

Adsorption studies on ground shells of hazelnut and almond

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Abstract

Adsorption behaviour of Ni(II), Cd(II) and Pb(II) from aqueous solutions by shells of hazelnut and almond were investigated. The structural properties and surface chemistry of the shells were characterized using sorption of nitrogen and Boehm titration. The equilibrium time was found to be 120 min. The equilibrium adsorption capacity of shells were obtained by using linear Langmuir and Freundlich adsorption isotherms. The equilibrium adsorption level was determined to be a function of the solution contact time, concentration and temperature. The thermodynamic parameters have been determined. The negative values of free change (ΔG) indicated the spontaneous nature of the adsorption of Ni(II), Cd(II) and Pb(II) onto shells of hazelnut and almond and the positive values of enthalpy change (ΔH) suggested the endothermic nature of the adsorption process. The best correlation coefficients were obtained for the pseudo second-order kinetic model. Ion exchange is probably one of the major adsorption mechanisms for binding divalent metal ions to the shells of hazelnut and almond. The selectivity order of the adsorbents is Pb(II) > Cd(II) > Ni(II). © 2007 Elsevier B.V. All rights reserved.

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1. Introduction

Heavy metals are nowadays among the most important pollutants in surface and ground water. They are extremely toxic elements, which can seriously affect plants and animals and have been involved in causing a large number of afflictions [1]. Therefore, the elimination of these metals from water and wastewaters is important to protect public health. For this reason, development of a new, flexible and environmentally friendly process for treatment of water and industrial effluents is major challenge [2]. The treatment methods, such as chemical precipitation, membrane filtration, reverse osmosis, ion exchange and adsorption have been practiced for the removal of heavy metals [3]. But these methods are not economical and do not exhibit high treatment efficiency, especially at metal concentrations in range of 0.01–0.1 g/L [4].

The adsorption phenomenon has still been found economically appealing for the removal of toxic metals from waste water by choosing some adsorbents under optimum operation conditions. Scattered research has already been conducted on a wide

variety of adsorbents. Some of the reported low-cost adsorbents include [5,6]; bark/tannin-rich materials, lignin, chitin, chitosan, dead biomass, sawdust, peat moss, modified wool, modified cotton. A wide variety of materials such as rice husk [7], fly ash [8], pine bark [9], sawdust [10] and animal bone [11] are being used as low cost alternatives to expensive adsorbents. Most of these materials contain functional groups associated with proteins, polysaccharides and cellulose as major constituents. Metal uptake is believed to occur through sorption process involving the functional group mentioned above [12]. The cost of these biomaterials is negligible compared with the cost of activated carbon or ion-exchange resins. Man-made synthetic ion exchange resins are marketed for US\$ 30–50/kg. With the same performance, natural new biosorbents could cost less than US\$ 30–50/kg [13]. The concentration limits for classification of hazardous waste-containing metals vary for different metals. The permissible limit of Ni(II), Cd(II) and Pb(II) is 20.0, 1.0 and 0.01 mg L⁻¹ or mg kg⁻¹ in water or soil [5,14].

The investigation reported here deals with equilibrium studies of shells of hazelnut and almond, which is a very cheap and readily available material for the removal of Ni(II), Cd(II) and Pb(II) from aqueous solutions. The effects of contact time, initial adsorbate concentration and temperature on the removal of Ni(II), Cd(II) and Pb(II) were evaluated. The thermodynamic parame-

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ters and the adsorption kinetics of Ni(II), Cd(II) and Pb(II) were also calculated and discussed.

2. Materials and methods

2.1. Adsorbate preparation

All the compounds used to prepare reagent solutions were analytic reagent grade. The stock solution of Ni(II), Cd(II) and Pb(II) (1000 mg L⁻¹ for each ion) is prepared by dissolving a weighed quantity of the respective nitrate salts in distilled water.

2.2. Adsorbent preparation

The shells of hazelnut (SH) and almond (SA) were obtained commercially and used for the preparation of adsorbent. It was washed several times with distilled water to remove surface impurities and then dried at 373 K for 24 h. The shells were ground and sieved with a blender (waring commercial) to increase the surface area. The chemical and physical characteristics of the adsorbents are presented in Table 1. The structural properties and surface chemistry of the shells were characterized using sorption of nitrogen and Boehm titration. Shells were analysed for BET surface area using Quanto Chrome Monosorb Analyser (USA). Elemental analysis was carried out with Fisons Instruments EA 1108 CHNS-O. A pH-meter (Jenway 3010) was used for pH of adsorbent. The surface functional groups containing oxygen were determined according to Boehm titration [15,16] (Table 1).

