



King Saud University
Arabian Journal of Chemistry

www.ksu.edu.sa
www.sciencedirect.com



ORIGINAL ARTICLE

Adsorptive removal of cadmium from aqueous solution by cork biomass: Equilibrium, dynamic and thermodynamic studies



Fouad Krika^a, Nouredine Azzouz^a, Mohamed Chaker Ncibi^{b,*}

^a Department of Process Engineering, Faculty of Sciences and Technology, University of Jijel, BP 98 Ouled Aissa, Jijel, Algeria

^b COVACHIMM, EA 3592 Laboratory, University of Antilles and Guyane, BP 250, 97157 Pointe à Pitre Cedex, Guadeloupe, France

Received 31 May 2011; accepted 10 December 2011

Available online 17 December 2011

KEYWORDS

Adsorption;
Cork biomass;
Cadmium;
Equilibrium;
Kinetics;
Modeling;
Thermodynamics

Abstract The removal of toxic metal, cadmium, by using adsorption into Algerian cork biomass was investigated. The biosorption process was studied with respect to contact time, particle size, pH and temperature. The results showed that equilibrium was reached within 1 h. The used biosorbent gave the highest adsorption capacity at pH 6. The experimental isotherm data were analyzed and modeled. The maximum adsorption capacity, Langmuir's q_{\max} , improved from 9.65 to 14.77 mg/g as the temperature increased from 20 to 40 °C. The enthalpy ΔH° and entropy ΔS° values were respectively estimated at 110.47 kJ mol⁻¹ and 0.3795 kJ K⁻¹ mol⁻¹ for the process, which reflects the endothermic nature and the spontaneous feasibility of the present sorption system. Besides, the adsorption kinetics was found to follow the second-order model, suggesting therefore a possible chemisorption process.

© 2011 Production and hosting by Elsevier B.V. on behalf of King Saud University. This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/3.0/>).

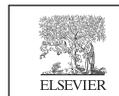
1. Introduction

Water contaminated by heavy metals remains a serious environmental and public problem (Gaballah and Kilbertus, 1998). Industrial wastewater often contains considerable amount of heavy metals and organic pollutants that would endanger public health and the environment if discharged without adequate treatment. The heavy metals are of special concern because they are non-degradable and therefore persistent (Namasivayam and Ranganathan, 1995). Cadmium is one of the heavy metals with a greatest potential hazard to humans and environment (Wase and Forster, 1997). It makes its way to water bodies through wastewater from metal plating industries, industries of Cd–Ni batteries, phosphate fertilizer, min-

* Corresponding author. Address: Laboratoire COVACHIMM, EA 3592 Université des Antilles et de la Guyane, BP 250, 97157 Pointe à Pitre Cedex, Guadeloupe, France. Tel.: + 590 590 48 30 50; fax: + 590 590 48 30 72.

E-mail address: ncibi_mc@yahoo.com (M.C. Ncibi).

Peer review under responsibility of King Saud University.



Production and hosting by Elsevier

ing, pigments, stabilizers and alloys (Low and Lee, 1991). Poisoning of cadmium in humans causes high blood pressure, kidney damage and destruction of testicular tissue and red blood cells (Parker, 1980). In small amounts cadmium is associated with hypertensive diseases and considered as carcinogenic to men (Schroeder, 1965).

Development of technically simple and economically attractive methods of industrial waste purification is one of the most important priorities of the 21st century (Volesky, 2001). Many chemical methods such as chemical precipitation (Navarro et al., 2005), electro-flotation (Gao et al., 2004), ion-exchange (Lacour et al., 2002) and reverse osmosis (Qdais and Mousab, 2004) have been used for the removal of heavy metals. However, these processes are economically non feasible especially in developing countries. The adsorption process has been found to be economically appealing for the removal of heavy metals with better removal efficiency from wastewater (Rao and Moonis, 2009). The optimisation of adsorption methods should be carried out, first of all, by choosing or developing inexpensive adsorbents selective to the contaminants to be removed. Different types of biomasses (or adsorbents of natural origin) have been studied for the last two decades and adsorption characteristics of many of them have been widely investigated (Figueira et al., 2000; Loukidou and Zouboulis, 2001).

These biomaterials present different type of functional groups, such as carboxylic, sulphates, phosphates and amino groups, which are the binding site for the ion-exchange and complexation reactions.

The aim of the present study was to investigate the efficiency of removing cadmium ions from aqueous solutions using cork as biosorbent. Several factors affecting this process are considered. Adsorption of cadmium was studied at different contact time and particle size; the influence of pH on cadmium biosorption was carried out. The adsorption capacity of cork biomass toward cadmium was investigated and adsorption isotherms were determined.

