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Kinetic and equilibrium study for the sorption of cadmium(II) ions from aqueous phase by eucalyptus bark

Ilhem Ghodbane, Loubna Nouri, Oualid Hamdaoui*, Mahdi Chiha

Department of Process Engineering, Faculty of Engineering, University of Annaba, P.O. Box 12, 23000 Annaba, Algeria

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Abstract

The efficiency of eucalyptus bark as a low cost sorbent for removing cadmium ions from aqueous solution has been investigated in batch mode. The equilibrium data could be well described by the Langmuir isotherm but a worse fit was obtained by the Freundlich model. The five linearized forms of the Langmuir equation as well as the non-linear curve fitting analysis method were discussed. Results show that the non-linear method may be a better way to obtain the Langmuir parameters. Maximum cadmium uptake obtained at a temperature of 20 °C was 14.53 mg g⁻¹. The influence of temperature on the sorption isotherms of cadmium has been also studied. The monolayer sorption capacity increased from 14.53 to 16.47 when the temperature was raised from 20 to 50 °C. The ΔG° values were negative, which indicates that the sorption was spontaneous in nature. The effect of experimental parameters such as contact time, cadmium initial concentration, sorbent dose, temperature, solution initial pH, agitation speed, and ionic strength on the sorption kinetics of cadmium was investigated. Pseudo-second-order model was evaluated using the six linear forms as well as the non-linear curve fitting analysis method. Modeling of kinetic results shows that sorption process is best described by the pseudo-second-order model using the non-linear method. The pseudo-second-order model parameters were function of the initial concentration, the sorbent dose, the solution pH, the agitation speed, the temperature, and the ionic strength.

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Keywords: Sorption; Cadmium(II); Eucalyptus bark; Langmuir isotherm; Pseudo-second-order model; Linear analysis; Non-linear analysis

1. Introduction

The increase of industrial activities has intensified environmental pollution problems and the deterioration of several ecosystems with the accumulation of many pollutants, especially heavy metals. Effluents containing heavy metals are discharged from various industrial processes. These pollutants concentration must be reduced to meet ever increasing legislative standards, and recovered where feasible. According to World Health Organization (WHO) the metals of most immediate concern are aluminum, chromium, manganese, iron, cobalt, nickel, copper, cadmium, mercury, and lead. Cadmium is one of the toxic metals and has received a great deal of attention. Cadmium may be found in wastewater discharges from the plating industry, the manufacture of cadmium–nickel batteries, fertilizers, pesticides, lead mining, pigments and dyes, and textile oper-

ations [1–3]. This metal is a non-essential and non-beneficial element for plants and animals. Ingestion of soluble cadmium compounds causes a number of health problems and the EPA (U.S. Environmental Protection Agency) lists cadmium compounds as carcinogenic [4]. The drinking water guideline value recommended for this element by WHO and American Water Works Association (AWWA) is 0.005 mg L⁻¹ [5]. Ingestion of cadmium above its permissible limit causes erythrocyte destruction, nausea, salivation, diarrhea and muscular cramps, renal degradation, chronic pulmonary problems, and skeletal deformity [5].

Many physicochemical techniques for removing cadmium from wastewaters include chemical precipitation, carbon adsorption, ion exchange, evaporation, and membrane processes [6]. The selection of a particular treatment technique depends notably on a number of factors, e.g. waste type and concentration, other constituents, level of clean-up required and economics. However, these technologies are generally practical and cost-effective only with concentrated wastewater, and are ineffective when applied to low strength wastes with heavy metal

* Corresponding author. Tel.: +213 71 59 85 09; fax: +213 38 87 65 60.
E-mail address: ohamdaoui@yahoo.fr (O. Hamdaoui).

Nomenclature

b	Langmuir constant related to the free energy of sorption (L mg^{-1})
b_M	Langmuir constant related to the free energy of sorption (L mol^{-1})
C_e	the equilibrium concentration of the solute in the bulk solution (mg L^{-1})
C_0	the initial concentration of the solute in the bulk solution (mg L^{-1})
ΔG°	Gibb's free energy change (kJ mol^{-1})
h	initial sorption rate ($\text{mg g}^{-1} \text{ min}^{-1}$)
K_F	Freundlich constant indicative of the relative sorption capacity of the sorbent ($\text{mg}^{1-1/n} \text{ L}^{1/n} \text{ g}^{-1}$)
K_1	Lagergren pseudo-first-order rate constant (min^{-1})
K_2	the pseudo-second-order rate constant ($\text{g mg}^{-1} \text{ min}^{-1}$)
n	Freundlich constant indicative of the intensity of the sorption
q	the amount of solute sorbed at any time t (mg g^{-1})
q_e	the amount of solute sorbed per unit weight of sorbent at equilibrium (mg g^{-1})
q_m	the maximum sorption capacity (mg g^{-1})
R_g	universal gas constant ($\text{J mol}^{-1} \text{ K}^{-1}$)
R_L	dimensionless separation factor of Hall
R^2	coefficient of determination
t	time (min)
T	temperature (K)

ions concentrations less than 100 mg L^{-1} [7]. Thus, biosorption technology, utilizing natural materials or industrial and agricultural wastes to passively remove cadmium from aqueous media, offers an efficient and cost-effective alternative compared to traditional chemical and physical remediation and decontamination techniques. A number of agricultural waste and by-products have been studied in the literature for their capacity to remove cadmium from aqueous solutions, such as bagasse sugar [8], sawdust [9], rice husk [10], spent grain [11], pine bark [12], rice polish [13], tree fern [14], modified corn cobs [15], etc. Therefore there is a need for the search of low cost and easily available biomaterials, which can sorb cadmium. Eucalyptus bark has been successfully used for the removal of chromium anions from industrial waste and a sorption capacity of 45 mg g^{-1} was found [16].

In this study, the removal of cadmium ions from aqueous phase by eucalyptus bark was investigated in batch process. Kinetic data and equilibrium isotherms were determined and analyzed. The five linearized forms of the Langmuir equation (Table 1) as well as the non-linear curve fitting analysis method were discussed. Pseudo-second-order model was evaluated using the six linear forms (Table 5) as well as the non-linear curve fitting analysis method.