2.3. Adsorption experiments

The sorption of heavy metal ions (HMI) on SH and SA were studied by the batch technique. A known weight (2 g) of SH and SA were equilibrated with 100 mL of the HMI solution of known concentration in a stoppered pyrex glass flask at a fixed temperature in a thermostated shaking waterbath (Nuve ST 400)

Table 1
Physical and chemical properties of SH and SA used in the experiments

	SH	SA
Parameters		
Moisture content (%)	5.49	4.73
Ash content (%)	2.10	0.67
pH (1% solution)	4.99	5.185
Water soluble components (%)	7.41	5.64
Insoluble components (%)	86.68	89.25
Total loss of ignition (%)	81.10	92.71
Particle size (mm)	0.8	1.2
Surface area (BET) (m ² /g)	4.31	4.11
Bulk density (g/mL)	0.46	0.61
C content (%)	42.67	53.38
H content (%)	4.74	6.26
Results of Boehm titration in mmol/g		
Carboxylic	0.3187	0.0415
Lactonic	0.0755	0.4298
Phenolic	0.7931	0.9732
Basic	0.0000	0.0000

for a certain period of time. After reaching the equilibrium, the suspension was filtrated with a syringe (Acrodisc LC 25 mm (0.45 μm)) and then the metal solution was analysed by AAS (Unicam model 929). In order to obtain the sorption capacity, the amount of ions adsorbed per mass unit of adsorbent (q_e in milligram of heavy metal ions per gram of adsorbent) was evaluated using the following expression (1):

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

where C_0 and C_e are the concentrations of heavy metal ions at initial and equilibrium, respectively, concentration (mg L⁻¹), V the volume of the aqueous phase (L), and m is the amount of the adsorbent used (g).

3. Result and discussion

3.1. Effect of contact time

There are many factors which can contribute to the adsorbate concentration effect. The first and important one is that adsorption sites remain unsaturated during the adsorption reaction. The second cause can be the aggregation/agglomeration of adsorbent particles at higher concentrations. Such aggregation would lead to a decrease in the total surface area of the sorbent particles available for HMI adsorption and an increase in the diffusional path length [17]. The effect of contact time is shown Figs. 1 and 2.

The results reveal that the rate of percent HMI removal are higher at the beginning. That is probably due to the larger surface area of shells at the beginning for the adsorption of HMI. 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 [18].

Most of the maximum percent HMI removal were attained after about 120 min of stirring time. There does not seem to be much benefit from a stirring time longer than 120 min. Therefore, equilibrium time of 120 min was selected for all further

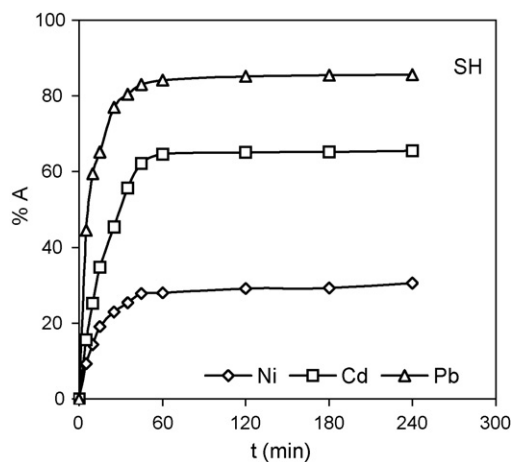


Fig. 1. Percent removal of HMI vs. time on SH (initial HMI concentration = 100 mg/L; temperature = 298 K; SH concentration = 10 g/L; agitation speed = 150 rpm).

