

Removal of heavy metals from aqueous solution by sawdust adsorption

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Abstract

The adsorption of lead, cadmium and nickel from aqueous solution by sawdust of walnut was investigated. The effect of contact time, initial metal ion concentration and temperature on metal ions removal has been studied. The equilibrium time was found to be of the order of 60 min. Kinetics fit pseudo first-order, second-order and intraparticle diffusion models, hence adsorption rate constants were calculated. The adsorption data of metal ions at temperatures of 25, 45 and 60°C have been described by the Freundlich and Langmuir isotherm models. The thermodynamic parameters such as energy, entropy and enthalpy changes for the adsorption of heavy metal ions have also been computed and discussed. Ion exchange is probably one of the major adsorption mechanisms for binding divalent metal ions to the walnut sawdust. The selectivity order of the adsorbent is $\text{Pb(II)} \approx \text{Cd(II)} > \text{Ni(II)}$. From these results, it can be concluded that the sawdust of walnut could be a good adsorbent for the metal ions from aqueous solutions.

Key words: adsorption; heavy metals; sawdust; kinetic; thermodynamic parameters

Introduction

The use of low-cost adsorbents has been investigated as a replacement for costly current methods. Natural materials or waste products from certain industries with a high capacity for heavy metals can be obtained, employed, and disposed of with little cost. Heavy metals are often discharged by a number of industries, such as metal plating facilities, mining operations and tanneries, this can lead into the contamination of freshwater and marine environment (Low and Lee, 2000; Bailey *et al.*, 1999). Heavy metals are not biodegradable and can lead to accumulation in living organisms, causing various diseases and disorders (Bailey *et al.*, 1999).

It is well known that some metals are harmful to life, such as antimony, chromium, copper, lead, manganese, mercury, cadmium, etc., they are significantly toxic to human beings and ecological environments (Doris *et al.*, 2000).

Generally, the techniques employed for heavy metal removal include precipitation, ion exchange, adsorption, filtration, electrodeposition, reverse osmosis (Rao *et al.*, 2000). However, most of them do not lead to a satisfactory depollution considering the operational costs (Marchetti *et al.*, 2000). Precipitation methods are particularly reliable but require large settling tanks for the precipitation of voluminous alkaline sludges and a subsequent treatment is needed. Ion exchange has the advantage of allowing the recovery of metallic ions, but it is expensive and sophisticated.

Adsorption on solid-solution interface is an important means for controlling the extent of pollution due to heavy metal ions. The use of activated carbon and ion exchange resins is not suitable for developing countries due to their high capital and operational costs (Raji and Anirudhan, 1997). This has encouraged research into discovering materials that are both efficient and cheap.

Interest has recently arisen in the investigation of some unconventional methods and low cost materials for scavenging heavy metal ions from industrial waste waters (Gloaguen and Morvan, 1997). In general, an adsorbent can be assumed as “low cost” if it requires little processing, is abundant in nature, or is a by-product or waste material from industry (Bailey *et al.*, 1999). Some of the reported low-cost adsorbents include bark, tannin-rich materials, lignin, chitin, chitosan, peat moss, moss, modified wool and cotton. Insoluble starch xanthates have been found to be very useful to remove heavy metal ions from solutions (Rao *et al.*, 2000). Agricultural waste materials such as spent grain (Low and Lee, 2000), polymerized onion skin (Kumar and Dara, 1981), rice husks (Khalid and Ahmad, 1999), bark and sawdust (Doris *et al.*, 2000; Marchetti *et al.*, 2000; Gloaguen and Morvan, 1997; Duvnjak and Al-Asheh, 1998; Ajmal *et al.*, 1998), maize cobs (Okieimen *et al.*, 1987), wheat bran (Bulut and Baysal, 2006) have been studied to investigate their effectiveness in binding heavy metal ions.

The adsorption of heavy metals by these materials might be attributed to their proteins, carbohydrates, and phenolic compounds which have carboxyl, hydroxyl, sulfate, phosphate, and amino groups that can bind metal ions.

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This article reported the efficiency of very commonly available tree sawdust of walnut in Turkey for the removal of toxic heavy metal ions such as Pb(II), Cd(II) and Ni(II) from aqueous solutions.