2. Experimental

2.1. Materials

The cork powder used was supplied by the Algerian company "EPE/ JIJEL Etanchetés SPA". Particle size fractions were obtained by sieving and the experiments were carried out with the size fractions with a particle diameters of ($d_1 < 0.08$; $0.08 < d_2 < 0.1$; $0.1 < d_3 < 0.16$ and $0.16 < d_4 < 0.2$ mm). Atomic absorption spectrometer AAS (Shimadzu AA-6200) with hollow cathode lamp and air acetylene flame was used for determining cadmium concentration. A HANNA instrument (pH 211) pH meter was used for pH measurements. A magnetic stirrer (Heidolph-RZR-2020) was used to agitating the samples.

2.2. Preparation of solution

All the chemicals used were of analytical reagent grade. Distilled water was used throughout the experimental studies. A stock cadmium solution for desired concentration was prepared by dissolving cadmium nitrate $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ in distilled water. Working standard was prepared by progressive dilution of stock cadmium solutions using distilled water.

ACS reagent grade HCl, NaOH and buffer solutions (E. Merck) were used to adjust the solution pH.

2.3. Biosorption studies

The adsorption experiments were carried out by batch process. 0.05 g of biosorbent was placed in Erlenmeyer flasks with 50 mL solution of metal ions of desired concentration. The entirety was agitated during a certain time at 250 rpm. Once the operation time had elapsed, the liquid phase was taken out, and then filtered through filter paper (Double Boxing rings 102) and final concentration of metal ion was determined in the filtrate by atomic absorption spectrometry (AAS). The amount of metal ions adsorbed at equilibrium per unit mass of biosorbent was determined according to the following equation:

$$q_e = \frac{(C_0 - C_e) \cdot V}{m} \quad (1)$$

Where, m is the mass of adsorbent (g), V is the volume of the solution (L), C_0 is the initial concentration of metal (mg/L), C_e is the equilibrium concentration of the adsorbate (mg/L) in solution and q_e is the metal quantity adsorbed at equilibrium (mg/g).

For the calculation of cadmium rate adsorption (R), the following expression was used:

$$R(\%) = \frac{(C_0 - C_e)100}{C_0} \quad (2)$$

2.4. Effect of contact time

Batch biosorption tests were done at different contact time at the initial metal ion concentration of 10 mg/L, and biosorbent concentration of 0.05 g in 50 mL solution, at 25 °C. The solid was kept in contact with the solution for different time periods (10; 20; 30; 40; 50; 60; 70; 80; 90 and 100 min), the solution of the specified flask was taken out and filtered. The concentration of metal was determined by AAS.

2.5. Effect of particles size

The effect of the biosorbent particle size (between 0.05 and 0.2 mm) on the adsorption capacity of cork biomass was investigated at 25 °C using 0.05 g of adsorbent, 50 mL of solution and cadmium concentration of 10 mg/L. The mixtures were shaken, and after equilibrium, the solutions were filtered. The concentration of metal ions was then determined.

2.6. Effect of pH

The effect of pH on the sorption of cadmium was studied by batch process as follows: 100 mL of metal solution was taken in beaker. The desired pH of solution was adjusted by adding dilute solution of HCl and NaOH. Then, 50 mL of these solutions were taken in Erlenmeyer flasks and mixed with 0.05 g of adsorbent. After equilibrium, the final concentration of metal ions was determined and the rate of metal adsorbed was calculated.

2.7. Equilibrium studies

Equilibrium isotherm studies were conducted for 1 h at 20, 30 and 40 °C using a constant amount of biosorbent (0.05 g) in 50 mL solution of pH 6 and for initial metal concentrations between 10 and 100 mg/L. The samples were then filtered and analysis was performed as mentioned before.

3. Results and discussions

3.1. Effect of contact time

The results obtained from the biosorption rate tests are shown in Fig. 1. It revealed that the rate of adsorption increased with increasing contact time. It was noticed that the maximum rate of cadmium elimination equals 29.9%. The extent of sorption increased rapidly during the initial stage and then became slower at later stage till the equilibrium is attained. Equilibrium time for the sorption of cadmium was found to be 60 min. These data are important because equilibrium time is one of the key parameters for economical wastewater treatment application (Kadirvelu and Namasivayam, 2003). Thus, the agitation time was fixed at 100 min for the rest of the batch experiments to make sure that equilibrium was reached. This equilibrium time is shorter than those usually employed for the adsorption of cadmium by other adsorbent materials. Indeed, times of 24 h were proposed for adsorption systems involving chitin (Benguella and Benaissa, 2002), chitosan (Becker et al., 2000), Baker's yeast (Vasudevan et al., 2003) or *Pinus pinaster* bark (Vazquez et al., 2002). Furthermore, other sorbents needed even longer time to reach the equilibrium state like 72 h for some carbonaceous material (Hanzlik et al., 2004) and even 3–5 days for an activated carbon (Leyva-Ramos et al., 1997).