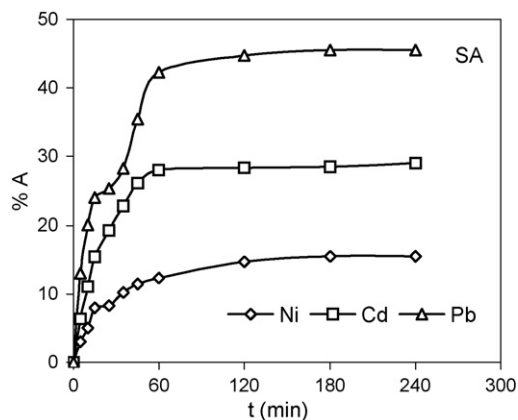


Fig. 2. Percent removal of HMI vs. time on SA (initial HMI concentration = 100 mg/L; temperature = 298 K; SA concentration = 10 g/L; agitation speed = 150 rpm).

studies. Similar results were reported using spent grain [19] and modified barks [2] as the adsorbent.

3.2. Adsorption kinetics

It is well known that the rate of the sorption process is modified by several parameters such as the structural properties of the adsorbent (i.e. porosity, specific area, particle size, etc.), the properties of the metallic ions (ionic radius, number of coordination, and speciation), metallic ions concentration, chelates formation between metallic ions, and the adsorbent, etc. In order to determine the adsorption kinetics of HMI, the first-order and second-order kinetics models were checked. The first-order rate expression of Lagergren based on solid capacity is generally expressed as follows [2,20,21] (2):

$$\log(q_e - q_t) = \log q_e - \left(\frac{k_{pf}t}{2303} \right) \quad (2)$$

where q_e and q_t are the amounts of HMI adsorbed (mg g^{-1}) at equilibrium and at time t (min), respectively, and k_{pf} is the adsorption rate constant of pseudo first-order sorption (min^{-1}). In most cases, the first-order equation of Lagergren did not apply well throughout the whole range of contact times and is generally applicable over the initial 20–30 min of the sorption process. The plotting of $\log(q_e - q_t)$ versus time deviated considerably from the theoretical data after a short period [22]. The plots

and intercepts of curves were used to determine the first-order constant k_{pf} and capacity q_e (Table 2).

Recently, Ho and Mc Kay reported that most of the sorption system followed a pseudo second-order kinetic model [14,18,23] which can be expressed as (3):

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

where k_{ps} is the adsorption rate constant pseudo second-order adsorption ($\text{g mg}^{-1} \text{min}^{-1}$). The values of k_{ps} were determined from the slope of the plots t/q_t versus time and thus are given in Table 2. The correlation coefficients for the linear plots are superior to 0.99 in all the systems. The sorption system is not a first-order reaction and that a pseudo second-order model can be considered. The letter is based on the assumption that the rate-limiting step may be a chemical sorption involving valance forces through sharing or exchange of electrons between adsorbent and adsorbate. It provides the best correlation of data.

The rate constant for intraparticle diffusion (k_{id}) is given by Weber Morris (4) [2,17]:

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

where C is the intercept. Best-fit straight (plots are not shown) that do not pass through the origin indicating that there are an initial boundary layer resistance. The result also indicates that adsorption of HMI on SH and SA is not diffusion controlled [5]. All the plots have the same general features of an initial curved portion followed by a linear portion and a plateau. The initial curved portion is attributed to the bulk diffusion 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 shell are both responsible for the uptake of HMI [2].

k_{id} is a characteristic of the rate of 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 the greater the boundary layer effect [24]. The deviation of the curves from the origin also indicates that intraparticle transport is not the only rate-limiting step [2]. The values of rate constants (k_{id}) are presented in Table 2.

Table 2
Adsorption kinetic parameters of HMI on SH and SA

Adsorbent	HMI	Pseudo first-order			Pseudo second-order			Intraparticle diffusion	
		k_{pf} (min^{-1})	q_e (mg g^{-1})	R^2	k_{ps} ($\text{g mg}^{-1} \text{min}^{-1}$)	q_e (mg g^{-1})	R^2	k_{id} ($\text{mg g}^{-1} \text{min}^{1/2}$)	R^2
SH	Ni(II)	0.06	1.31	0.9704	0.16	1.58	0.9992	0.1218	0.9326
	Cd(II)	0.08	4.77	0.9407	0.29	3.49	0.9966	0.4054	0.956
	Pb(II)	0.07	3.05	0.9858	1.19	4.36	0.9998	0.1315	0.9395
SA	Ni(II)	0.03	0.65	0.9729	0.04	0.86	0.9987	0.0616	0.9456
	Cd(II)	0.07	1.78	0.9495	0.11	1.55	0.9973	0.1692	0.986
	Pb(II)	0.04	2.21	0.8968	0.14	2.47	0.9961	0.3218	0.9714