1 Materials and methods

1.1 Sawdust preparation and chemicals

The sawdust of walnut was obtained commercially and used for the preparation of adsorbent. It was washed with distilled water to remove surface impurities and dried at 100°C for 24 h, ground and sieved with Waring Commercial Marka Lab. Blender to increase the surface area. The adsorbents were used as raw materials.

All chemicals were of analytical grade. Stock solutions of heavy metal ions (HMI) (1000 mg/L) were prepared from Pb(NO₃)₂, (CH₃COO)₂·Cd₂H₂O and Ni(NO₃)₂ (Merck).

A water bath shaker (Model 400, Nuve ST) was used for all the adsorption experiments. Filtration process was performed with Acrodisc LC 25 mm (0.45 µm). Atomic absorption spectrometer (AAS) (Model 929, Unicam) was used to analyze the concentrations of HMI. Elemental analysis (EA) was carried out with an EA 1108 Fisons instruments. The surface area was determined by a single-point N₂ gas adsorption method using a model micromeritics Flow Sorb 11.2300.

1.2 Batch adsorption experiments

The batch technique was selected to obtain equilibrium data because of its simplicity. Batch adsorption were performed at different temperatures and initial HMI concentrations to obtain equilibrium isotherms. For isotherm studies, adsorption experiments were carried out by shaking 2 g of sawdust samples with 100 ml flasks filled with 100 ml of HMI solution at a concentration range 10–200 mg/L at a fixed temperature in a thermostated shaker bath for a known period of time. After equilibrium the suspension was filtered with syringe and the metal solution then was analyzed using AAS. In order to obtain the adsorption capacity, the amount of ions adsorbed per mass unit of sawdust (mg/g) was evaluated using the following expression:

$$q_e = (C_0 - C_e)V/m \quad (1)$$

where q_e is the amount adsorbed at equilibrium (mg/g), C_0 is the initial metal ions concentration (mg/L), C_e is the equilibrium metal ions concentration (mg/L), V is the volume of the aqueous phase (L), and m is the amount of the sawdust used (g).

For adsorption kinetic the mixture of the test solution 250 ml (100 mg/L) and sawdust (5 g) was stirred in a shaker at 150 r/min and 25°C continuously for 4 h. Separate samples for HMI were drawn after 5, 10, 15, 25, 35, 45, 60, 120, 180 and 240 min intervals. The suspension was filtered. The HMI concentrations were then analyzed using AAS.

2 Results and discussion

2.1 Elemental analysis of adsorbent

Elemental analysis was carried out with an EA 1108 Fisons instruments. A sample of adsorbent was put in an oven at 1273 K under oxygen to obtain a quick and completed compustion. H₂O and CO₂ were released and conducted in a copper oven at 293 K, then passed through a 2-m column with helium vector gas, and analyzed by a catharameter dedector. The results are shown in Table 1.

Table 1 Physical and chemical properties of walnut of sawdust used in the experiments

Item	
Moisture content (%)	90.00
Bulk density (g/ml)	0.63
Total loss of ignition (%)	97.00
Organic and inorganic components (%)	89.77
Insoluble components (%)	10.23
Surface area (BET) (m ² /g)	0.72
C content (%)	47.07
H content (%)	5.65

2.2 Effect of contact time and adsorption kinetics

To establish an appropriate contact time between the sawdust and metallic ion solution, adsorption capacities of metal ion were measured as a function of time (Fig.1). The plot reveals that the rate of the percentage of HMI removal is higher at the beginning. That is probably due to the larger surface area of the sawdust being available at beginning for the adsorption of metals. As the surface adsorption sites become exhausted, the uptake rate is controlled by the rate at which the adsorbate is transported from the exterior to the interior sites of the adsorbent particles. The rate of HMI removal was attained after approximately 1 h stirring. It does not seem to be much benefit from a stirring time longer than 1 h. Therefore, equilibrium time of 1 h was selected for all further studies. This is rather as compared with the results obtained with other adsorbents referred to literature (Table 2).

Adsorption is a physical-chemical process that the mass transfers a solute (adsorbate) from the fluid phase to the adsorbent surface (Silva *et al.*, 2004). A study of kinetics of adsorption is desirable as it provides information about the mechanism of adsorption, which is important for efficiency of the process (Jain *et al.*, 2003).