Table 1

Freundlich and Langmuir isotherms and their linear forms

Isotherm	Linear form	Plot
Freundlich ^a	$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e$	$\ln q_e$ vs. $\ln C_e$
Langmuir-1 ^b	$\frac{1}{q_e} = \frac{1}{b q_m} \frac{1}{C_e} + \frac{1}{q_m}$	$1/q_e$ vs. $1/C_e$
Langmuir-2 ^b	$\frac{C_e}{q_e} = \frac{1}{q_m} C_e + \frac{1}{q_m b}$	C_e/q_e vs. C_e
Langmuir-3 ^b	$q_e = -\frac{1}{b} \frac{q_e}{C_e} + q_m$	q_e vs. q_e/C_e
Langmuir-4 ^b	$\frac{q_e}{C_e} = -b q_e + b q_m$	q_e/C_e vs. q_e
Langmuir-5 ^b	$\frac{1}{C_e} = b q_m \frac{1}{q_e} - b$	$1/C_e$ vs. $1/q_e$

^a $q_e = K_F C_e^{1/n}$.

^b $q_e = \frac{q_m b C_e}{1 + b C_e}$.

2. Materials and methods

2.1. Sorbent and sorbate

Eucalyptus bark used in the present work was collected in autumn 2005 from adult trees from the University Scientific Campus of Sidi-Amar, Annaba, Algeria. The collected bark was washed with permuted water several times to remove dirt particles and water soluble materials. The washing process was continued till the wash water contained no color. The washed materials were then completely dried in an oven at 80°C for 24 h. The dried barks were then cut into small pieces, crushed, and sieved to eliminate fine particles ($<0.5 \text{ mm}$). The obtained material was washed repeatedly with distilled water (conductivity $0.5 \mu\text{S cm}^{-1}$ and pH 6) until the wash water contained no color and its UV–vis absorbance (200–700 nm) was equal to zero and electric conductivity and pH remain constant. Finally, the obtained material was then dried in an air circulating oven at 80°C for two days and stored in a desiccator until use.

Cadmium(II) solutions of desired concentration have been prepared by dissolving the appropriate amount of its sulfate ($3\text{CdSO}_4 \cdot 8\text{H}_2\text{O}$, Fluka) in distilled water (conductivity $0.5 \mu\text{S cm}^{-1}$ and pH 6). All Chemicals used in this study were of analytical grade.

2.2. Equilibrium isotherms

Equilibrium isotherms were determined by contacting a fixed mass of eucalyptus bark (2 g) with 500 mL of cadmium(II) solutions in beakers. A range of cadmium(II) concentrations ($25\text{--}300 \text{ mg L}^{-1}$) was tested. A series of such beakers was then stirred using mechanical stirrers at a constant speed of 400 rpm in a water bath with temperatures 20, 30, 40, and 50°C , respectively. After agitating the beakers for 2 h, the reaction mixtures were filtered through filter paper, and then the filtrates were analyzed for the remaining cadmium(II) concentration with atomic absorption spectrometry (Perkin-Elmer A310).

All experiments were conducted in triplicate, and sometimes repeated again and the mean values have been reported.

2.3. Kinetics

The initial concentration of cadmium(II) solution was 100 mg L^{-1} for all experiments, except for those carried out to examine the effect of the initial concentration of cadmium. For kinetic studies, the batch method was used because of its simplicity. For cadmium removal kinetic experiments, 2 g of eucalyptus bark was contacted with 0.5 L of cadmium solution in a beaker agitated vigorously by a mechanic stirrer using a water bath maintained at a constant temperature. The stirring speed was kept constant at 400 rpm. At predetermined intervals of time, samples of the mixture were withdrawn at suitable time intervals, and filtered through a paper filter. These were analyzed by atomic absorption spectrometry (Perkin-Elmer A310) for cadmium concentration.

Sorption experiments carried out to investigate the effect of pH were conducted by using a volume of 0.5 L of solution having 100 mg L^{-1} of Cd(II) concentration with a sorbent mass of 2 g at 20°C . The solution pH was adjusted using $0.1 \text{ N H}_2\text{SO}_4$ aqueous solution.

In all the experiments in which the effect of agitation speed was studied, the initial cadmium concentration, sorbent mass, and solution temperature were 100 mg L^{-1} , 2 g, and 20°C , respectively. The stirring speed was varied from 0 (without stirring) to 1000 rpm.

The influence of ionic strength on the sorption of cadmium by eucalyptus bark was studied with a constant initial concentration of 100 mg L^{-1} , sorbent mass of 2 g, solution volume of 0.5 L, and temperature of 20°C . The ionic strength of the cadmium solution was modified using different dosages of Na_2SO_4 (0 – 10 g L^{-1}).

All experiments were conducted in triplicate, and sometimes repeated again and the mean values have been reported.

2.4. Determination of active sites

Acidic and basic sites on eucalyptus bark were determined by the acid–base titration method proposed by Boehm [17]. The total acid sites matching the carboxylic, phenolic, lactonic and carbonylic and quinonic sites [17] were neutralized using alkaline solutions (0.1 N NaOH , 0.1 N NaHCO_3 , $0.1 \text{ N Na}_2\text{CO}_3$, and $0.1 \text{ N NaOC}_2\text{H}_5$) while the basic sites were neutralized with a 0.1 N HCl solution. The carboxylic and lactonic sites were titrated with a $0.1 \text{ N Na}_2\text{CO}_3$ solution, the carboxylic sites were determined with a 0.1 N NaHCO_3 solution, and the phenolic sites were estimated by difference [18]. The carbonylic and quinonic sites were titrated with NaOC_2H_5 .

The acidic and basic sites were determined by adding 50 mL of 0.1 N titrating solution and 1 g of eucalyptus bark to a 50 mL volumetric flask. The flask was slowly agitated and partially immersed in a constant temperature water bath set at 25°C and it was left there for 5 days. Afterward, a sample of 10 mL was titrated with 0.1 N HCl or NaOH solution. The titration was carried by triplicate using a potentiometer, Orion, model EA940.

