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Adsorption Isotherm and Kinetic Modeling of Chlordecone on Activated Carbon Derived from Date Stones

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ABSTRACT

Environment contamination by pesticides is a major issue threatening human health. Adsorption is one of the most effective processes for removing pesticides, such as the organochlorine compounds chlordecone. The objective of this study was to determine the rate of chlordecone adsorption from drinking water by date stones-based activated carbon (C.A.). This laboratory scaleexperimental study was performed during March 2016 to September 2016 in the Laboratory of Water and Environmental Sciences, Lebanese University-Faculty of Public Health. The used activated carbon was derived from date stones and activated chemically by phosphoric acid.In order to determine the adsorption efficacity of chlordecone on activated carbon derived from date stones, a mixture of 0.5g of activated carbon and 100 ml of chlordecone concentration 100 μ g/l was studied under differentpH values ranging from 2 to 10 and contact time (15, 30, 45, 60, 90, 120, 150, 180). In addition, 0.5 g of activated carbon were exposed to different initial chlordecone concentration (50, 75, 100, 250, 750) in order to determine the chlordecone concentration effect on the adsorption mechanism. The rate of residual pesticides was determined using liquid chromatography coupled to a UV/visible detector. The kinetic data were analyzed by applying pseudo-first-order and pseudo-second-order models. The applicability of Langmuir and Freundlich adsorption isotherms was evaluated to better understand the adsorption process. The results revealed that the equilibrium data were perfectly represented using Langmuir II and Freundlich isotherms. The maximum multilayer adsorption capacity was found to be at pHZPC and a contact time 90 min. The kinetic data followed closely the pseudo-second-order model. Results from this study suggest that the activated carbon produced from date stones residue is an effective, low cost and locally available adsorbent for removing chlordecone from aqueous systems. This study imposed a conclusion of great concern since activated carbon from natural resources is considered as a renewable and cheaper precursor compared to the commercially available activated carbons.

KEYWORDS: adsorption, activated carbon, chlordecone, isotherm, kinetics.

INTRODUCTION

The long term environmental problems raised by application of highly chlorinated pesticides have been of great concern since the 1960s [1]. However, some chlorinated compounds, whose pollution potential has long

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been underestimated, are now known to pose serious human health and environmental problems. Such is the case for chlordecone $C_{10}Cl_{10}O$, who was extensively used to control a wide range of pests.

In May 2009, chloredecone was included in Annex A of the Stockholm Convention on Persistent Organic Pollutants.

Notwithstanding, the current residual chlordecone contamination still has negative impacts on human health, the environment and local economy. An example of this is the French West Indies FWI (Guadeloupe and Martinique), where chloredecone was used in banana plantations to control the weevil, *Cosmopolites sorditus*[2].

Due to its strong persistence in natural environments, its high resistance to chemical reactions and microbiological degradations, around 8-9% of the cultivation areas of Guadaloupe contain CLD concentrations higher then 1mg/kg in topsoil, and some banana fields exhibit CLD content higher than 9 mg/kg. Chlordecone has a strong affinity for lipids, accumulates in food chain [3;4]

Several methods are available for pesticides removal such as photocatalytic degradation [5;6], biological oxidation [7], aerobic degradation [8], nanofiltration membranes [9], ozonation[10] and adsorption[11;12].

Adsorption on activated carbon is the widest spread technology used to deal with purification of water contaminated by pesticides.

Commercially available activated carbons are still considered expensive due to the use of non-renewable and relatively expensive starting material such as coal. This has led a growing research interest in the production of activated carbons from renewable and cheaper precursors. To our knowledge, the adsorption of chlordecone in the solutions using date stones-based activated carbon was not studied.

In this work, we attempt to use date palm stones as low-cost, abundantly available and renewable precursor for production of activated carbon as adsorbent for the removal of pesticide from aqueous solutions. The date palm may be the world's oldest food-producing plant known to humans. Palm trees are abundant in several countries in the world such as Iraq, Saudi Arabia, Iran, Egypt, Algeria and other Mediterranean countries. Pits of date palm (seed) are a waste product of many industries, after technological transformation of the date fruits [13;14] or their biological transformation [15;16]. Date stones represent about 10% of the date weight. Any attempt to reutilize this waste will be useful.