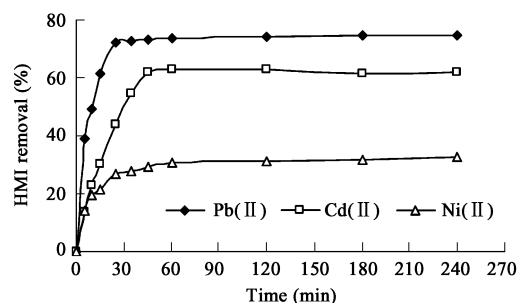


Fig. 1 Removal of HMI vs. time. Initial concentration of HMI 100 mg/L; $m=5$ g; $V=250$ ml; $T=25^\circ\text{C}$.

Table 2 Contact time for different adsorption systems

Metallic ions solution	Adsorbent	Contact time	References
Pb(II), Ni(II), Cd(II), Cu(II)	Leaf, stem and root phytomass of <i>Quercus ilex</i> L.	3 d	Prasad and Freitas, 1999
Ni(II), Cd(II), Cu(II)	Pine bark	24 h	Duvnjak and Al-Asheh, 1998
Pb(II), Cd(II), Hg(II)	Polyacrylamide grafted hydrous tin(IV) oxide gel	5 h	Anirudhan <i>et al.</i> , 2001
Pb(II), Ni(II), Cd(II), Cu(II)	Modified barks	2 h	Gaballah <i>et al.</i> , 1998
Pb(II), Cd(II)	Spent grain	2 h	Low and Lee, 2000
Cu(II)	Sawdust of mangifera indica	90 min	Ajmal <i>et al.</i> , 1998
Pb(II), Cd(II), Cu(II)	Modified cellulosic materials	20 min	Okieimen <i>et al.</i> , 1987

Various adsorption kinetic models have been used to describe the adsorption of metal ions. The first-order kinetic process has been used for reversible reaction with an equilibrium being established between liquid and solid phases. The pseudo first-order rate by Lagergren has also widely been used (Taty-Costodes *et al.*, 2003; Bulut and Aydın, 2006). The adsorption rate expression of Lagergren is as follows.

$$\lg(q_e - q_t) = \lg q_e - k_{pf}/2.303t \quad (2)$$

where q_e is the amount adsorbed (mg/g) at equilibrium, q_t is the amount adsorbed (mg/g) at time t and k_{pf} is the adsorption rate constant (min^{-1}). In most cases, the first-order equation of Lagergren did not apply well throughout the whole contact time and is generally applicable over the initial 20–30 min of the adsorption process. The plotting of $\lg(q_e - q_t)$ versus time deviated considerably from the theoretical data after a short period (Fig.2). The plots and intercepts of curves were used to determine the first-order constant k_{pf} , capacity q_e and the corresponding linear regression correlation coefficient R_1^2 values (Table 3).

Recently, McKay and Ho (1999), Vadivelan and Kumar (2005) reported that most of the adsorption system followed a pseudo second-order kinetic model which can be expressed as:

$$t/q_t = 1/k_{ps}q_e^2 + t/q_e \quad (3)$$

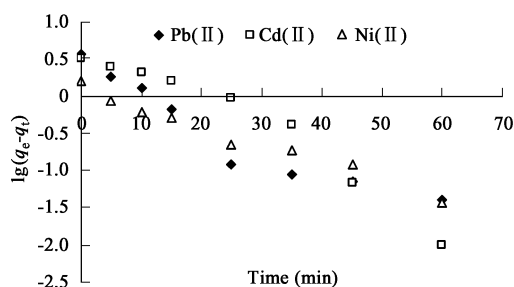


Fig. 2 Pseudo first-order adsorption kinetics of Pb(II), Cd(II) and Ni(II) on sawdust of walnut. Initial concentration of HMI 100 mg/L; $m=5$ g; $V=250$ ml; $T=25^\circ\text{C}$.

where k_{ps} is the adsorption rate constant ($\text{g}/(\text{mg}\cdot\text{min})$). Plots of t/q_t versus time (Fig.3) suggest that the values of k_{ps} and corresponding linear regression correlation coefficient R_2^2 values were determined from the slope of the plots. The results are given in Table 3. The correlation coefficients for the second-order kinetics model (R_2^2) are greater 0.99, indicating the applicability of this kinetics equation and the second-order nature of adsorption process of HMI onto sawdust. Similar phenomena was observed in HMI onto modified sawdust of walnut (Bulut and Tez, 2003). So a pseudo-second order model can be considered. The later is based on the assumption that the rate limiting step may be a chemical adsorption involving valance forces through sharrin or exchange of electrons between adsorbent and adsorbate. It provides the best correlation of data.

