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Removal of Pb(II) from wastewater using wheat bran

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Abstract

The adsorption of Pb(II) ions from aqueous solutions on wheat bran (WB) has been investigated as a function of initial concentration, adsorbent dose, adsorbent particle size, agitation speed, temperature, contact time and pH of solution. The equilibrium process was described well by the Langmuir isotherm model with maximum sorption capacities of 69.0, 80.7 and 87.0 mg g^{-1} of Pb(II) on wheat bran at 20, 40 and 60 °C, respectively. Thermodynamic parameters, i.e. ΔG^0, ΔH^0 and ΔS^0 have also been calculated for the system and the sorption process was found to be endothermic. Good correlation coefficients were obtained for the pseudo second-order kinetic model. The metal ion could be stripped by addition of 0.5 M HCl, making the adsorbent regeneration and its reutilization possible.

Keywords: Wheat bran; Adsorbtion; Pb(II); Removal; Wastewater

1. Introduction

The presence of toxic heavy metal ions in industrial wastewaters has generated considerable concern in recent years. Heavy metal contamination exists in aqueous waste streams of many industries, such as metal plating facilities, mining operations and tanneries. The soils surrounding many military bases are also contaminated and pose a risk of metal ground water and surface water contamination. Among the toxic heavy metal ions which present potential danger to human health are copper, lead, cadmium, chromium and mercury (Bailey et al., 1999; Gloaguen and Morvan, 1997a). These heavy metals are not biodegradable and tend to accumulate in living organisms, causing various diseases and disorders. The cost of removal of heavy metals from industrial effluents and waste waters using ion exchange resins is exorbitant and many chemical methods such as chemical precipitation, electroflotation and reverse osmosis have been used for the removal of heavy metals. All these methods are generally expensive. Adsorption at a solid solution interface is an important means for controlling the extent of pollution due to metallic species of industrial effluents. Cost is an important parameter for comparing the sorbent materials (Raji and Anirudhan, 1997). Hence, the usage of indigenous biodegradable resources for treating hazardous waste would be less expensive (Prasad and Freitas, 2000; Ajmal et al., 2003). For this purpose, sun flower stalks (Sun and Shi, 1998), rice husk (Khalid et al., 1999), almond husk (Hasar, 2003), sawdust (Ajmal et al., 1998), barks (Gloaguen and Morvan, 1997a; Gaballah and Kilbertus, 1998), spent grain (Low et al., 2000), etc. have been used. Most of these materials contain functional groups associated with proteins, polysaccharides and cellulose as major constituents. Metal uptake is believed to occur through a sorption process involving the functional groups mentioned above (Hasar, 2003). The cost of these biomaterials is negligible compared with the cost of activated carbon or ion-exchange resins which are in the range of approximately \$2.0–4.0 kg^{-1} (Al-Asheh and Duvnjak, 1998).

Lead is a hazardous waste and is highly toxic to humans, plants and animals. It causes plant and animal death as well as anemia, brain damage, mental deficiency, anorexia, vomiting and malaise in humans (Gaballah and Kilbertus, 1998; Low et al., 2000). Lead is a substitute for calcium in bony tissues and accumulates there. The presence of lead in drinking water is known to cause various types of serious health problems leading to death in extreme cases (Volesky, 1993). The permissible limit of Pb is 0.01 mg L^{-1} in water

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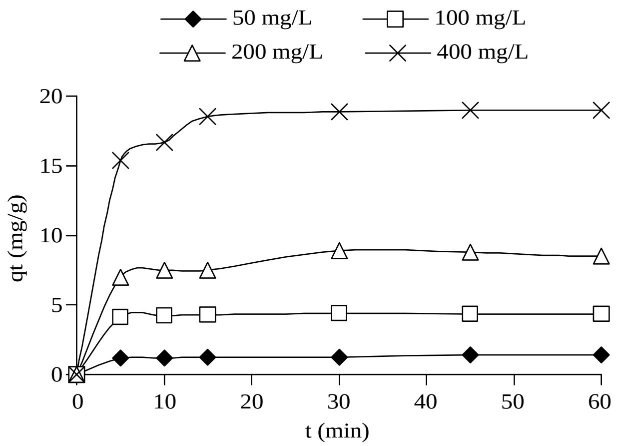

Fig. 1. The rate of adsorption of Pb(II) by wheat bran at different initial concentrations.

