

Heavy metal adsorption by modified oak sawdust: Thermodynamics and kinetics

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Abstract

This paper describes the adsorption of heavy metal ions from aqueous solutions by oak (*Quercus coccifera*) sawdust modified by means of HCl treatment. Our study tested the removal of three heavy metals: Cu, Ni, and Cr. The optimum shaking speed, adsorbent mass, contact time, and pH were determined, and adsorption isotherms were obtained using concentrations of the metal ions ranging from 0.1 to 100 mg L⁻¹. The adsorption process follows pseudo-second-order reaction kinetics, as well as Langmuir and D–R adsorption isotherms. The paper discusses the thermodynamic parameters of the adsorption (the Gibbs free energy, entropy, and enthalpy). Our results demonstrate that the adsorption process was spontaneous and endothermic under natural conditions. The maximum removal efficiencies were 93% for Cu(II) at pH 4, 82% for Ni(II) at pH 8, and 84% for Cr(VI) at pH 3.

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1. Introduction

Heavy metal pollution occurs in many industrial wastewaters such as those produced by metal plating facilities, mining operations, battery manufacturing processes, the production of paints and pigments, and the glass production industry. This wastewater commonly includes Cu, Ni, Cr, Cd, and Pb. These heavy metals are not biodegradable and their presence in streams and lakes leads to bioaccumulation in living organisms, causing health problems in animals, plants, and human beings. Excessive human intake of Cu leads to severe mucosal irritation and corrosion, widespread capillary damage, hepatic and renal damage, and central nervous system irritation followed by depression [1]. Severe gastrointestinal irritation and possible necrotic changes in the liver and kidney can also occur. The effects of Ni exposure vary from skin irritation to damage to the lungs, nervous system, and mucous membranes [2]. Hexavalent chromium (Cr(VI)) is known to be a strong oxidant and to be highly toxic [3]. Some heavy metals are also known carcinogens. Therefore, the removal of excess heavy metal ions from wastewater is essen-

tial to protect human and environmental health. As a result, the removal of toxic heavy metal ions from sewage and from industrial and mining effluents has been widely studied in recent years.

The most widely used methods for removing heavy metals are chemical or electrochemical precipitation, both of which pose a significant problem in terms of disposal of the precipitated wastes [4,5], and ion-exchange treatments, which do not appear to be economical [6]. It has been reported that some aquatic plants [7,8], wood materials [9–11], agricultural by-products [12], clay [13], natural zeolite [14], turba (partially decomposed vegetable matter) [15,16], microorganisms [17–19], and other low-cost adsorbents [20] have the capacity to adsorb and accumulate heavy metals. Adsorption capacities ranged from 1.79 to 146 mg g⁻¹ for Cu(II), from 7.54 to 138 mg g⁻¹ for Ni(II), and from 33.44 to 47.4 mg g⁻¹ for Cr(VI) (Table 1). Although the use of aquatic plants, microorganisms, and wood-based materials such as sawdust and bark increases the COD of water, acid-modification of these adsorbents decreases this problem [17]. However, problems with the aforementioned solutions make it necessary to develop easily available, inexpensive, and equally effective alternatives for wastewater treatment.

Sawdust is one possible material because it is produced in large quantities at sawmills as a solid waste. Sawdust contains primarily lignin and cellulose. Interest in the use of sawdust

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Table 1
Heavy metal removal capacities (mg g^{-1}) for various methods, and cost comparisons