3.2. Effect of particles size

The contact surface between any sorbent and the liquid phase plays an important role in the phenomena of sorption. According to Fig. 2, the results showed that the rate of cadmium biosorption increases with the reduction in the diameter of the particles, which is probably due to the increase of the number of active sites and thus the increase of the biosorbent surface. The maximum rate elimination of cadmium (i.e.

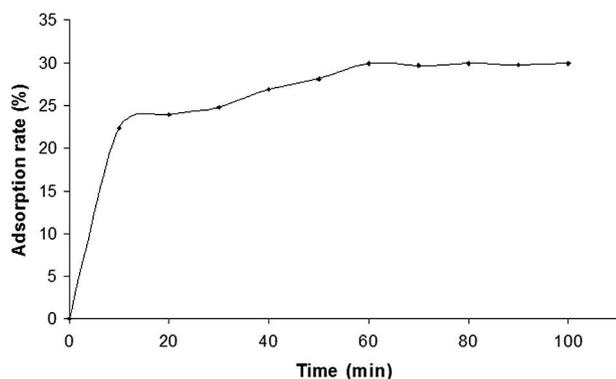


Figure 1 Effect of contact time cadmium ions sorption onto cork biomass ($C_0 = 10$ mg/L, $m = 0.05$ g, $T = 25$ °C, agitation rate = 250 rpm, $d_1 < 0.08$ mm).

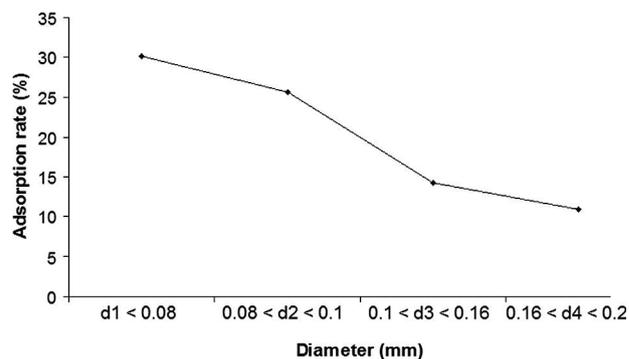


Figure 2 Effect of biosorbent particle size on cadmium biosorption onto cork biomass ($C_0 = 10$ mg/L, $m = 0.05$ g, $T = 25$ °C, agitation rate = 250 rpm).

30.19%) was reached using the fine particle (diameter less than 0.08 mm). Similar results have been reported for the adsorption of cadmium using manganese nodule residue (Agrawal and Sahu, 2006) and vegetable wastes (Azouaou et al., 2008).

3.3. Effect of pH

The pH of the aqueous solution is an important controlling parameter in the adsorption process. The binding of metal ions with surface functional groups was strongly pH dependent (Lee and Davis, 2001). The percentage sorption of cadmium on cork powder increased with the increase of pH, attaining a maximum at pH 6 (Fig. 3). Availability of negatively charged groups on the adsorbent surface is necessary for the sorption of metals (Ajmal et al., 2005). Sorption at pH 2 was limited since the sorbent surface potentially gained a global positive charge due to the presence of H^+ and H_3O^+ . In such conditions, hydrogen and hydronium ions compete with metal ions (Luef et al., 1991) resulting in active sites to become protonated to the virtual exclusion of metal binding on the sorbent surface (Low et al., 1993). Hence, at higher H^+ concentration, the sorbent surface becomes more positively charged thus reducing the attraction between sorbent and metal cations (Aldov et al., 1995). In contrast, as the pH increases, more negatively charged surface becomes available thus facilitating

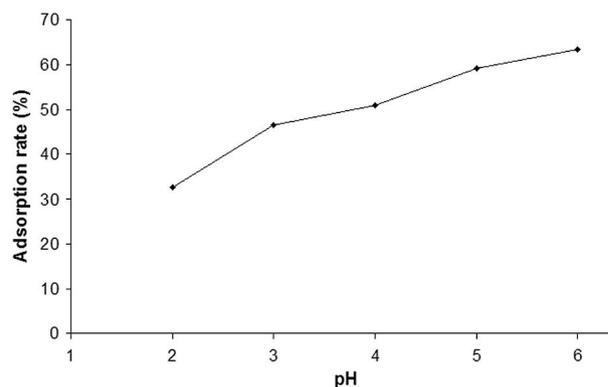


Figure 3 Effect of initial pH on cadmium biosorption by cork powder ($C_0 = 10$ mg/L, $m = 0.05$ g, $T = 25$ °C, agitation rate = 250 rpm, $d_1 < 0.08$ mm).

greater metal uptake and therefore metal sorption tends to increase significantly by increasing pH.