Therefore, the purpose of this work was to evaluate the adsorption potential of date stones-based activated carbon for chlordecone. The equilibrium and kinetic data of the adsorption process were then studied to understand the adsorption mechanism of chlordecone molecules onto the prepared activated carbon.

MATERIALS AND METHODS

Chlordecone Pestanal® was purchased from Sigma-Aldrich (Schnelldorf, Germany) with a purity of 99.7%. Chlordecone is a non-ionic organochloride insecticide/fungicide that is slightly soluble in water, however, it is readily soluble in hydrocarbon solvents, alcohols and ketones [17]. The chemical structure of chlordecone is shown in Figure 1.

The activated carbons used were obtained from date stones bought from Tripoli, Lebanon. The collected date stones were soaked in phosphoric acid H_3PO_4 solution (60% concentration) with an impregnation ratio of H_3PO_4 : date stones of 7:4. Impregnation ratio is defined as the ratio of the weight of H_3PO_4 to the weight of date stones. The liquid/solid mixture was heated at 104°C (which corresponds to the boiling point of phosphoric acid) for 2h.

The slurry was then oven dried at 80°c for 3h, so as to achieve adsorption of the H3PO4 on to the date stones. The activation of the dried impregnated with phosphoric acid date stones was performed in a stainless steel vertical tubular reactor placed in a tube furnace at 450°c for 2h. The obtained char was washed with hot distilled water in order to achieve a neutral pH solution and then dried at 105°C for 2h. The product was finally ground and characterized[18].

The prepared activated carbons were characterized by selected adsorption properties including Iodine number and Methylene Blue number, and chemical property including the pH of point of zero charge. The details of characterization methods are illustrated as follows.

Iodine number is defined as the milligrams of iodine adsorbed by one gram of activated carbon. Basically, iodine number is a measure of the micropore content of activated carbon (0 to 20 Å) by adsorption of iodine from solution. Iodine number of the prepared carbon was determined as follows: 0.2g of activated carbon was weighed and added to a conical flask containing 20 ml of 0.02N iodine solution. The flask was shaken for 4-5 min and then filtered. 10 ml of the filtrate was titrated with 0.1N sodium thiosulfate solution till it becomes colorless. The iodine number was then calculated by using the following equation:

$$Q(I2) = \frac{\left[C0 - \frac{Cn \times Vn}{2 \times VI2}\right] \times MI2 \times Vads}{mCA}$$

Where Q_{I2} is iodine number (mg/g), V_n is the volume of sodium thiosulfate solution required for sample titrations (ml), C_n is the concentration of sodium thiosulfate solution (0.1 mol/L), C_0 is the initial concentration of iodine solution (0.02 mol/L), V_{I2} is the titrated volume of iodine solution (10ml), M_{I2} is the molar mass of iodine (253.81 g/mol), V_{abs} is the adsorption volume of iodine solution, m_{CA} is the mass of activated carbon (g) [19].

Methylene blue number is one of the most widely recognized probe molecules for assessing the removal capacity of the specific carbon for moderate-size pollutant molecules (≥ 1.5 nm). Methylene blue adsorption test was conducted by mixing 0.3g of the prepared activated carbon with 100 ml of 1200 mg/l methylene blue solution. After agitation during 24h, the suspension was filtered and the methylene blue residual concentration was measured at 620 nm, using an UV/vis spectrophotometer [18].

The pH of point of zero charge (pH_{ZPC}) was determined by adding 0.1 g of the prepare activated carbon to a series of Erlenmeyer flasks that contained 50 ml of distilled water. Before adding the adsorbent, the pH of the solutions was adjusted to be in the range 1.0-9.0 by the addition of 0.1 M NaOH or 0.1 M HNO₃ solutions. These Erlenmeyer flasks were then rotated for an hour in a shaker, and the pH values were measured at the end of the test. The pH of the suspensions is represented as a function of the initial pH of the solutions.