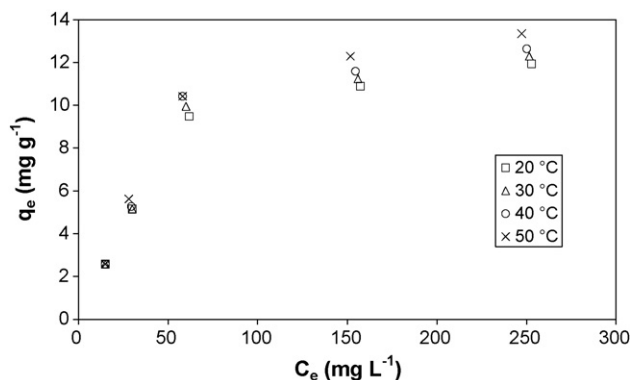


Fig. 1. Equilibrium isotherms of cadmium sorption by eucalyptus bark at different temperatures.

3. Results and discussion

3.1. Equilibrium isotherms

The dynamic sorptive separation of metals from solution by eucalyptus bark can be successfully represented by a good description of the equilibrium separation of metal between two phases. Fig. 1 presents the amount of cadmium sorbed at 20, 30, 40, and 50°C plotted against its concentration in liquid phase at equilibrium. Isotherm data obtained with a range of initial Cd(II) concentration showed an increase in the amount of Cd(II) sorbed when the initial metal concentration was raised from 25 to 300 mg L^{-1} . Additionally, the amount of metal sorbed increased following an increase in temperature from 20 to 50°C . The shape of the curves clearly indicated that the isotherms for all temperatures belong to L-type according to the classification of equilibrium isotherm in solution by Giles et al. [19].

Several mathematical models can be used to describe experimental data of sorption isotherms. The equilibrium data were modeled with the Langmuir and Freundlich models. Linear regression is frequently used to determine the best-fitting isotherm, and the method of least squares has been used for finding the parameters of the isotherms. However, the Langmuir isotherm can be linearized as five different types (Table 1). The more-popular linear forms used are Langmuir-1 and Langmuir-2. The linear form of the Freundlich model is also shown in Table 1.

The sorption data for cadmium by eucalyptus bark at different temperatures were analyzed by a regression analysis to fit the Freundlich and the five linearized expression of Langmuir isotherm models. The details of these different forms of linearized Langmuir equations and the method to estimate the Langmuir constants q_m and b from these plots were explained in Table 1. Out of the five different types of linearized Langmuir isotherm equations, Langmuir-1 and Langmuir-2 are the most frequently used by several researchers because of the minimized deviations from the fitted equation resulting in the best error distribution. Values of the Langmuir constants and the Freundlich parameters are presented in Table 2 for the sorption of cadmium by eucalyptus bark at 20, 30, 40, and 50°C . The linear analysis using different linear forms of the Langmuir equation

Table 2
Parameters of the Langmuir and Freundlich isotherms obtained using the linear method

Isotherm		T (°C)			
		20	30	40	50
Langmuir-1	$b (\times 10^3 \text{ L mg}^{-1})$	9.92	8.95	7.93	6.76
	$q_m (\text{mg g}^{-1})$	20.58	22.52	25.25	29.67
	R^2	0.979	0.977	0.970	0.960
Langmuir-2	$b (\times 10^3 \text{ L mg}^{-1})$	18.26	17.76	17.68	16.72
	$q_m (\text{mg g}^{-1})$	14.71	15.27	15.77	16.92
	R^2	0.983	0.977	0.972	0.971
Langmuir-3	$b (\times 10^3 \text{ L mg}^{-1})$	17.62	18.16	19.63	18.44
	$q_m (\text{mg g}^{-1})$	14.97	15.19	15.18	16.30
	R^2	0.727	0.637	0.544	0.594
Langmuir-4	$b (\times 10^3 \text{ L mg}^{-1})$	12.80	11.60	10.70	11.00
	$q_m (\text{mg g}^{-1})$	17.62	19.09	20.74	21.30
	R^2	0.727	0.637	0.544	0.594
Langmuir-5	$b (\times 10^3 \text{ L mg}^{-1})$	9.20	8.10	6.90	5.50
	$q_m (\text{mg g}^{-1})$	21.73	24.3	28.14	35.00
	R^2	0.979	0.977	0.970	0.960
Freundlich	n	1.92	1.88	1.86	1.81
	$K_F (\text{mg}^{1-1/n} \text{ L}^{1/n} \text{ g}^{-1})$	0.796	0.778	0.783	0.774
	R^2	0.878	0.866	0.849	0.858

will significantly affect calculations of the Langmuir parameters. The values of the coefficient of determination obtained from Langmuir-2 expression indicate that there is strong positive evidence that the sorption of cadmium by the biosorbent follows the Langmuir isotherm.

Additionally, the equilibrium data were further analyzed using the linearized form of Freundlich equation using the same set experimental data. The calculated Freundlich isotherm constants and the corresponding coefficient of determination values were shown in Table 2. From Table 2, if just the linear form of Langmuir-2 is used for comparison, Langmuir-2 was more suitable for the experimental data than was the Freundlich isotherm because of the higher value of the coefficient of determination. In contrast, if using the linear form of the other Langmuir equations, the Freundlich isotherm was more suitable for the experimental data than was the Langmuir isotherm in most cases, especially in the cases of Langmuir-3 and Langmuir-4. This suggests that Langmuir-2 isotherm could be well represented the experimental sorption data, while a worse fit of the equilibrium isotherms is obtained using Freundlich equation.

On the other hand, the sorption equilibrium isotherms for cadmium by eucalyptus bark was analyzed by non-linear curve fitting analysis method, using MicrocalTM Origin[®] software, to fit both the Langmuir and Freundlich models. Table 3 shows the isotherm parameters obtained using the non-linear method. The Langmuir model constants obtained from the non-linear and linear methods are different. It seems that the best fit was obtained by the Langmuir-2 expression as compared with other linear expressions because it had the highest coefficient of determination and because the model parameters were closer to those obtained using the non-linear method. The parameters of the Freundlich equation determined by linear and non-linear analysis are different. Moreover, the obtained results indicate that the Langmuir model gave an acceptable fit to the experimental data than the Freundlich equation. Thus, it will be more appropriate to use non-linear method to estimate the parameters involved in the isotherm equation.

