



Equilibrium and kinetics of cadmium adsorption from aqueous solutions using untreated *Pinus halepensis* sawdust

L. Semerjian*

Department of Civil and Environmental Engineering, American University of Beirut, P.O. Box 11-0236, Beirut, Lebanon

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ABSTRACT

Untreated *Pinus halepensis* sawdust has been investigated as an adsorbent for the removal of cadmium from aqueous solutions. Batch experiments were carried out to investigate the effect of pH, adsorbent dose, contact time, and metal concentration on sorption efficiency. The favorable pH for maximum cadmium adsorption was at 9.0. For the investigated cadmium concentrations (1–50 mg/L), maximum adsorption rates were achieved almost in the 10–20 min of contact. An adsorbent dose of 10 g/L was optimum for almost complete cadmium removal within 30 min from a 5 mg/L cadmium solution. For all contact times, an increase in cadmium concentration resulted in decrease in the percent cadmium removal (100–87%), and an increase in adsorption capacity (0.11–5.36 mg/g). The equilibrium adsorption data were best fitted with the Freundlich isotherm ($R^2 = 0.960$). The kinetics of cadmium adsorption was very well described by the pseudo-second-order kinetic model ($R^2 > 0.999$).

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1. Introduction

Heavy metals may reach watercourses either naturally through a variety of geochemical processes or by direct discharge of municipal and industrial wastewater. At elevated concentrations, soluble metal compounds can be deleterious to human health as well as to aquatic and marine environments. Cadmium (Cd) is one of the heavy metals considered to be toxic to humans and aquatic life. One of the major sources of surface water contamination by heavy metals such as Cd, is urban and agricultural wastewaters or stormwater runoffs as Cd is used in a number of industries, such as welding and soldering, photography, production of iron, steel and cement, use of superphosphate fertilizers and pesticides, and production of nickel–cadmium batteries. Chronic exposure to Cd can affect the nervous system, liver, cardiovascular system and may lead to renal failure and death in mammals and humans [1]. Because of the associated adverse effects, international regulatory agencies have promulgated effluent standards limiting heavy metal discharges, including Cd, into surface waters as well as into municipal sewers. However, the cost of complying with pollution control legislation is tremendously high and sometimes not affordable, particularly by small industries and developing countries. Therefore, there is a great need for new and cost-effective processes for heavy metal removal from wastewaters and stormwaters.

Traditionally, the most widely applied methods for heavy metal removal from wastewaters are chemical and electrochemical precipitation [2,3], cationic and anionic ion-exchange resins, membrane filtration, and sorption [4]. Whereas, some methods such as ion-exchange and reverse osmosis are costly, others such as precipitation techniques have problems for disposal of metal-containing sludge. Sorption methods are considered flexible, easy to operate, with much less sludge disposal problems. Besides different types of commercial adsorbents such as granular activated carbon or powdered activated carbon, several low-cost adsorbents generated by forestry and agricultural activities able to sequester heavy metals from contaminated waters have been extensively studied. Efficient removal of copper (Cu), zinc (Zn), arsenic (As), cadmium (Cd), chromium (Cr), iron (Fe), lead (Pb), mercury (Hg), vanadium (V) and nickel (Ni) has been achieved with low-cost adsorbents in bench scale studies such as biomass waste from biological wastewater treatment systems [5,6]; cotton ball [7]; pollens [8]; teak leaves powder [9]; black gram husk [10]; grape stalk [11]; peat [12]; fly ash [13]; wood barks [14,15]; various types of sawdust [4,16–22]. In previous research specifically related to Cd adsorption, several natural adsorbents, including algal biomass [1,23–26], peat moss [27,28], bark [15,29–31], sugar beet pulp [32], poplar wood sawdust [22], walnut sawdust [33] and treated *Pinus sylvestris* sawdust [34] have been investigated for their ability to sequester Cd from water or wastewater.

The objective of the present study is to investigate the feasibility of alternative sawdust as an adsorbent for the removal of Cd from wastewaters. Sawdust of *Pinus halepensis*, a common pine tree in Lebanon, is evaluated without any chemical pretreatment as an

* Tel.: +961 1 34 79 52; fax: +961 1 74 44 62.