(Karacan and Gürkan). Various low cost adsorbents such as onion skin (Kumar and Dara, 1981), tea leaves (Orhan and Büyükgüngör, 1993) and peat moss (Ho et al., 1996) are known to adsorb Pb(II) ions from solutions in their native state and with suitable chemical treatment, the adsorption capacity can be significantly enhanced (Raji and Anirudhan, 1997).

The wheat bran of wheat is the shell of the wheat seed and is the site of the most nutrients in wheat. This bran is usually removed in the processing of wheat into flour, however, the bran is retained for 'whole wheat' types of flour. Wheat bran and other related grain products are already well known to be nutritionally beneficial foods. These foods are rich in complex carbohydrates, fiber, iron, vitamin B, and many other nutrients vital for a healthy diet. Lately, researchers have investigated wheat bran not for its nutritional aspects, but for its anti-cancer properties—specifically in preventing colon cancer (Farajzadeh and Monji, in press).

The present work deals with a series of experiments to assess the utility of wheat bran as an adsorbent for the removal of Pb(II) from aqueous solution. The effects of initial adsorbate concentration, adsorbent doses, particle size, agitation speed, temperature and pH on the removal of Pb(II) have been studied.

2. Material and methods

2.1. Adsorbent

The starting material, wheat bran, was obtained commercially by Souteastern Anatolia of Turkey and used for the preparation of adsorbent. It was washed with distilled water and then dried. The surface area of the wheat bran was determined by the nitrogen adsorption (BET method) using Quantocrome Nova 1200.

2.2. General procedure for adsorption studies

The sorption of Pb(II) on wheat bran was studied using a batch technique. The general method used for this study is described as follows. The stock solution of $Pb(NO_3)_2$ at a concentration of 1000 mg L^{-1} of Pb(II) was used in all experimental runs. A known weight of wheat bran was equilibrated with Pb(II) solutions of known concentrations in a stopped pyrex glass flask at a fixed temperature in a thermostatic shaker bath (150 rpm) for a known period of time. After equilibration, the suspension was centrifuged in a stopped tube for 5 min at 2000 rpm and the metal solution then was analyzed with an Unicam model 929 Atomic Absorption Spectrometer (AAS).

The effects of several parameters, such as initial metal concentration, sorbent doses, temperature, sorbent size, agitation speed and solution pH on the adsorption were studied. The effect of pH on metal ion removal was carried out using 0.5 g of wheat bran in a 50 mL metal ion solution. The pH of the solution was adjusted between the range 1.85 and 7.01 with 0.1 N NaOH or 0.1 N HCl (Low et al., 2000; Shubha et al., 2001). Pb(II) ions in solution precipitate as lead hydroxides over a pH of 7 (Ajmal et al., 1998). Thus, the sorption studies were not carried out at pH higher than 7.

2.3. Desorption experiments

To make the adsorption process more economical, it would be necessary to regenerate the spent adsorbent. After the attainment of equilibrium, the supernatants were carefully decanted and desorption experiments were carried out by using either distilled water or an aqueous medium of 0.5 M HCl. Experiments were performed by shaking 1 g of wheat bran with 100 ml of solution (Gloaguen and Morvan, 1997a). To regenerate, the same procedure was followed for three cycles. All the experiments were performed in duplicate and mean values are presented.

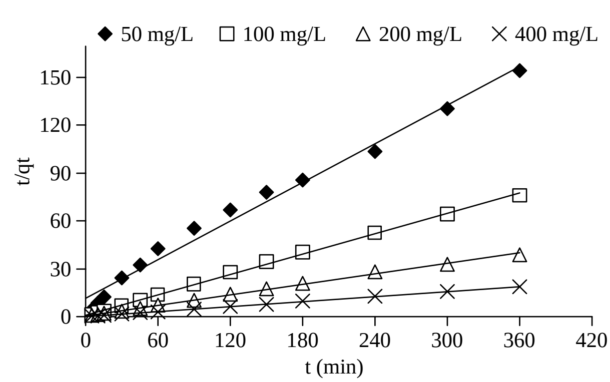

Fig. 2. Pseudo second-order sorption kinetics of Pb(II) on wheat bran at different initial concentrations.

Table 1
Effect of wheat bran concentration on the removal of Pb(II) with different initial concentrations

C_0 (mg L^{-1})	200		400		600		1000	
AD[a] (g L^{-1})	mg g^{-1}	%A	mg g^{-1}	%A	mg g^{-1}	%A	mg g^{-1}	%A
5	38.34	95.86	77.76	97.20	111.55	92.96	117.96	48.98
10	19.13	95.67	39.10	97.74	57.89	96.48	95.55	95.55
20	9.45	94.49	19.63	98.17	25.69	85.62	49.19	98.38
40	4.50	90.02	9.71	97.14	14.38	95.85	24.75	99.00
60	3.08	92.43	6.52	97.81	9.54	95.39	16.56	99.37

[a] Adsorbent dose.

