-5	1.45	0.361	0.550	0.911		40
MCM-41-SH/SO_3H-6	2.49	0.606	0.327[b]	-		65

[a] oxidation on air
[b] the values were calculated from the total concentration of sulfur bearing groups
[c] concentration determined by elemental analysis

As it is illustrated on Fig. 3.3, linear correlation exists between H_2O_2 concentration and –SO_3H loading on MCM-41-SH/SO_3H-X. So it can be expected that adding MCM-41-SH to 5 mM solution of H_2O_2 will follow complete oxidation of the surface layer to –SO_3H groups. Nevertheless such transformation is not observed for any concentration of H_2O_2 and can only be achieved when the concentration of thiol groups at the surface is low [201]. Such a restriction, in case of mild oxidation with H_2O_2, is generally attributed to formation of disulfide groups stable to oxidation [215]. To explain increasing in oxidation stability of immobilized layer on TSFH its FTIR, XPS and TPD-MS spectra were studied.

3.2 FTIR spectra of MCM-41-SH/SO_3H-X

FTIR spectra of MCM-41-SH/SO_3H-X samples show characteristic peaks of stretching (2982, 2929, 2898 and 2858 cm^{-1}) and deformation (1450, 1411 and 1344 cm^{-1}) vibrations of aliphatic CH_2-groups. This is evidence of MCM-41-SH/SO_3H-X stability against a destructive effect of oxidation. Low-intense adsorption of S–H stretching band from propylthiol was also registered at 2569 cm^{-1} for MCM-41-SH only (see Fig. 3.4). Due to low intensity of this band it is hidden in background of other MCM-41-SH/SO_3H-X samples. Instead they show characteristic asymmetric vibrational modes of -SO_3H group at 1367 cm^{-1}.

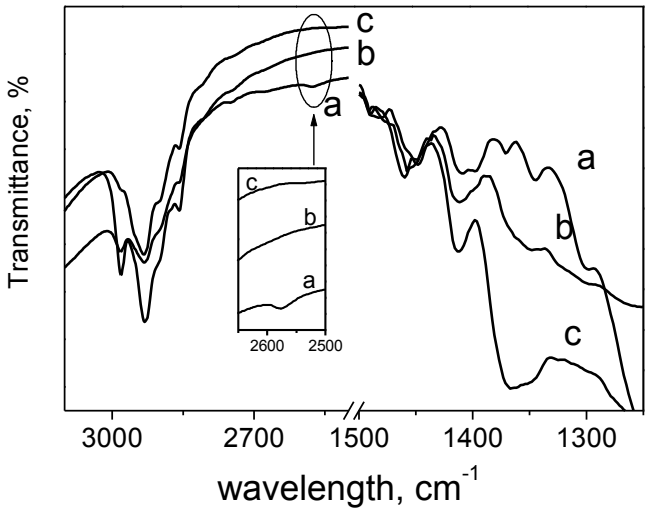


Fig. 3.4. Fragments of FTIR spectra of MCM-41-SH (a), MCM-41-SH/SO_3H-4 (b) and MCM-41-SH/SO_3H-6 (c)

3.3 XPS study of MCM-41-SH/SO_3H-X

As an alternative approach to confirm the above titration results, we have performed XPS analysis of the same series or materials. XPS spectra (S2p core level) of MCM-41-SH/SO_3H-X series were fitted using doublets $2p_{1/2}$ and $2p_{3/2}$ separated by a spin-orbit splitting of 1.2 eV. The S($2p_{1/2}$) peak area was constrained to be one half of the area from major S($2p_{3/2}$) band. For MCM-41-SH sample the energy of the major band in the doublet is observed at 163.3±0.1 eV (Fig. 3 a) and it is typically attributed to S(II) in mono- or poly-sulfide species [162]. This position remains constant for the whole MCM-41-SH/SO_3H-X set, while the peak area decreases with increasing of oxidation rate of the immobilized layer. For oxidized MCM-41-SH/SO_3H-X samples together with doublet at 165 eV another asymmetric peak at higher energy is observed (Fig. 3.5).

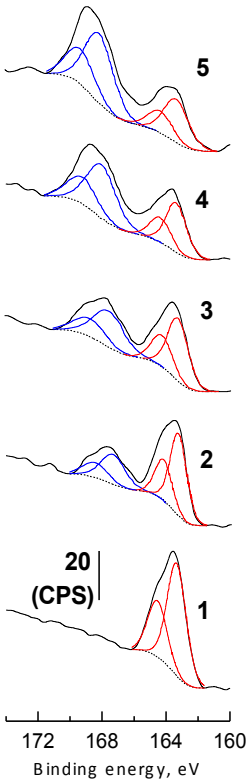


Fig. 3.5. XPS spectra (S_{2p} core level) of MCM-41-SH (*1*), MCM-41-SH/SO_3H-3 (*2*), MCM-41-SH/SO_3H-4 (*3*), MCM-41-SH/SO_3H-5 (*4*), MCM-41-SH/SO_3H-6 (*5*)

The intensity of this peak is growing with increasing of oxidation degree of the immobilized layer, Fig.3.5. The later peak is shifted by 5 eV to higher binding energy in respect to the position of S(II) one, and attributed to S(VI) sulfur species in alkylsulphonic fragments [162]. Consequently, XPS data confirms formation of alkylsulfonic acid species on the MCM-41-SH/SO_3H-X surface. Similar to the results of conductimetric titration, XPS data denote incomplete transformation of propylthiol into propylsulfonic groups under H_2O_2 treatment: spectrum of MCM-41-SH/SO_3H-6 sample that was obtained in highest concentration of H_2O_2 is still characterized with both S(II) and S(VI) bands, Fig.3.5.

The XPS data cannot be used directly for quantitative determination of concentration of bonded species because of unavailability of the standards (and because this technique is only analyzing the extreme surface of the materials), but the ratio of intensities (*h*) for different XPS peaks correlates with the concentration ratio for corresponded fragments. Table 3.2 summarized the results obtained form XPS spectra

of different MCM-41-SH/SO_3H-X samples together with data obtained from their conductimetric titration. Better correlation between S(VI)/S(II) ratio and ω_H+, % is observed for data obtained from the peak intensities but not from mass concentration according to the quantification report of XPS spectra analyzer.

Table 3.2.

Data from the XPS spectra

Sample	Height (*h*) of the peak, cm		S(VI)/S(II), %		Results of conductimetric determination		
	S(II)	S(VI)			*C*(SH), mmol g^{-1}	*C*(SO_3H), mmol g^{-1}	ω_H+, %
MCM-41-SH/SO_3H-6	1.7	2.6	60	68[a]	0.33	0.61	65
MCM-41-SH/SO_3H-5	2.1	1.9	48	65[a]	0.55	0.36	40
MCM-41-SH/SO_3H-4	2.4	1.5	38	48[a]	0.60	0.35	37
MCM-41-SH/SO_3H-3	4.4	1.6	26	40[a]	0.74	0.19	21

[a]Mass concentration according to the quantification report of XPS spectra analyzer

Both the ratio of S(VI) to S(II) peak intensities in XPS spectra of MCM-41-SH/SO_3H-X and concentrations of –SO_3H to -SH found from conductimetric measurements are in linear correlation with the quantity of oxidizing agent used for MCM-41-SH/SO_3H-X synthesis, Fig. 3.6.

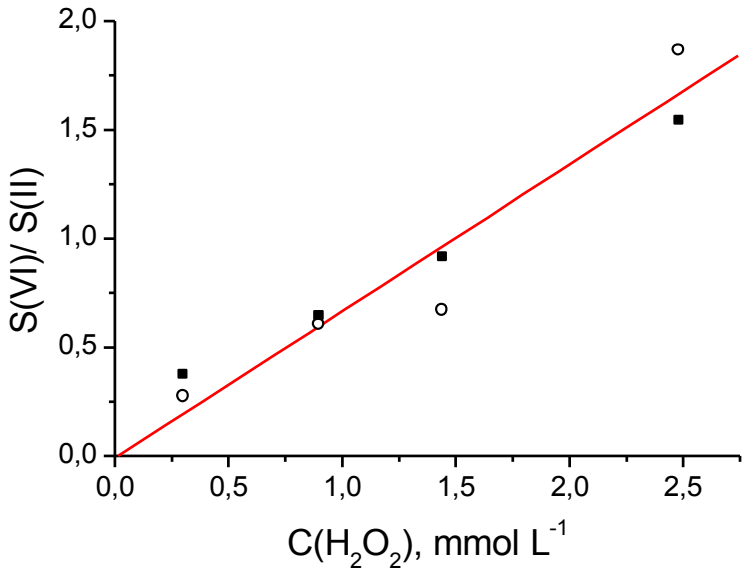


Fig. 3.6. Correlation of –SO_3H to –SH ratio, calculated from conductimetric titration curves (hollow circles) and heights of XPS peaks (solid squares), with concentration of

added H_2O_2

It is generally believed that oxidation of immobilized –SH groups leads not only to $–SO_3H$ but also to disulfide moieties (type 1-3 on scheme 3.1). By formation of more stable to oxidation disulfides is commonly explained by incomplete transformation of –SH to $–SO_3H$ under H_2O_2 treatment [201]. From XPS spectra -SH and –S-S– groups cannot be differentiated: XPS bands of hydrosulfide and polysulfides are typically overlapped as far as the binding energies of mono- and polysulfides differ within 1 eV. There also is no direct evidence for absolute selectivity of back-conductimetric titration used in this research to determine concentration of –SH groups. Therefore the methods applied above cannot prove or refute the presence of disulfide bridges on TSFH surface.

3.4 Study of MCM-41-SH/SO_3H-X by TPD-MS

In order to reveal the products of incomplete oxidation of immobilized thiols, the method of thermo-programmed desorption with mass spectroscopy detection (TPD-MS) was applied. Some results of TPD-MS study of MCM-41-SH/SO_3H-X is presented on Fig. 3.7. Under thermal treatment MCM-41-SH/SO_3H-X samples release H_2S, H_2S_2, SO_2 and CH_3-CH=CH_2. Hydrogen sulfide is observed for all MCM-41-SH/SO_3H-X samples at high enough temperature (337°C), Fig.3.7. This peak is asymmetric and has an evident arm at 400°C. Also all samples discharge H_2S_2 at 440-450°C but intensity thermal desorption of this compound is very low (less than 5% from H_2S intensity). H_2S_2 can only be generated from thermal decomposition of disulfides like 1-3 (scheme 3.1). So from TPS-MS spectra of MCM-41-SH/SO_3H-X it can be suggested that the contribution of disulfide moieties to the composition of the immobilized layer on oxidized MCM-41-SH is not significant. In this context, the hypothesis of disulfide bridge formation as explanation of incomplete –SH to $–SO_3H$ transformation seems to be wrongful, at least for MCM-41-SH/SO_3H-X materials, synthesized by co-condensation, where propylthiol groups are incorporated into the matrix during the sol-gel synthesis.

Under thermal treatment the MCM-41-SH/SO_3H-X samples, sulfur dioxide is released, Fig 3.7. The intensity of its discharge is growing with the rate of MCM-41-SH/SO_3H-X oxidation. For the maximal oxidized sample its intensity predominates over that of hydrogen sulfide peak.

Similarly to the thermal desorption of hydrogen sulfide, the discharge of sulfur dioxide has two temperature extremes at 256°C and 400°C. Existence of several maximums of discharge for hydrogen sulfide and sulfur dioxide suggest different mechanisms of their generation.

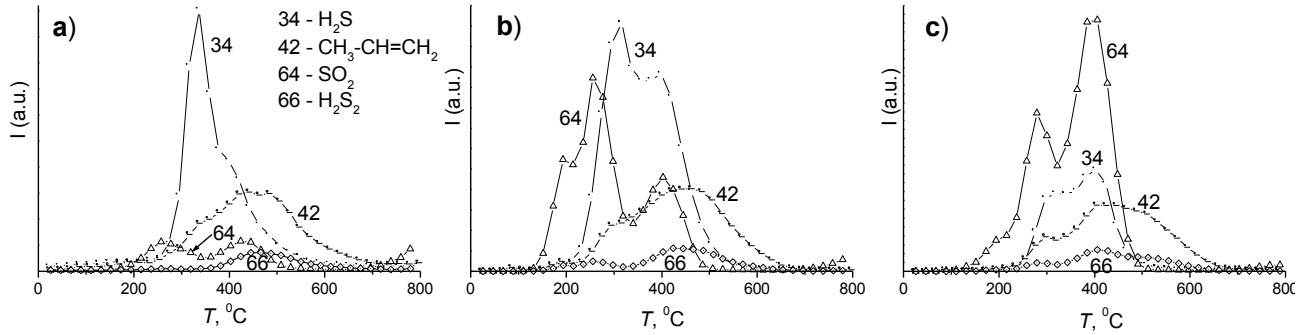
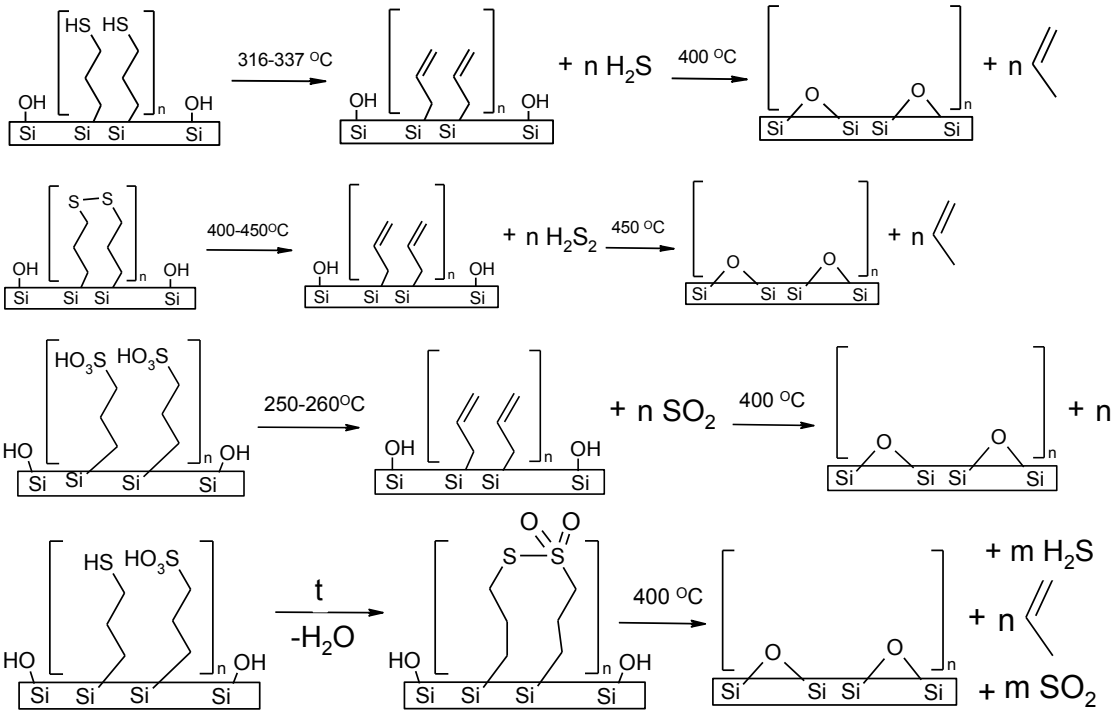