E-mail address: ls07@aub.edu.lb.

alternate Cd adsorbent as it contains various organic compounds (lignin, cellulose, and hemicellulose) with polyphenolic groups that might be useful for binding heavy metal ions. Batch experiments are carried out for kinetic studies on the removal of Cd from aqueous solutions. The influence of various contributing parameters such as pH, adsorbent concentration, contact time, and initial Cd concentration is investigated. Three adsorption isotherm models (Langmuir, Freundlich, and Generalized equation) are used to study the fit of the experimental equilibrium data obtained in the study, and several kinetic models are used to evaluate the mechanism of adsorption.

2. Materials and methods

2.1. Adsorbent

Sawdust of *P. halepensis* (also known as Aleppo pine), a pine tree species abundantly available in Lebanon, was obtained from the Mechanical Engineering wood shop at the American University of Beirut (AUB). The raw sawdust was sieved through a 1.18 mm sieve (US standard No. 16), washed repeatedly with distilled water to remove surface and soluble impurities, and dried at 100 °C for 48 h. The dried sawdust was not subjected to further processing or chemical treatment which might enhance its adsorptive capacity in an attempt to evaluate the Cd adsorption properties of a low-cost unprocessed sawdust, abundantly available in Lebanon.

2.2. Preparation of cadmium solutions and analytical methods

Several aqueous solutions with varying concentrations of cadmium (1–50 mg/L) were prepared by proper dilutions of a stock 1000 mg/L certified cadmium reference solution (Cd metal in 2% nitric acid, Fisher Scientific, NJ). Recovered Cd concentrations in prepared aqueous solutions as well as residual Cd levels in experimented sawdust-Cd solution mixtures were analyzed by direct flame atomic absorption spectrometry using a flame atomic absorption spectrophotometer (Thermo Electron Corporation, M series AAS) equipped with auto-sampler (CETAC, ASX-510, USA) and an in-line dilutor (Thermo Electron Corporation, ID100, USA). The method detection limit of adopted analytical procedure is 0.05 mg/L Cd.

2.3. Batch experiments

Batch adsorption experiments were carried out at constant temperature (23 ± 1 °C) by adding different amounts of raw *P. halepensis* sawdust (1–50 g/L) to 125 mL conical flasks containing aqueous solutions with varying initial Cd concentrations (1–50 mg/L). pH values of sawdust-Cd aqueous solutions were adjusted to desired levels (pH 1–12) using 0.5N HCl or 0.5N NaOH. The flasks were shaken on an orbit shaker (Lab-Line, model 3520, USA) at 200 rpm for varying durations (10 min–24 h) to study the influence of contact time between adsorbent and Cd on adsorption efficiency. After specified contact times, aliquots of sawdust-Cd aqueous solutions were filtered through 11.0 cm filter papers (Whatman No. 5), and the filtrates were analyzed for residual Cd using flame AAS for adsorption efficiency assessment and isotherm analysis. Adsorption efficiency was expressed as a percentage of adsorbed metal compared to initial metal concentration, whereas adsorption capacity was expressed as amount of Cd adsorbed per mass unit of sawdust using the following equations, respectively:

$$\text{Cd removal efficiency (\%)} = \frac{C_i - C}{C_i} \times 100 \quad (1)$$

$$q(\text{mg/g}) = \frac{(C_i - C)V}{m} \quad (2)$$

where C_i and C are the initial and residual concentrations of Cd in mg/L, q is the adsorption capacity in mg/g, V is the volume of Cd solution in L, and m is the adsorbent mass in g.

2.4. Adsorption isotherm models

Adsorption isotherms are important to describe the adsorption mechanism of a solute on adsorbent surface thus aid in optimizing the design of a specific adsorption process. In the present study, the equilibrium data obtained for Cd removal using raw *P. halepensis* sawdust was tested with three isotherm models available in the literature to reveal the best fitting isotherm. Adopted isotherm models were Langmuir, Freundlich, and Generalized isotherm equations. Isotherm coefficients and correlation coefficients (R^2) were computed from linearized equations of these isotherms in Microsoft Excel.