3. Results and discussion

Wheat bran's surface area (particle size = 500 μm) was found to be 8.65 m^2 g^{-1} using the BET method. Although this value is low compared with other adsorbents such as activated carbon, which has a surface area of 1000–1500 m^2 g^{-1}, 500–800 m^2 g^{-1} and 700–1400 m^2 g^{-1} for gas and vapor adsorption coals, water purifying coals and color removing coals, respectively (Güzel, 1991), WB is cheaper than activated carbon, and therefore advantageous from an economical point view.

3.1. Effect of the initial sorbate concentration and contact time

There are many factors which can contribute to the sorbate 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 sorbent particles at higher concentrations. Such aggregation would lead to a decrease in the total surface area of the sorbent particles available for metal adsorption and an increase in the diffusional path length. The particle interaction brought about at high sorbent concentrations may also desorb some of the metal ions, which are loosely and reversibly bound to the sorbent surface (Katsumata et al., 2003).

The effect of the initial sorbate concentration (namely 50, 100, 200 and 400 mg L^{-1}) is shown in Fig. 1 ([WB] = 10 g L^{-1}, particle size = 1000 μm, temperature = 20 °C, agitation speed = 150 rpm, contact time = 60 min). The maximum removal of Pb(II) was attained after about 60 min of stirring time. There does not seem to be much benefit from a stirring time longer than 60 min, so stirring times above 60 min were ignored. Therefore, an equilibrium time of 60 min was selected for all further studies. With an increase in the initial concentration of metal ions from 50 to 400 mg L^{-1} the extent of removal increased from 56% (1.41 mg g^{-1}) to 95% (18.98 mg g^{-1}) for Pb(II). The kinetic rate constant was determined using these data assuming a pseudo-second order model. This can be expressed as (1);

$$t/q_t = 1/k + t/q_e \qquad (1)$$

where t is the contact time (min), q_t and q_e are the quantities of sorbate sorbed at time t and at equilibrium (mg g^{-1}), respectively, and k is the rate constant (g mg^{-1} min; Low et al., 2000; Ho and Mc Kay, 1999). Plots of t/q_t versus t for Pb(II)-wheat bran systems are shown in Fig. 2. The rate constants were determined to be 0.10, 1.15, 2.48 and 17.09 g mg^{-1} min when the initial concentrations of the systems were 50, 100, 200 and 400 mg L^{-1}, respectively.

Table 2
Effect of wheat bran particle size on the removal of Pb(II) with different initial concentrations

PS[a] (μm)	C_0 = 200 mg L^{-1}		C_0 = 500 mg L^{-1}	
	%A	mg g^{-1}	%A	mg g^{-1}
1500	93.62	46.81	78.6	98.25
1000	96.43	48.22	91.14	113.92
500	98.35	49.17	97.69	122.11

[a] Particle size.

3.2. Effect of adsorbent dose on the adsorption process

Adsorbent dosage is an important parameter because this determines the capacity of an adsorbent for a given initial concentration of the adsorbate. The effect of wheat bran dose on the adsorption of Pb(II) is presented in Table 1 (particle size = 1000 μm, temperature = 20 °C, agitation speed = 150 rpm, contact time = 60 min). The data indicate

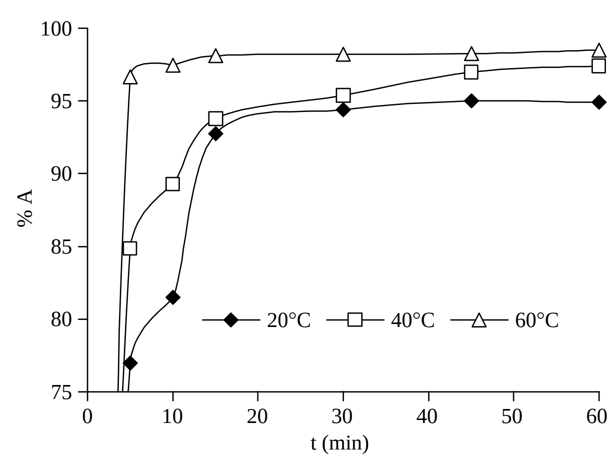

Fig. 3. Effect of temperature on the removal of Pb(II) with different initial concentrations.