Material	Sources	Cu(II)	Ni(II)	Cr(VI)	Pb(II)	Zn(II)	Cd(II)	Capacity per unit cost ($\text{mg US}\$^{-1}$) ^a
Chemical precipitation (NaOH)	[5]	9.5	9.6		8.0	7.9	6.2	99, 100, 85, 83, 65
Ion-exchange resin (Dowex50 W)	[6]	146	138	–	425	154	270	608, 575, 1770, 640, 1124
<i>Ceratophyllum demersum</i>	[7]	6.2		–	44.8	14.0	–	NA
Modified pine bark	[10]	–	20.58	–	–	–	–	NA
Natural zeolite	[14]	8.9	–	–	–	8.5	–	NA
<i>Rhizopus nigricans</i>	[17]	–	–	46.18	–	–	–	NA
<i>Thuja orientalis</i>	[18]	19.23	–	–	–	–	–	NA
<i>Mucor hiemalis</i>	[19]	–	–	47.4	–	–	–	NA
Wool	[20]	–	–	41.15	–	–	–	NA
Olive cake	[20]	–	–	33.44	–	–	–	NA
Activated carbon (Sigma C-3014)	[32]	2.23	–	–	–	1.23	1.51	15, 9, 10
Maple sawdust	[33]	1.79	–	–	3.19	–	–	NA
Sphagnum moss peat	[34]	12.4	7.54	–	12.3	–	–	NA
Modified oak sawdust	Present study	3.22	3.29	1.70	–	–	–	2450, 2500, 1294

NA: not available.

^a Order of costs matches the order of the ions, from left to right.

as an adsorbent has been stimulated by the good results that have been obtained [9]. In this context, oak (*Quercus coccifera*) sawdust is particularly interesting in Turkey because of its high availability and low-cost; oak sawdust costs approximately US\$ 0.07–\$0.10 kg^{-1} (Demir Corporation sawmill in Turkey), versus \sim US\$ 96 kg^{-1} for NaOH (a chemical precipitation agent; EMD Chemicals Pellets (ACS) 500 g; US\$ 48.47), US\$ 390 kg^{-1} for ion-exchange resins (Dowex(r) 50WX8-100 ion-exchange resin 500 g; US\$ 195.30), and \sim US\$ 145 kg^{-1} for activated carbon (charcoal, activated coconut, EMD Chemicals 500 g; US\$ 77.40) [21]. In addition, it is a renewable resource, and does not need to be regenerated after it has been used to capture the metals.

However, treatment with unmodified oak sawdust is also likely to create a high COD in the wastewater. Thus, our goal in the present study was to determine whether acid-modified oak sawdust would have an acceptable adsorption efficiency for removing Cu(II), Ni(II), and Cr(VI) and would thus offer an effective and economical alternative to more expensive treatments.

2. Materials and methods

2.1. Adsorbents and reagents

Acid-modified oak (*Quercus coccifera*) sawdust treated with HCl was used in this study. The adsorbents were obtained from the Demir Corporation sawmill in Turkey's Konya city. Structural analyses of this material were performed using the Van Soest method [22] (Table 2). The proportions of lignin increased and cellulosic materials, hemicellulosic materials, and extractives decreased during the modification process. This change is beneficial because previous research [23] has demonstrated that heavy metals are adsorbed by lignin rather than by cellulose and hemicellulose. All the chemical compounds used to prepare the reagent solutions were of analytic grade (Merck, Whitehouse Station, NJ). The stock solutions of the three metals used in this study (1000 mg L^{-1}) were prepared by dissolving weighed quantities of NiCl_2 , CuCl_2 , and $\text{K}_2\text{Cr}_2\text{O}_7$ salts in twice-distilled

water. Concentrations of the metal solutions ranged from 0.1 to 100 mg L^{-1} . Before mixing these solutions with the adsorbent, we created test solutions with pH values ranging from 2 to 9 (to permit a determination of the optimal pH for adsorption) by adding 0.1 M NaOH or 0.1 M HNO_3 . After we selected the optimal pH, we only tested one pH value in all subsequent adsorption tests.

2.2. Instruments

A thermal stirrer (ZHWHY-200B, ZHICHENG Analytical Co., Ltd) was used for the batch adsorption experiments. The metal solutions were filtered through 0.45- μm membrane filters (Millipore Corp., Bedford, Mass.) after settling. The filtrates were then analyzed using an inductively coupled plasma spectrometer (Optima 4300DV ICP, Perkin-Elmer, Boston, MA). The pH measurements were performed using a digital ion analyzer with a combination electrode (Multi 340i, WTW, Weilheim, Germany).