2.4.1. Langmuir isotherm

Langmuir isotherm is represented in terms of fractional coverage (θ) as given by Eq. (3), and rearranged to the linear form given by Eq. (4) where b is the adsorption equilibrium constant in L/mg related to the apparent energy of adsorption, q_m is the quantity of adsorbate required to form a single monolayer on unit mass of adsorbent in mg/g, and q_e is the amount adsorbed on unit mass of the adsorbent (mg/g) when the equilibrium concentration is C_e (mg/L).

$$\theta = \frac{q_e}{q_m} = \frac{bC_e}{1 + bC_e} \quad (3)$$

$$\frac{C_e}{q_e} = \frac{1}{bq_m} + \left(\frac{1}{q_m}\right) C_e \quad (4)$$

Thus, a plot of C_e/q_e versus C_e should yield a straight line if Langmuir isotherm is obeyed by the adsorption equilibrium. q_m and b values will be calculated from the slope and intercept of the graphed line, respectively. A further analysis of the Langmuir equation can be made using a dimensionless equilibrium parameter, the separation factor R_L as given by Eq. (5):

$$R_L = \frac{1}{1 + bC} \quad (5)$$

For a favorable adsorption, the value of R_L should lie between 0 and 1; $R_L > 1$ represents an unfavorable adsorption, $R_L = 1$ represents linear adsorption, whereas $R_L = 0$ translates into irreversible adsorption [16].

2.4.2. Freundlich isotherm

The Freundlich isotherm is expressed by Eq. (6) where K_f ($\text{mg}^{1-1/n} \text{L}^{1/n} \text{g}^{-1}$) and n_f are the Freundlich equilibrium constants which can be determined from the plot of $\log q_e$ versus $\log C_e$ on the basis of the linear form of Freundlich equation (Eq. (7)).

$$q_e = K_f C_e^{n_f} \quad (6)$$

$$\log q_e = \log K_f + n_f \log C_e \quad (7)$$

2.4.3. Generalized isotherm

The generalized isotherm is a combination of Langmuir and Freundlich isotherms and depends on the value of cooperative binding constant (N_b). The linear form of the generalized isotherm is expressed in Eq. (8) where, K_G is the saturation constant in mg/L, N_b is the cooperative binding constant, and Q_m is the maximum adsorption capacity of adsorbent in mg/g as obtained from the Langmuir isotherm model. Related isotherm constants are obtained from the slope and intercept of the plot of $\log [(Q_m/q_e) - 1]$ versus

$\log C_e$.

$$\log \left(\frac{Q_m}{q_e} - 1 \right) = \log K_G = N_b \log C_e \quad (8)$$

2.5. Adsorption kinetics

The process of pollutant removal from an aqueous phase by any adsorbent can be explained by using kinetic models and examining the rate-controlling mechanism of the adsorption process. The study of adsorption kinetics is desirable as it provides information about the dynamics of the adsorption process in terms of the order and the rate constant which are of significance in designing and modeling an efficient adsorption operation. Various adsorption kinetic models have been used in the literature to describe the adsorption of metal ions [4,16,18,33]. It has been reported that most adsorption systems follow a pseudo-second-order kinetic model expressed in Eq. (9) [35] where k_2 is the second-order adsorption rate constant in g/(mg min) computed from the linear plot of t/q_t versus t .

$$\frac{t}{q_t} = \left(\frac{1}{k_2 q_e^2} \right) + \frac{t}{q_e} \quad (9)$$

Additionally, the possibility of intra-particle diffusion was explored using the intra-particle diffusion model given in Eq. (10) [36], where k_{id} is the rate constant for intra-particle diffusion estimated from plotting q_t versus $t^{1/2}$.

$$q_t = k_{id} t^{1/2} \quad (10)$$

Elovich kinetic model (Eq. (11)) is also considered where α is the initial adsorption rate in mg/(g min), and β (g/mg) is the desorption constant related to the extent of the surface coverage and activation energy for chemisorptions. Both kinetic constants (α and β) will be estimated from the slope and intercept of the plot q_t versus $\ln t$.

$$q_t = \frac{1}{\beta} \ln(\alpha\beta) + \frac{1}{\beta} \ln t \quad (11)$$

3. Results and discussion

3.1. Factors affecting efficiency of metal adsorption on sawdust

3.1.1. Effect of initial pH of suspension on sorption efficiency

In previous studies, pH has been referred as an important influencing factor for heavy metal adsorption on sawdust. In a certain pH range, most metal adsorption increases with increasing pH up to a certain pH value and then decreases with further increasing pH. Therefore, there is a favorable pH range for the adsorption of every metal on a specific adsorbent [4,16,18,20]. In this study, the effect of pH on Cd adsorption by *Pinus halepensis* sawdust is investigated by varying the pH of Cd solution (5 mg/L)–sawdust (20 g/L) suspension from 1 to 12, and shaking the suspensions for varying contact times