The pH_{ZPC} is the point where the curve of pH final vs pH initial intersects the line pH initial=pH final [20].

The effect of solution pH was studied by agitating 0.5 g of activated carbon prepared from date stones and 100 ml of chlordecone concentration 100 μ g/l using shaker at room temperature. The pH of the various solutions was adjusted from 2 to 10 by adding NaOH or HCl solutions. The suspensions were stirred for 2h.

The effect of contact time was performed by adding fixed amount of 0.5 g of activated carbons into 100 ml solution containing 100 μ g/l of chlordecone. The suspensions were stirred for different time intervals (15, 30, 45, 60, 90, 120, 150, 180 min).

The effect of initial chlordecone concentration was carried out using 250 ml Erlenmeyer flask containing 100 ml test solution of 50, 75, 100, 250 and 750 μ g/l of initial chlordecone concentration. 0.5 g of activated carbon was added. Then, the flasks were shaken at room temperature for 2 h.

The analysis of pesticide residues was performed by following these steps:

• Liquid-liquid extraction:

100 ml of the sample was mixed with 10 ml of hexane/acetone mixture (8.5/1.5 ml) and stirred for 10 min. The supernate was then decant and evaporated to dryness using the RapidVap Vacuum Evaporation System. 5 ml of methanol was then added and evaporated to dryness in order to ensure the total absence of hexane/acetone solution. 2 ml of methanol was finally added to the residues for injection.

• Quantification of chlordecone:

Samples (100 μ l) were injected and analyed with liquid chromatography Agilent Technologies coupled to a UV/visible detector. The column used for analysis was C18 column, 100 mm long and 3 micrometers inner diameter. Chlordecone was eluted with a water-methanol gradient changing as following:

Time (min)	Water (%)	Methanol (%)
0	100	0
10	100	0
13	0	100
25	0	100
30	100	0

Table 1: HPLC g	gradient.
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The flow rate was adjusted to 0.8 ml/min and the wavelength was set at 225 nm.

A chlordecone curve was obtained from area integrated peak counts derived from chromatograms produced by known concentrations of chlordecone (10, 25, 50, 100 μ g/L per injection)[21].

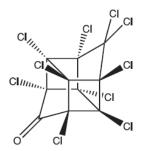


Fig. 1: Chemical structure of chlordecone.

RESULTS AND DISCUSSION

The knowledge of the characteristics of the activated carbon is necessary to contribute to the comprehension of many phenomena, like adsorption, desorption, or others. Table 2 represents some of the most important characteristics.

The results of analysis of the activated carbon (Table 2) showed that the percentage of iodine adsorption is 62 %. This indicated a high affinity of the activated carbon prepared from date stones for removing small sized contaminants.

The percentage of methylene blue adsorption is 32 %. The presence of high amount of micropores on the surface of the activated carbon indicates that the prepared sorbents show a good possibility for chlordecone to be trapped and adsorbed into the surface of the pores [22].

The pH_{ZPC} of activated carbon prepared from date stones was found to be 3. The significance of pH_{ZPC} of activated carbon surface is that it will have a positive charge at solution pH less than its pH_{ZPC} and thus be a surface on which anion may be adsorbed. On the other hand, if the solution pH is greater than that of pH_{ZPC} of activated carbons, the surface of the carbons will bear negatively charged and cations may be adsorbed on the surface.