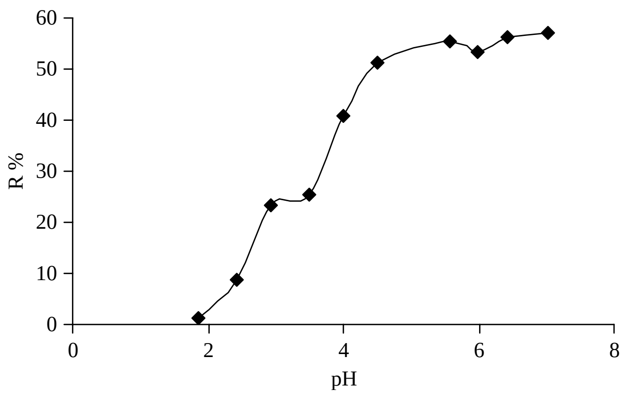

Fig. 4. Effect of pH on the removal of Pb(II) on wheat bran.

Table 3
Adsorption capacities for some adsorbents for Pb(II) (Bailey et al., 1999)

Adsorbent	Adsorption capacities (mg g^{-1})
Black oak bark	153.3
Redwood bark	6.8
Chitosan	796
Rice hulls	11.40
Zeolite	155.4
Bentonite	6
Rastunsuo	20.03
Xanthated sawdust	31.1
Chlorella minutissima	9.74
Formaldehyde-polymerized peanut skins	205

that the amount of lead ions adsorbed on WB (mg g^{-1}) decreased with increasing dose of adsorbent. This may be due to the greater availability of the exchangeable sites, or surface area, at higher concentrations of the adsorbent and the decreased amount of adsorbate per adsorbent (mg g^{-1}) with increased dose of adsorbent is basically due to adsorption sites remaining unsaturated during the adsorption reaction (Bailey et al., 1999; Yu et al., 2000). It can be observed from the Table 1 that WB prepared in different batches produced reproducible data with identical experimental conditions.

3.3. Effect of particle size

The study was also carried out using wheat bran of different particle sizes (500, 1000 and 1500 μm). It is evident from the results summarized in Table 2 ([WB] = 10 g L^{-1}, temperature = 20 °C, agitation speed = 150 rpm, contact time = 60 min) that for wheat bran milling to a particle size of 500 μm would be suitable for adsorption. The removal of Pb(II) increased with a decrease in particle size, probably because of the larger surface area available. The mechanism of Pb(II) uptake is one of adsorption onto the external sites of a non-porous adsorbent (Al-Asheh and Duvnjak, 1998).

3.4. Effect of agitation speed

The studies were carried out at 100, 150 and 200 rpm agitation([WB] = 10 g L^{-1}, particle size = 1000 μm, temperature = 20 °C, contact time = 60 min). The sorption capacity of wheat bran for Pb(II) increased with increasing agitation speed. %A (% adsorption) was found to be 93.47, 95.41 and 95.98 for 100, 150 and 200 rpm agitation, respectively. An enhanced sorption rate at higher shaking speeds is probably due to an increase in the mobility of sorbing species (Anirudhan and Raji, 1996).

3.5. Effect of temperature

The removal of Pb(II) from solution by wheat bran was measured after 60 min of agitation at different temperatures, namely 20, 40 and 60 °C. The results are shown in Fig. 3 ([WB] = 10 g L^{-1}, particle size = 1000 μm, agitation speed = 150 rpm, contact time = 60 min). The sorption capacity of wheat bran for Pb(II) increased with increasing temperature indicating that the sorption process was endothermic in nature. The increase in uptake of metal ions with temperature may be due to the desolvation of the sorbing species and change in the size of the pores (Raji and Anirudhan, 1997) and further evidence that intraparticle diffusion plays an important role in the rate-determining step in the adsorption of Pb(II) on WB is confirmed by the temperature dependence of the rate of adsorption (Al-Asheh and Duvnjak, 1998).