The essential characteristics of the Langmuir isotherm can be expressed in terms of dimensionless constant separation factor

Table 3
Parameters of the Langmuir and Freundlich isotherms obtained using the non-linear method

Isotherm		T (°C)			
		20	30	40	50
Langmuir	$b (\text{L mg}^{-1}) \times 10^3$	20.69	20.68	21.23	20.22
	$q_m (\text{mg g}^{-1})$	14.53	15.03	15.45	16.47
	R^2	0.956	0.941	0.927	0.951
	$\Delta G^\circ (\text{kJ mol}^{-1})$	−18.88	−19.53	−20.24	−20.76
Freundlich	n	2.55	2.54	2.56	2.48
	$K_F (\text{mg}^{1-1/n} \text{ L}^{1/n} \text{ g}^{-1})$	1.456	1.497	1.574	1.555
	R^2	0.872	0.852	0.833	0.864

Table 4
Separation factor values for cadmium sorption by eucalyptus bark at different temperatures

$T (^{\circ}\text{C})$	$b (\times 10^3 \text{ L mg}^{-1})$	Initial cadmium concentration (mg L^{-1})				
		25	50	100	200	300
		R_L				
20	20.69	0.659	0.492	0.326	0.195	0.139
30	20.68	0.659	0.492	0.326	0.195	0.139
40	21.23	0.653	0.485	0.320	0.191	0.136
50	20.22	0.664	0.497	0.331	0.198	0.142

or equilibrium parameter, R_L , given by [20]

$$R_L = \frac{1}{1 + bC_0} \quad (1)$$

where b is the Langmuir constant (L mg^{-1}) and C_0 is the initial concentration of cadmium (mg L^{-1}).

The parameter R_L indicated the shape of isotherm as follows: $R_L > 1$ unfavorable; $R_L = 1$ linear; $0 < R_L < 1$ favorable; $R_L = 0$ irreversible.

The obtained R_L values, calculated using Langmuir constants determined by non-linear method, versus initial solute concentration at four different temperatures were shown in Table 4. From Table 4, it was observed that at all temperature conditions, sorption was found to be more favorable at higher concentrations. Also the value of R_L in the range of 0–1 at all initial metal concentrations and at all the four-solution temperature conditions confirms the favorable uptake of Cd(II) process.

3.1.1. Thermodynamic parameters

For designing sorption systems, the designer should be able to understand the changes that can be expected to occur and how fast will they take place. The rate of the reaction can be calculated from the knowledge of kinetic studies. But the change in reaction that can be expected during the process require the brief idea of thermodynamic parameters.

The Gibbs free energy change, ΔG° , is the fundamental criterion of spontaneity. The Gibbs free energy change (ΔG°) is the basic criterion of spontaneity, and a negative value indicates the reaction to be spontaneous. By using the equilibrium constant (b_M) obtained for each temperature from the Langmuir model using the non-linear method (Table 3), ΔG° can be calculated according to Eq. (2):

$$\Delta G^{\circ} = -R_g T \ln b_M \quad (2)$$

The thermodynamic parameter, ΔG° , is shown in Table 3. ΔG° is negative and decreases with increase in temperature indicating that sorption of cadmium by eucalyptus bark is spontaneous and spontaneity increases with increase in temperature.

3.2. Sorption kinetics

3.2.1. Effect of contact time and initial concentration of Cd(II)

The rate of metal removal is of great significance for developing sorbent-based water technology. In order to establish equilibration time for maximum uptake and to know the kinetics

of sorption process, the sorption of Cd(II) by eucalyptus bark was carried out using contact times ranging from 2 to 60 min and the results are shown in Fig. 2. It was observed that metal sorption occurred rapidly. The sorption efficiency of Cd(II) increased gradually with increasing contact times and reached a plateau afterwards. An increase in initial cadmium concentration leads to an increase in the sorption capacity of cadmium by eucalyptus bark. Equilibrium uptake increased with the increasing of initial metal ions concentration at the range of experimental concentration. This is a result of the increase in the driving force the concentration gradient, as an increase in the initial metal ion concentrations. For initial concentrations of 100 and 200 mg L^{-1} , the ability of eucalyptus bark to sorb maximum amount of Cd(II) within 25 min indicates that it is an effective biosorbent for the removal of Cd(II) from wastewater. When initial cadmium concentration was increased from 50 to 200 mg L^{-1} , the equilibrium sorption capacity increased from 5.15 to 10.89 mg g^{-1} .

Kinetics of cadmium sorption by eucalyptus bark can be modeled by the pseudo-first-order Lagergren equation and the pseudo-second-order model.

The pseudo-first-order equation (Eq. (3)) and the pseudo-second-order expression (Eq. (4)) are given by

$$\ln(q_e - q) = \ln q_e - K_1 t \quad (3)$$

$$q = \frac{K_2 q_e^2 t}{1 + K_2 q_e t} \quad (4)$$

where K_1 is the pseudo-first-order rate constant (min^{-1}), q_e the amount of cadmium sorbed at equilibrium (mg g^{-1}), q the amount of cadmium on the surface of eucalyptus bark at any

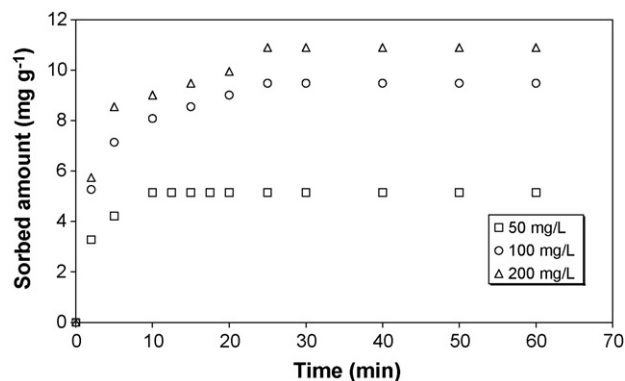


Fig. 2. Effect of initial concentration of metal on the sorption of cadmium by eucalyptus bark.