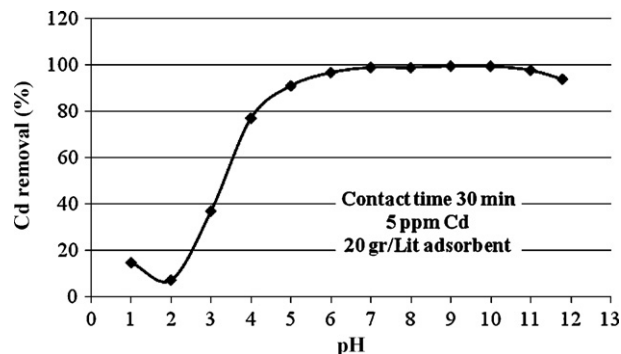


Fig. 1. Effect of pH variation on Cd removal through adsorption on *P. halepensis* sawdust.

(30, 60, 120, and 180 min). Irrespective of allowed contact times, the percent adsorption of Cd was minimal (<20%) at pH 1–2, significantly increased to 90% in the pH range 2–5, and reached >95% at pH range 6–11 with a maximum of >99% at pH 9–10, afterwards Cd removal efficiency started to slightly decline to <95% from pH 11–12. Thus, the favorable pH for maximum Cd adsorption on the adsorbent under study was at 9, and this pH value was selected to further investigate the influence of other contributing parameters on the sorption process. The effect of pH on Cd removal efficiency at 30 min contact time is illustrated in Fig. 1.

The effect of pH may be explained in terms of pH_{zpc} (zero point of charge) of the adsorbent, at which the adsorbent is neutral. The surface charge of the adsorbent is positive when suspension pH is below pH_{zpc} . Moreover at pH less than pH_{zpc} , the predominant metal species will be positively charged [M^{n+} and $M(OH)^{(n-1)+}$], thus, the uptake of metals in the pH range below pH_{zpc} is a $H^+ - M^{n+}$ (or $M(OH)^{(n-1)+}$) exchange process. An increase in pH above pH_{zpc} will show a slight increase in adsorption as long as the metal species are still positively charged or neutral even though the surface of the adsorbent is negatively charged. When both the surface charge of the adsorbent and metal species charge become negative, the adsorption will decrease significantly. Decrease in removal of metal ions at lower pH is apparently due to the higher concentrations of H^+ in the suspension, which compete with M^{n+} ions for the adsorption sites of sawdust. Decrease in adsorption at higher pH is due to the formation of soluble hydroxyl complexes. These observations in the current study are in accordance with earlier observations related to effect of varying pH on metal adsorption processes by low-cost adsorbents [4,20].

3.1.2. Effect of contact time on sorption efficiency

The effect of contact time on efficiency of Cd adsorption on sawdust is investigated to study the rate of Cd removal. For different values of initial Cd concentrations ranging from 1 to 50 mg/L, percentage removal of Cd by 10 g/L *Pinus halepensis* sawdust as a

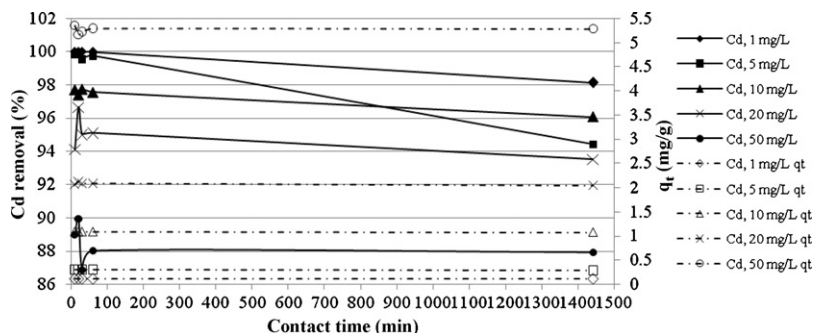


Fig. 2. Effect of contact time on Cd removal using sawdust at varying initial Cd concentrations.