2.3. Preparation and modification of adsorbents

The adsorbent used in this study was oak sawdust with a range of particle sizes. In accordance with ASTM Method D4749 [24,25]. We sieved the sawdust through a range of sieves, and used only the particles that passed through a 0.25-mm mesh in our study. The sieves were shaken for approximately 15 min, then the separated particles were stored. After sieving, the adsorbents were heated in an oven at 80–85 $^\circ\text{C}$ for 2 h.

Table 2

Structural analyses of the oak sawdust samples (wt.% daf)^a and COD created by sawdust before and after acid-modification

Adsorbent	Hemicellulose (%)	Cellulose (%)	Lignin (%)	Extractives ^b (%)	COD ($\text{mg O}_2 \text{L}^{-1}$)
Before	32.7	41.5	22.8	3.0	1800
After	32.5	38.2	26.8	2.5	90

^a daf: dry and ash free.

^b Alcohol–benzene extractives.

Table 3
Experimental conditions

	Metal ions	S (rpm)	Ms (g L ⁻¹)	t (h)	pH	C ₀ (mg L ⁻¹)
Effect of shaking speed, S (rpm)	Cu(II)	100–450	20	2	6	92
	Ni(II)	100–450	20	2	6	97
	Cr(VI)	100–450	20	2	4	79
Effect of adsorbent mass, Ms (g)	Cu(II)	250	5–80	2	6	92
	Ni(II)	250	5–80	2	6	97
	Cr(VI)	250	5–80	2	4	79
Effect of contact time, t (h)	Cu(II)	250	40	0–12	6	92
	Ni(II)	250	30	0–12	6	97
	Cr(VI)	250	60	0–12	4	79
Effect of pH	Cu(II)	250	40	4	2–9	92
	Ni(II)	250	30	8	2–9	97
	Cr(VI)	250	60	8	2–9	79
Effect of metal concentration, C ₀ (mg L ⁻¹)	Cu(II)	250	40	4	4	0.1–100
	Ni(II)	250	30	8	8	0.1–100
	Cr(VI)	250	60	8	3	0.1–100

For the modification process, HCl was used to increase the proportion of active surfaces and to prevent the elution of tannin compounds that would stain the treated water and that greatly increase COD. First, 0.5, 1.0, 2.0, 3.0, and 5.0 mol L⁻¹ HCl solutions were prepared. An accurately weighed (± 0.001 g) 25-g sample of oven-dried sawdust was washed several times with distilled water to remove any particles adhering to the surface and any water-soluble particles, then was oven-dried again at 85 °C. Following this operation, individual sawdust samples were poured into 500-mL conical flasks containing 250 mL of HCl solution, then were shaken at 200 rpm for 4 h at 298 K. The mixture was left overnight, then was filtered to remove the sorbent, which was washed several times with distilled water to provide neutral pH. The adsorbents were then oven-dried at 85 °C for 2 h. The maximum removal efficiency by this material (i.e., the sample that showed the greatest weight increase as a result of adsorption of the metals) was used to select the acid concentration that would be used in subsequent modification of the sawdust.

2.4. General procedures

We studied the effects of shaking speed, adsorbent mass, contact time, pH, and initial metal ion concentration on adsorption of each metal using the experimental conditions shown in Table 3. The sorption experiments were performed in a batch reactor using stoppered Pyrex glass flasks. The metal concentrations in the solutions were determined at the beginning (C_0) and end (C_e) of the shaking period. Eq. (1) was used to compute the percentage sorption of the metal:

$$\text{sorption (\%)} = \frac{C_0 - C_e}{C_0} \times 100 \quad (1)$$

Each experiment was replicated three times, and the mean values were used in our analyses. If the standard error (S.E.) were greater than 0.01, the test was repeated to control for errors. The deviation of the metal uptake per unit weight of sawdust (Δq_e)

was calculated as follows:

$$\Delta q_e (\%) = \frac{\sum_{i=1}^N |(q_{ei})_{cal} - (q_{ei})_{exp}| / (q_{ei})_{exp}}{N} \times 100 \quad (2)$$

where the subscripts “exp” and “cal” show the experimental and calculated values of q_e and N is the number of measurements.