Table 5
Linear forms of the pseudo-second-order kinetic model

Type	Linear form	Plot	Parameters
Type 1	$\frac{t}{q} = \frac{1}{K_2 q_e^2} + \frac{1}{q_e} t$	t/q vs. t	$q_e = 1/\text{slope}$; $K_2 = \text{slope}^2/\text{intercept}$; $h = 1/\text{intercept}$
Type 2	$\frac{1}{q} = \frac{1}{q_e} + \frac{1}{K_2 q_e^2} \frac{1}{t}$	$1/q$ vs. $1/t$	$q_e = 1/\text{intercept}$; $K_2 = \text{intercept}^2/\text{slope}$; $h = 1/\text{slope}$
Type 3	$q = q_e - \frac{1}{K_2 q_e} \frac{q}{t}$	q vs. q/t	$q_e = \text{intercept}$; $K_2 = -1/(\text{slope} \times \text{intercept})$; $h = -\text{intercept}/\text{slope}$
Type 4	$\frac{q}{t} = K_2 q_e^2 - K_2 q_e q$	q/t vs. q	$q_e = -\text{intercept}/\text{slope}$; $K_2 = \text{slope}^2/\text{intercept}$; $h = \text{intercept}$
Type 5	$\frac{1}{t} = -K_2 q_e + K_2 q_e^2 \frac{1}{q}$	$1/t$ vs. $1/q$	$q_e = -\text{slope}/\text{intercept}$; $K_2 = \text{intercept}^2/\text{slope}$; $h = \text{slope}$
Type 6	$\frac{1}{q_e - q} = \frac{1}{q_e} + K_2 t$	$1/(q_e - q)$ vs. t	$q_e = 1/\text{intercept}$; $K_2 = \text{slope}$; $h = \text{slope}/\text{intercept}^2$

time t (mg g^{-1}), t the time (min), and K_2 is the pseudo-second-order rate constant ($\text{g mg}^{-1} \text{min}^{-1}$).

The pseudo-second-order equation can be linearized to six different linear forms as shown in Table 5. Expression of type 6 was previously reported by Blanchard et al. [21] for the exchange reaction of divalent metallic ions onto NH_4^+ ions fixed onto zeolite particles. A type 1 expression as shown in Table 5 was previously reported by Ho [22,23]. This is the most used linearized form for the pseudo-second-order equation.

The initial sorption rate h ($\text{mg g}^{-1} \text{min}^{-1}$) is given by the following equation:

$$h = K_2 q_e^2 \quad (5)$$

The pseudo-first-order kinetic constant K_1 (min^{-1}) and the amount of cadmium sorbed at equilibrium q_e (mg g^{-1}) based on pseudo-first-order kinetics can be obtained from the plot of $\ln(q_e - q)$ versus t . The lower coefficient of determination value and the amount of cadmium sorbed at equilibrium determined using this model (Table 6) suggest that it is inappropriate to use this equation to represent the sorption of cadmium by eucalyptus bark.

Linear regression analysis using the six linear expressions of the pseudo-second-order equation was used to determine the model parameters for the sorption of cadmium onto eucalyptus bark for different initial metal concentrations. The obtained results were shown in Table 6. It was observed that the rate constant, the sorbed amount at equilibrium, and the initial sorption rate values obtained from the six linear forms of pseudo-second-order expressions were different. It is clear that transformations of non-linear pseudo-second-order kinetic model to linear forms implicitly alter their error structure and may also violate the error variance and normality assumptions of standard least-squares method. The very higher coefficient of determination value for type 1 expression suggests that the pseudo-second-order kinetic expression is the optimum kinetic expression to represent the uptake of cadmium by eucalyptus bark. Additionally, a type 1 pseudo-second-order expression predicts reasonably the theoretical q_e value. The lower determination coefficient value for type 6 pseudo-second-order expression suggests that it is not appropriate to use this type of linearization. The theoretical amount sorbed at equilibrium value for 100 mg L^{-1} initial Cd(II) concentration determined using this expression (type 6) is negative that is experimentally and practically impossible. The initial

sorption rate calculated using the type 6 expression is unacceptable since it is very different from those calculated using the five other linear expressions.

Additionally, the sorption kinetic uptake for cadmium by eucalyptus bark was analyzed by non-linear curve fitting analysis method, using MicrocalTM Origin[®] software, to fit the pseudo-second-order equation (Table 6). The pseudo-second-order model constants obtained from the non-linear and linear methods differed even when compared with the results of type 1 expression, which had the highest coefficient of determination (Table 6). It seems that the best fit was obtained by the expression of Ho (type 1) as compared with other linear expressions because it had the highest coefficient of determination and because the model parameters were closer to those obtained using the non-linear method. Thus it will be more appropriate to use non-linear method to estimate the parameters involved in the kinetic equation.

3.2.2. Effect of sorbent dose

The effect of a variation of sorbent mass on the kinetics of sorption of cadmium on eucalyptus bark is reported in Fig. 3, which shows a series of contact time curves for variation of mass of eucalyptus bark in the range of 0.5–8 g. The sorption of cadmium increased with an increase in sorbent dosage. This may be attributed to increased sorbent surface area and availability of more sorption sites resulting from the increase dose of the sorbent. But amount of metal sorbed per unit mass of sorbent decreased with increase in sorbent dose. At higher eucalyptus bark to solute concentration ratios, there is a very fast superficial

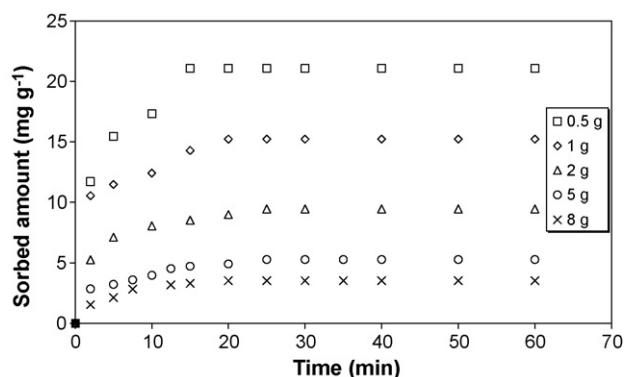


Fig. 3. Effect of sorbent dose on the sorption of cadmium by eucalyptus bark.