3.6. Effect of pH

The effect of pH on the removal of heavy metal was examined because the wastewater from the plating factory was of various pH values. Generally, it is considered that the wastewater from the plating factory is in the acidic range (Ajmal et al., 1998). Therefore, the effect on the removal of Pb(II) was investigated between the pH range of 1.85 and 7.01 (Fig. 4; [WB] = 10 g L^{-1}, particle size = 1000 μm,

Table 4
Freundlich and Langmuir constants at different temperature

T (°C)	Freundlich constants			Langmuir constants		
	$1/n$ (−)	k_f (L g^{-1})	R^2	Q_m (mg g^{-1})	b (L mg^{-1})	R^2
20	0.3993	9.21	0.8695	68.97	0.08	0.9913
40	0.4332	10.49	0.8475	80.65	0.10	0.9816
60	0.4845	10.06	0.8858	86.96	0.10	0.9698

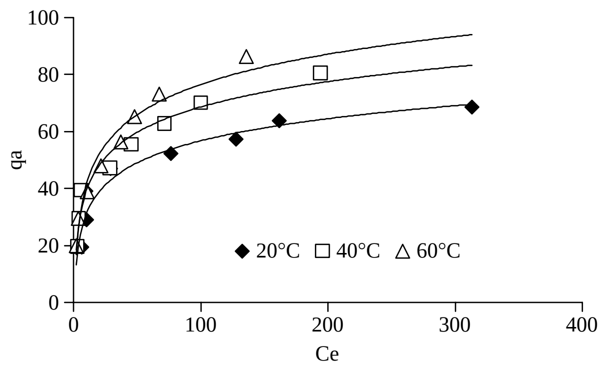

Fig. 5. Adsorption isotherms of Pb(II) on wheat bran at different temperature.

temperature = 20 °C, agitation speed = 150 rpm, contact time = 60 min). It can be observed that the Pb(II) adsorption by wheat bran increases with increasing pH. The lowest value of Pb uptake was obtained when the pH was minimum (about 2.0). This could be due to the excess hydrogen ions surrounding the binding sites making sorption unfavorable. A similar result was reported using spent grain as adsorbent (Low et al., 2000). For pH greater than 6 precipitation of Pb hydroxide occurred. All the other experiments were conducted without pH adjustment. A significant increase in the adsorption of Pb(II) ion on wheat bran was observed in a pH range from about 4 to 7.

3.7. Adsorption isotherms

The distribution of metal ions between the liquid phase and the solid phase can be described by several isotherm models such as the standard Langmuir isotherm model and the Freundlich isotherm model. The Langmuir model assumes that the uptake of metal ions occurs on a homogenous surface by monolayer adsorption without any interaction between adsorbed ions. The model can take the following linear form (2):

$$C_e/A_m = 1/b \times 1/Q_m + C_e/Q_m \quad (2)$$

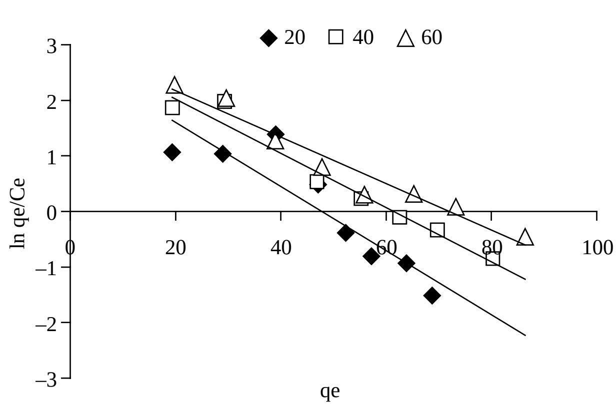

Fig. 6. Plots of $\ln(q_e/C_e)$ versus q_e for Pb(II) at different temperature using wheat bran.

Table 5
Equilibrium parameters (R_L)

C_0 (mg L^{-1})	20 °C	40 °C	60 °C
50	0.200	0.167	0.167
100	0.111	0.091	0.091
200	0.059	0.048	0.048
400	0.030	0.024	0.024
800	0.015	0.012	0.012

where C_e is the equilibrium concentration (mg mL^{-1}), A_m the amount adsorbed per amount of adsorbent (mg g^{-1}), b is the Langmuir equilibrium constant (L mg^{-1}) and Q_m is the amount of adsorbate required to form a monolayer (mg g^{-1}). The adsorption constants of the Langmuir isotherm Q_m obtained were 68.97, 80.65 and 86.96 mg g^{-1}, respectively, at 293, 313 and 333 K. The values compare favorably with some of those reported with other types of adsorbents (Table 3; Bailey et al., 1999).

The Freundlich model assumes that the uptake of metal ions occurs on a heterogeneous surface by monolayer adsorption. The model can be described by the following equations:

$$A_m = k_f C_e^{1/n} \quad (3)$$

or

$$\log(A_m) = \log(k_f) + 1/n \log(C_e) \quad (4)$$

k_f and n are Freundlich constants (Hasar, 2003).