3.4. Biosorption isotherms

The analysis of equilibrium data to monitor the adsorption process is quite important for design purposes. Adsorption isotherms express the mathematical relationship between the quantity of adsorbate and equilibrium concentration of adsorbate remaining in the solution at a constant temperature. Sorption data for wide range of adsorbate concentration are most conveniently described by sorption isotherms. The adsorption studies were carried out at 20, 30 and 40 °C to determine the adsorption isotherms and the isotherm parameters were evaluated using non-linear Langmuir and Freundlich models.

Langmuir adsorption isotherm is often used to describe the maximum adsorption capacity of adsorbent, which is a most important parameter for an adsorption system. The Langmuir equation (Langmuir, 1918) is written as follows:

$$q_e = \frac{q_{\max} K_L C_e}{1 + K_L C_e} \quad (3)$$

The above can be rewritten to the following linear form:

$$\frac{C_e}{q_e} = \frac{1}{K_L q_{\max}} + \frac{C_e}{q_{\max}} \quad (4)$$

where, q_{\max} (mg/g) is the maximum adsorption capacity. K_L (L/mg) is a constant related to the affinity of binding sites or bonding energy. q_{\max} denotes a practical limiting adsorption capacity when the surface of adsorbent is completely covered with adsorbate. The maximum adsorption capacity is compared in Table 1 with the data reported by other authors for cadmium biosorption. As can be seen, the maximum cadmium sorption value of cork is higher than those reported in the literature. This comparison indicates the great potential of cork for the removal of cadmium from wastewater.

The empirical Freundlich isotherm is based on adsorption on a heterogeneous surface. It is expressed by the following equation (Freundlich, 1906):

$$q_e = K_F \cdot C_e^{1/n} \quad (5)$$

Where K_F [(mg/l)·(l/mg)^{1/n}] and n (dimensionless) are the Freundlich constant and exponent related to the adsorption capacity and intensity, respectively. Eq. (5) is generally used at the linear form represented by:

$$\ln q_e = \ln K_F + \frac{1}{n} \cdot \ln C_e \quad (6)$$

The Langmuir and Freundlich isotherms for the adsorption of cadmium on the cork powder at different temperatures are presented in Fig. 4. The corresponding Langmuir and Freundlich parameters along with correlation coefficients are given in Table 2.

The experimental results are well fitted by the Langmuir model then the Freundlich model considering the values of regression coefficients presented in Table 2 which are higher than 0.99. The values of q_{\max} and K_L calculated from Langmuir plots were found to be 9.65 mg/g and 0.20 L/mg for the experiments carried out at 20 °C. The values of both q_{\max} and K_L increased with a rise in the solution temperature. The values of q_{\max} increased from 9.65 to 14.77 mg/g, when the solution temperature increased from 20 to 40 °C. The increasing trend was observed for the values of K_L depending upon the temperature of solution. The increase in the values of q_{\max} and K_L with temperature indicates that the cadmium ions are favourably adsorbed by cork powder at higher temperatures, which shows that the cadmium adsorption phenomenon is endothermic.

The essential feature of the Langmuir isotherm can be expressed in terms of dimensionless separation constant or equilibrium parameter (R_L), which is defined as:

$$R_L = \frac{1}{(1 + K \cdot C_0)} \quad (7)$$

The values of R_L indicate the type of isotherm to be irreversible ($R_L = 0$), favourable ($0 < R_L < 1$), linear ($R_L = 1$) or unfavourable ($R_L > 1$). The R_L values were found to be less than 1 and greater than 0 (Table 3) for all experiments carried out at different initial concentrations and temperatures. It is found that the adsorption of cadmium on cork powder is a favourable phenomenon. Thus, cork seems to have a good affinity for cadmium ions removal and its adsorption capacity increased as the temperature increases.

3.5. Thermodynamics studies

In the environmental engineering practice, thermodynamic parameters including standard enthalpy change (ΔH°), standard entropy change (ΔS°) and standard free energy change (ΔG°) should be considered in order to determine if the adsorp-

Table 1 Maximum adsorption capacities of cadmium from aqueous media using various sorbents.