Table 6

Pseudo-second-order kinetic parameters obtained by using the linear and non-linear methods for different initial cadmium concentrations

Type	Parameters	Initial cadmium concentration (mg L ⁻¹)		
		50	100	200
Type 1	K_2 (g mg ⁻¹ min ⁻¹)	0.381	57.78×10^{-3}	43.38×10^{-3}
	q_e (mg g ⁻¹)	5.22	9.83	11.36
	h (mg g ⁻¹ min ⁻¹)	10.37	5.59	5.60
	R^2	0.999	0.999	0.999
Type 2	K_2 (g mg ⁻¹ min ⁻¹)	0.140	58.61×10^{-3}	46.29×10^{-3}
	q_e (mg g ⁻¹)	5.46	9.78	11.29
	h (mg g ⁻¹ min ⁻¹)	4.16	5.61	5.90
	R^2	0.964	0.992	0.979
Type 3	K_2 (g mg ⁻¹ min ⁻¹)	0.145	57.04×10^{-3}	46.57×10^{-3}
	q_e (mg g ⁻¹)	5.44	9.82	11.29
	h (mg g ⁻¹ min ⁻¹)	4.31	5.51	5.93
	R^2	0.912	0.979	0.943
Type 4	K_2 (g mg ⁻¹ min ⁻¹)	0.131	55.68×10^{-3}	43.56×10^{-3}
	q_e (mg g ⁻¹)	5.49	9.85	11.37
	h (mg g ⁻¹ min ⁻¹)	3.97	5.41	5.63
	R^2	0.912	0.979	0.943
Type 5	K_2 (g mg ⁻¹ min ⁻¹)	0.133	57.23×10^{-3}	44.95×10^{-3}
	q_e (mg g ⁻¹)	5.49	9.8	11.33
	h (mg g ⁻¹ min ⁻¹)	4.01	5.56	5.77
	R^2	0.964	0.992	0.979
Type 6	K_2 (g mg ⁻¹ min ⁻¹)	0.174	91.7×10^{-3}	44.8×10^{-3}
	q_e (mg g ⁻¹)	5.23	-75.19	8.73
	h (mg g ⁻¹ min ⁻¹)	4.76	518.4	3.42
	R^2	0.999	0.917	0.971
Non-linear	K_2 (g mg ⁻¹ min ⁻¹)	0.153	54.57×10^{-3}	45.17×10^{-3}
	q_e (mg g ⁻¹)	5.42	9.87	11.32
	h (mg g ⁻¹ min ⁻¹)	4.49	5.32	5.79
	R^2	0.990	0.997	0.990
Lagergren	K_1 (min ⁻¹)	0.229	0.114	0.083
	q_e (mg g ⁻¹)	2.96	4.71	4.67
	R^2	1.000	0.985	0.902

sorption onto the sorbent surface that produces a lower solute concentration in the solution than when the biomaterial to solute concentration ratio is lower. This is because a fixed mass of eucalyptus bark can only sorb a certain amount of metal. Therefore, the more the sorbent dosage, the larger the volume of effluent that a fixed mass of eucalyptus bark can purify is. The decrease in amount of cadmium sorbed with increasing sorbent mass is due to the split in the flux or the concentration gradient between solute concentration in the solution and the solute concentration in the surface of the sorbent. Thus with increasing sorbent mass, the amount of cadmium sorbed onto unit weight of sorbent gets reduced, thus causing a decrease in sorption capacity with increasing sorbent mass concentration.

The experimental kinetic data were fitted to the pseudo-second-order equation using the non-linear curve fitting analysis method. The determined parameters of the model are shown in Table 7. The sorption of cadmium by eucalyptus bark was found to be well represented by the pseudo-second-order kinetic equation. Increasing the dose of eucalyptus bark enhanced the rate constant. However, the initial sorption rate and theoretical amount sorbed at equilibrium decreased with sorbent mass.

3.2.3. Effect of solution initial pH

The pH of metal solutions is the major parameter controlling metal sorption processes. In order to study the effect of this parameter on the metal sorption by eucalyptus bark, solution initial pH was varied within the range 2–5. This pH range was chosen in order to avoid metal solid hydroxide precipitation. The effect of solution initial pH on the sorption kinetics for Cd(II) on eucalyptus bark is shown in Fig. 4. As seen in this figure, Cd(II) sorption on eucalyptus bark was drastically reduced by decreasing the solution pH. The maximum Cd(II) sorption occurred

Table 7

Pseudo-second-order kinetic parameters obtained by using the non-linear method for different sorbent doses

Parameters	Sorbent mass (g)				
	0.5	1	2	5	8
K_2 ($\times 10^3$ g mg ⁻¹ min ⁻¹)	22.97	51.88	54.57	57.3	84.67
q_e (mg g ⁻¹)	22.29	15.53	9.87	5.65	3.87
h (mg g ⁻¹ min ⁻¹)	11.41	12.51	5.32	1.83	1.27
R^2	0.988	0.978	0.997	0.97	0.988

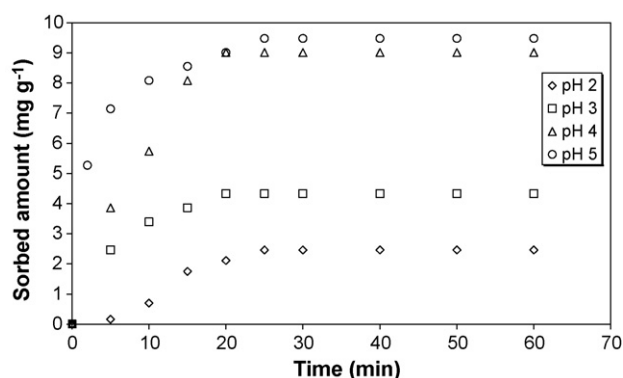


Fig. 4. Effect of solution initial pH on the sorption of cadmium by eucalyptus bark.

at pH 5 and Cd(II) was very slightly sorbed at pH values of 2 and 3.

According to the Cd(II) speciation diagram [24], Cd^{2+} is the predominant ionic species at pH less than 7. Thus, Cd(II) was sorbed on the eucalyptus bark as Cd^{2+} since all experiments were carried out at a pH < 6. The minimal sorption amount obtained at low pH is partly due to the fact that protons are strong competing sorbate because of their higher concentration and high mobility and partly to the fact that the solution pH influences the sorbent surface charge. The surface charge of the eucalyptus bark is positive at pH < PZC, is neutral at pH = PZC, and is negative at pH > PZC. At pH > PZC, the Cd^{2+} ions in solution are attracted to the surface of sorbent, thus favoring sorption. At higher pH values, the lower number of protons and greater number of negative charges results in greater cadmium sorption. The effect of pH on the sorption kinetics is attributed to electrostatic attraction existing between the eucalyptus bark surface and the Cd^{2+} ions in solution.