Fig. 3.7. TPD-MS study of MCM-41-SH/SO_3H-1 (a), MCM-41-SH/SO_3H-3 (b), MCM-41-SH/SO_3H-6(c)

Predominance of the low-temperature H_2S discharge for lightly oxidized MCM-41-SH/SO_3H-X (where x=1 and 3) assign the peak observed at 320-330°C to the thermal decomposition of thiol groups in accordance with the scheme (3.2). H_2S_2 is generated form decomposition of dipropyldisulfides (type 1, scheme 3.1), according to scheme 3.3. Peak of SO_2 discharge observed form MCM-41-SH/SO_3H-X at low-temperature (260°C) is assign to the thermal decomposition of propylsulfonic acid groups according to scheme 3.4. As far as high-temperature peaks for hydrogen sulfide and sulfur dioxide discharge is observed at the same temperature (400°C) simultaneous decomposition of the surface fragment reviling both of these gases can be suggested. This fragment is presented on scheme 3.1 as thiosulfonate with formula 4. Formation and thermal decomposition of immobilized thiosulfonate under TPD-MS is presented by scheme 3.5.



The shape of H_2S and SO_2 thermo-desorption curves depends on MCM-41-SH/SO_3H-X oxidation degree. For lightly oxidized sample (MCM-41-SH/SO_3H-1), containing mostly propylthiol groups, the low-temperature shoulder of H_2S discharge (at 320°C) is twice as intensive as the high-temperature one (at 400°C), Fig.3.7. Contrary, the intensity of high-temperature shoulder of H_2S discharge for MCM-41-SH/SO_3H-6, having only 35% of –SH group left, is higher than a low-temperature one. For later sample sulfonic acid micro-environment for residual –SH moieties is more likely than for the first one. This microenvironment can stabilize –SH fragment due to the formation of thiosulphonate, according to scheme 3.5. Similar effect is observed for SO_2 thermo-desorption curve. For MCM-41-SH/SO_3H-6 sample the high temperature shoulder as twice as high of low-temperature one, Fig.3.7.

Consequently, MCM-41-SH/SO_3H-X samples in all degree of surface oxidation have bi-functional nature of immobilized layer with 0 to 65% of propylsulphonic and from 35 to 100% of propylthiol groups. No essential amount of dipropyldisulfide is detected for any samples with oxidation degree from 0 to 65%, so stabilization towards complete oxidation by H_2O_2 cannot be explained by the surface disulfide formation.

Contrary, neighbor –SH and –SO_3H fragments stabilized each other probably due to formation of thiosulphonate.

3.5 Effect of exposition to an oxic atmosphere (air)

The proposed conductimetric technique was used to determine composition of immobilized layer on MCM-41-SH/SO_3H-2.X samples obtained from MCM-41-SH/SO_3H-2.0 by its oxidation on air. Figure 3.8 shows the curves of conductimetric titration of MCM-41-SH/SO_3H-2.X samples with a base, which were disposed on air during different periods of time.

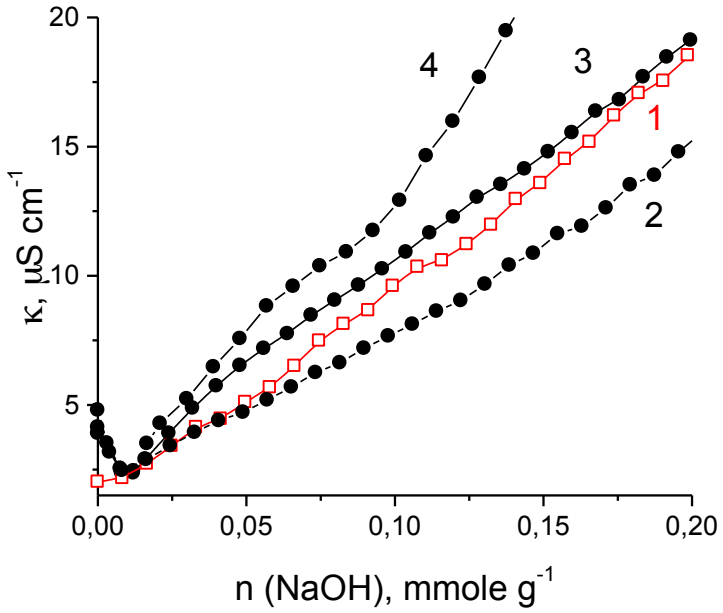


Fig. 3.8. Curves of conductimetric titration of MCM-41-SH (1), MCM-41-SH/SO_3H-2.1 (2), MCM-41-SH/SO_3H-2.2 (3) and MCM-41-SH/SO_3H-2.3 (4) with NaOH

Table 3.3

Concentrations of different sulfur groups in MCM-41-SH/SO_3H-2.X series

Sample	$C(H_2O_2)$, mmol L^{-1}	C(-SO_3H), mmol g^{-1}	C(-SH), mmol g^{-1}	ΣC_L, mmol g^{-1}	ΣC_L [b], mmol g^{-1}	ω_{H^+}, %
MCM-41-SH/SO_3H-2.1	0[a]	0.015±0.003	0.572±0.024	0.587±0.027	0.63	3
MCM-41-SH/SO_3H-2.2						2
MCM-41-SH/SO_3H-2.3						2

[a] oxidation on air
[b] concentration determined by elemental analysis

As it can be seen from the figure, a typical minimum for sulfonic acid groups is observed at each titration curve. The results for all the curves are in close agreement, stating the presence of 15 μmol $g^{-1}$of sulfonate groups and 572 μmol g^{-1} of thiol groups. Comparison of these curves with the curve of the sample, which was kept in atmosphere of argon, shows that disposition of thiol groups on air provokes insignificant oxidation, which doesn't increase with prolongation of the contact.

3.6 Conclusions

The proposed single instrumental method is applicable for detection of thiol and sulfonic acid groups simultaneously present at the surface of silica-based mesoporous organic-inorganic materials containing up to 1 m g^{-1} of propylthiol groups and 15-600 μmol g^{-1} of sulfonic acid groups. Reliability of the obtained results is confirmed by the repeatable coincidence of the total concentration of thiol and sulfonic acid groups calculated by conductimetric titration, which in turn agrees with the data of elemental analysis. It is demonstrated that thiol and sulfonic acid groups are present at the surfaces of all studied samples except the one that was synthesized in conditions of inert atmosphere. The concentrations of strong acid moieties calculated from conductimetric titration curves were found to be in linear proportion to the quantity of added oxidant, which prove the transformation of one groups into others. But still, in agreement with the XPS and TPD-MS data, the proposed method of titration proves incomplete transformation of thiol groups to sulfonic acid moieties (65%), even at 100-fold molar excess of oxidant. TPD-MS analysis of MCM-41-SH/SO_3H-X samples did not reveal any formation of disulfide bonds during oxidation by hydrogen peroxide. On the contrary, it was suggested that thiol groups surrounded by sulfonic groups are stable to oxidation by hydrogen peroxide owing to the formation of thiosulfonate bonds. At the same time, it is also shown that thiol-functionalized materials synthesized on air contain small concentrations of sulfonic acid groups (up to 3 % of the total concentration of sulfur-containing groups) and are not likely to further oxidation by being disposed on air in room conditions for 2 months.

Chapter IV

Une gamme d'adsorbants à base de silice mésoporeuse fonctionnalisée par des groupements thiol a été préparée par co-condensation de mercaptopropyltriméthoxysilane et de tétraéthoxysilane en présence de bromure de cétyltriméthylammonium utilisé comme tensioactif directeur de structure. Après élimination du tensioactif, ils ont été partiellement oxydés à des degrés divers afin d'obtenir des matériaux bi-fonctionnalisés contenant à la fois des fonctions thiol et acide sulfonique (MCM-41-SH/SO_3H). L'hybride organique/inorganique obtenu a été appliqué pour l'élimination des espèces du chrome selon un mécanisme de réduction-sorption impliquant la réduction de Cr(VI) par les groupes thiol et l'immobilisation du Cr(III) résultant sur les fonctions acide sulfoniques. Ces réactions sont fortement influencées par le pH, et les conditions optimales pour une séquestration efficace du chrome résultent d'un compromis à trouver entre des valeurs de pH suffisamment faibles pour assurer une réduction quantitative de Cr(VI), mais pas trop faibles pour permettre la fixation de Cr(III) sur les groupements sulfonate. Cet optimum est atteint pour un pH entre 2 et 3. L'effet du rapport solide/solution et des quantités relatives des groupements SH et $–SO_3H$ a également été examiné. Même si la réduction de Cr(VI) par les groupements thiol conduit à la formation d'acides sulfonique, leur quantité n'est pas suffisante pour assurer l'immobilisation quantitative des espèces Cr(III) produites. L'immobilisation quantitative est seulement atteinte avec des matériaux contenant déjà des groupements acide sulfonique avant leur mise en contact avec des solutions de Cr(VI). La spéciation redox des espèces du soufre et du chrome a été analysée par spectroscopie des photoélectrons X (XPS) et utilisée afin de confirmer le mécanisme proposé.

4 Cr(VI) reduction and concomitant Cr(III) immobilization on bifunctionalized mesoporous silica containing both thiol and sulfonic acid moieties (MCM-41-SH/SO_3H)

4.1 Sorption of Cr(III) on mesoporous silicas functionalized with thiol or sulfonic acid groups

In acidic medium, where Cr(III) species are positively charged (Cr^{3+}, or more accurately the Cr(III) aqua complex $Cr(H_2O)_6^{3+}$), sulfonic acid-functionalized mesoporous silica (MCM-41-SH,SO_3H-6) is likely to immobilize these cations due to favorable electrostatic interaction between $Cr(H_2O)_6^{3+}$ and sulfonate groups. This is illustrated in Figure 4.1, showing a pH dependence of the process (see part A). At rather low solid-to-solution ratio (i.e., 0.8 g L^{-1}), the sorption yield decreased when decreasing pH in the range studied (see curve "c" on Fig. 4.1.A) because of much higher amount of competing H^+ species (-SO_3H groups less dissociated). This effect was also observed, but less marked, at higher solid-to-solution ratio (i.e., 6 g L^{-1}), indicating maximum adsorption capacities at pH > 2.5 (see curve "d" on Fig. 4.1. A). Similar pH trend was reported for Cr(III) adsorption on phosphonic acid functionalized adsorbents [216]. Note that in the investigated pH range and Cr(III) concentration, speciation calculations show that both $Cr(H_2O)_6^{3+}$ and $Cr(OH)(H_2O)_5^{2+}$ species are likely to exist so that both these cations are expected to participate to the binding process (see, Fig. 1.3., Chapter I). Strictly speaking, the hydroxylated forms of Cr(III) (e.g., $Cr(OH)(H_2O)_5^{2+}$) are also likely to interact with the surface silanol groups, but this reaction is expected to start at pH values above 4.5 [217]. Even if the exact sorption mechanism cannot be stated unambiguously from these data, the process can be explained by the next scheme: (a) in strong acidic media where immobilized sulfonic acid is not ionized, no Cr(III) adsorption is possible; (b) at pH > 2, electrostatic interactions become possible and Cr(III) is likely to be bound to sulfonate moieties; (c) in weakly acidic conditions where the silica surface starts to be positively-charged (Fig. 1.3., Chapter I), additional

chromium adsorption can be due to $Cr(OH)(H_2O)_5^{2+}$ binding to silanol/silanolate groups.