Sorbents	q_{\max} (mg/g)	References
Algerian Cork	9.65	This study
Activated carbon from <i>C. pentandra</i> hulls	19.60	Rao et al. (2006)
Tea-industry waste	11.26	Cay et al. (2004)
Olive cake	10.56	Doyurum and Celik (2006)
Chitosan	8.54	Becker et al. (2000)
Granular activated carbon F400	8.00	Mohan et al. (2007)
<i>Pinus halepensis</i> sawdust	7.35	Semerjian (2010)
Date pits	6.50	Banat et al. (2003)
Oak bark char	5.40	Mohan et al. (2007)
Hazelnut shell	5.42	Cimino et al. (2000)
Tannic acid modified activated carbon	2.46	Ucer et al. (2006)
Bagasse fly ash	2.00	Gupta et al. (2003)
Pine bark char	0.34	Mohan et al. (2007)

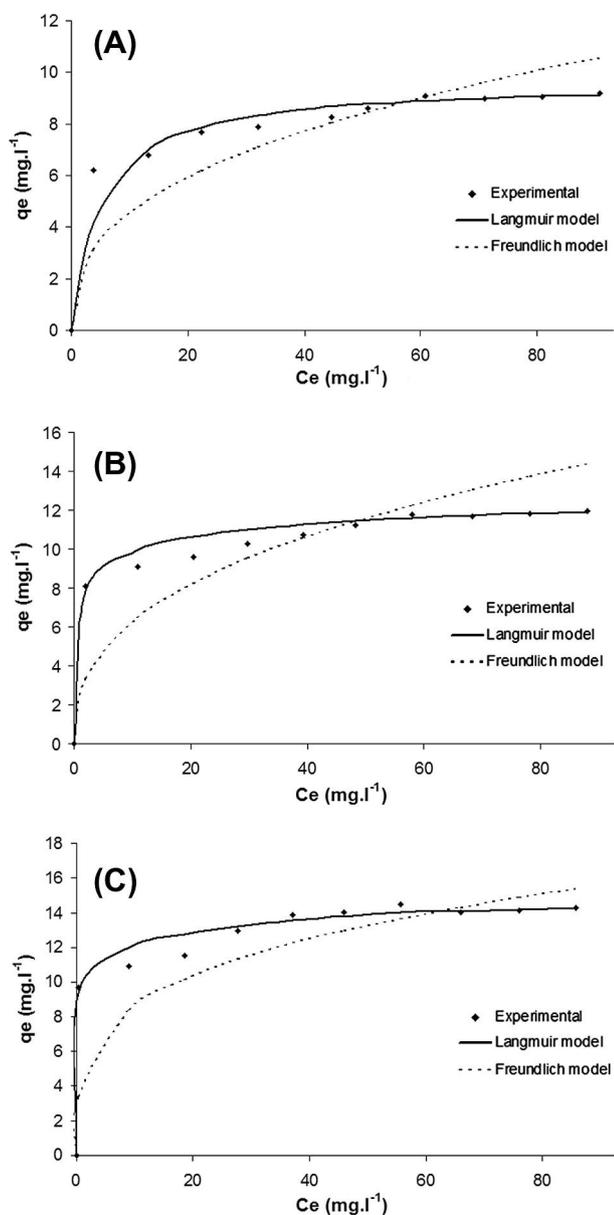


Figure 4 Adsorption isotherms modelling related to the bio-sorption of cadmium onto cork powder at 20 °C (A), 30 °C (B) and 40 °C (C) [$C_0 = 10\text{--}100\text{ mg/L}$, $m = 0.05\text{ g}$, $d_1 < 0.08\text{ mm}$, pH 6].

tive removal process will occur spontaneously. Thus, (ΔH°) and (ΔS°) were obtained from the Van't Hoff equation:

$$\ln(K_c) = \frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} \quad (8)$$

Table 3 The values of R_L based on the Langmuir isotherm for cadmium ions adsorption.

C_0 (mg/L)	R_L values with respect to temperature (°C)		
	20	30	40
10	0.33	0.30	0.24
20	0.20	0.18	0.14
30	0.14	0.13	0.09
40	0.11	0.11	0.07
50	0.09	0.08	0.06
60	0.08	0.07	0.05
70	0.07	0.06	0.04
80	0.06	0.05	0.03
90	0.05	0.04	0.02
100	0.04	0.03	0.01

where, ΔS° and ΔH° were calculated from the slope and intercept of linear plots of $\log K_c$ versus $1/T$ (data not shown). Equilibrium constant (K_c) was calculated from the following relationship:

$$K_c = \frac{C_{Ae}}{C_e} \quad (9)$$

where, C_{Ae} and C_e are the equilibrium concentrations of metal (mg/L) on adsorbent and in solution, respectively.