3. Results and discussion

3.1. Effect of shaking speed

Because shaking consumes energy and affects the adsorption efficiency, it is important to determine the optimal speed that should be used in wastewater treatment. The maximum removal efficiencies were obtained at 250 rpm: 87, 82, and 80% for Cu(II), Ni(II), and Cr(VI), respectively (Fig. 1). Fig. 1 indicates that the adsorption values for the Cu, Ni, and Cr ions were lowest at 100 rpm and increased as the shaking speed increased to 250 rpm, then declined slightly as speed increased to 450 rpm. This effect can probably be attributed to the decrease in boundary layer thickness around the adsorbent particles that results from

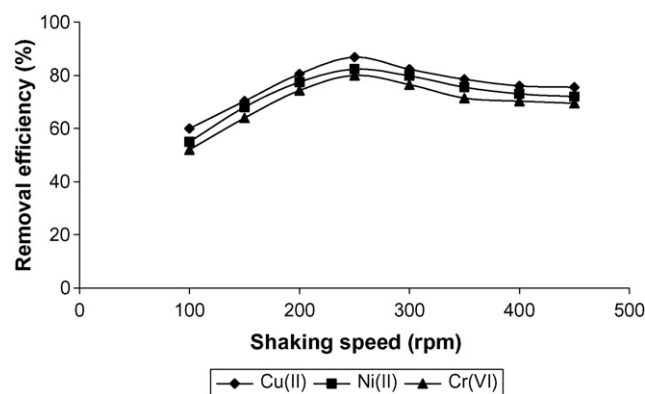


Fig. 1. Effect of shaking speed on the metal-removal efficiencies of modified sawdust.

Table 4
Changes in the values of the diffusion coefficients (k_s and k_d) as a function of shaking speed

Shaking speed (rpm)	External diffusion coefficient	Intraparticle diffusion coefficients ($\text{mg g}^{-1} \text{min}^{-0.5}$)		
	$k_s (\times 10^{-4} \text{ m min}^{-1})$	k_{d1}	k_{d2}	k_{d3}
Cu(II)				
150	3.42	0.1100	-0.0100	-
250	4.00	0.1220	-0.0140	-
350	3.85	0.1200	-0.0120	-
450	3.65	0.1150	-0.0110	-
Ni(II)				
150	4.00	0.2000	0.0275	-0.0278
250	5.00	0.2290	0.0282	-0.0286
350	4.75	0.2200	0.0280	-0.0283
450	4.52	0.2150	0.0277	-0.0280
Cr(VI)				
150	2.23	0.0265	-0.0123	-
250	3.00	0.0278	-0.0134	-
350	2.88	0.0275	-0.0130	-
450	2.65	0.0273	-0.0127	-

increasing the degree of mixing. When the mixture was shaken, the solid particles moved around rapidly in the solution, and this increased the concentration of heavy metals near the surface of the solid particles, possibly to a level near that of the bulk concentration. Because heavy metal diffusion to the boundary layer between adsorbent particles and the surrounding solution would increase with increased shaking, the external mass transfer speed of the metals would increase and equilibrium would be reached more rapidly. However, when the shaking speed rose above 250 rpm, diffusion speeds decreased. This may occur because the high shaking speed provided sufficient additional energy to break newly formed bonds between the metal ions and the adsorbent surface. Table 4 shows that shaking speed also significantly affected the coefficients of diffusion of metal ions.

3.2. Effect of mass of adsorbent

Fig. 2 shows that adsorption increased gradually with increasing adsorbent mass, to a maximum at 40 g L^{-1} for Cu(II), 30 g L^{-1} for Ni(II), and 60 g L^{-1} for Cr(VI). After this maxi-