The adsorbate species are most likely transported from the bulk of the solution into the solid phase through an inparticle diffusion process, which often is the rate-limiting step in many adsorption processes. The possibility of intraparticle diffusion was explored by using the intraparticle diffusion model (Doğan *et al.*, 2004).

The rate constant for intraparticle diffusion (k_{id}) is given by Weber Morris (Anirudhan *et al.*, 2001):

$$q_t = k_{id}t^{1/2} \quad (4)$$

where q_t is the amount adsorbed (mg/g) at time t (min).

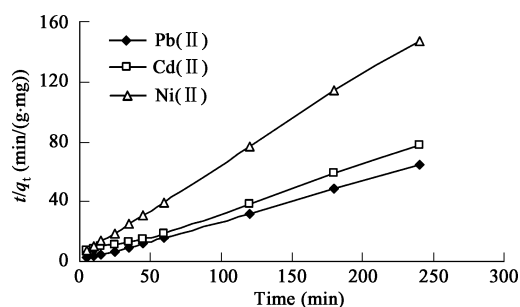


Fig. 3 Pseudo second-order adsorption kinetics of Pb(II), Cd(II) and Ni(II) on sawdust of walnut. Initial concentration of HMI 100 mg/L; $m=5$ g; $V=250$ ml; $T=25^\circ\text{C}$.

Table 3 Adsorption kinetic parameters of Pb(II), Cd(II) and Ni(II) on sawdust

HMI	Pseudo first-order kinetic model			Pseudo second-order kinetic model		
	k_{pf} (min^{-1})	q_e (mg/g)	R_1^2	k_{ps} ($\text{g}/(\text{mg}\cdot\text{min})$)	q_e (mg/g)	R_2^2
Pb(II)	0.08	2.24	0.9053	1.54	3.78	0.9996
Cd(II)	0.09	5.35	0.9379	0.28	3.32	0.9936
Ni(II)	0.06	1.23	0.9776	0.24	1.67	0.9997

R^2 is the correlation coefficient.

Plots of q versus $t^{1/2}$ are shown in Fig. 4 for different heavy metal ions. All the plots have the same general features that an initial curved portion is followed by a linear portion and a plateau. The initial curved portion is attributed to the bulk diffusion of the linear portion to the intraparticle diffusion and the plateau to the equilibrium. This indicates that transport of heavy metal ion from solution through the particle solution interface, into the pores of the particle as well as the adsorption on the available surface of sawdust are both responsible for the uptake of heavy metal ions (Jain, 2001).

Rate constants (k_{id}) characteristic of the adsorption in the region where intraparticle diffusion is rate controlling. Extrapolation of the linear portions of the plots back to the axis provides intercepts which are proportional to the extent of the boundary layer thickness, i.e., the larger the intercept is, the greater is the boundary layer effect (Mckay *et al.*, 1980).

The deviation of the curves from the origin also indicates that intraparticle transport is not the only rate-limiting step (Jain, 2001). The values of k_{id} of Pb(II), Cd(II) and Ni(II) is 0.9891, 0.9284 and 0.8853 $\text{mg}/(\text{g}\cdot\text{min})^{1/2}$, respectively.

2.3 Adsorption isotherms

The equilibrium adsorption isotherm is of importance in the design of adsorption systems (Wang *et al.*, 2005). The adsorption isotherm for the metal ions onto sawdust at the temperature of 25, 45 and 60°C is shown in Fig. 5. The adsorption data indicate linear distribution in the initial concentration range of 10–200 mg/L. It is evident that, for the same equilibrium time, the metal ions adsorbed are higher for greater values of initial concentration of metal

ions. This is obvious because more efficient utilization of the adsorptive capacities of the adsorbent is expected due to a greater driving force (by a higher concentration gradient pressure) (Jain, 2001).