The very useful relationship between standard free energy change and equilibrium constant is given by the following equation:

$$\Delta G^\circ = -RT \cdot \ln(K_c) \quad (10)$$

where, T (K) is the absolute temperature, R (8.3145 J/mol K) gas constant, ΔG° is the standard free energy change.

The positive values of ΔH° (Table 4) suggest endothermic nature of adsorption and cadmium ions are adsorbed more efficiently on cork powder at higher temperatures. The standard free energy change (ΔG°) of the process decreases with increase in temperature, which indicates that the process is spontaneous and spontaneity increases with increase in temperature. The positive values of standard entropy change (ΔS°) shows the increase in randomness at the solid/solution interface during the adsorption of cadmium.

3.6. Kinetic studies

A quantitative understanding of the sorption is possible with the help of kinetic models. The pseudo-first-order kinetic model, as expressed by Lagergren (1898), can be written as:

$$\log(q_e - q_t) = \log q_e - k_1 t / 2.303 \quad (11)$$

where q_e and q_t are the amounts of metal sorbed (mg g^{-1}) at equilibrium and at time t , respectively, and k_1 is the pseudo-first-order equilibrium rate constant (1/min). A plot of \log

Table 2 Langmuir and Freundlich constants for cadmium ions adsorption onto cork biomass.

Temperature (°C)	Langmuir			Freundlich		
	q_{\max} (mg/g)	K_L (l/mg)	r^2	$1/n$	K_F (mg/l)/(l/mg) $^{1/n}$	r^2
20	9.65	0.20	0.996	1.88	2.61	0.703
30	12.48	0.23	0.996	2.60	2.62	0.637
40	14.77	0.31	0.996	4.60	3.69	0.413

Table 4 Thermodynamic parameters for the adsorption of cadmium ions on cork powder at different temperatures.

T (°C)	ΔG° (kJ/mol)	ΔH° (kJ/mol)	ΔS° (kJ/mol K)	r^2
20	-0.72 ± 0.08	110.47 ± 9	0.3795 ± 0.05	0.959
30	-4.51 ± 0.3			
40	-8.31 ± 0.7			

Table 5 Pseudo-first-order and pseudo-second-order kinetic constants for the adsorption of cadmium ions on cork powder.

k_1 (1/min)	Pseudo-first-order			Pseudo-second-order			
	$q_{e(\text{theo})}$ (mg/g)	$q_{e(\text{exp})}$ (mg/g)	r^2	k_2 (g/mg min)	$q_{e(\text{theo})}$ (mg/g)	$q_{e(\text{exp})}$ (mg/g)	r^2
0.089	1.85	3	0.939	0.3113	3.21	3	0.991

$(q_e - q_t)$ vs. t gives straight line confirming the applicability of the pseudo-first-order rate equation.

Pseudo-second-order sorption rate equation (Ho et al. 1996) may be expressed as follows

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \quad (12)$$

k_2 is the pseudo-second-order sorption rate constant (g/mg min). Straight line plot of t/q_t vs. t indicates the applicability of pseudo-second-order model.

The results have been analyzed using Eqs. (11) and (12). The experimental data fitted well with both equations. The values of $q_{e(\text{theo})}$ calculated from these models were compared with experimental values $q_{e(\text{exp})}$ (Table 5). It was found that for pseudo-first-order kinetic model the values of $q_{e(\text{theo})}$ and $q_{e(\text{exp})}$ differed appreciably. On the other hand, values of $q_{e(\text{theo})}$ are very close to $q_{e(\text{exp})}$ for pseudo-second-order model. The values of correlation coefficients (r^2) are very high for pseudo-second-order model as compared to pseudo-first-order rate model (0.99 and 0.93, respectively). It is therefore confirmed that sorption of cadmium on cork follows the pseudo-second-order rate equation.

4. Conclusions

The present study showed that the cork is a low cost biosorbent available abundantly in Algeria. The sorption of cadmium onto cork powder was studied. It has been established that this biomaterial has an acceptable sorption capacity toward the toxic metal ion. Based upon the experimental results of this study, the following conclusions can be drawn:

- The removal rate increased with increasing contact time and reached the equilibrium state within 60 min.
- The adsorption is favoured by an increase of pH. The optimum pH was determined as 6. At this pH, the removal rate of cadmium ions was found to be 64.48%.
- The extent of the removal of cadmium is directly related to the particle size of cork biomass. It was observed that the removal rate increases with the decrease of the diameter of the biosorbent in the suspension.
- The results related to adsorption isotherms showed that the equilibrium data fitted very well to the Langmuir model. It was observed that the isotherm constant increased with increasing temperature. The values of q_{max}

increased from 9.65 to 14.77 mg g⁻¹, when the solution temperature increased from 20 to 40 °C, which proves that the adsorption process is endothermic.