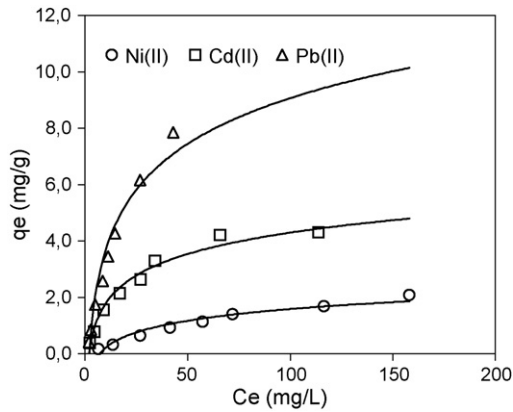


Fig. 3. Adsorption isotherm of HMI on SH (298 K) (temperature = 298 K; SH concentration = 10 g/L; agitation speed = 150 rpm; contact time = 120 min).

3.3. Adsorption isotherms

The adsorption isotherm for HMI on SH and SA at 298 K was shown in Figs. 3 and 4. The adsorption data indicate that there is a linear distribution in the initial concentration range of 10–200 mg L⁻¹. 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) [2].

Adsorption information for a wide range of adsorbate concentrations are most frequently described by adsorption models, such as Langmuir or Freundlich isotherm, which relate adsorption density q_e (metal uptake per unit weight of adsorbent) to equilibrium adsorbate concentration in the bulk fluid phase, C_e . Adsorption data of Pb (II), Cd (II) and Ni (II) onto SH and SA at different temperatures (298, 318 and 333 K) (plots at 318 and

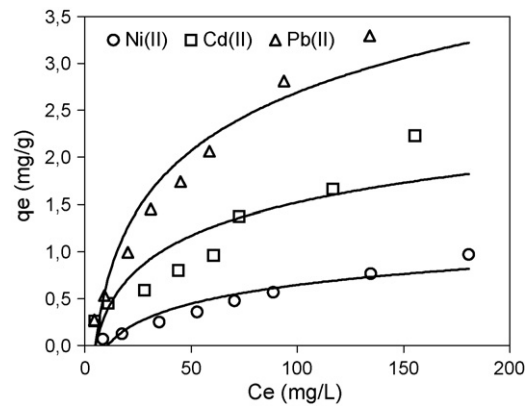


Fig. 4. Adsorption isotherm of HMI on SH (298 K) (temperature = 298 K; SA concentration = 10 g/L; agitation speed = 150 rpm; contact time = 120 min).

333 are not shown) have been analysed with the help of Langmuir and Freundlich models to evaluate the mechanistic details associated with the adsorption process [2].

Langmuir's isotherm model is valid for monolayer adsorption onto a surface containing a finite number of identical sites. 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 that there is no transmigration of adsorbate in the plane of the surface [2], which is represented by (5):

$$\frac{C_e}{q_e} = \frac{1}{bQ^0} + \frac{C_e}{Q^0} \quad (5)$$

where q_e is the amount of heavy metal ions adsorbed per unit mass of sorbent (mg g⁻¹) at equilibrium liquid phase concentration (C_e) of heavy metal ion (mg L⁻¹). Q^0 (mg g⁻¹) and b (L mg⁻¹) are Langmuir constants indicating sorption capacity and energy of adsorption, respectively. The plots of C_e/q_e versus C_e at different temperatures were found to be linear indicating

Table 3
Adsorption constants for the sorption of Pb(II), Cd(II) and Ni(II) on SH and SA at different temperatures