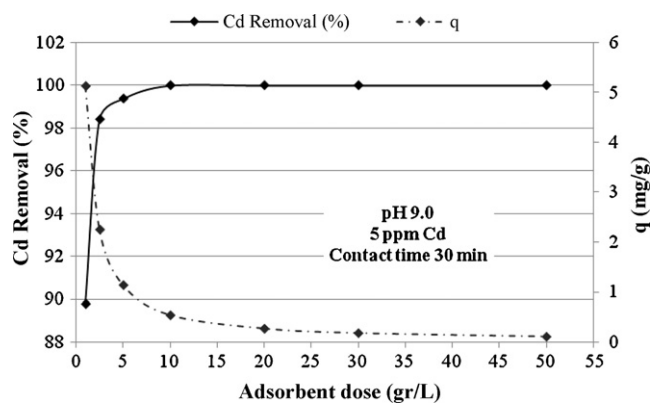


Fig. 3. Effect of adsorbent dose on Cd removal using sawdust at 30 min contact time.

function of contact time at pH of 9.0 is illustrated in Fig. 2. From the plots, it is evident that for the investigated varying initial concentrations of Cd, maximum adsorption rates (97.7–100%) are achieved almost in the first 10 min of contact for Cd concentrations of 1, 5, and 10 mg/L, and in 20 min of contact for Cd concentrations of 20 and 50 mg/L. A further increase in the contact time has a negligible effect on the rate of Cd adsorption. The rate of metal removal is higher in the beginning due to a larger surface area of the sawdust being available for metal adsorption. Later as the adsorbed material forms a monolayer, the capacity of the adsorbent gets exhausted and then the uptake rate is controlled by the rate at which the metal is transported from the exterior to the interior sites of the adsorbent particles. The rate of adsorption decreases in later stages probably due to the slow pore diffusion of the solute ion into the bulk of the adsorbent. It is noted that after 24 h of mixing, adsorption started decreasing as the capacity of the adsorbent was exhausted.

3.1.3. Effect of adsorbent concentration on sorption efficiency

The effect of sawdust concentration, varying from 1 to 50 g/L, onto Cd adsorption is depicted in Fig. 3. It is apparent that the percent removal of metal ions increases with increasing weight of sawdust due to the greater availability of surface area and thus exchangeable sites. However, once almost all Cd is adsorbed, the contribution of additional sawdust will be insignificant. Almost complete Cd removal was achieved within 30 min from a 5 mg/L Cd solution at pH 9.0 in the presence of 10 g/L adsorbent. On the other hand, the adsorption capacity, the amount adsorbed per unit mass of adsorbent, decreases mainly due to un-saturation of adsorption sites through the adsorption reaction. Another reason may be due to the particle interaction, such as aggregation, resulting from high sorbent concentration. Such aggregation would lead to decreases in total surface area of the sorbent and an increase in diffusion path length [4]. It can be noted from Fig. 3 that adsorption capac-

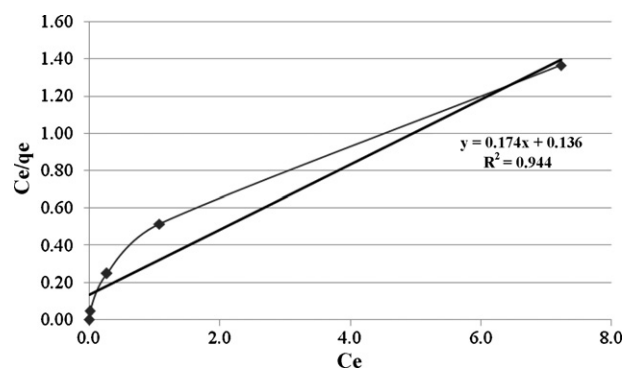


Fig. 5. Langmuir isotherm model for Cd adsorption onto *Pinus halepensis* sawdust.

ity, q , decreased from 5.13 to 0.11 mg/g as sawdust concentration increased from 1 to 50 g/L.