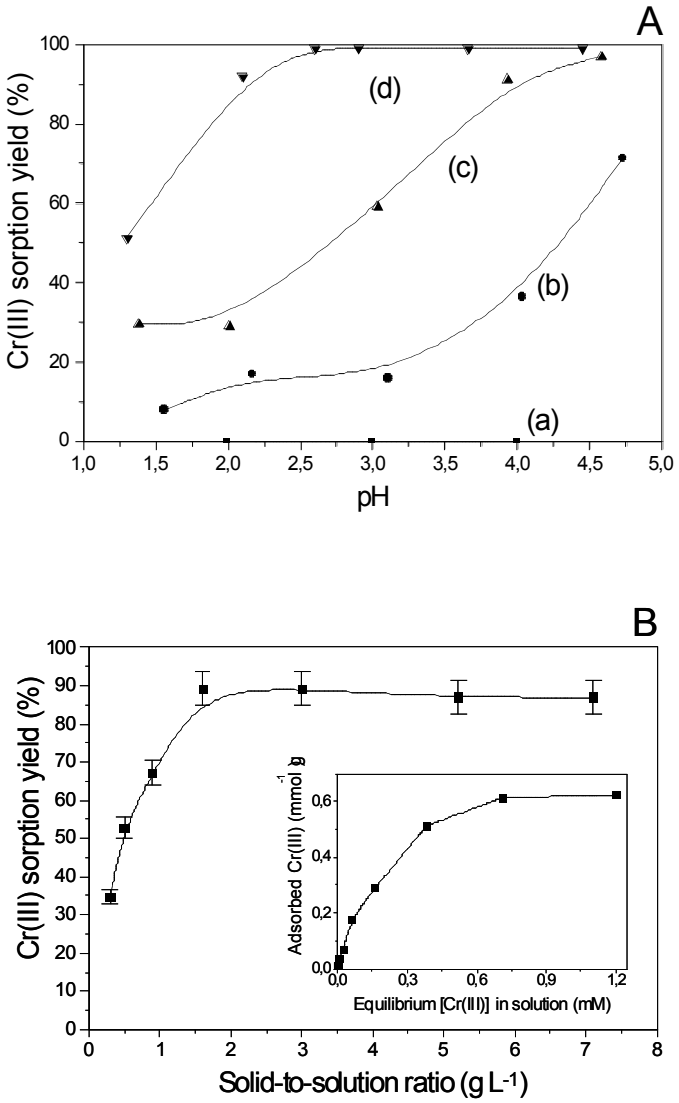


Fig. 4.1. (A) Variation of Cr(III) sorption yields as a function of pH, using various adsorbents: MCM-41-SH (a), MCM-41-SH/SO_3H-1 (b), and MCM-41-SH/SO_3H-6 (c, d); experimental conditions: solid-to-solution ratios of 0.8 g L^{-1} (a-c) or 6 g L^{-1} (d); starting Cr(III) concentration in solution equal to 50 μM. (B) Variation of Cr(III) sorption yields on MCM-41-SH/SO_3H-6 at pH 2 as a function of the solid-to-solution ratio (Inset: adsorption isotherm obtained in the same conditions).

The effect of solid-to-solution ratio is better shown on Part B of the figure 4.1 (from data obtained at pH 2). Adsorption yields of about 90% were observed down to

1.5 g L^{-1} of adsorbent whereas lower contents of materials in suspension gave rise to lower Cr(III) adsorption (e.g., 53% at 0.5 g L^{-1}, a value corresponding yet to an excess of sulfonate groups with respect to the amount of chromium in solution). These results indicate that rather high contents of adsorbent would be necessary to enable the uptake of all Cr(III) species from dilute solutions (the sorption yield being function of pH) and that the experimentally observed capacities are much lower than the amount of binding sites in the material. On the other hand, the uptake process was very fast as equilibrium was reached within 1 min, indicating the presence of minimal mass transfer resistances in agreement with other observations made for metal ion binding to ordered mesoporous silica bearing organo-functional groups [189, 191]. Cr(III) sorption to MCM-41-SH/SO_3H-6 at pH 2 was further characterized by drawing the corresponding isotherm (inset in Fig. 4.1.B) indicating a maximum adsorption capacity of 32 mg g^{-1} (0.62 mmol g^{-1}), which is of the same order of magnitude as those reported for other cation-exchanger bearing sulfonic acid (see Fig. 1.7 in Chapter I) and solid-phase extractants used for Cr(III) removal (for comparison see Table 1.8 in Chapter I). This value corresponds to an adsorbed quantity exactly equal to the amount of sulfonic acid groups in the material (as determined by titration, more details in Chapter IV), confirming again the optimal accessibility to binding sites in ordered mesoporous adsorbents [189, 191].

By comparison and unsurprisingly, no Cr^{3+} binding to thiol-functionalized mesoporous silica (MCM-41-SH) was detected, at least when the adsorbent was prepared in inert atmosphere (see curve "a" on Fig. 4.1. A). This indicates that Cr^{3+} is not likely to be complexed by thiol groups (under these conditions) and further confirms negligible binding to the surface silanol groups in acidic medium. Interestingly, some Cr^{3+} binding was observed on thiol-functionalized mesoporous silica, which was prepared without strict atmosphere control (i.e., in air), but the uptake yield was significantly lower than that observed on MCM-41-SH/SO_3H-6 (compare curves "b" and "c" on Fig. 4.1. A). This can be explained by the assumption that materials preparation in the presence of oxygen (especially the template removal step in acidic medium) has led to a bi-functionalized system containing both thiol and sulfonic acid

groups (named afterwards MCM-41-SH/SO_3H-1). The existence of both these groups was demonstrated by XPS (Fig. 4.2), by means of the S_{2p} lines located at 163.4 eV (-SH) and at 168.5 eV (-SO_3H) [191].

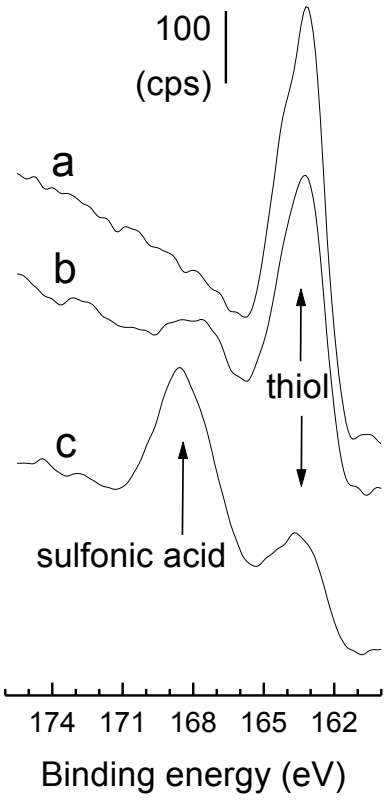


Fig. 4.2. XPS spectra (S_{2p} core-level) of MCM-41-SH (a) MCM-41-SH/SO_3H-1 (b) and MCM-41-SH/SO_3H-6 (c).

Comparison of curves "a" and "c" in Figure 4.2 clearly indicates the successful, yet incomplete, oxidation of MCM-41-SH into MCM-41-SH/SO_3H-1 when treating MCM-41-SH by H_2O_2. When preparing the thiol-functionalized adsorbent in air, curve "b" in Figure 4.2 indicates the presence of a small contribution of the S_{2p} line located at 168.5 eV, pointing out the oxidation of some thiol groups into hexavalent sulfur in the course of the material preparation procedure. From acid-base titration, one can evaluate that about 25% of thiol groups have been oxidized into MCM-41-SH/SO_3H-1. All these observations explain the results depicted on Figure 4.1.A and especially the intermediary behavior of MCM-41-SH/SO_3H-1 in comparison to MCM-41-SH and MCM-41-SH/SO_3H-6 adsorbents with respect to Cr^{3+} binding.

4.2 Reduction of Cr(VI) and subsequent immobilization of Cr(III) on bi-functionalized (thiol + sulfonic acid groups) mesoporous silicas

4.2.1 Possible reduction of Cr(VI) and partial Cr(III) sequestration

Thiol-functionalized material prepared without taking care about oxic atmosphere has been chosen for the first tests because this solid contains already both organo-functional groups of interest (thiol and sulfonic acid). Figure 4.3.A shows that adding MCM-41-SH/SO_3H-1 particles into Cr(VI) solutions results in the uptake of some chromium species. The process starts at pH lower than 5 to increase rapidly when decreasing pH, giving rise to a maximal effectiveness of about 55% sequestration at pH 1-2. Chemical analyses after equilibration have revealed the presence of both Cr(III) and Cr(VI) in the supernatant solution. Cr(VI) concentration in solution was found to sharply decrease with lowering pH (Fig. 4.3. B). This demonstrates the possible reduction of Cr(VI) by thiol groups immobilized in the mesoporous material, in agreement with observations made with other thiol-containing solids, and this process is more quantitative at lower pH values. Such pH dependence is consistent with the variation of the apparent potentials for Cr(VI)/Cr(III) redox couple (i.e., increasing when decreasing pH, see Fig. 1.2 in chapter I).

On the opposite, the remaining amount of Cr(III) in solution was found to be more important when decreasing pH (see Fig. 4.3. B, in agreement with pH effect on Cr(III) binding to MCM-41-SH/SO_3H, Fig. 4.1. A), suggesting that an optimal pH would have to be found on the basis of a compromise between a value low enough to ensure quantitative Cr(VI) reduction and not too low to enable Cr(III) sequestration.

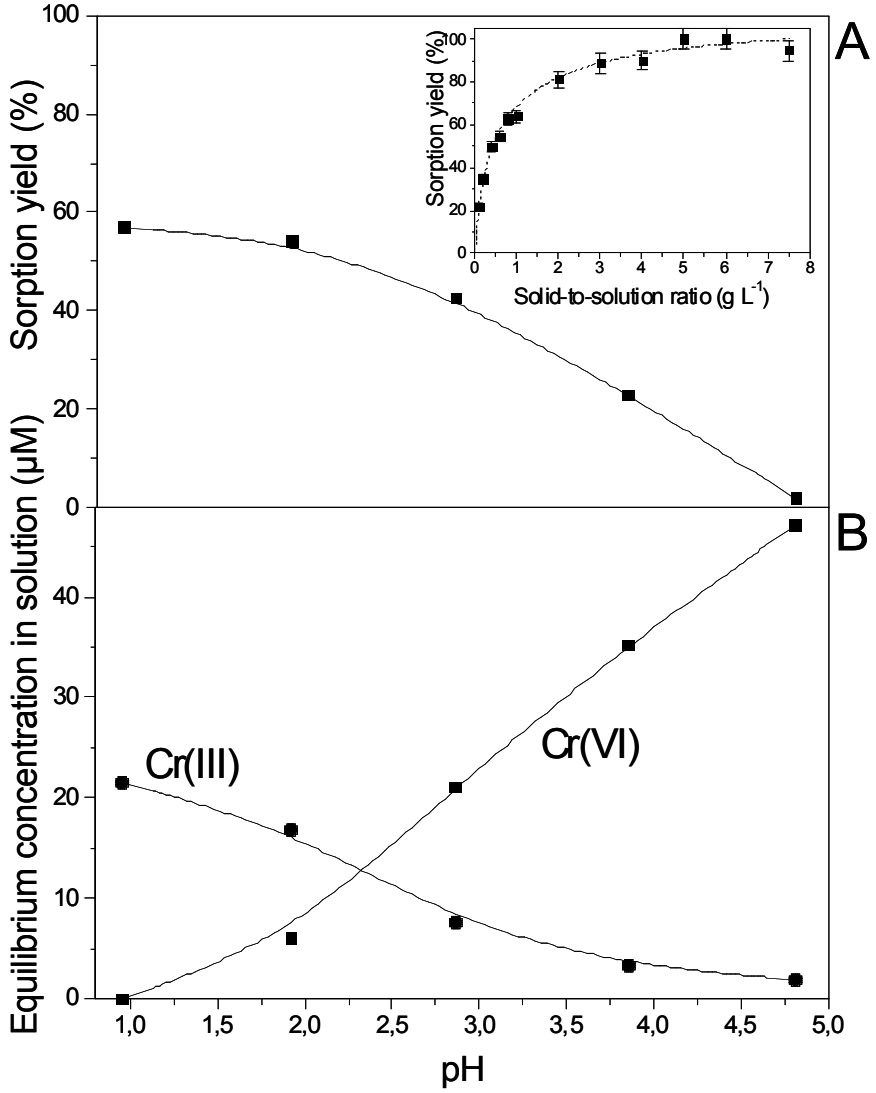


Fig. 4.3. Variation as a function of pH of (A) total chromium sorption yield and (B) equilibrium concentration of Cr(VI) and Cr(III) in solution after reaction with MCM-41-SH/SO_3H-1; (experimental conditions: solid-to-solution ratios of 0.5 g L^{-1}; starting Cr(VI) concentration in solution equal to 50 µM.)

Inset in part (A): variation of chromium sorption yields at pH 2 as a function of the solid-to-solution ratio.

XPS analysis of the solid phase has been carried out to evidence the speciation of adsorbed chromium. As shown on Figure 4.4, the signal obtained for a sample having reacted with chromium in equimolar ratio to thiol groups was at the noise level (curve

"a"). The experiment was thus repeated using a large excess of Cr(VI) in solution and the resulting spectra (curve "b") was now visible, consisting of two main peaks corresponding to $2p_{3/2}$ and $2p_{1/2}$ core levels of chromium. The main $2p_{3/2}$ peak was located at a binding energy of 577.3 eV, which corresponds to Cr(III) on the basis of values ranging between 577 and 577.5 eV for $Cr2p_{3/2}$ reported for Cr(III)-containing materials [67, 218, 219]. The $Cr2p_{1/2}$ signal located at 586.7 eV also supports the existence of Cr(III) [218]. This demonstrates that Cr(VI) species have been indeed reduced by thiol groups and that the adsorbed species are really in the form of Cr(III) on the material. This appears to be advantageous in comparison to the commonly used activated carbon adsorbents for which the presence of both Cr(III) and the more toxic Cr(VI) species has been identified on the solid [67].

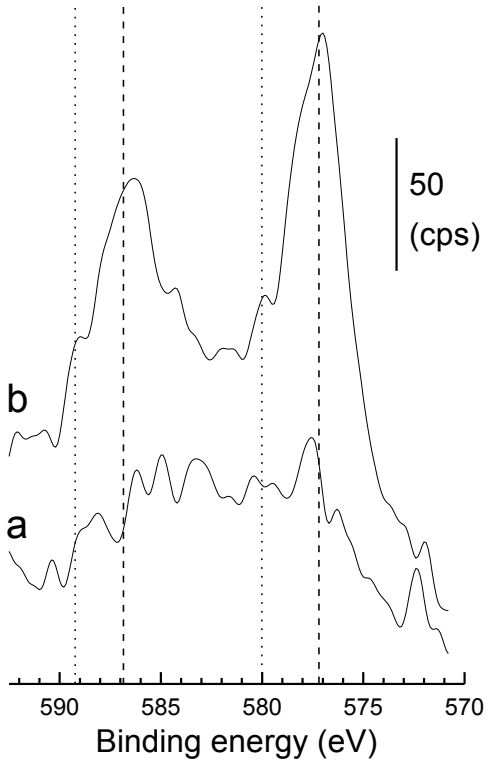


Fig. 4.4. XPS spectra (Cr_{2p} core-level) of MCM-41-SH/SO_3H-1 after contacting (a) equimolar and (b) large excess (0.5 M) quantities of Cr (VI) with respect to thiol groups.