The concentrations of total acid and basic sites on the surface of eucalyptus bark are displayed in Table 8. Of the four types of acid sites, the carboxylic and quinonic sites are the dominant acidic oxygenated sites. The total acidic sites are much higher than the total basic sites. Acidic sites are protonated in acidic conditions explaining the low sorption of cadmium by eucalyptus bark at low pH.

The experimental results for different solution pH were modeled by the pseudo-second-order equation using the non-linear curve fitting analysis method. The determined parameters of the model are given in Table 9. The sorption of cadmium by eucalyptus bark was found to be well represented by the pseudo-second-order kinetic equation. The initial sorption rate

Table 8
Concentration of active sites on eucalyptus bark surface

Acidic sites	
Total (mequiv. g^{-1})	1.198
Carboxylic (mequiv. g^{-1})	0.100
Lactonic (mequiv. g^{-1})	0.085
Phenolic (mequiv. g^{-1})	0.000
Carboxylic and quinonic (mequiv. g^{-1})	1.013
Basic sites (mequiv. g^{-1})	0.088

Table 9

Pseudo-second-order kinetic parameters obtained by using the non-linear method for different solution pH

Parameters	pH			
	2	3	4	5
$K_2 (\times 10^3 \text{ g mg}^{-1} \text{ min}^{-1})$	12.81	49.76	27.53	54.57
$q_e (\text{mg g}^{-1})$	3.73	4.85	9.30	9.87
$h (\text{mg g}^{-1} \text{ min}^{-1})$	0.18	1.17	2.38	5.32
R^2	0.886	0.986	0.920	0.997

and theoretical amount sorbed at equilibrium decreased with the decrease in solution pH.

3.2.4. Effect of agitation speed

The effect of varying the agitation speed range was investigated for sorption of cadmium using eucalyptus bark. The other process variables were kept constant while a series of experiments was undertaken with different agitation speeds of 60, 300, 400, 600, and 1000 rpm. Fig. 5 shows a plot of cadmium uptake against time at various agitation speeds for the sorption of Cd(II) on eucalyptus bark. Results show that the high amount of cadmium sorbed at equilibrium (9.48 mg g^{-1}) is obtained with an agitation speed of 400 rpm that assures a good diffusion of ions toward eucalyptus bark particles.

The amount of cadmium sorption increases with the increase of the agitation speed from 0 to 400 rpm. When increasing the agitation speed, the diffusion rate of metal ions from the bulk liquid to the liquid boundary layer surrounding sorbent particles became higher because of an enhancement of turbulence and a decrease of the thickness of the liquid boundary layer.

The sorption kinetic results for cadmium by eucalyptus bark at different agitation speeds was analyzed by non-linear curve fitting analysis method to fit the pseudo-second-order kinetic model. Table 10 shows the model parameters obtained using the non-linear curve fitting analysis method. The values of the rate constant increased from 16.9×10^{-3} to $54.57 \times 10^{-3} \text{ g mg}^{-1} \text{ min}^{-1}$ with an increase in the agitation rate from 0 to 400 rpm. The values of initial sorption rate increase from 0.52 to $5.32 \text{ mg g}^{-1} \text{ min}^{-1}$, and the values of equilibrium

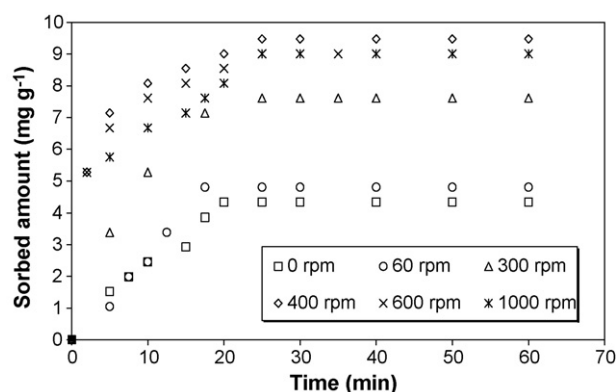


Fig. 5. Effect of agitation speed on the sorption of cadmium by eucalyptus bark.

Table 10

Pseudo-second-order kinetic parameters obtained by using the non-linear method for different agitation speeds

Parameters	Stirring speed (rpm)					
	0	60	300	400	600	1000
K_2 ($\times 10^3$ g mg $^{-1}$ min $^{-1}$)	16.9	12.44	17.2	54.57	60.31	24.22
q_e (mg g $^{-1}$)	5.57	6.41	8.95	9.87	9.34	9.84
h (mg g $^{-1}$ min $^{-1}$)	0.52	0.51	1.38	5.32	5.26	2.35
R^2	0.938	0.911	0.978	0.997	0.994	0.984

sorption capacity increase 5.57–9.87 mg g $^{-1}$, for an increase in agitation speed from 0 to 400 rpm.

3.2.5. Effect of ionic strength

In water, salt is present in a wide range of concentrations depending on the source and the quality of the water. The presence of salt or co-ions in solution can affect the sorption of metal ions. The effect of salt concentration (ionic strength) on the amount of cadmium sorbed by eucalyptus bark was analyzed over the Na₂SO₄ concentration range from 0 to 10 g L $^{-1}$. Sorption kinetics was carried out for cadmium initial concentration of 100 mg L $^{-1}$, solution volume of 0.5 L, and a sorbent mass of 2 g. The obtained results are shown in Fig. 6. It was seen that the increase in the salt concentration resulted in a decrease of cadmium sorption by eucalyptus bark. This trend indicated that the sorbing efficiency decreased when Na₂SO₄ concentration increased in the cadmium solution, which could be attributed to the competitive effect between cadmium ions and cations from the salt (Na⁺) for the sites available for the sorption process. As the concentration of salt is increased from 0 to 10 g L $^{-1}$, the amount of cadmium sorbed onto eucalyptus bark decreased from 9.48 to 2.93 mg g $^{-1}$. Another reason is the influence of the great ionic strength on the activity coefficient of cadmium, which reduce its transfer to the sorbent surface.