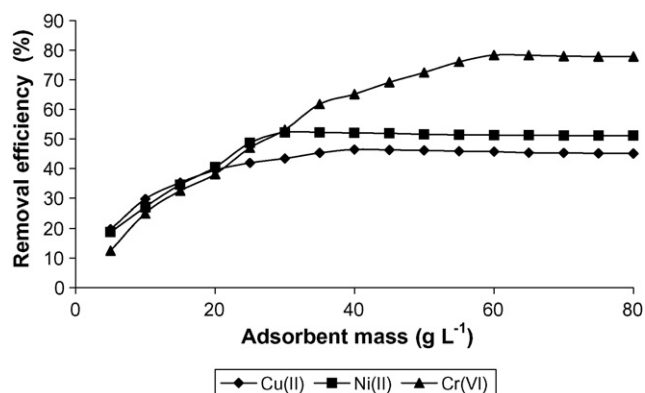


Fig. 2. Effect of the mass of adsorbent on the metal-removal efficiencies of modified sawdust (shaking speed, 250 rpm; temperature, 293 K).

imum equilibrium value, the removal efficiency did not increase with increasing adsorbent mass. These results suggest that the relationship between adsorbent dosage and removal efficiency was related to increases in the number of adsorption sites, and that increasing this number had no effect after equilibrium was reached.

3.3. Effect of contact time

For a fixed concentration of heavy metals and a fixed adsorbent mass, the retention of heavy metals increased with increasing contact time. Fig. 3 shows that the adsorption rate initially increased rapidly, and that the optimal removal efficiencies were reached within about 2 h: 56, 78, and 72% for Cu(II), Ni(II), and Cr(VI), respectively. However, the equilibrium (maximum) value was attained at around 4 h for Cu(II) and 8 h for Ni(II) and Cr(VI), with adsorption rates of 62, 88, and 81%, respectively. In addition, the removal efficiencies decreased by about 4–10% with increasing contact time after equilibrium had been reached. This probably resulted from saturation of adsorbent surfaces with heavy metals followed by adsorption and desorption processes that occur after saturation.

3.4. Effect of pH

The effect of pH on the adsorption of Cu(II), Ni(II), and Cr(VI) by the modified sawdust is presented in Fig. 4. The pH of the aqueous solution was clearly an important parameter that controlled the adsorption process. Maximum removal efficiency reached 93% for Cu(II) at pH 4, 82% for Ni(II) at pH 8, and 84% for Cr(VI) at pH 3. At pH lower than 8, the dominant forms of Cu and Ni were Cu(II) and Ni(II); Cu(OH)₂ and Ni(OH)₂ were present as precipitates at pH greater than 8. Based on these results, the divalent Cu and Ni were bound to active surfaces on the adsorbent by O²⁻ ions and released H⁺ into the solution, thereby decreasing the pH [23]:



where Ar is a functional group of the modified sawdust, such as the carboxylic groups of polysaccharides, the phenolic groups of

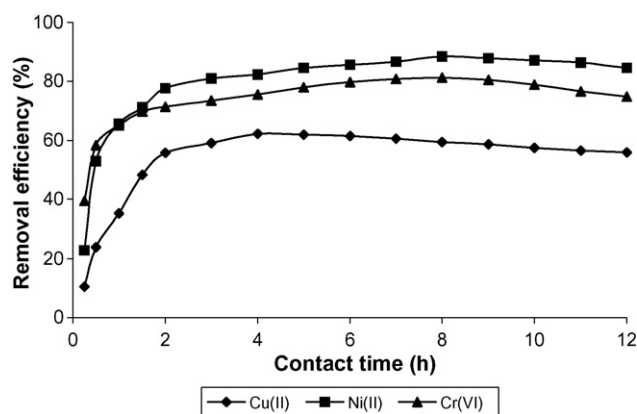


Fig. 3. Effect of contact time on the removal of heavy metals. The dosage of modified sawdust: 40 g L^{-1} for Cu(II), 30 g L^{-1} for Ni(II), and 60 g L^{-1} for Cr(VI); the shaking speed was 250 rpm and the temperature was 293 K.