The Langmuir treatment is based on the assumption that a maximum adsorption corresponds to a saturated monolayer of solute molecules on the adsorbent surface, that the energy of adsorption is constant, and there is no transmigration of adsorbate in the plane of the surface (Jain, 2001), which is represented by:

$$q_e = Q^0 b C_e / (1 + b C_e) \quad (5)$$

and, the linear form of the equation can be written as

$$C_e/q_e = 1/bQ^0 + C_e/Q^0 \quad (6)$$

where q_e is the amount of heavy metal ions adsorbed per unit mass of adsorbent (mg/g) at equilibrium liquid phase concentration of heavy metal ion (mg/L). Q^0 and b are Langmuir constants indicating adsorption capacity and energy, respectively. The plots of C_e/q_e versus C_e at different temperatures were found to be linear, this indicates the applicability of the Langmuir model. The statistical significance of the correlation coefficient (R^2) for C_e/q_e versus C_e was the criteria by which the fitting of the data to Langmuir isotherm was tested. It demonstrates monolayer coverage of adsorbate at the outer surface of the adsorbent. The parameters Q^0 and b have been calculated and the results are represented in Table 4. It shows that the adsorption of HMI onto sawdust is a monolayer type one that does not fully cover the surface of the sawdust. As seen from Table 3, Langmuir isotherm fits well with the experimental data. This may be due to homogenous distribution of active sites on the walnut sawdust, since the Langmuir equation assumes that the surface is homogenous (Wang *et al.*, 2005).

The Freundlich equation has been widely used for isothermal adsorption. This is a special case for heterogeneous surface energies in which the energy term (b) in the Langmuir equation varies as a function of surface coverage (q_e) strictly due to variations in heat of adsorption (Jain, 2001). The Freundlich equation has the general form:

$$q_e = K_f C_e^{1/n} \quad (7)$$

The logarithmic form of the equation is:

$$\lg q_e = \lg K_f + 1/n \lg C_e \quad (8)$$

where q_e is the amount of heavy metal ion adsorbed per unit mass of adsorbent (mg/g) at equilibrium, C_e is

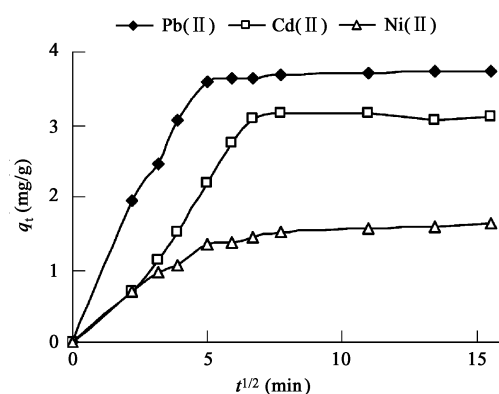


Fig. 4 Intraparticle diffusion plots at different HMI on sawdust of walnut. Initial concentration of HMI 100 mg/L; $m=5$ g; $V=250$ ml; $T=25^\circ\text{C}$.

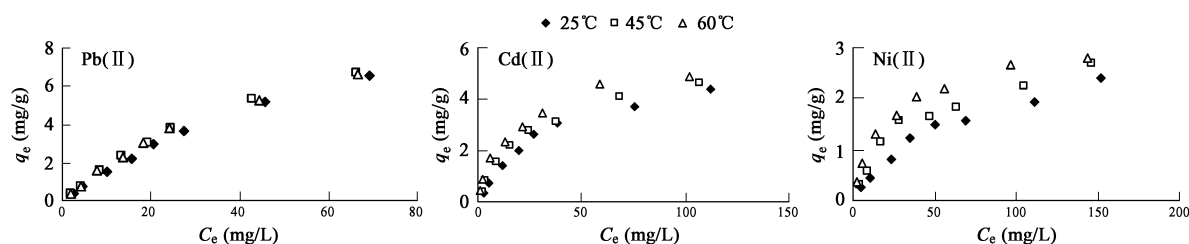


Fig. 5 Adsorption isotherms of Pb(II), Cd(II) and Ni(II) on sawdust of walnut.