3.1.4. Effect of initial cadmium concentration on sorption efficiency

The effect of initial Cd concentration (1–50 mg/L) was investigated at pH of 9.0 in the presence of 10 mg/L sawdust, and recorded outcomes are illustrated in Fig. 4. The plots reveal that for all contact times, an increase in the Cd concentration from 1 to 50 mg/L results in a decrease in the percent metal removal from 100% to 87%, and an increase in adsorption capacity from 0.11 to 5.36 mg/g. The decrease in the percentage removal of Cd can be attributed to saturation of available active sites on the adsorbent above a certain concentration of metal. The increase in adsorption capacity may be due to the higher adsorption rate and the utilization of all available active sites for adsorption at higher metal concentration.

3.2. Adsorption isotherm study

As previously mentioned, adsorption isotherms aid in describing the adsorption mechanism of Cd on the surface of the adsorbent under study. Adsorption isotherms are characterized by specific constants that express the surface properties and affinity of adsorbent towards the adsorbed pollutant. In the present study, three equilibrium models are analyzed and results are discussed in the following sections.

3.2.1. Langmuir isotherm

The isotherm data have been linearized and plotted in accordance to Langmuir equation given as Eq. (4) (Fig. 5). The Langmuir constant, q_m , which is a measure of monolayer adsorption capacity of sawdust is calculated as 7.35 mg/g and Langmuir constant, b , which denotes adsorption energy, is calculated as 0.7818 L/mg. The dimensionless parameter, R_L is found in the range 0.1215–1.0 ($0 < R_L < 1$) which confirms favorable Cd adsorption process using *P. halepensis* sawdust. At low Cd concentration (1 mg/L), $R_L = 1$ thus

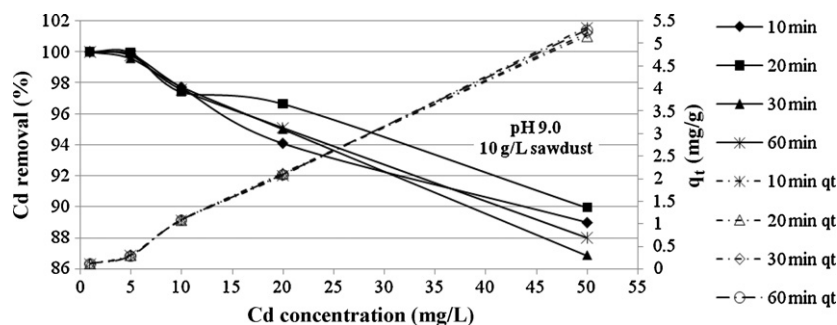


Fig. 4. Effect of initial Cd concentration on Cd removal using sawdust at varying contact times.

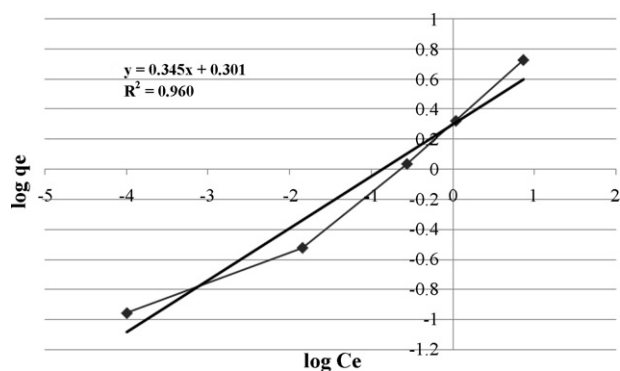


Fig. 6. Freundlich isotherm model for Cd adsorption onto *Pinus halepensis* sawdust.

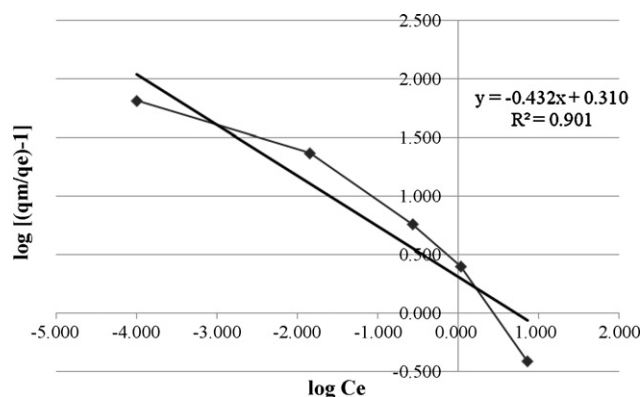


Fig. 7. Generalized isotherm model for Cd adsorption onto *Pinus halepensis* sawdust.