Cr(III) is expected to be immobilized via favorable interaction with the sulfonate groups in the MCM-41-SH/SO_3H-1 material. The binding process is most probably

more complicated than a simple ion exchange of Cr^{3+} species at sulfonic acid centers in the material as total desorption cannot be achieved (i.e., only 60% desorption in a solution made of 2M HCl, as measured after Cr(VI) reduction / Cr(III) sorption on MCM-SH/SO_3H-1). No attempt was made to characterize the exact coordination of Cr(III) in the material but this could involve the participation of silanol groups, as suggested from IR spectroscopic measurements (decrease in the absorption band of free silanol groups at 3750 cm^{-1} observed after reductive adsorption of Cr(VI) on MCM-SH/SO_3H). It should be also noted that the presence of a small contribution of Cr(VI) cannot be discarded from XPS data (possible contribution of $Cr2p_{3/2}$ signal around 579.5-580 eV [218, 219], which could be due to some impregnation of Cr(VI) (that wasn't washed out after excess treatment).

4.2.2 Influence of solid-to-solution ratio

Sorption yields can be dramatically improved by increasing the solid-to-solution ratio (see inset in Fig. 4.3.A), as expected from a higher amount of organo-functional groups to reduce Cr(VI) and to immobilize the generated Cr(III) species. These data show that quantitative uptake (i.e., 100% sorption yield) was reached at about 5 g L^{-1}, a solid-to-solution ratio corresponding to an excess of about 2 orders of magnitude of organo-functional groups in the adsorbent with respect to the initial amount of Cr(VI) in solution. In fact, the variation in sorption yields for Cr(VI) on MCM-41-SH/SO_3H-1 (inset in Fig. 4.3.A) follows a trend rather similar as that for Cr(III) sorption on most fully oxidized sample MCM-41-SH/SO_3H-6 (Fig. 4.1.B), suggesting that the limiting step would be the immobilization of Cr(III) species arising from Cr(VI) reduction and not the redox transformation of Cr(VI) by thiol groups. This is also sustained by the fact that complete Cr(VI) reduction was already achieved at a solid-to-solution ratio of 1 g L^{-1}, although only 64% of the generated Cr(III) species were bonded to the adsorbent in these conditions.

Again, pH was found to play an important role in the reduction-sorption process (Fig. 4.5) and the trend was similar as that observed with less solid in suspension (Fig. 4.3) except that both Cr(VI) reduction and Cr(III) immobilization steps were much more

quantitative. The ideal pH range was 2-3, higher values leading to incomplete Cr(VI) reduction and lower values to non quantitative Cr(III) immobilization. Taking into account this duality, the optimal pH values seem to be closer to 2 than to 3 because this situation ensures a low amount of remaining chromium species in solution that is in the form of the less toxic Cr(III) (at pH 3, the remaining chromium is Cr(VI)).

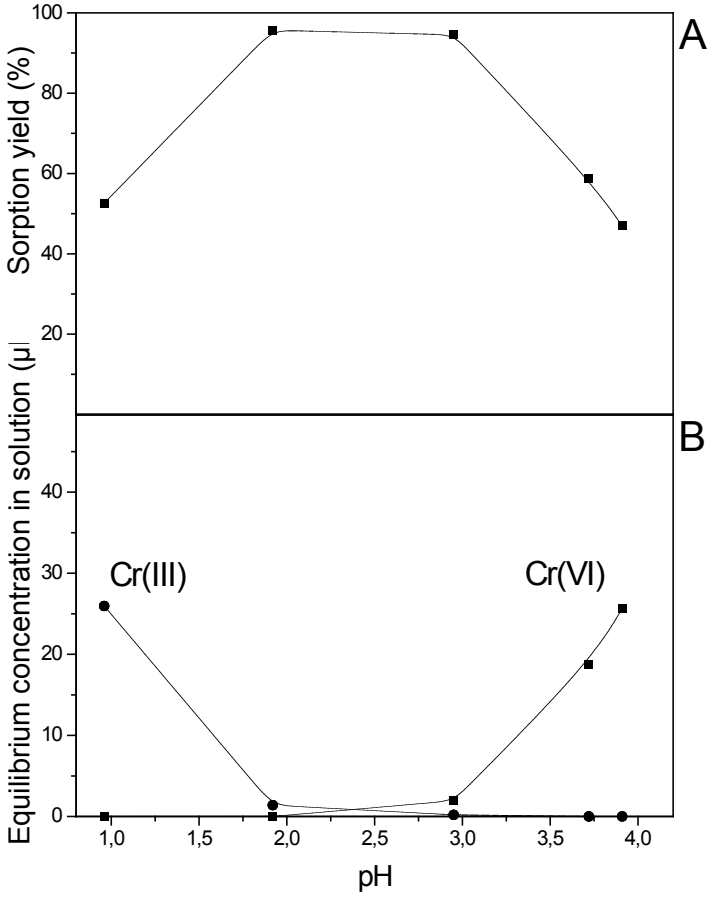


Fig. 4.5. Variation as a function of pH of (A) total chromium sorption yield and (B) equilibrium concentration of Cr(VI) and Cr(III) in solution after reaction with MCM-41-SH/SO_3H-1); experimental conditions: solid-to-solution ratios of 7.5 g L^{-1}; starting Cr(VI) concentration in solution equal to 50 µM.

4.2.3 Overall mechanism and optimization of the process

It is clear from the above results that MCM-41-SH/SO_3H-1 is likely to reduce Cr(VI) via its thiol groups and to immobilize Cr(III) species generated by this reaction via its sulfonate groups. One could be surprised, however, that Cr(III) sorption yield

was better when allowing MCM-41-SH/SO_3H-1 to react with Cr(VI) than directly with Cr(III) (compare data on Fig. 4.3.A with curve "b" on Fig. 4.1.A). For example at pH 2, 0.8 g L^{-1} of MCM-41-SH/SO_3H-1 was likely to immobilize less than 20% of Cr(III) from a 50 µM solution whereas 0.5 g L^{-1} of MCM-41-SH/SO_3H-1 in 50 µM of Cr(VI) gave rise to more than 50% binding of reduced chromium. This suggests that reaction of thiol groups with Cr(VI) would have increased the amount of sulfonate groups in the material (in agreement with increased Cr(III) binding capacities observed with adsorbent containing higher amounts of sulfonate groups, see Fig. 4.1.A). To demonstrate that point, experiments have been performed with the aid of MCM-41-SH (i.e. a thiol-functionalized mesoporous silica containing no oxidized groups), thus maintaining the reduction ability of the material but not its sequestration properties (no sulfonate groups in the starting material). In that case, Cr(VI) reduction was always quantitative (at pH 2.2) and some of the generated Cr(III) species were indeed sequestrated in the material, in a proportion reaching up to about 35 % depending on the solid-to-solution ratio (see part "a" on Fig. 4.6). Meanwhile, XPS measurements made on the solid before and after reaction point out an oxidation of some thiol groups into sulfonic acid moieties (decrease in the S_{2p} line located at 163.4 eV (-SH) with concomitant increase of that situated at 168.5 eV (-SO_3H), as much more pronounced as high was Cr(VI) concentration in solution, see Fig. 4.7).

One can rationalize the above data by the following equation (4.1):

$$\text{MCM-41-SH} + 2\,HCrO_4^- + 8\,H^+ \rightarrow \text{MCM-41-}SO_3H + 2\,Cr^{3+} + 5\,H_2O \qquad (4.1)$$

This equation does support all the trends observed beforehand. First, the redox process involving oxidation of thiol groups by Cr(VI) is more quantitative at low pH values. At this stage sulfonic acid groups are generated and they are likely to interact with Cr^{3+} cations produced concomitantly. The stoechiometry of the reaction indicates however that only one sulfonic acid group is formed when 2 Cr^{3+} cations are produced, so that all these cations cannot be retained by the material (only 35 % sequestrated in the best cases, see part "a" on Fig. 4.6). This also explains why the use of a bi-

functionalized material containing both thiol and sulfonic acid groups (i.e., MCM-41-SH/SO_3H) gave rise to better performance for the sequestration process (inset in Fig. 4.3.A).

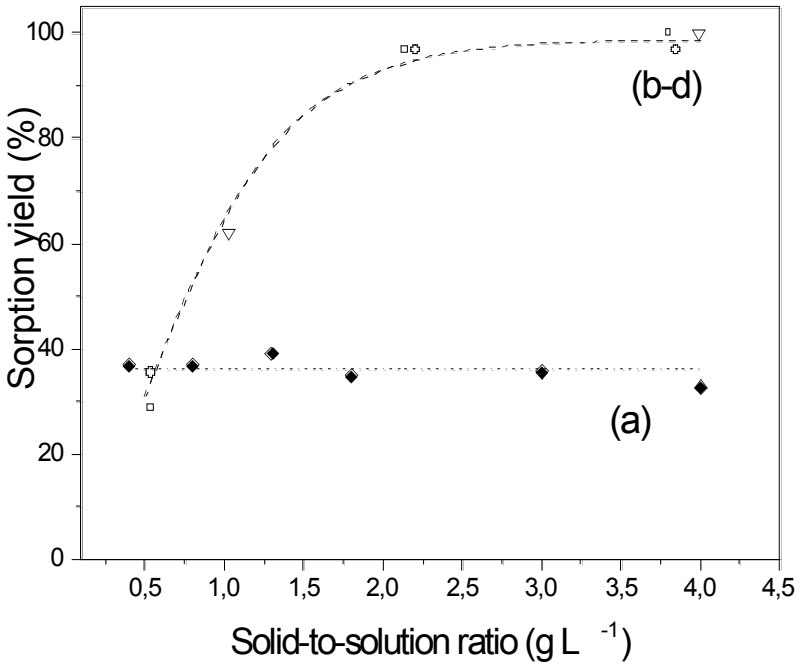


Fig. 4.6. Variation of chromium sorption yields, as a function of the solid-to-solution ratio, using MCM-41-SH/SO_3H-X particles suspended in 50 µM Cr(VI) solution at pH 2.2: (a) MCM-41-SH, (b, ○) MCM-41-SH/SO_3H-2, (b, □) MCM-41-SH/SO_3H-3, (b, ∇) MCM-41-SH/SO_3H-5.

In attempt to optimize the performance of the reduction/sequestration scheme, we have thus evaluated the influence of the SH/SO_3H ratio on the sorption yields (see parts "b-d" on Fig. 4.6)). As shown, the presence of sulfonic acid groups in the starting material is of major importance to reach the best performance (sorption yields close to 100 % under optimized conditions and at high solid-to-solution ratio), but their amount relative to the thiol group content is not critical as no distinguishable variation was found between MCM-41-SH/SO_3H-X samples respectively oxidized at 15, 20, and 40 % (for more information see Table 3.1). Only little amounts of sulfonate groups are thus necessary to ensure efficient reduction-sorption in the adsorbent. As reduction is equally

quantitative in all cases, one can conclude that the limiting step in total sequestration of chromium is always the binding of the reduced products (i.e., Cr^{3+}).

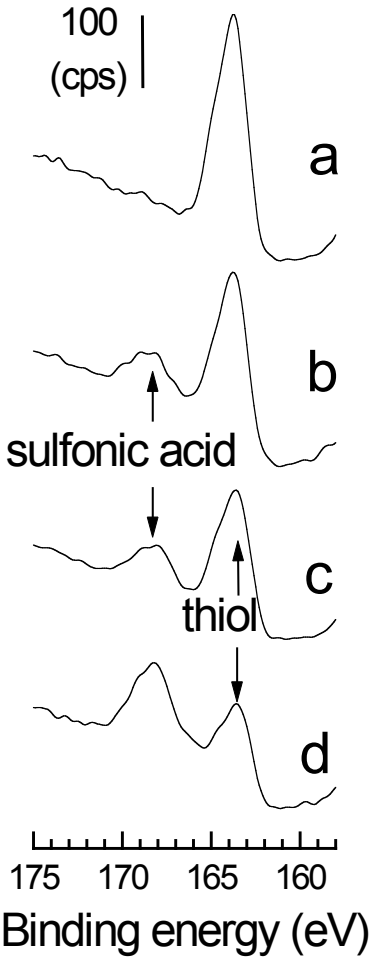


Fig. 4.7 . XPS spectra (S_{2p} core-level) of MCM-41-SH after reaction with solutions containing Cr(VI) at increasing concentrations: (a) 50 μM, (b) 2 mM, (c) 5 mM and (d) 0.5 M.

4.3 Conclusions

Once optimized (adsorbent at a content higher than 5 g L^{-1}, pH 2.2), the reduction-sorption process using MCM-41-SH/SO_3H-1 is efficient enough to ensure residual chromium concentrations as low as the tolerance level accepted for industrial wastes (0.05-0,1 mg L^{-1}, see Table 1.2), holding great promise for wastewater treatment by reducing the volume of toxic sludges with respect to the conventional reduction-

precipitation method in pH conditions mimicking those of leather tanning wastewaters [220]. Although the adsorbent capacity is not overwhelming (yet of the same order of magnitude) in comparison to conventional sorbents in common use, especially activated carbon, the bi-functionalized material ensures selective and complete removal of the toxic Cr(VI) species, which are quantitatively reduced and immobilized exclusively in the form of Cr(III). This is also advantageous in comparison to anion exchangers that can suffer from competition with other anions such as sulfate, nitrate or phosphate. Further works seem to be necessary to associate stronger ligands for Cr(III) to the thiol-functionalized mesoporous adsorbent to improve sorption yields at lower solid-to-solution ratios.