Adsorbent	HMI	T (K)	Freundlich constants			Langmuir constants		
			K_F	n	R_F^2	Q^0 (mg g ⁻¹)	b (L mg ⁻¹)	R_L^2
SH	Ni(II)	298	0.05	1.28	0.9861	3.83	0.007	0.9702
		318	0.08	1.38	0.9736	3.84	0.011	0.9817
		333	0.21	1.80	0.9451	3.92	0.031	0.9821
	Cd(II)	298	0.31	1.61	0.9417	5.42	0.039	0.9904
		318	0.39	1.66	0.8700	5.45	0.053	0.9815
		333	0.51	1.87	0.9456	5.47	0.066	0.9947
	Pb(II)	298	0.45	1.25	0.9772	16.23	0.023	0.9526
		318	0.64	1.39	0.9765	16.24	0.039	0.9806
		333	0.89	1.43	0.9865	16.46	0.056	0.9829
SA	Ni(II)	298	0.01	1.12	0.9968	3.11	0.003	0.9526
		318	0.02	1.22	0.9872	3.15	0.005	0.9602
		333	0.10	1.76	0.9647	3.22	0.020	0.9828
	Cd(II)	298	0.09	1.67	0.9697	3.18	0.010	0.7244
		318	0.13	1.67	0.9851	3.40	0.017	0.9220
		333	0.17	1.70	0.9519	3.74	0.022	0.9557
	Pb(II)	298	0.10	1.35	0.9878	5.43	0.011	0.9906
		318	0.25	1.55	0.9388	5.45	0.031	0.9884
		333	0.90	2.46	0.9514	5.48	0.101	0.9961

Table 4
Adsorption capacities for some adsorbents reported in the literatures (mg g⁻¹)

Adsorbent	Pb(II)	Cd(II)	Ni(II)	Reference
SH	16.23	5.42	3.83	Present study
SA	5.43	3.18	3.11	Present study
Barks of Larix	21.06	–	9.7	[18]
Sawdust	15.77	15.27	–	[17]
Rice hulls	11.4	21.4	–	[14]
Stem of <i>Quercus ilex</i> L.	0.75	0.36	0.58	[21]

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 sorbent. The parameters Q^0 and b have been calculated and the results are represented in Table 3. This shows that the adsorption of HMI onto shells is a monolayer type one that does not fully cover the surface of the shell. The adsorption constants of the Langmuir isotherm Q^0 obtained as 3.83, 5.42, 16.23 and 3.11, 3.18, 5.43 for Pb(II), Cd(II) and Ni(II), respectively on SH and SA at 298 K. The values compare favourably with some of those reported with other types of adsorbents (Table 4).

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 [2]. The Freundlich equation has the general form (6):

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \quad (6)$$

where q_e is the amount of heavy metal ion adsorbed per unit mass of sorbent (mg/g) at equilibrium and C_e is the equilib-

rium concentration of heavy metal ion (mg L⁻¹); K_F and n are Freundlich constants related to adsorption capacity and adsorption intensity, respectively. The plots of $\log q_e$ versus $\log C_e$ 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 [2]. The Freundlich parameters and the results are represented in Table 3. 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.

3.4. Adsorption mechanism

Ion exchange may be the principal mechanism for the removal of HMI. The major components of the polymeric material in shell 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.

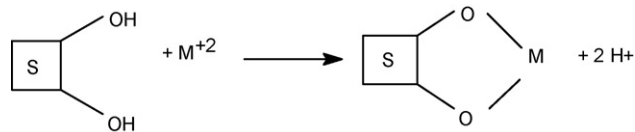
Based on the structure of these phenolic compounds, a possible mechanism of ion exchange could be considered as a divalent heavy metal ion (M^{2+}) that attaches itself to two adjacent hydroxyl groups and two oxyl groups which could donate two pairs of electrons to metal ions, forming four coordination number compounds and releasing two hydrogen ions into solution (Scheme 1) [18].

3.5. Effect of temperature and thermodynamic parameters

To determine the effect of temperature on the adsorption of HMI, experiments were also conducted at 298, 318 and 333 K.