- The enthalpy ΔH° and entropy ΔS° values were found equal to 110.47 kJ mol⁻¹ and 0.3795 kJ K⁻¹ mol⁻¹ for the process. The negative value of (ΔG°) reflects the feasibility and spontaneous nature of that process.
- The kinetics models for the adsorption of cadmium on cork powder confirms better applicability of pseudo-second-order rate equation as evident from regression coefficient.

References

- Agrawal, A., Sahu, K.K., 2006. Kinetic and isotherm studies of cadmium adsorption on manganese nodule residue. *J. Hazard. Mater.* 137, 915–924.
- Ajmal, M., Rao, R.A., Khan, M.A., 2005. Adsorption of copper from aqueous solution on *Brassica cumpestris* (mustard oil cake). *J. Hazard. Mater.* 122, 177–183.
- Aldov, I., Fourest, E., Volesky, B., 1995. Desorption of cadmium from algal biosorbent. *Can. J. Chem. Eng.* 73, 516–522.
- Azouaou, N., Sadaoui, Z., Mokaddem, H., 2008. Removal of cadmium from aqueous solution by adsorption on vegetable wastes. *J. Appl. Sci.* 24, 4638–4643.
- Banat, F., AL-Asheh, S., Makhadmeh, L., 2003. Kinetics and equilibrium study of cadmium ion sorption onto date pits: an agricultural waste. *Adsorpt. Sci. Technol.* 21, 245–260.
- Becker, T., Schlaak, M., Strasdeit, H., 2000. Adsorption of nickel (II), zinc (II) and cadmium(II) by new chitosan derivatives. *React. Funct. Polym.* 44, 289–298.
- Benguella, B., Benaissa, H., 2002. Cadmium removal from aqueous solutions by chitin: kinetic and equilibrium studies. *Water Res.* 36, 2463–2474.
- Cay, S., Uyanik, A., Ozasik, A., 2004. Single and binary component adsorption of copper(II) and cadmium(II) from aqueous solutions using tea-industry waste. *Sep. Purif. Technol.* 38, 273–280.
- Cimino, G., Passerini, A., Toscano, G., 2000. Removal of toxic cations and Cr(VI) from aqueous solution by hazelnut shell. *Water Res.* 34, 2955–2962.
- Doyurum, S., Celik, A., 2006. Pb(II) and Cd(II) removal from aqueous solutions by olive cake. *J. Hazard. Mater.* B138, 22–28.
- Figueira, M.M., Volesky, B., Ciminelli, V.S., 2000. Biosorption of metals in brown seaweeds biomass. *Water Res.* 34, 196–204.
- Freundlich, H.M., 1906. Over the adsorption in solution. *Z. Phys. Chem.* 57, 385–470.