Table 2: Adsorptive and chemical properties of prepared activated carbon

Parameter	Value
Iodine Number (% of adsorption)	62.5
Methylene blue Number (% of adsorption)	32
pH _{ZPC}	3

The effect of the solution pH on the on the adsorption of chlordecone on activated carbon prepared from date stones was examined under the following conditions: an initial chlordecone concentration of 100 μ g/l, 0.50 g of adsorbent, at room temperature, and constant contact time 120 min. The initial solution pH range was adjusted between 2 and 10. The experimental results are shown in Figure 2. We note that the adsorption capacity increases when the pH increases to reach a peak at pH = 3, close to the pH_{ZPC} of the activated carbon where the surface charge is neutral; it decreases then. Thus, when the pH = pH_{ZPC} chlordecone would mainly bind the activated carbon by hydrophobic interactions. At pH value lower than pH_{ZPC}, very low amounts of the molecule are adsorbed because at pH <pH_{ZPC}, adsorption of protons would induce a steric hindrance and lower the affinity of the molecule for the surface and at pH >pH_{ZPC} electrostatic repulsion between the negative surface of the activated carbon and the molecule would occur. On the other hand, the adsorption capacity re increases from a pH value of 5. This is due to the formation of chlordecone hydroxide (C₁₀ Cl₁₀ (OH)₂) by substitution of the carbonyl function with two alcohol groups. The chlordecone hydrate formed is much more hydrophilic than chlordecone and may have a higher affinity for activated carbon prepared from date stones surface [22].

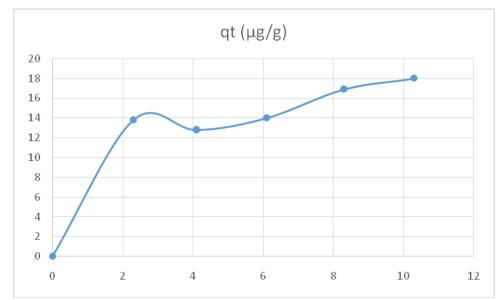


Fig. 2: Effect of solution pH on adsorption of chlordecone on the prepared activated carbon

The effect of contact time on the sorption of chlordecone by activated carbon was investigated for time periods from 15 min up to 3 h. From Figure 3, it is concluded that rate of chlordecone adsorption is fast at the initial stages of the contact time, and thereafter, it becomes slower near the equilibrium at t = 90 min. This may

be due to the availability of initial large number of vacant surface active sites for sorption during the first 90 min, and after a lapse of time, the remaining vacant surface sites are difficult to be occupied due to repulsive forces between chlordecone adsorbed on solid surface and chlordecone from solution. In order to study the kinetic of chlordecone adsorption on prepared activated carbon, pseudo-first-order and pseudo-second-order were tested [23].

The pseudo-first order equation [24]:

$$\log(q_{\rm e} - q_t) = \log q_{\rm e} - \frac{k_1}{2.303}t\tag{1}$$

The pseudo-second-order equation[25]:

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e} t$$
(2)

Where q_e and q_t refer to the amount of solute (mg/g) adsorbed at equilibrium and at any time t (min), respectively, k_1 is the equilibrium rate constant of pseudo-first order sorption (1/min), k_2 is the equilibrium rate constant of pseudo-second order adsorption (g/mg min). A linear plot of log (q_e - q_t) against time allows to obtain the rate constant k_1 (Figure 4). The pseudo-first order rate constant k_1 and q_{ecalc} determined from the model are presented in Table 3 along with the corresponding correlation coefficient. It can be seen that there is no agreement between q_e experimental and q_e calculated values for the pseudo-first order model.

The equilibrium adsorption capacity (q_e) , and the second-order constant k_2 can be determined experimentally from the slope and intercept of plot t/q_t versus t (Figure 5). The k_2 and q_{ecalc} determined from the model are presented in Table 3 along with the corresponding correlation coefficient. It was seen that the pseudo-second order model better represented the adsorption kinetics with a higher correlation coefficient and the calculated q_e value agreed with the experimental q_e value (table 3). This suggests that the adsorption of chlordecone follows pseudo-second-order kinetics. Pseudo-second order kinetic model implies that the predominant process here is chemisorption, which involves a sharing of electrons between the adsorbate and the surface of the adsorbent [26].