Chapter V

D'après les résultats présentés dans le chapitre III, il apparait que les silices mésoporeuses fonctionnalisées par des groupements thiol et acide sulfonique présentent des propriétés de réduction-sorption vis-à-vis du chrome(VI). Ceci est rendu possible dans une gamme de pH appropriée (certes limitée, i.e., pH 2-3) grâce à la réduction de Cr(VI) par le groupe thiol et l'immobilisation des espèces Cr(III) résultantes par le biais d'interactions électrostatiques favorables avec les entités sulfonates. Le processus fonctionne assez bien mais souffre au final de deux restrictions : la stoechiométrie de la transformation redox (limitant les propriétés de piégeage du matériau), et la faiblesse des interactions entre les Cr(III) et les groupements sulfonates. Pour contourner ces limitations, ce chapitre traite du potentiel que représente l'utilisation d'un gel de silice organiquement modifié portant des groupements mercaptopropyle et ethylènediaminetriacetate (SiO_2-SH/ED3A) susceptibles de jouer respectivement le rôle de réduction de Cr(VI) et de séquestration des espèces Cr(III) ainsi formées. On peut espérer une amélioration des résultats sur base d'une interaction potentiellement plus forte entre Cr(III) et les groupements ED3A qu'entre Cr(III) et les groupements sulfonates. Le mécanisme de séquestration inclut toujours la réduction de Cr(VI) par des groupements thiol (SH) et l'immobilisation subséquente des espèces Cr(III) ainsi générées, mais cette fois l'immobilisation a lieu par complexation de Cr(III) avec les ligands éthylènediaminetriacetate (ED3A). La valeur de pH la plus appropriée (1-3) pour une réduction-sorption complète de Cr(VI) par SiO_2-SH/ED3A provient d'un compromis entre la réduction complète de Cr(VI) par SH, qui requiert des valeurs de pH assez basses, et la complexation quantitative de Cr(III) par ED3A, qui est favorisée dans des milieux moins acides. De tels adsorbants bi-fonctionnels sont considérés comme sensiblement plus efficaces que ceux portant seulement des groupements thiol. Le procédé de réduction-sorption est caractérisé par une cinétique rapide, ceci permettant une utilisation efficace de l'adsorbant SiO_2-SH/ED3A dans des conditions dynamiques (expériences en colonne). Le suivi de la quantité des espèces du chrome immobilisées sur le solide a été réalisé par spectrométrie de fluorescence X et par spectrométrie UV-visible. L'étude de l'influence de

la force ionique et de la présence de métaux lourds a révélé peu d'interférence dans l'élimination de Cr(VI).

5 Cr(VI) removal via reduction-sorption by SiO_2-SH/ED3A

5.1 Adsorbent preparation and characteristics

Attachment of mercaptopropyl groups (SH), on one hand, and ethylenediaminetriacetate moieties (ED3A), on the other hand, onto the silica surface requires two distinct grafting procedures. The first one is the "classical" grafting reaction of MPTMS on silica in refluxing toluene (see section 2.3.4) but special care should be taken to avoid complete coverage of the whole silica surface to enable further immobilization of ED3A groups, which can be easily made by adjusting the MPTMS/silica ratio [192]. Then, ED3A groups were attached to the SiO_2-SH material by reaction with the ED3A-silane coupler in water-methanol medium, as described in section 2.3.5). Again, it was possible to adjust the amount of immobilized groups by tuning the ED3A-silane coupler-to-silica ratio (see Fig. 5.1). A maximum ED3A content of *ca.* 0.7 mmol g^{-1} was achieved.

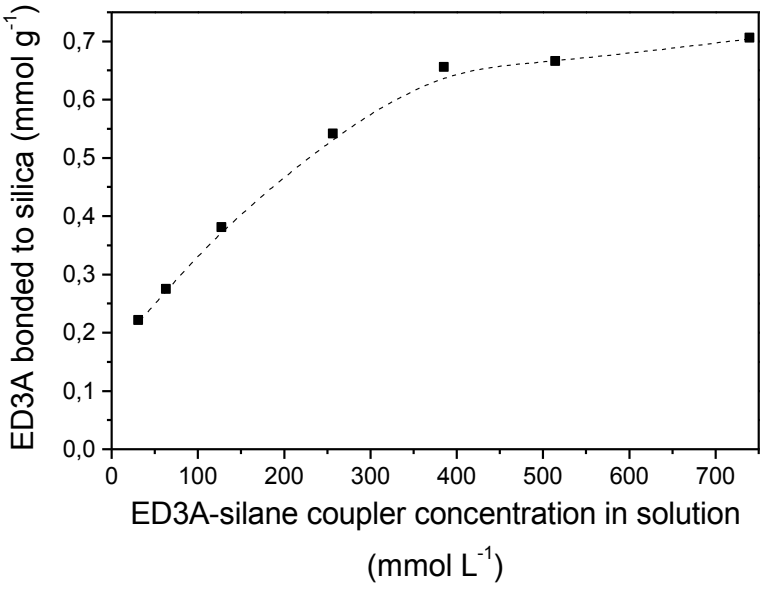


Fig. 5.1. Variation of the amount of ED3A groups attached to the silica surface, as a function of the concentration of the ED3A-silane coupler solution.

When using the SiO_2-SH material instead of bare silica, the amount of immobilized ED3A groups was lower due to the presence of SH groups occupying a significant portion of the silica surface. This is confirmed by chemical analysis, indicating the presence in the final bi-functional adsorbent (SiO_2-SH/ED3A) of SH groups (0.38 ± 0.02 mmol g^{-1} from elemental analysis; 0.40 ± 0.03 mmol g^{-1} from silver titration), and ED3A groups (0.39 ± 0.02 mmol g^{-1}, from elemental analysis).

The presence and the integrity of the organo-functional groups were further checked by FTIR (see Fig. 5.2). The spectra of thiol-bearing samples were characterized by C-H stretching vibrations of the propyl chains at 2855 and 2960 cm^{-1} and a weak vibration corresponding to the -SH group at 2578 cm^{-1} [221]. The ED3A-groups can be identified via the vibration of their carboxylate/carboxylic acid moieties, leading to a band at 1728 cm^{-1} (COOH) and two others (COO^-) at 1631 cm^{-1} (this latter being superimposed to that of weakly physi-sorbed water [222]) and 1405 cm^{-1}, in agreement with previous observations [223], whereas the characteristic band of ED3A at 1332 cm^{-1} [224] was almost invisible because it was located too close to the huge signal corresponding to siloxane moieties in the 1000 to 1300 cm^{-1} range [221].

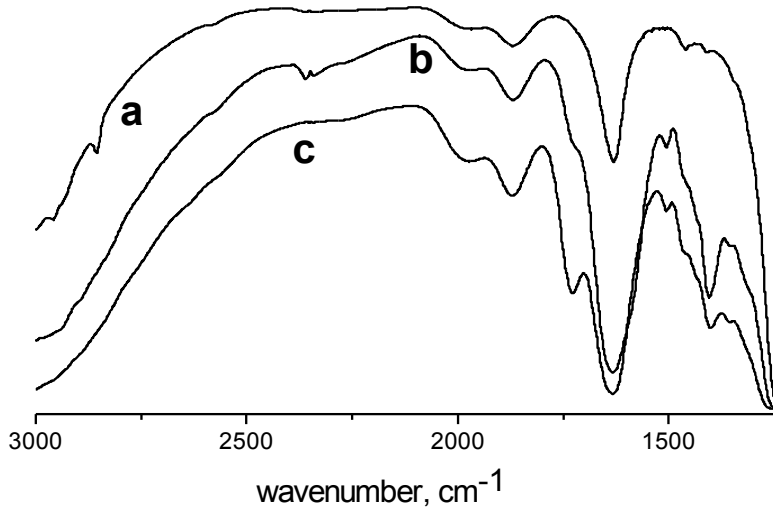


Fig. 5.2. FTIR spectra of SiO_2-SH (a), SiO_2-SH/ED3A (b) and SiO_2-ED3A (c) in the 1250-3000 cm^{-1} range.

5.2 Batch sorption experiments

5.2.1 Cr(III) sorption on SiO_2-ED3A

Cr(III) species (Cr^{3+}, or more accurately the aqua complex $Cr(H_2O)_6^{3+}$ in acidic medium) can be immobilized on SiO_2-ED3A and, as illustrated in Figure 5.3 (part a), this process is pH-dependent. As shown, no adsorption was observed at pH than 2.5, but sorption yields increased then rapidly at pH 3, to reach maximum values above pH 5. The sorption process is expected to be due to metal-ligand complex formation (on the basis of known Cr(III)-chelate complexes with chelators such as *N*-(2-hydroxyethyl)ethylenediaminetriacetic acid (HEDTA) or ethylenediaminetetraacetic acid (EDTA)), but one cannot exclude a contribution of non-selective bonding of $Cr(H_2O)_6^{3+}$ species to silanolate groups, especially at higher pH values (i.e., above pH 4 [217]). The accumulation process is very slow, requiring several hundreds of hours to reach significant sorption yields (see curve a in Fig. 5.4). This is explained by the kinetic inertness of $Cr(H_2O)_6^{3+}$ ions with respect to ligand exchange reactions (see section 1.4.2), which constitutes the rate-determining step in complex formation of Cr(III) with ethylenediaminetriacetic acid. On the other hand, one should mention that no measurable Cr(III) uptake was observed up to pH 4, using the SiO_2-SH adsorbent, confirming the absence of any interaction between thiol groups and Cr(III) species (discussed in section 3.1).

5.2.2 Cr(VI) reduction-sorption on SiO_2-SH/ED3A

While no interaction between the SiO_2-ED3A material and Cr(VI) species was observed, Figure 5.3 (part b) reveals that using the bi-functionalized SiO_2-SH/ED3A adsorbent led to significant chromium uptake, especially between pH 1 and 3.

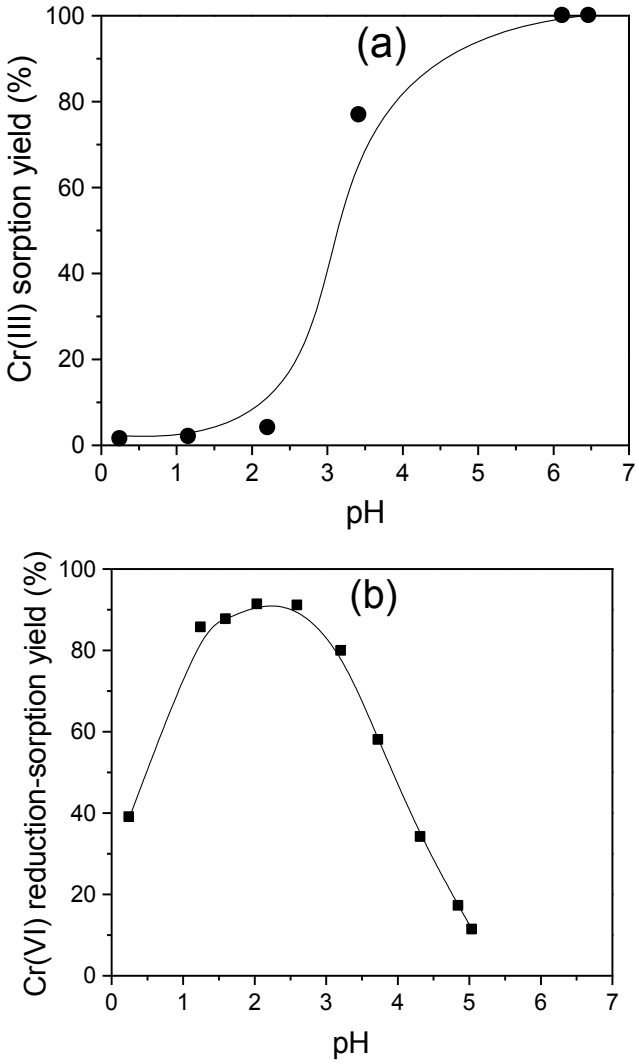


Fig. 5.3 (a) Variation of Cr(III) sorption yields as a function of pH, using the SiO_2-ED3A adsorbent; experimental conditions: solid-to-solution ratio of 2.0 g L^{-1}, starting Cr(III) concentration in solution equal to 100 μM (25 mL solution). (b) Variation of Cr(VI) reduction-sorption yields as a function of pH, using the SiO_2-SH/ED3A adsorbent; experimental conditions: solid-to-solution ratio of 2.0 g L^{-1}, starting Cr(VI) concentration in solution equal to 100 μM (25 mL solution).

One already knows that thiol-functionalized silica (i.e., SiO_2-SH) is likely to reduce Cr(VI) species (discussed in section 3.2), in agreement with observations made with other thiol-containing solids [71, 225]. The reaction can be described by equation (5.1):

$$SiO_2\text{-}SH + 2\,HCrO_4^- + 8\,H^+ \rightarrow SiO_2\text{-}SO_3H + 2\,Cr^{3+} + 5\,H_2O \qquad (5.1)$$

This equation indicates that Cr(VI) reduction is favoured at lower pH values (consistent with thermodynamical predictions). This explains the right part of the curve (Fig. 5.3, part b), indicating dramatic decrease in sorption yields above pH 3 (to reach almost zero at pH 5), because the medium was not acidic enough for thiol groups to reduce Cr(VI) species. This is also confirmed by solution-phase analyses, revealing that all the remaining chromium species in solution are in the Cr(VI) form.