- Gaballah, I., Kilbertus, G., 1998. Recovery of heavy metal ions through decontamination of synthetic solutions and industrial effluents using modified barks. *J. Geochem. Explor.* 62, 241–286.
- Gao, P., Chen, X., Shen, F., Chen, G., 2004. Removal of chromium(VI) from wastewater by combined electrocoagulation–electroflotation without a filter. *Sep. Purif. Technol.* 43, 117–123.
- Gupta, V.K., Jain, C.K., Ali, I., Sharma, M., Saini, V.K., 2003. Removal of cadmium and nickel from wastewater using bagasse fly ash—a sugar industry waste. *Water Res.* 37, 4038–4044.
- Hanzlik, J., Jehlika, J., Sebek, O., Weishauptova, Z., Machovic, V., 2004. Multi-component adsorption of Ag(I), Cd(II) and Cu(II) by natural carbonaceous materials. *Water Res.* 38, 2178–2184.
- Ho, Y.S., Wase, D.A., Forster, C.F., 1996. Kinetic studies of competitive heavy metal adsorption by sphagnum moss peat. *Environ. Technol.* 17, 71–77.
- Kadirvelu, K., Namasivayam, C., 2003. Activated carbon from coconut coirpith as metal adsorbent: adsorption of Cd(II) from aqueous solution. *Adv. Environ. Res.* 7, 471–478.
- Lacour, S., Bollinger, J.C., Serpaud, B., Chantron, P., Arcos, R., 2002. Removal of heavy metals in industrial wastewaters by ion-exchanger grafted textiles. *Anal. Chim. Acta* 428, 121–132.
- Lagergren, S., 1898. About the theory of so-called adsorption of soluble substances. *K. Sven. Vetenskapsakad. Handl.* 24, 1–39.
- Langmuir, I., 1918. The adsorption of gases on plane surfaces of glass, mica and platinum. *J. Am. Chem. Soc.* 40, 1361–1403.
- Lee, S.M., Davis, A.P., 2001. Removal of Cu(II) and Cd(II) from aqueous solution by seafood processing waste sludge. *Water Res.* 35, 534–540.
- Leyva-Ramos, R., Rangel-Mendez, J.R., Mendoza-Barron, J., Fuentes-Rubio, L., Guerrero-Coronado, R.M., 1997. Adsorption of cadmium(II) from aqueous solution onto activated carbon. *Water Sci. Technol.* 35, 205–211.
- Loukidou, M.X., Zouboulis, A.I., 2001. Comparison of two biological treatment processes using attached-growth biomass for sanitary landfill leachate treatment. *Environ. Pollut.* 111, 273–281.
- Low, K.S., Lee, C.K., Lee, K.P., 1993. Sorption of copper by dye-treated oil-palm fibers. *Bioresour. Technol.* 44, 109–112.
- Low, K.S., Lee, C.K., 1991. Cadmium uptake by the moss. *Bioresour. Technol.* 38, 1–6.
- Luef, E., Prey, T., Kubicek, C.P., 1991. Zinc biosorption by fungal waste mycelia. *Appl. Microbiol. Biotechnol.* 34, 688–692.
- Mohan, D., Pittman, C.U., Bricka, M., Smith, F., Yancey, B., Mohammad, J., Steele, P.H., Alexandre, M.F., Gomez, V., Gong, H., 2007. Sorption of arsenic, cadmium, and lead by chars produced from fast pyrolysis of wood and bark during bio-oil production. *J. Colloid Interface Sci.* 310, 57–73.
- Namasivayam, C., Ranganathan, K., 1995. Removal of Cd(II) from wastewater by adsorption on waste Fe(III)/Cr(III) hydroxide. *Water Res.* 29, 1737–1744.
- Navarro, R., Wada, S., Tatsumi, K., 2005. Heavy metal precipitation by polycation-polyanion complex of PEI and its phosphonome-thylated derivative. *J. Hazard. Mater.* B123, 203–209.
- Parker, S.P., 1980. *Encyclopedia of Environmental Science*. McGraw-Hill, New York.
- Qdaisi, H.A., Moussab, H., 2004. Removal of heavy metals from wastewater by membrane processes: a comparative study. *Desalination* 164, 105–110.
- Rao, M.M., Ramesh, A., Rao, G.P., Seshiah, K., 2006. Removal of copper and cadmium from the aqueous solutions by activated carbon from *Ceiba pentandra* hulls. *J. Hazard. Mater.* 129, 123–129.
- Rao, R.A., Moonis, A.K., 2009. Biosorption of bivalent metal ions from aqueous solution by an agricultural waste: kinetics, thermodynamics and environmental effects. *Colloids Surf. A* 332, 121–128.
- Schroeder, H.A., 1965. Cadmium as a factor in hypertension. *J. Chronic. Dis.* 18, 647–656.
- Semerjian, L., 2010. Equilibrium and kinetics of cadmium adsorption from aqueous solutions using untreated *Pinus halepensis* sawdust. *J. Hazard. Mater.* 173, 236–242.
- Ucer, A., Uyanik, A., Aygun, S.F., 2006. Adsorption of Cu(II), Cd(II), Zn(II), Mn(II) and Fe(II) ions by tannic acid immobilized activated carbon. *Sep. Purif. Technol.* 47, 113–118.
- Vasudevan, P., Padmavathy, V., Dhingra, S.C., 2003. Kinetics of biosorption of cadmium on Baker's yeast. *Bioresour. Technol.* 89, 281–287.
- Vazquez, G., Gonzalez-Alvarez, J., Freire, S., Lopez-Lorenzo, M., Antorrena, G., 2002. Removal of cadmium and mercury ions from aqueous solution by sorption on treated *Pinus pinaster* bark: kinetic and isotherms. *Bioresour. Technol.* 82, 247–251.
- Volesky, B., 2001. Detoxification of metal-bearing effluents: biosorption for the next century. *Hydrometallurgy* 59, 203–216.
- Wase, D.A., Forster, C.F., 1997. *Biosorbents for Metal Ions*. Taylor and Francis, London.