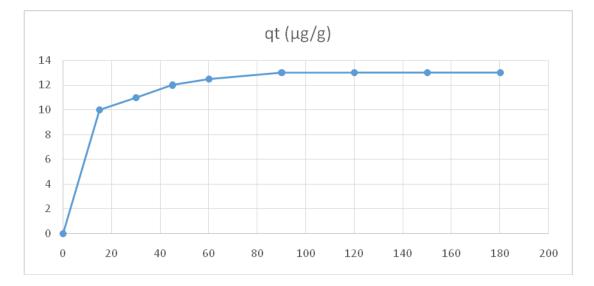


Fig. 3: Effect of contact time on adsorption of chlordecone on the prepared activated carbon

Table 3: kinetic model parameters for the adsorption of chlordecone onto activated carbon.

Kinetic model	Parameters	Value	
Pseudo-first order	Qe,exp (µg/l)	13	
	K _{1 (1/min)}	0.04	
	Qe,cal (µg/l)	5.99	
	R^2	0.9867	
Pseudo-second order	Qe,exp (µg/l)	13	
	K _{2 (g/µg min)}	0.014	
	Qe,cal (µg/l)	13.4	
	\mathbb{R}^2	0.9996	

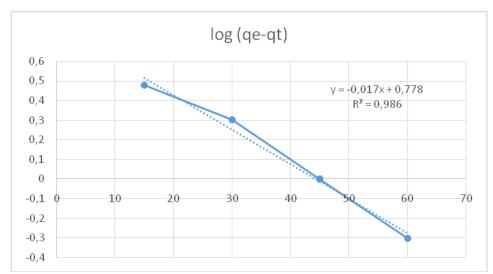


Fig. 4: Pseudo-first-order kinetic for adsorption of chlordecone on activated carbon prepared from date stones.

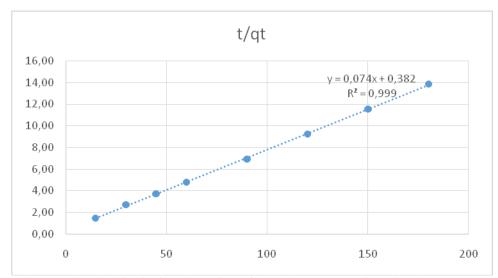


Fig. 5: Pseudo-second-order kinetic for adsorption of chlordecone on activated carbon prepared from date stones.

Activated carbon was equilibrated with chlordecone solutions of different concentrations 500-1000 ppb for 2h at ambient temperature in order to study the effect of initial chlordecone concentration. After filtration and extraction, the final concentrations of chlordecone in solutions were measured.

The Langmuir and Freundlich adsorption isotherms, often used to describe the sorption of solutes from a liquid phase, were applied to our experimental results. Linear form of Langmuir equation can be expressed as follows [27]:

$$\frac{ce}{qe} = \frac{1}{q0b} + \frac{ce}{q0} \tag{3}$$

Where Ce is the equilibrium concentration ($\mu g/L$), qe is the amount of chlordecone sorbed at equilibrium, b is the sorption constant (L/ μg) at a given temperature, q₀ is the maximum sorption capacity $\mu g/g$.

The plot of specific adsorption (C_e/q_e) against the equilibrium concentration (C_e) shows that the adsorption obeys the Langmuir model Figure 6.

The Langmuir constants Q_0 and b were determined from the slope and intercept of the plot. The essential characteristics of the Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor $R_L[28]$ that is given by Eq.

$$RL = \frac{1}{1+bc0}$$

(4)

Where C_0 is the highest initial concentration of adsorbate ($\mu g/L$), and b ($L/\mu g$) is Langmuir constant.

The value of RL indicates the shape of the isotherm to be either unfavorable (RL >1), linear (RL =1), favorable (0 < RL < 1), or irreversible (RL =0). The RL values between 0 and 1 indicate favorable adsorption. The

value of RL in the present investigation was found to be 0.021 indicating that the adsorption of chlordecone on activated carbon is favorable.

The Langmuir model is basically developed to describe the sorption processes where no interaction between sorbate species occur on sites having the same sorption energies independent of surface coverage [29]. Maximum adsorption capacity q_0 of chlordecone onto activated carbon was 232.55µg/L. RL value was calculated as 0.02, which is greater than zero and less than unity, showing favorable adsorption of chlordecone onto activated carbon with H3PO4 under optimal conditions.