On the other hand, Cr(III) species (generated by Cr(VI) reduction by thiol groups) are immobilized on the adsorbent, as ascertained by XPS analysis (via $Cr2p_{3/2}$ and $Cr2p_{1/2}$ signals located respectively at binding energies of 577.3 eV and 586.7 eV, which are characteristics of Cr(III) [218]). This confirms that Cr(VI) species have been really reduced by thiol groups and that the adsorbed species are in the form of Cr(III) on the material. Actually, the generated Cr(III) species are likely to interact with either ED3A groups (via complex formation) or sulfonic acid moieties (via ion exchange/electrostatic interactions), as illustrated in the following equations:

$$SiO_2\text{-}SO_3H + Cr^{3+} \rightarrow SiO_2\text{-}SO_3^-,Cr^{3+} + H^+ \qquad (5.2a)$$

$$SiO_2\text{-ED3A} + Cr^{3+} \rightarrow SiO_2\text{-ED3A-}Cr^{3+} \qquad (5.2b)$$

At this stage it is difficult to distinguish unambiguously between these 2 processes but several features tend to indicate that the ED3A chelate plays an important role. First, the stoechiometry of the redox reaction (Eq. 5.1) shows that 2 Cr(III) species are formed when only one SO_3H is generated whereas sorption yields as high as 90% have been observed (Fig. 5.3), demonstrating that ion exchange (Eq. 5.2a) cannot be the only process explaining Cr(III) immobilization and, therefore, complex formation with ED3A should occur. Secondly the pH range for effective reduction-sorption using SiO_2-SH/ED3A (i.e., in the 1-3 range, see Fig. 5.3) is significantly larger than for SiO_2-SH (i.e., between pH 2 and 3 for MCM-SH/SO_3H-X), indicating more efficient Cr^{3+} binding in acidic medium for the SiO_2-SH/ED3A sorbent, which can be explained by complex

formation with ED3A (even at pH values as low as 0.5–1, consistent with highly stable Cr(III) complexes with HEDTA [170] or EDTA [226] in strongly acidic media).

Kinetics associated to Cr(VI) reduction and subsequent Cr(III) immobilization onto SiO_2-SH/ED3A are very fast (see curve b in Fig. 5.4), showing steady state values for maximum sorption yields in less than 15 min (i.e., the first measured data). This supports the idea of fast binding of freshly generated Cr(III) in the form of Cr^{3+} species, which are formed close to ED3A groups in the porous material and thereby likely to undergo rapid complexation, contrary to as-prepared solutions of Cr(III) in which chromium is in the form of $Cr(H_2O)_6^{3+}$ which requires slow ligand exchange before being complexed with the ED3A chelate (as supported by curve a in Fig. 5.2).

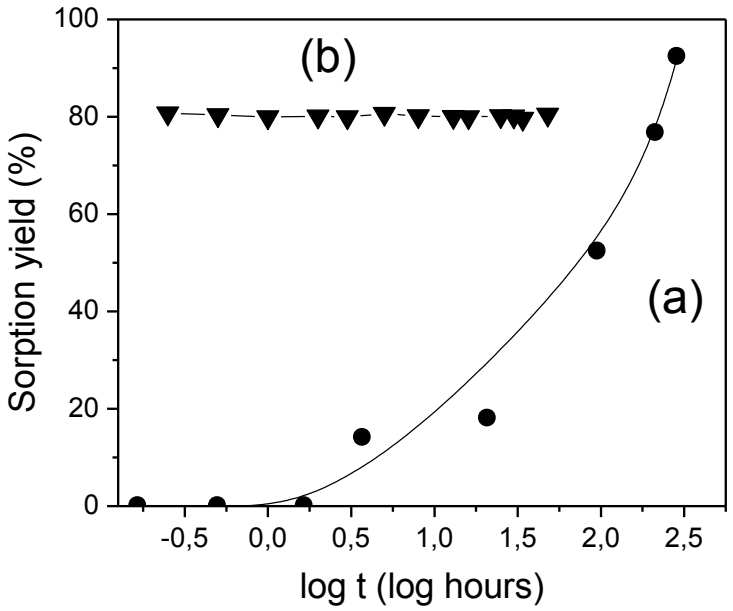


Fig. 5.4. Effect of contact time between (a) a Cr(III) solution and the SiO_2-ED3A adsorbent, or (b) a Cr(VI) solution and the SiO_2-SH/ED3A adsorbent, on the chromium sorption yields; experimental conditions: solid-to-solution ratios of 4.0 g L^{-1} (a) or 2.0 g L^{-1} (b), starting Cr(III) and Cr(VI) concentrations in solution equal to 192 µM and 100 µM, respectively (25 mL solution), and pH in the medium equal to 5.0 (a) or 2.5 (b).

5.2.3 Performance of the adsorbents

Figure 5.5.A shows the variation of SiO_2-SH/ED3A (curve a) and SiO_2-SH (curve b) sorbent capacities as a function of the initial Cr(VI) concentration in solution. The data demonstrate clear advantage of the bi-functional adsorbent: while the sorption capacity for SiO_2-SH rapidly leveled off at about 0.15 mmol g^{-1}, that of SiO_2-SH/ED3A rapidly grew up to 0.4 – 0.5 mmol g^{-1} in the same conditions. A maximum value of 0.69 mmol g^{-1} (SiO_2-SH/ED3A) is even reached in the presence of a large excess of Cr(VI) in solution. Even more overwhelming is the comparison of adsorption isotherms (see inset in Fig. 5.5 A), showing that negligible amounts of remaining chromium in solution were observed with SiO_2-SH/ED3A up to a capacity of about 0.4 mmol g^{-1} (with a Langmuir H-type isotherm), contrary to SiO_2-SH for which significant chromium uptake was only visible with non negligible equilibrium chromium concentrations in solution (type S isotherm). This further confirms the above hypotheses of Cr(III) immobilization onto SiO_2-SH/ED3A (Eqs. 5.2a & 5.2b): a strong binding to ED3A chelates (which are indeed present in the material at a content of 0.4 mmol g^{-1}) via complex formation (Eq. 5.2a) and then a weaker binding to the generated sulfonic acid species via ion exchange/electrostatic interactions (Eq. 5.2b). Only this second (weak interaction) binding process was likely to occur with the mono-functionalized SiO_2-SH material. These results also suggest the formation of a 1:1 complex between Cr(III) and ED3A on silica, consistent with the stoechiometry of the corresponding Cr(III)-HEDTA complex in solution.

Figure 5.5.B shows that SiO_2-SH/ED3A is likely to decrease the residual chromium concentration below low threshold values, but this requires the use of solid/solution ratios high enough. For instance, working in a solution containing initially 0.1 mM Cr(VI), the use of SiO_2-SH/ED3A contents increasing from 2 to 4 and then to 6 g L^{-1} resulted in sorption yields of 88, 97, and 99 %, respectively. The adsorbent is thus likely to reduce chromium concentration under the µM concentration level. In view of the importance of the solid-to-solution ratio (Fig. 5.5.B) and considering the fast sorption kinetics (Fig. 5.4.b), flow-through experiments could be

even more effective for chromium removal via reduction-sorption on such bi-functional porous material (see section 5.3).

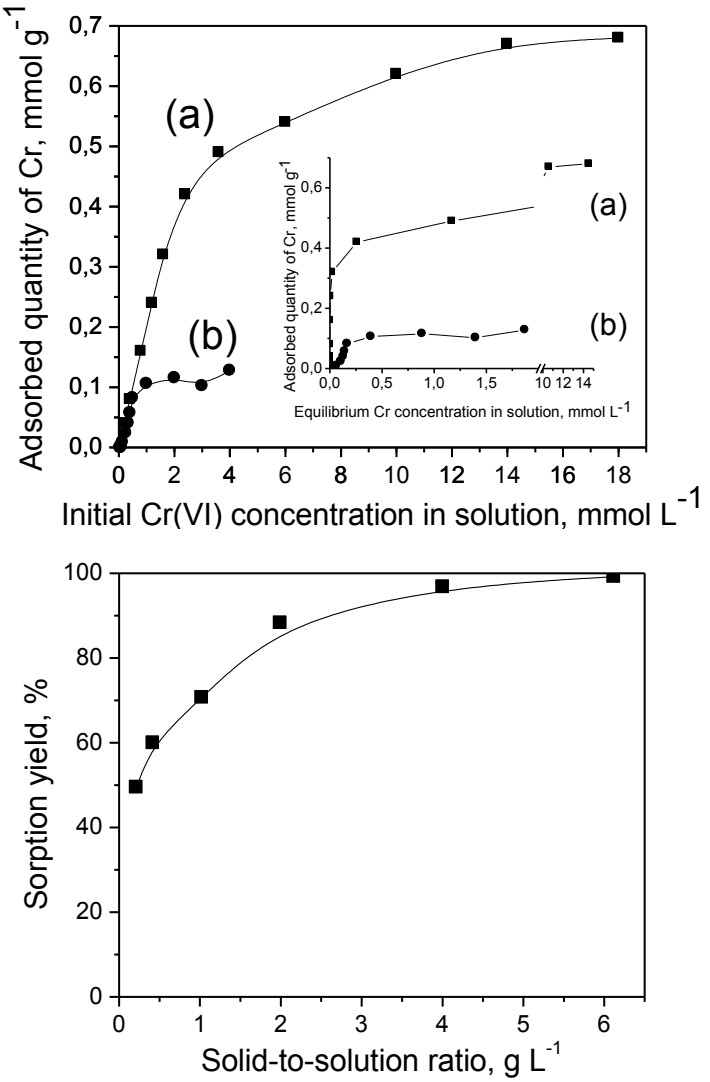


Figure 5.5. (A) Variation of the amount of adsorbed chromium on (a) SiO_2-SH/ED3A and (b) SiO_2-SH, as a function of the initial Cr(VI) concentration in solution (25 mL solution at pH 2.5, containing 125 mg of adsorbent); the corresponding isotherms (i.e., same variations given versus the equilibrium chromium concentrations in solution) are given in the inset. (B) Variation of chromium sorption yields, as a function of the solid-to-solution ratio, using SiO_2-SH/ED3A particles suspended in 50 mL of 100 µM Cr(VI) solution at pH 3.0.

5.2.4 Solid phase analysis after reduction-sorption experiments

An additional feature to support the existence of two forms of adsorbed Cr(III), and the best performance of SiO_2-SH/ED3A compared to SiO_2-SH, is provided by the optical analysis of adsorbent samples treated with Cr(VI) solutions of increasing concentration. The reduction-sorption of chromium started earlier using the bi-functional SiO_2-SH/ED3A adsorbent and led to the observation of much intense colour as a result of higher contents of adsorbed species (see Fig. 5.6).

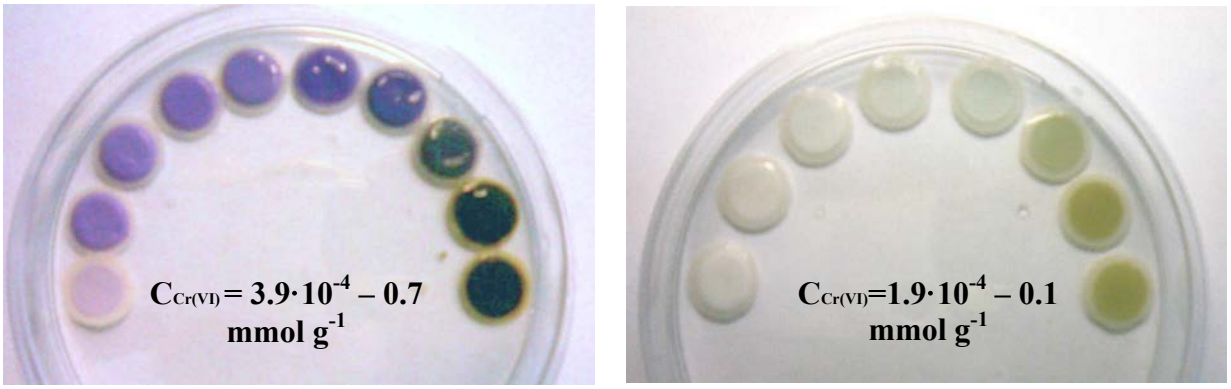


Fig. 5.6. Illustration of colour changes of (A) SiO_2-SH/ED3A and (B) SiO_2-SH materials after reduction-sorption of increasing amounts of Cr(VI) species.

One can distinguish the characteristic blue/violet colour of the Cr(III)-ED3A complex on SiO_2-SH/ED3A, the intensity of which increasing as high was the chromium loading. This is more quantitatively evidenced from recording UV-Vis diffuse spectra (see Fig. 5.7) for which the main peak at 565 nm was found to increase linearly up to a chromium loading of 0.4 mmol g^{-1} (corresponding to the content of ED3A groups in the material) and then tended to level off.

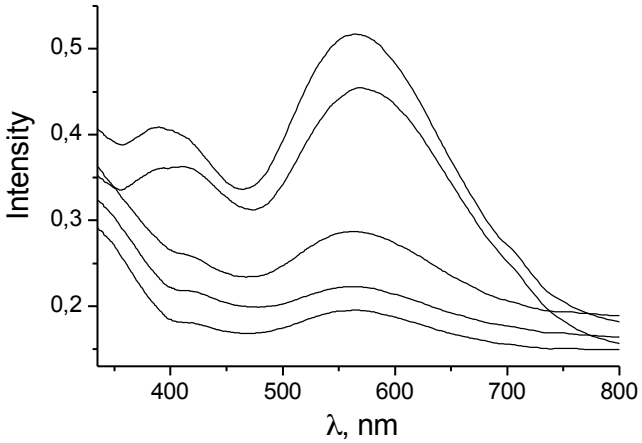


Fig. 5.7. UV-Vis diffuse reflectance spectra of Cr(VI)-treated SiO_2-SH/ED3A at various chromium contents, ranging from 0.04 to 25 mg g^{-1}.

At higher chromium loadings, an additional coloured contribution appeared (see the three last spots on the right of Fig. 5.6.A), which corresponds to the greenish-yellow colour typical of the SiO_2-SO_3^-,Cr^{3+} ion pair formed when using the mono-functionalized SiO_2-SH adsorbent (see Fig. 5.6.B). This confirms the two forms of adsorbed Cr(III) on SiO_2-SH/ED3A and that the firstly formed one corresponds to the more stable SiO_2-ED3A-Cr(III) complex.

From the analytical point of view, adsorbed Cr(III) on SiO_2-SH/ED3A can be quantitatively determined by XRF, showing a linear relation of the signal intensity and chromium content in the adsorbent in the whole range up to 0.6 mmol g^{-1} (or 30 mg g^{-1}, as shown on Fig. 5.8). These values correspond well to those calculated from solution-phase analyses (by difference with respect to starting chromium concentrations in solution), checking thereby that mass balance was maintained during the reduction-sorption process.