The experimental results for different salt concentrations were modeled by the pseudo-second-order equation using the non-linear curve fitting analysis method. The determined parameters of the model are given in Table 11. The sorption of cadmium by eucalyptus bark was found to be well represented by the pseudo-second-order kinetic equation. The initial sorption rate and theoretical amount sorbed at equilibrium decreased with the increase in ionic strength.

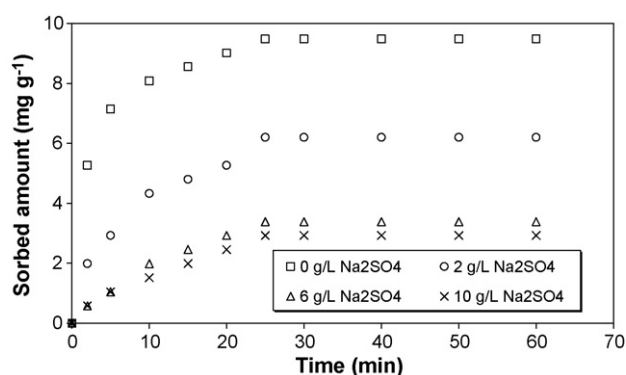


Fig. 6. Effect of ionic strength on the sorption of cadmium by eucalyptus bark.

Table 11

Pseudo-second-order kinetic parameters obtained by using the non-linear method for different ionic strength

Parameters	Mass of Na ₂ SO ₄ (g)			
	0	1	3	5
K_2 ($\times 10^3$ g mg $^{-1}$ min $^{-1}$)	54.57	22.37	20.66	22.71
q_e (mg g $^{-1}$)	9.87	7.13	4.34	3.77
h (mg g $^{-1}$ min $^{-1}$)	5.32	1.14	0.39	0.32
R^2	0.997	0.986	0.974	0.972

3.2.6. Effect of temperature

The temperature dependence of cadmium ions sorption by eucalyptus bark was studied with a constant initial cadmium ion concentration of 100 mg L $^{-1}$ at 400 rpm at various temperatures (20, 30, 40, and 50 °C). The temperature has two main effects on the sorption processes. Increasing temperature is known to increase the diffusion rate of the sorbate within the pores as a result of decreasing solution viscosity and will also modify the equilibrium capacity of the sorbent for a particular sorbate. Fig. 7 shows the variation of the sorbed amount versus time at various temperatures. The present data show that by increasing temperature from 20 to 50 °C the necessary time of equilibrium does not change. The equilibrium sorption capacity slightly increases (from 9.48 to 10.42 mg g $^{-1}$) when the temperature of cadmium solutions increases from 20 to 50 °C.

The kinetic data were correlated with the pseudo-second-order rate model by using the non-linear curve fitting analysis method and the obtained parameters are listed in Table 12. The theoretical amount sorbed at equilibrium slightly increased with the increase in temperature.

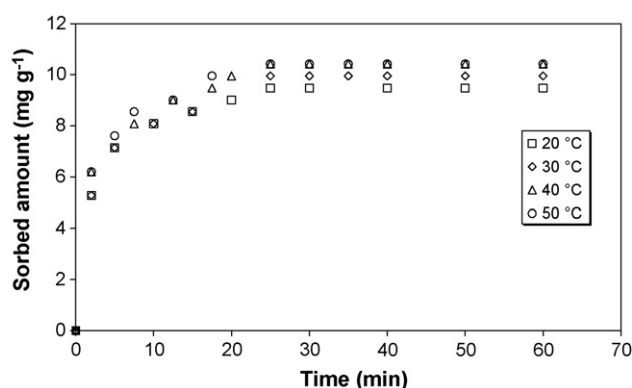


Fig. 7. Effect of temperature on the sorption of cadmium by eucalyptus bark.

Table 12

Pseudo-second-order kinetic parameters obtained by using the non-linear method for different temperatures

Parameters	Temperature (°C)			
	20	30	40	50
$K_2 (\times 10^3 \text{ g mg}^{-1} \text{ min}^{-1})$	54.57	53.85	53.08	52.17
$q_e (\text{mg g}^{-1})$	9.87	10.21	10.76	10.83
$h (\text{mg g}^{-1} \text{ min}^{-1})$	5.32	4.68	6.15	6.12
R^2	0.997	0.988	0.989	0.992

3.3. Comparison of Cd(II) removal with different sorbents reported in literature

The sorption capacity of eucalyptus bark for the removal of Cd(II) have been compared with those of other sorbents reported in literature. The values of the monolayer sorption capacities of the present investigation are comparable with that reported for the sorption of cadmium by Petiolar felt-sheath of palm [25], tea-industry waste [26], chitin [27], sugar beet pulp [28], NaOH-treated spent grain [11], and oxidized corncob [29].

4. Conclusion

The removal of cadmium from aqueous solution using eucalyptus bark has been investigated under different experimental conditions in batch process. The analysis of equilibrium data show that it is not appropriate to use the coefficient of determination of the linear regression method for comparing the best-fitting isotherm. Non-linear curve fitting analysis method was found to be the more appropriate method to determine the isotherm parameters. Langmuir-2 is the most used linear form which had the highest coefficient of determination compared with other Langmuir linear equations. The Freundlich isotherm gives a worse fit of the equilibrium data. Maximum cadmium uptake obtained at a temperature of 20 °C was 14.53 mg g⁻¹. The influence of temperature on the sorption isotherms of cadmium has been also studied. The monolayer sorption capacity increased from 14.53 to 16.47 when the temperature was raised from 20 to 50 °C. Thermodynamic parameters show that the sorption of cadmium onto eucalyptus bark was spontaneous in nature.

The sorption kinetics is found dependent upon contact time, initial dye concentration, sorbent dose, solution initial pH, ionic strength, temperature, and agitation speed. The sorption process followed pseudo-second-order rate kinetics. Non-linear curve fitting analysis method was found to be the more appropriate method to determine the rate kinetic parameters. Among the six linear expressions of the pseudo-second-order kinetic model, a type 1 expression very well represent the kinetic uptake of cadmium by eucalyptus bark.

Eucalyptus bark, a low cost material, may be particularly appropriate for the treatment of small quantities of wastewaters containing cadmium and the data reported here should be useful for the design of batch or stirred-tank flow reactors.

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