The Freundlich isotherm [30] is an empirical equation employed to describe heterogeneous systems. The linear form of Freundlich equation is expressed:

$$\ln qe = \ln kf + \frac{1}{n}\ln Ce \tag{5}$$

Where K_F and n are Freundlich constants with $K_F (\mu g/g(L/\mu g)^{1/n})$ is the adsorption capacity of the sorbent and n giving an indication of how favorable the adsorption process. The magnitude of the exponent 1/n gives an indication of the favorability of adsorption. Values of n>1 represent favorable adsorption condition. Values of K_F and n are calculated from the intercept and slope of the plot.

Graphic presentations of the adsorption isotherms of chlordecone onto activated carbon prepared under the optimal conditions along with its validation with Freundlich isotherm at ambient temperature is illustrated in Figure 7.

The values of isotherm constants are given in table 4, the R^2 values show that the Langmuir and freundlich isotherms fitted quite well with the experimental data with a high correlation coefficient $R^2=0.9$.

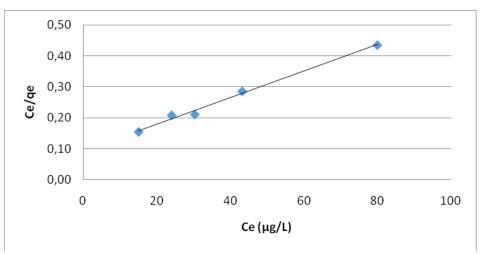


Fig. 6: Langmuir adsorption isotherm of chlordecone on activated carbon

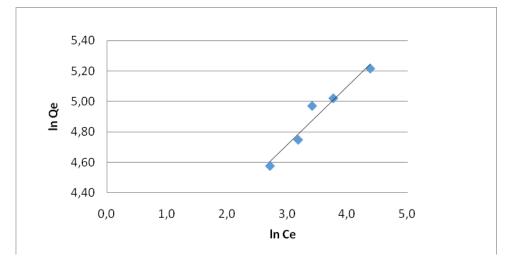


Fig. 7: Freundlich adsorption isotherm of chlordecone on activated carbon

Isotherms	Parameter	Value
Langmuir	$q_0 (\mu g/g)$	232.55
	b (L/µg)	0.05
	R _L	0.02
	\mathbb{R}^2	0.99
Freundlich	K _f	35.24
	n	2.6
	\mathbb{R}^2	94.92

Table 4: equilibrium model parameters for adsorption of chlordecone onto optimal activated carbon

Conclusion:

The present study shows that activated carbon prepared from date stones, using chemical activation by phosphoric acid, constitutes a good adsorbent for removing chlordecone from aqueous systems. The aspects of the adsorption under different parameters (different pH of the media, different contact time between chlordecone and activated carbon, different initial chlordecone concentration) were evaluated. The adsorption capacity reached a peak at pH = 3, close to the pH_{ZPC} of the activated carbon. Besides, it was concluded that rate of chlordecone adsorption is fast at the initial stages of the contact time, and thereafter, it becomes slower near the equilibrium at t= 90 min. The equilibrium data were also studied and fitted to the Langmuir and Freundlich isotherm models and the maximum adsorption capacity calculated from the Langmuir isotherm was equal to 232.55 (μ g/g). The suitability of the kinetic models for the adsorption of chlordecone obeyed pseudo-second-order adsorption kinetics. Thus, the present study conclude that date stones derived activated carbon prepared under the conditions listed above is a low cost and locally available adsorbent for environmental protection purpose. Based on the satisfied results obtained by this study, further work concerning a widest range of micropollutants (organochlorine pesticides, polycyclic aromatic hydrocarbons, polychlorinated biphenyls, drugs residues...) can be studied in order to solve the large encountered environmental problems.

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This study has contributed to increase the knowledge about the use of activated carbon derived from date stone in removing or decreasing the concentration of chlordecone pesticides from drinking water by the application of adsorption mechanism.

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