Cd adsorption is linear. The plot in Fig. 5 yields a high coefficient of determination ($R^2 = 0.944$) which indicates a good agreement between the experimental values and isotherm parameters, and confirms the monolayer Cd adsorption on *P. halepensis* sawdust.

3.2.2. Freundlich isotherm

Freundlich equilibrium constants were determined from the plot of $\log q_e$ versus $\log C_e$ (Fig. 6) on the basis of the linear form of Freundlich equation (Eq. (7)). The values for K_f and n_F are 2.213 and 4.194, respectively. A higher value of coefficient of determination ($R^2 = 0.960$) is obtained compared to Langmuir isotherm which indicates a better agreement between the experimental values and isotherm parameters for Cd adsorption on *P. halepensis* sawdust.

3.2.3. Generalized isotherm equation

The generalized isotherm constants N_b and K_G are calculated from the slope and intercept of the plot of $\log [(q_m/q_e) - 1]$ versus $\log C_e$ as shown in Fig. 7. From the current experimental data, the values of N_b and K_G are 0.432 and 2.042, respectively. The coefficient of determination obtained from the generalized isotherm model is 0.901 thus less than R^2 values obtained with Langmuir and Freundlich isotherm equations. This denotes that the experimental data better obey the Freundlich and Langmuir isotherms.

3.3. Adsorption kinetics study

The experimental data were tested with pseudo-second-order, intra-particle diffusion, and Elovich kinetic models in order to understand the kinetics of Cd removal using *P. halepensis* sawdust as an adsorbent.

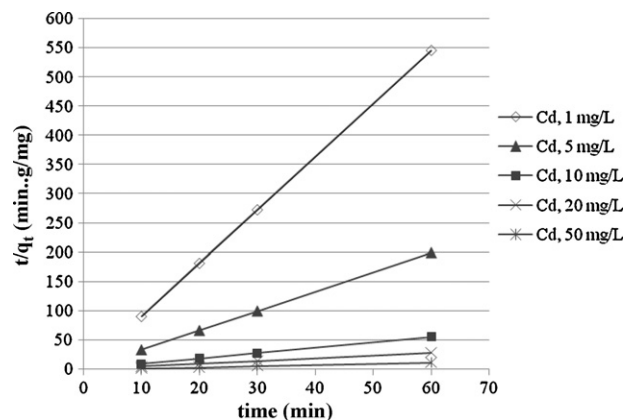


Fig. 8. Pseudo-second-order plot for Cd adsorption onto *Pinus halepensis* sawdust.

Table 1

Kinetic parameters for pseudo-second-order and Elovich kinetic models for Cd adsorption onto *Pinus halepensis* sawdust.

C_i (mg/L)	Experimental q_e (mg/g)	Pseudo-second-order kinetic model		
		k_2	q_e	R^2
1	0.11	1.6×10^{15}	0.11	1
5	0.30	-3.7×10^{14}	0.30	1
10	1.08	2.14×10^{14}	1.08	1
20	2.09	-7.38	2.09	0.999
50	5.30	0.736	5.32	0.999

3.3.1. Pseudo-second-order kinetics

Cadmium adsorption kinetics onto *P. halepensis* sawdust was tested with the pseudo-second-order kinetic model by plotting t/q_t versus t as shown in Fig. 8. From this plot the second-order rate constant, k_2 , the estimated equilibrium capacity, q_e , and the coefficient of determination (R^2) were calculated for the initial Cd concentration ranging from 1 to 50 mg/L as summarized in Table 1. The calculated q_e values show a very good agreement with the experimental values with R^2 values exceeding 0.999. This indicates that the pseudo-second-order kinetic model describes well Cd removal using the sawdust under study.