Table 4 Adsorption constants for the adsorption of Pb(II), Cd(II) and Ni(II) on sawdust at different temperatures

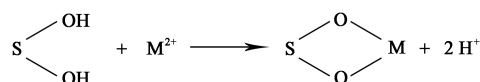
HMI	Temperature (°C)	Freundlich constant			Langmuir constant			
		K	n	R^2	q_e	Q^0	b	R^2
Pb(II)	25	0.19	1.16	0.9904	6.54	15.90	0.01	0.9558
	45	0.22	1.20	0.9881	6.68	13.81	0.01	0.9872
	60	0.27	1.25	0.9873	6.66	12.15	0.02	0.9882
Cd(II)	25	0.24	1.50	0.9498	4.39	5.76	0.03	0.9895
	45	0.35	1.66	0.9485	4.65	5.69	0.04	0.9937
	60	0.49	1.82	0.9530	4.90	5.70	0.06	0.9943
Ni(II)	25	0.11	1.51	0.9767	2.40	3.29	0.01	0.9754
	45	0.17	1.74	0.9437	2.68	3.22	0.03	0.9780
	60	0.29	2.03	0.9524	2.79	3.19	0.05	0.9970

the equilibrium concentration of heavy metal ion (mg/L); K_f and n are Freundlich constant related to adsorption capacity and adsorption intensity, respectively. The plots of $\lg q_e$ versus $\lg C_e$ at different temperatures were found to be linear indicating the applicability of the Freundlich model. The intercept of the line is roughly an indicator of the adsorption capacity, and the slope is an indication of adsorption intensity (Jain, 2001). The Freundlich parameters and the results are represented in Table 4. The value K_f of sawdust for Pb(II), Cd(II) and Ni(II) at 25, 45 and 60°C increase and follows the order 0.19, 0.22, 0.27; 0.24, 0.35, 0.49 and 0.11, 0.17 and 0.29, respectively. It is well known that the Langmuir isotherm corresponds to a dominant ion exchange mechanism while the Freundlich isotherm shows adsorption-complexation reactions taking place in the adsorption process.

2.4 Adsorption mechanism

Ion exchange may be the principal mechanism for the removal of HMI. The major components of the polymeric material in sawdust are lignin, tannins or other phenolic compounds. From the nature of the material which are efficient in capturing heavy metal ions, it can be speculated that lignin, tannins or other phenolic compounds are the active ion exchange compounds and that active sites are the phenolic groups of those compounds.

Based on the structure of these phenolic compounds, a possible mechanism of ion exchange could be considered as a divalent heavy metal ion (M^{2+}) attaches itself to two adjacent hydroxyl groups and two oxyl groups which could donate two pairs of electrons to metal ions, forming four coordination number compounds and releasing two hydrogen ions into solution (Schema 1) (Doris *et al.*, 2000).



Schema 1

2.5 Thermodynamic parameters

Thermodynamic parameters such as free energy change (ΔG^0), enthalpy change (ΔH^0) and entropy change (ΔS^0) were calculated from the variations of the thermodynamic distribution coefficient, K_0 with change in temperature. K_0 for the adsorption reaction was determined by the method of Biggar and Chung (Gaballah *et al.*, 1997; Anirudhan and Raji, 1997), by plotting $\ln q_e/C_e$ versus q_e and extrapolating the line to zero (Fig.6).

The free energy change (ΔG^0) for the interaction of sawdust with Pb(II), Cd(II) and Ni(II) calculated as $\Delta G^0 = -RT \ln K_0$. From the variations of ΔG^0 with temperature, the standard enthalpy, ΔH^0 and ΔS^0 were computed using the following equation (Raji and Anirudhan, 1997).

$$\Delta G^0 = \Delta H^0 - T \Delta S^0 \quad (9)$$

Table 5 contains the values of thermodynamic parameters. Positive values of ΔH^0 suggest the endothermic nature of the adsorption and the negative values of ΔG^0 indicate the spontaneous nature of the adsorption process. However, the negative value of ΔG^0 decreased with an increase in temperature, indicating that the spontaneous nature of adsorption is inversely proportional to the temperature. The positive values of ΔS^0 show the increased randomness at the solid/solution interface during the adsorption process. The adsorbed water molecules, which are displaced by the adsorbate species, gain more translational energy than is lost by the adsorbate ions, thus allowing the prevalence of randomness in the system. The enhancement of adsorption