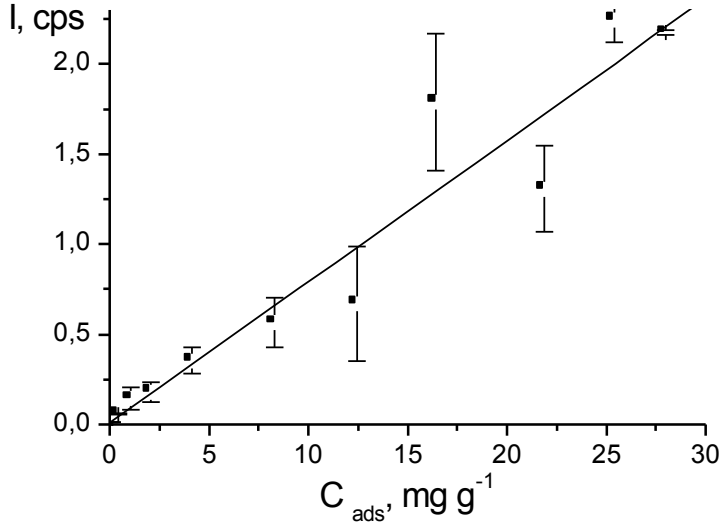


Fig. 5.8. Dependence of intensity of the chromium signal (from XRF spectra) on the chromium content in the adsorbent.

5.3 Column sorption experiments

The potential for SiO_2-SH/ED3A to remove Cr(VI) from wastewaters in dynamic conditions was evaluated in model experiments using toxic metal concentrations in the mM range. Typical results are illustrated on Figure 5.9, for two chromium concentrations and three distinct flow rates. Both the variations of the remaining chromium concentrations in the eluate and the adsorbed chromium on the material have been plotted, respectively on parts A and B of the figure, as a function of the solution volume passed through the column.

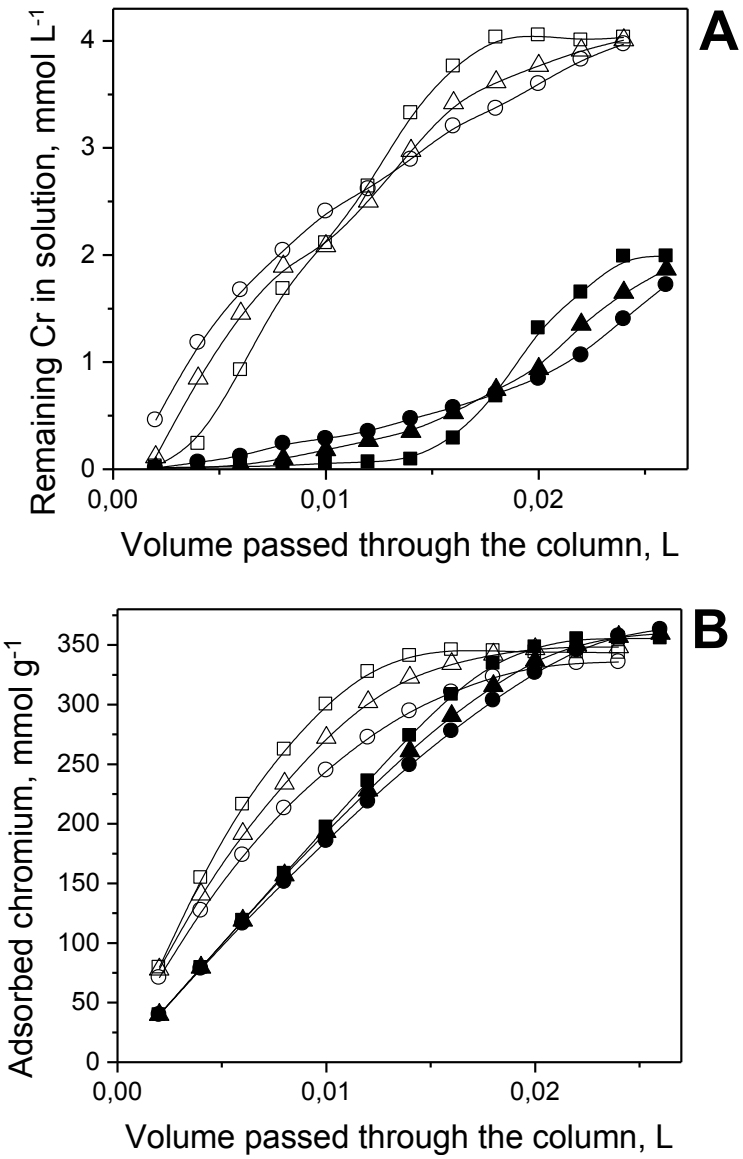


Fig. 5.9. Cr(VI) reduction-sorption onto SiO_2-SH/ED3A in dynamic mode. Variation of (A) the concentration of remaining (non adsorbed) chromium in solution at the output of the column, and (B) the amount of adsorbed chromium onto the solid phase, as a function of the solution volume passed through the column; the experiments have been performed at two Cr(VI) concentrations (2 mM (■,▲,●) and 4 mM (□,Δ,○), at pH 2.5), and three different flow rates (0.1 mL min^{-1} (■,□), 0.4 mL min^{-1} (▲,Δ), and 1.0 mL

Several conclusions can be drawn from these results. First, if the maximum sorption yields are independent on the solution flow rate (in the 0.1 – 1.0 mL min^{-1} range), this parameter has some effects on the overall speed of the reduction-sorption process, especially more marked at 4 mM Cr(VI) than at 2 mM. This can be evidenced

from the breakthrough data (Fig. 5.9.A) in which the S-shaped curves were more well-defined at lower flow rates, as expected from longer contact times for reaching steady-state. This is also evident from adsorbent capacity variations (Fig. 5.9.B), showing that higher flow rates required larger solution volumes to fill the column. Secondly, the maximum uptake capacity was *ca.* 0.37 mmol g^{-1} (i.e., near the content of ED3A groups in the material), suggesting that only the strong chelating ED3A groups are likely to retain Cr(III) species that have been reduced by thiol groups. In such dynamic conditions, the lability of the SiO_2-SO_3^-,Cr^{3+} ion pair does not allow the durable immobilization of Cr(III) species via electrostatic interactions with sulfonic acid moieties. This confers definite advantage to the SiO_2-SH/ED3A adsorbent over the previously reported SiO_2-SH/SO_3H one, which cannot be used in column (no measurable Cr(III) retention). Thirdly, under optimal conditions (i.e., low flow rates), there exists an inverse relationship between the breakthrough volume and the chromium solution concentration (i.e., 0.02 L for [Cr(VI)] = 2 mM, and 0.01 L for [Cr(VI)] = 4 mM, see Fig. 5.9.A), suggesting that the chromium concentration does not affect the kinetics of the reduction-sorption process.

To establish optimal volume suitable for effective concentration of Cr (VI) different volumes of solutions (10-1000 mL) with constant amount of Cr (VI) (10 μmole) were passed through at the column filled with SiO_2-SH/ED3A. As shown in Figure 5.10 (curve 2), the sorption efficiency decreases by 15% while volume is increasing to 100 mL. While diluting solution to 500 mL, sorption efficiency remains constant (71-75%) but it is reduced sharply (10%) when the volume of Cr(VI) solution passed through the column is 1000 mL. Efficiency of Cr (VI) reduction (curve 1, Fig. 5.10) exceeds 90% when low volumes (10-25 mL) are passed through the column and is reduced up to 80% when 1000 mL are used.

Apparently, dilution of Cr (VI) solution has little effect on reduction ability of SiO_2-SH/ED3A column, but the sorption efficiency of reductively-generated Cr (III) is somewhat reduced when solution is diluted to 500 mL and is rather low (56%) when diluted to 1000 mL.

Despite this fact, distribution coefficients (see inset Fig. 5.10) are increasing with increasing of the volume of Cr(VI) solution. The value of distribution coefficient at passing 0,5 L of Cr(VI) solution (1 mg L^{-1}) is 10^4 mL g^{-1}, indicating a promising application of SiO_2-SH/ED3A for the removal of chromium from solutions with low concentrations of Cr (VI).

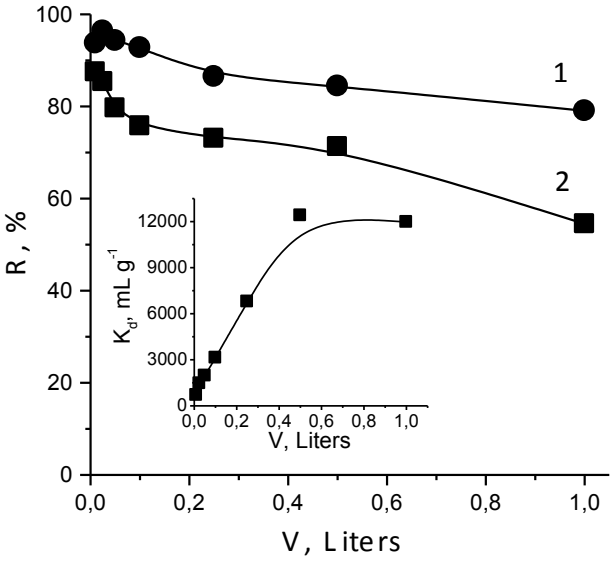


Fig. 5.10. Efficiency of Cr(VI) reduction (1) and sorption (2) after interaction with SiO_2-SH/ED3A in dynamic mode versus the volume of Cr(VI) solution;
Inset: corresponding variation of distribution coefficients ($m_{SiO_2\text{-}SH/ED3A}$ = 100 mg, $n_{Cr(VI)}$ = 10 μmole, ν = 1 mL min^{-1})

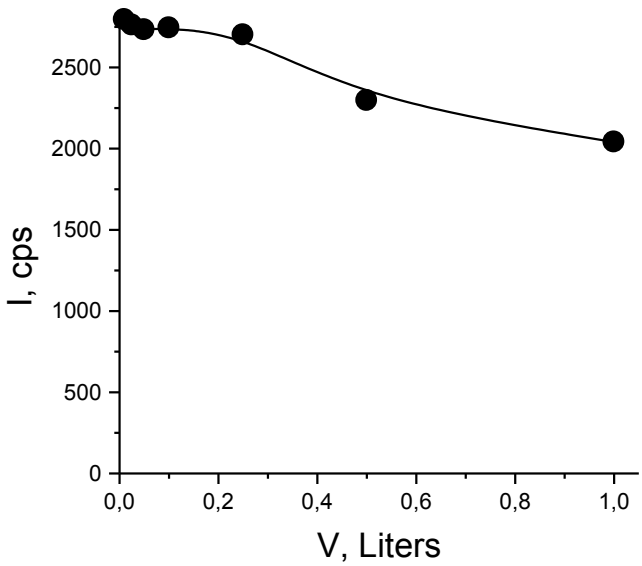


Fig. 5.11. Dependence of intensity of the chromium signal (Kα line of Cr in XRF spectra) on Cr(VI) solution volume ($m_{SiO_2\text{-}SH/ED3A}$ = 100 mg, $n_{Cr(VI)}$ = 10 μmole, ν = 1 mL $min^{-}1$, pH=2,5)

It should be mentioned that the intensity of Kα lines of Cr (XRF), adsorbed on the surface SiO_2-SH/ED3A from different volumes also varies slightly in case when solution is diluted to 250 mL (see Figure 5.11). The value of the signal intensity obtained after concentration of Cr (VI) from 500 and 1000 mL differ by 500 conventional units and cannot be considered as a method error. Thus, under the conditions of described experiment (4-fold excess of ED3A groups to amount of

chromium, the volume rate = 1 mL min^{-1}, column d∅ = 6 mm and $m_{SiO_2\text{-}SH/ED3A}$ = 100 mg) efficiency of chromium adsorption is sufficient in case of passing 250 mL of Cr (VI) solution. This makes it possible to apply columns filled with SiO_2-SH/ED3A for adsorptiomn of toxic Cr(VI0 from diluted solutioins.

5.4 Influence of the presence of concomitant foreign species

The effect of high ionic strength on the adsorbent capacity was first considered in static conditions, by working in excess Cr(VI), for which a decrease in the reduction-sorption capacity by about 40 % was observed at high ionic strength (>0.5M, see Fig. 5.12). At the same time, distribution coefficients (Kd values) were found to decrease by a factor of about 2 (see inset in Fig. 5.12), but remained rather high, even at high ionic strength (e.g., 435 mL g^{-1} in the presence of 1 M NaCl). This behaviour can be rationalized by considering the reduction-sorption mechanism discussed above. Indeed, only Cr(III) species weakly bonded to $-SO_3^-$ moieties contribute to the loss in capacity (i.e., from 0.69 to 0.43 mmol g^{-1}). This confirms again the major importance of the strong ED3A chelates in maintaining the immobilization properties of the bi-functional adsorbent.

Because ED3A-functionalized materials are likely to adsorb other metal ions, we have then investigated the possible effect of the presence of such species, which can be present along with chromium in typical acidic wastewaters (e.g., from electroplating). Figure 5.13.A shows that under pure thermodynamic competition conditions (i.e., excess adsorbent over solute), the presence of foreign species (Fe(III), Cu(II), Ni(II)) at concentrations ranging from half to twice as that of chromium did not dramatically affect the sorption yields (less than 20 % decrease when interfering species were two times in excess over Cr(VI)), even if these species were likely to bind to the material (Fig. 5.13.B) but at ca. 10 times lower contents in comparison to chromium. More importantly, pH was found to play a major role on the selectivity series.