3.3.2. Intra-particle diffusion model

Adsorbate species are most likely transported from the bulk of the solution into the solid phase through an intra-particle diffusion process, which often may be the rate-limiting step in many adsorption processes [18]. The possibility of intra-particle transport in the current study was explored by using the Weber–Morris equation (Eq. (10)). Plots of $t^{1/2}$ versus q_t are shown in Fig. 9 for the initial Cd concentration ranging from 1 to 50 mg/L. From these

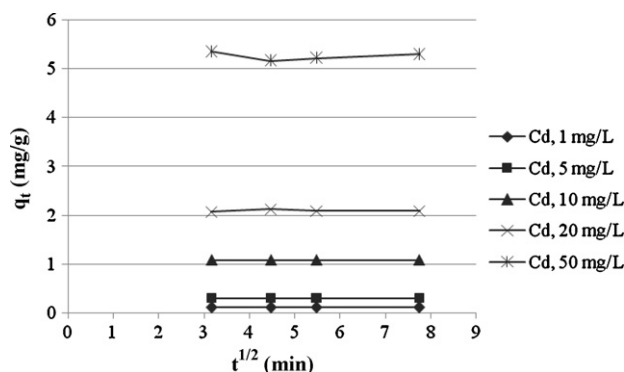


Fig. 9. Intra-particle diffusion plot for Cd adsorption onto *Pinus halepensis* sawdust.

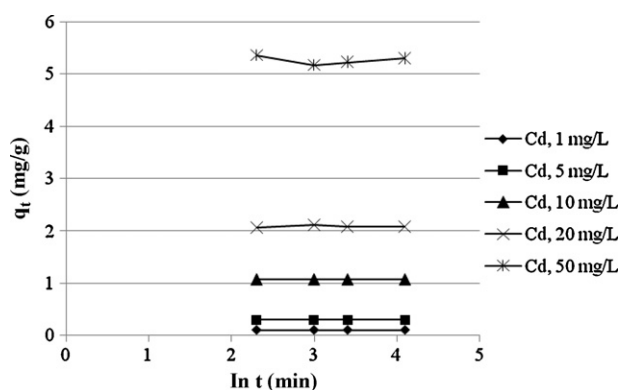


Fig. 10. Elovich model plot for Cd adsorption onto *Pinus halepensis* sawdust.

plots the intra-particle diffusion rate constant, k_{id} were calculated to range between -0.004 and $3 \times 10^{-17} \text{ mg}/(\text{g min})^{1/2}$. It is observed that linearity is not applied for all Cd concentrations, even though some linearity is present when Cd concentration equals 1 mg/L, thus it cannot be stated that the intra-particle diffusion process is the unique rate-limiting step occurring during sorption of Cd onto *P. halepensis* sawdust. The deviation of plots from the origin indicates that there are other sorption steps occurring in this adsorption process [37].

3.3.3. Elovich kinetic model

Cadmium adsorption kinetics onto *P. halepensis* sawdust was also tested with the Elovich kinetic model (Eq. (11)) by plotting $\ln t$ versus q_t as shown in Fig. 10. Recorded R^2 values are very low (-0.2 to 0.065) which indicates that the experimental data do not fit the Elovich kinetic model and Cd removal using the sawdust under study cannot be described using this model.

4. Conclusions

Untreated sawdust of *P. halepensis*, a common pine tree in Lebanon, has proven to be a promising adsorbent for the removal of cadmium from aqueous solutions. Metal sorption and removal efficiency may be influenced by a number of factors, such as pH, adsorbent dose, contact time, and initial metal concentration. Cadmium adsorption by *P. halepensis* sawdust is highly pH-dependent, and the favorable pH for maximum Cd adsorption on the adsorbent under study was at 9.0. For the investigated varying initial Cd concentrations, maximum adsorption rates (97.7–100%) were achieved almost in the first 10 min of contact for Cd concentrations of 1, 5, and 10 mg/L, and in 20 min of contact for Cd concentrations of 20 and 50 mg/L. A further increase in the contact time had a negligible effect on the rate of Cd adsorption. Also, it was apparent that the percent removal of Cd increases with increasing weight of sawdust due to the greater availability of surface area and thus exchangeable sites. However, once almost all Cd is adsorbed, the contribution of additional sawdust will be insignificant. For all contact times, an increase in Cd concentration from 1 to 50 mg/L resulted in a decrease in the percent Cd removal from 100% to 87%, and an increase in adsorption capacity from 0.11 to 5.36 mg/g at pH of 9.0 in the presence of 10 mg/L *P. halepensis* sawdust. The equilibrium adsorption data were tested with three isotherm models and were best fitted with the Freundlich isotherm ($R^2 = 0.960$). The kinetics of Cd adsorption was very well described by the pseudo-second-order kinetic model with R^2 values exceeding 0.999.

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