Table 5
Values of thermodynamic parameters for the sorption of Pb(II), Cd(II) and Ni(II) on SH and SA

Adsorbent	HMI	T (K)	b (L mol ⁻¹)	ln b	ΔG^0 (kJ mol ⁻¹)	ΔS^0 (J mol ⁻¹ K ⁻¹)	ΔH^0 (kJ mol ⁻¹)			
SH	Ni(II)	298	434.45	6.07	-15.05	158.54	32.49			
		318	657.55	6.49	-17.15					
		333	1825.88	7.51	-20.79					
	Cd(II)	298	4428.95	8.40	-20.80			110.73	12.21	
		318	5935.25	8.69	-22.97					
		333	7452.78	8.92	-24.69					
	Pb(II)	298	4682.72	8.45	-20.94	142.11	21.41			
		318	8018.64	8.99	-23.77					
		333	11623.92	9.36	-25.92					
	SA	Ni(II)	298	146.78	4.99			-12.36	199.00	47.29
				299.42						
			318		5.70			-15.07		
333		1168.33	7.06	-19.56	118.28	17.76				
Cd(II)		298	1146.58	7.04			-17.45			
			1899.73							
		318		7.55	-19.96					
Pb(II)		333	2416.82	7.79	-21.57	233.32	50.55			
		298	2320.64	7.75	-19.20					
		6133.12								
	318		8.72	-23.06						
	333	20699.28	9.94	-27.51						



Scheme 1. S: shell of hazelnut or almond.

The degree of adsorption increases with increased temperature, indicating that the adsorption is endothermic. The free energy of adsorption (ΔG^0) can be related with the equilibrium constant K (L mol^{-1}) corresponding to the reciprocal of the Langmuir constant, b , by the following Eq. (7). The values of enthalpy change (ΔH^0), and entropy change (ΔS^0), for the adsorption process were calculated, using Eq. (8) [14,25–28]:

$$\Delta G^0 = -RT \ln b \quad (7)$$

$$\ln b = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \quad (8)$$

Thus, a plot of $\ln b$ versus $1/T$ should be a straight line. ΔH^0 and ΔS^0 values were obtained from the slope and intercept of this plot, respectively [25].

Table 5 presents 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 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 the energy lost by the adsorbate ions, thus allowing the prevalence of randomness in the system. The enhancement of adsorption at higher temperatures may be attributed to the enlargement of pore size and/or activation of the adsorbent surface [2].

3.6. 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 others, a series of experiments has been designed to study the effect of the presence of a combination of several metals on the ability of adsorbent to adsorb one specific metal. Shell of hazelnut and almond can effectively bind a number of heavy metal ions but it would be doubtful that all ions have been equally bound. Furthermore, considering the shell as a complex material with many possible binding sites, the main question is to know whether different ions could be bound in the same site [18]. Table 6 shows the percentage of sorption each ion in the presence of other. The general binding affinity of the barks for the metals studied, in order decreasing affinity is: $\text{Pb(II)} > \text{Cd(II)} > \text{Ni(II)}$.

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 [21]. The difference in the adsorption behaviour of Pb(II) and Cd(II)

Table 6
Competition among metal ions (% A)

Adsorbent	Ni(II)	Cd(II)	Pb(II)
SH	26.14	39.80	–
	35.99	–	76.71
	–	39.54	67.89
	23.92	39.44	60.63
SA	11.10	16.16	–
	5.00	–	35.74
	–	16.93	46.27
	12.60	34.64	54.76

compared Ni(II) may also be explained by the different affinity of metal ions for the donor atoms present in the structure of shell. The binding capacity of individual ion depends on a number of factors such as ionic potential, ionic radius, chemical properties and hydrolysis [19].

4. Conclusion

This work demonstrates the wonderful capacity of chelating HMI and justifies the approach of using a waste for the treatment of another waste and to resolve an environmental problem so as to protect life conditions for future generations. The following conclusions can be drawn based on the investigation of HMI removal by SH and SA adsorption. First of all SH and SA appears to be a promising adsorbent for removal of HMI from wastewater. At these adsorption levels, a process using shell for the removal and recovery of a heavy metal ions is potentially more economical than current process technology.

Secondly, the adsorption of HMI depends on their initial concentrations, temperature and contact time. The kinetics of HMI on SH and SA follows the pseudo second-order model.

Thirdly, isothermal data of HMI sorption on shell can be modeled by both Langmuir and Freundlich isotherms. The capacity of shell for adsorption of certain metals can be calculated by using these models.

The data obtained from adsorption isotherms at different temperatures were used to calculate thermodynamic quantities such as ΔG^0 , ΔH^0 and ΔS^0 . The results indicate that HMI onto SH and SA is spontaneous and physical in nature. SH and SA, which is an inexpensive and easily available material, can be an alternative for more costly adsorbents used for HMI removal in waste-water treatment processes.

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