The parameters related to fitting the Freundlich or Langmuir isotherm models to the experimental data at different temperatures are summarized in Table 4 and the adsorption isotherms in Fig. 5. The Langmuir model was found to be suitable according to the obtained results. The essential characteristics of a Langmuir isotherm can be described by a dimensionless constant separation factor or equilibrium parameter, R_L which is defined by (5) (Anirudhan and Raji, 1999);

$$R_L = 1/(1 + bC_0) \quad (5)$$

where C_0 is initial metal ion concentration (mg L^{-1}) and b is the Langmuir constant. The separation factor R_L indicates the isotherm shape as:

$R_L < 1$ unfavorable
$R_L > 1$ unfavorable
$R_L =$ linear
$0 < R_L < 1$ unfavorable
$R_L = 0$ irreversible

Table 6
Thermodynamic parameters for adsorption of Pb(II) on wheat bran

T (K)	ln K_0	ΔG^0 (kj mol^{-1})	ΔH^0 (kj mol^{-1})	ΔS^0 (j mol^{-1} K)
293	2.4366	−5.93	11.55	60.00
313	2.9994	−7.80		
333	3.0174	−8.35		

Table 7
Desorption and regeneration data

Number of cycles	HCl				Water			
	Adsorption		Desorption	Recovery	Adsorption		Desorption	Recovery
	mg g^{-1}	%	mg g^{-1}	%	mg g^{-1}	%	mg g^{-1}	%
1	46.81	93.62	12.98	27.73	46.60	93.20	1.35	27.85
2	45.75	91.49	91.49	28.37	30.31	91.49	3.11	42.82
3	44.08	90.17	90.17	29.45	25.63	51.26	3.69	50.64

The R_L at different concentrations and temperatures (Table 5) are between 0 and 1 indicating a highly favorable adsorption.

The standard free energy change, ΔG^0, ΔH^0 and ΔS^0 for the interaction of Pb(II)-wheat bran was calculated from the variations of the thermodynamic distribution coefficient, K_0 with change in temperature. K_0 for the adsorption reaction was determined by plotting $\ln q_e/C_e$ versus q_e and extrapolating to zero q_e (Fig. 6). ΔG^0 for the interaction of wheat bran with Pb(II) was calculated as (6);

$$\Delta G^0 = -RT \ln K_0 \quad (6)$$

From the variations of ΔG^0 with temperature, the standard enthalpy, ΔH^0 and entropy, ΔS^0 were computed using the following equation (Raji and Anirudhan, 1997) (7):

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \quad (7)$$

The thermodynamic parameters are given in Table 6. The positive values of ΔH^0 suggest the endothermic nature of the process. The values of $\Delta G^0 < 0$, which suggests that the process is feasible and spontaneous with a high preference of metal ions for wheat bran. The positive values of ΔS^0 show the increased randomness at the solid/solution interfaces during the adsorption of metal ions on wheat bran and also reflects the affinity of the adsorbent material for the metal ions under consideration. It is also suggested that the positive values of entrophy indicate some structural changes in the adsorbate and adsorbent (Ajmal et al., 2003).

3.8. Desorption and regeneration

To make the adsorption process more economical it is necessary to regenerate the spent adsorbent. The desorption and regeneration data for wheat bran and Pb(II) are summarized in Table 7. In the first cycle, only 1. 35 mg g^{-1} desorption took place in distilled water whereas 12.98 mg g^{-1} desorption was observed in 0.5 M HCl. Even if the sorption capacities decrease with increasing number of cycles, it is remarkable that the WB already used, then reactivated, preserved its ability for sorption. This capacity for reactivation could constitute a technical and/or an economical argument for the utilization of WB in waste water detoxification processes (Gloaguen and Morvan, 1997b).

4. Conclusion

The aim of this paper was to investigate the ability of WB to remove Pb ions from aqueous solutions. Under batch conditions equilibrium was attained within 60 min. It was found that the adsorption performance of WB is affected by initial metal concentration, sorbent dose, temperature, sorbent size, agitation speed and solution pH. Biosorption efficiencies increased with increasing contact time, temperature and agitation speed and decreased with increasing sorbent size. The equilibrium data were described satisfactorily by the Langmuir and Freundlich isotherm models and the capacity of WB for adsorption of Pb(II) can be calculated using these models. Adsorption of Pb(II) onto WB is an endothermic and spontaneous process.

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