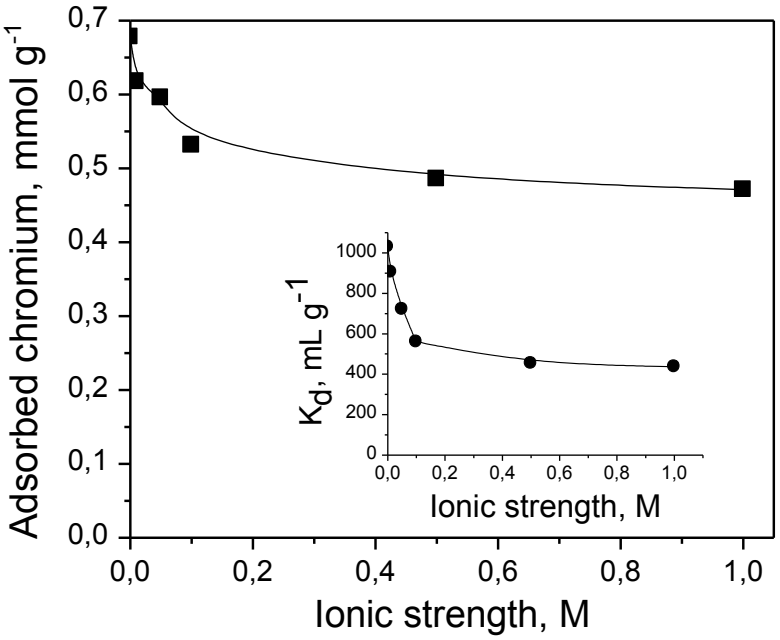


Fig. 5.12. Influence of the ionic strength on adsorption capacity SiO_2-SH/ED3A adsorbent versus Cr(VI) (2.0 g L^{-1}; starting Cr(VI) concentration in solution equal to 2 mM; pH 2.5), and corresponding variation of distribution coefficients (inset).

This has been considered here by studying desorption of a SiO_2-SH/ED3A column previously loaded with chromium (as Cr(VI) for immobilization by reduction-sorption) and various other metal species, following a pH-gradient elution process (see inset in Fig. 5.14).

The results (Fig. 5.14) clearly shows a selectivity series in which adsorbed Cr(III) appears to be the most stable species: Pb(II) < Co(II) < Fe(III) < Ni(II), < Cu(II) < Cr(III). In such pH-gradient desorption experiment, the pH value for half-desorption yield is commonly used to compare the stability of immobilized complexes [91]. According to data from Fig. 5.14, this value decreased in the following order for metal ions tested here: Pb (4.2), Co (2.3), Fe(1.8), Ni and Cu (1.6), and no measurable data was available for chromium as less than 10 % Cr(III) was desorbed at pH 1.5 (the lowest pH tested here). This means that only Cu(II), Ni(II) and Fe(III) could interfere with Cr(VI) if present in solution in high excess over Cr(VI). In agreement with data presented in Figure 5.1 (curve b), chromium species only started to desorb at very low pH values. For instance, at pH 1.6, more than 90 % of chromium is still bonded to the

adsorbent, when other metal species are desorbed at yields ranging from 50 to 100 % (Fig. 5.14).

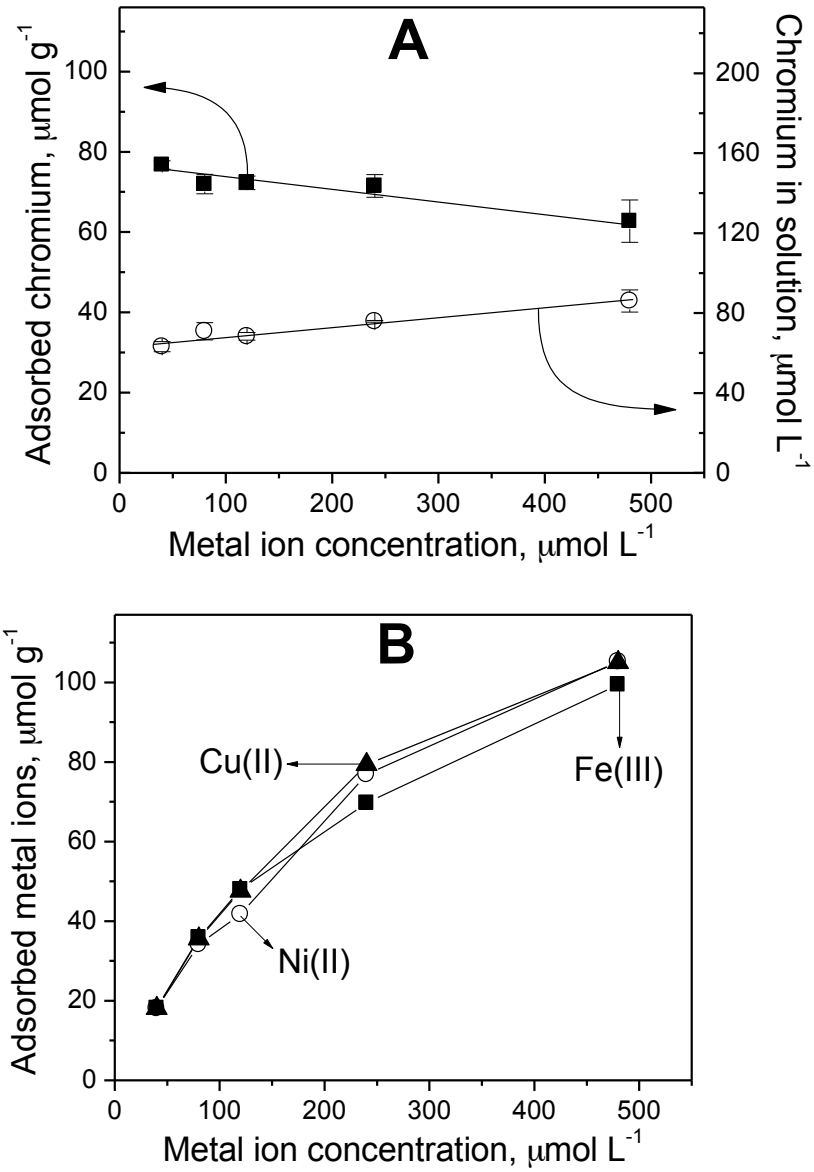


Fig. 5.13. (A) Influence of the presence of metal species (Cu(II), Ni(II), and Fe(III), in mixture) at increasing concentrations, on Cr(VI) reduction-sorption yields using the SiO_2-SH/ED3A adsorbent (2.0 g L^{-1}; starting Cr(VI) concentration in solution equal to 233 μM; pH 2.5), expressed as both the amount of adsorbed chromium and the remaining quantity of chromium in solution, as a function of the foreign metal species concentration. (B) Variation of the amounts of Cu(II) (▲), Ni(II) (○), and Fe(III) (■), adsorbed on the SiO_2-SH/ED3A material, as a function of their initial concentration in solution, as measured from experiments performed in the same conditions as in (A).

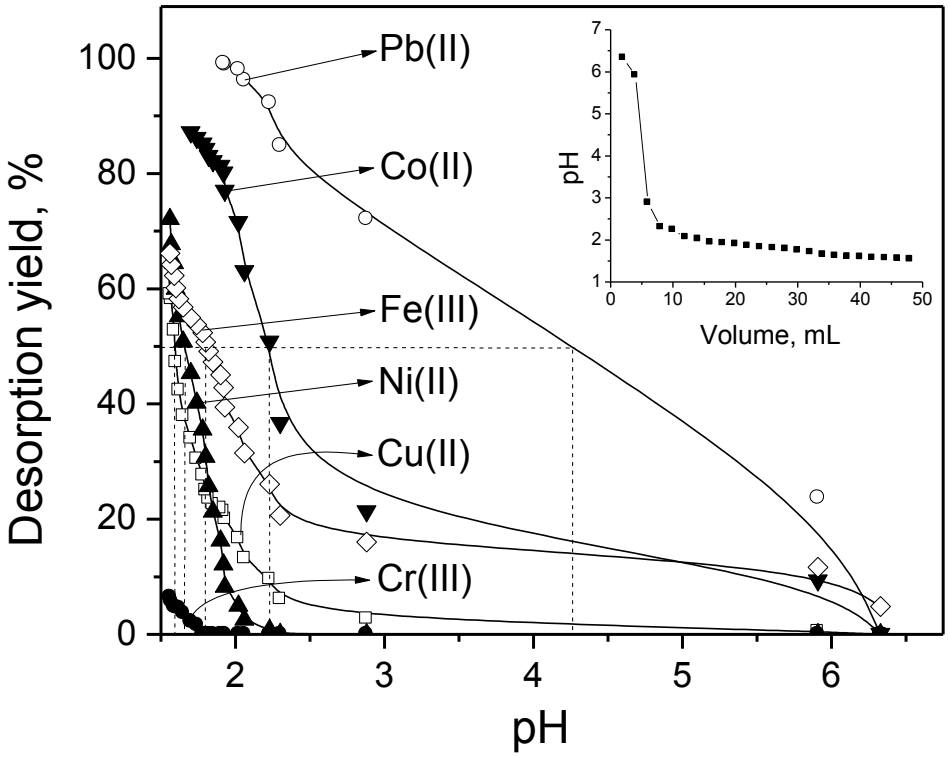


Fig. 5.14. Variations of the desorption yields, as a function of pH, of a column made of 100 mg of SiO_2-SH/ED3A material pre-treated with a solution (25 mL) containing 80 μM of various metal species; desorption was made at a flow rate of 1.0 mL min^{-1} in a pH-gradient elution mode (see variation in pH values as a function of the elution volume in the inset). Metal species were Pb(II) (○), Co(II) (▼), Fe(III) (◊), Ni(II) (▲), Cu(II) (□), and Cr(VI) (adsorbed as Cr(III) species, ●).

5.5 Conclusion

Adequately engineered bi-functional silica adsorbents, SiO_2-SH/ED3A, bearing one component designed to reduce toxic Cr(VI) (thiol groups in this case) and another one specifically selected for immobilizing the so-generated, yet less toxic, Cr(III) species (i.e., ethylenediaminetriacetate moieties), have proven to offer good performance for the efficient removal of chromium from aqueous medium, according to a reduction-sorption mechanism. Actually, the produced Cr(III) species can be sequestrated in the material via either complexation with the ethylenediaminetriacetate

ligand (ED3A) or ion exchange/electrostatic interactions with sulfonic acid moieties generated concomitantly to Cr(VI) reduction by thiol groups. The strong chelate properties of ED3A towards Cr(III) species, however, gave rise to significant improvement (in terms of operational pH range, durable adsorbent capacity, and low residual chromium concentration in solution) in comparison to the former SiO_2-SH/SO_3H material suffering form weak interactions between Cr(III) and the sulfonic acid groups. This has been notably exploited here in dynamic mode (column experiments) for which the presence of ED3A groups was essential to immobilize the reduced Cr(III) species on the adsorbent, which were not retained by "simple" electrostatic interactions with sulfonate moieties. Cr(VI) reduction and subsequent Cr(III) uptake was also possible in the presence of other metal species and the immobilized Cr(III) was found to be more stable at lower pH values than the other metal ions. Finally, optical (UV-vis) and spectroscopic (XRF) techniques can be used to quantify the adsorbed species and to distinguish between the strong ED3A-Cr^{3+} complex and the weaker SO_3^-,Cr^{3+} ion pair on the solid

General conclusions

This work propose bifunctionalized silica-based adsorbents MCM-SH,SO_3H-X and SiO_2-SH/ED3A as effective adsorbents for selective removal of Cr(VI). For this purpose, the methods of synthesis of corresponding mono-and bifunctional materials are developed. In order to distinguish between the concentrations of both mercaptopropyl and propylsulfonic acid groups which are simulteniously present at the surface of MCM-SH,SO_3H-X the method of conductometric titration has been proposed. It allows detecting existence of sulfonic acid groups in such low concentrations as 15-600 μmole g^{-1}, which is suitable for surveillance of thiol-containing adsorbents. Using conductimetric method, it is shown that prolonged exposure of thiol-containing adsorbent to an oxic atmosphere doesn't cause the formation of sulfonic acid groups. The contents of MCM-SH,SO_3H-X layers are precised using spectroscopic methods (TPDMS, IR and XPS), which confirmed bifunctionality and various ratios of -SH and-SO_3H groups at their surfaces.

It is evaluated that bifunctuanalized adsorbents operate much more effective than the corresponding monofunctionalized silica-based materials. It is shown that the presence of minor amounts (0.2 mmol g^{-1}) of binding groups (e.g. SO_3H) helps to improve the efficency of sorption up to 100%. Although the adsorption capacities (20-30 mg g^{-1}) are found to be not greater (yet of the same order of magnitude) than those for conventional sorbents, the proposed bifunctionalized adsorbents help to reduce toxic Cr(VI) (thiol groups) and selectively immobilize the so-generated, yet less toxic, Cr(III). In case of MCM-SH,SO_3H-X, the binding of Cr(III) is achieved by ion exchange with SO_3H groups, while at the surface of SiO_2-SH/ED3A, the binding mainly occurs through complexation with ED3A groups (if the quantity of Cr(VI) exceeds the molar ratio with ED3A, the binding of Cr(III) excess is reached by ion-exchange with the generated SO_3H groups). Due to the reductive sorption mechanizm of Cr(VI) sequestration, the selectivity of bifunctionalized adsorbents is higher in comparison to conventional Cr(VI) adsorbents. It is shown that high concentrations of either

competing anions (high ionic strength is typical for wastewaters from plating industry) or heavy metals doesn't prevent the efficiency of Cr(VI) removal. The selectivity of Cr(VI) extraction is based on the kinetic inertness of Cr(III)ED3A complex at the applied conditions (pH=1-3).

Both bifunctionalized adsorbents are advantageous in comparison to anion exchangers that can suffer from competition with other anions such as sulfate, nitrate or phosphate. Besides they operate under conditions typical for industial wastewaters (pH = 1-3), which facilitate the process of wastewater treatment. Experiments in dynamic mode revealed the possibility to use SiO_2-SH/ED3A for column treatment of Cr(VI) contaminated waters. It was shown that such column can be used for complete sequestration of Cr(VI) from solutions with Cr(VI) concentrations as low as the tolerance level accepted for industrial wastes (0.05-0,1 mg L^{-1}). Pre-concentration of Cr(VI) at the surface of SiO_2-SH/ED3A in combination with X-ray fluorescence analysis can also be used for creation of a test method of Cr(VI) detection. Occurrence of characteristic color of Cr(III)ED3A complex in the phase of SiO_2-SH/ED3A after interaction with solutions containing Cr(VI) allows detecting its presence visually.

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