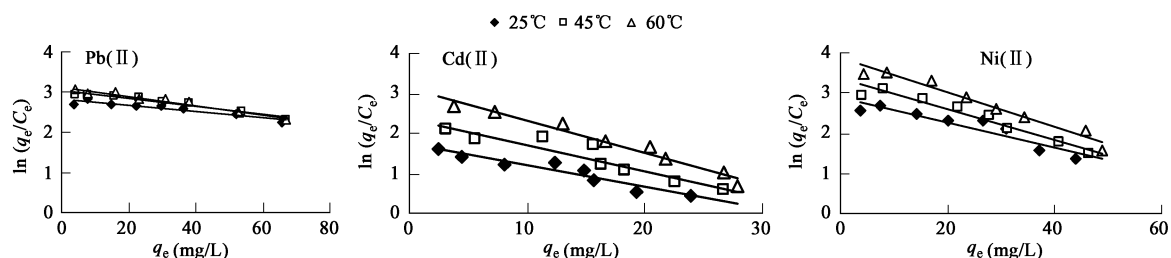
Fig. 6 Plots of $\ln(q_e/C_e)$ versus q_e for Pb(II), Cd(II) and Ni(II).

Table 5 Values of thermodynamic parameters for the adsorption of Pb(II), Cd(II) and Ni(II)

HMI	Temperature (K)	K_0	$\ln K_0$	ΔG^0 (cal/mol)	ΔS^0 (cal/(mol·K))	ΔH^0 (cal/mol)
Pb(II)	25	16.95	2.83	-1675.72	11.33	1696.8
	45	20.70	3.03	-1914.55		
	60	22.87	3.13	-2071.03		
Cd(II)	25	17.64	2.87	-1699.4	24.01	5479.3
	45	27.94	3.33	-2104.11		
	60	46.99	3.85	-2547.43		
Ni(II)	25	5.64	1.73	-1024.38	29.76	7879.6
	45	10.81	2.38	-1503.84		
	60	23.10	3.14	-2077.65		

at higher temperatures may be attributed to the enlargement of pore size and/or activation of the adsorbent surface (Jain, 2001).

2.6 Competition among metal ions

In wastewaters, the metals of interest are usually found with a number of other metals. To test the binding of each metal ion in the presence of other metals. Sawdust of walnut can effectively bind a number of heavy metal ions but it would be doubtful that all ions have been equality bound. Furthermore, considering the sawdust as a complex material with many possible binding sites, the main in the same site. Table 6 shows the percentage of adsorption each ion in the presence of other. The general binding affinity of the sawdust for the metals studied, in order decreasing affinity is Pb(II)≈Cd(II)>Ni(II).

While it is clear that some of the metal ions compete with one another for bark binding sites, it is of interest to note that the binding of Pb (II) is relatively unaffected by other metals (Gloaguen and Morvan, 1997). The difference in the adsorption behaviour of Pb(II) and Cd(II) compared Ni(II) may also be explained by the different affinity of metal ions for the donor atoms present in the structure of sawdust.

Table 6 Competition among metal ions

HMI	Adsorption (%)		
Ni(II)-Cd(II)	25.98	43.33	43.26
Ni(II)-Pb(II)	27.55	64.32	
Cd(II)-Pb(II)	48.50	55.82	
Ni(II)/Cd(II)/Pb(II)	27.98	43.86	

3 Conclusions

The following conclusions can be drawn based on the investigation of HMI removal by sawdust adsorption. First of all sawdust appears to be a promising adsorbent for removal of HMI from wastewater. At these adsorption levels, a process using sawdust for the removal and recovery of a heavy metal ions is potentially more economical than current process technology. Secondly, adsorption of heavy metal ions depends on their initial concentrations, temperature and contact time. Thirdly, isothermal data of HMI adsorption on sawdust can be modeled by both Langmuir and Freundlich isotherms. The capacity of sawdust for adsorption of certain metals can be calculated by using these models.

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