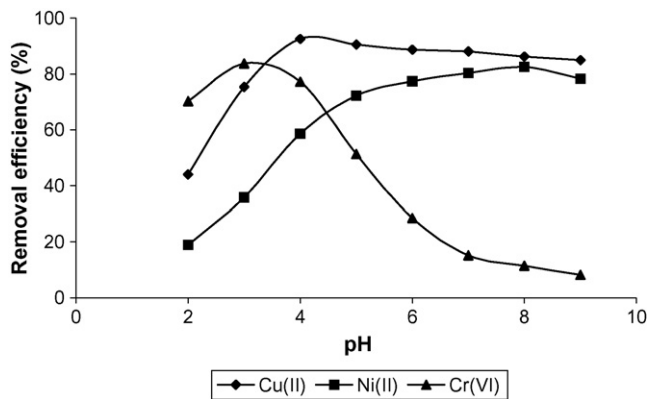


Fig. 4. Effect of pH on the Cu(II), Ni(II), and Cr(VI) removal percent by modified sawdust (dosage of modified sawdust: 40 g L⁻¹ for Cu(II), 30 g L⁻¹ for Ni(II) and 60 g L⁻¹ for Cr(VI); shaking speed: 250 rpm and temperature: 293 K).

lignin, and hemicellulosic material, and M represents metal ions. Adsorption of hexavalent Cr(VI) varies as a function of pH, with H₂CrO₄, HCrO₄⁻, Cr₂O₇²⁻, and CrO₄²⁻ ions present as dominant species [23]. At pH 3, HCrO₄⁻ was the dominant species. The surface charge of modified sawdust should be positive at low pH, and this should promote the binding of the negatively charged HCrO₄⁻ ions. The HCrO₄⁻ species are most easily exchanged with OH⁻ ions at active surfaces under acidic conditions:



3.5. Determination of adsorption isotherms

Equilibrium adsorption isotherms (capacity studies) are of fundamental importance in the design of adsorption systems since they indicate how metal ions are partitioned between the adsorbent and liquid phases at equilibrium as a function of metal concentration. When an adsorbent comes into contact with a metal ion solution, the concentration of metal ions on the surface of the adsorbent will increase until a dynamic equilibrium is reached; at this point, there is a clearly defined distribution of metal ions between the solid and liquid phases. Heavy metal ion concentrations ranged from 0.1 to 100 mg L⁻¹ with a fixed adsorbent mass and pH for each heavy metal. As metal concentrations increased, the removal efficiencies decreased from 98% to 80% for Cu(II), 98% to 66% for Ni(II), and 97% to 66% for Cr(VI). Thus, increasing the initial heavy metal concentrations in the solutions decreased the removal efficiency. It is likely that a given mass of adsorbent material has a finite number of adsorption sites, and that as metal concentrations increase, these sites become saturated. That is, there is some metal concentration that produces the maximum adsorption for a given adsorbent mass, and thereafter, adding more metal cannot increase adsorption because no more sites are available: all are occupied. Another cause may have been a progressive decrease in the proportion of covalent interactions and an increase in the proportion of electrostatic interactions at sites with a lower affinity for heavy metals as the initial heavy metal concentrations increased. The heavy metal adsorption

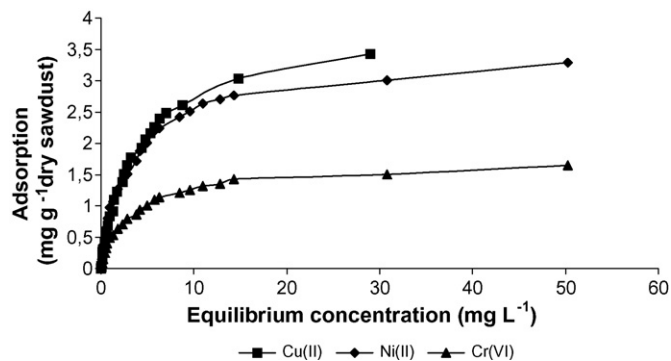


Fig. 5. Adsorption isotherms for the modified sawdust using different initial metal concentrations (heavy metal concentration range: 0.1–150 m L⁻¹, dosage of modified sawdust: 40 g L⁻¹ at pH 4 for Cu(II), 30 g L⁻¹ at pH 8 for Ni(II), and 60 g L⁻¹ at pH 3 for Cr(VI); shaking speed, 250 rpm; temperature, 293 K).

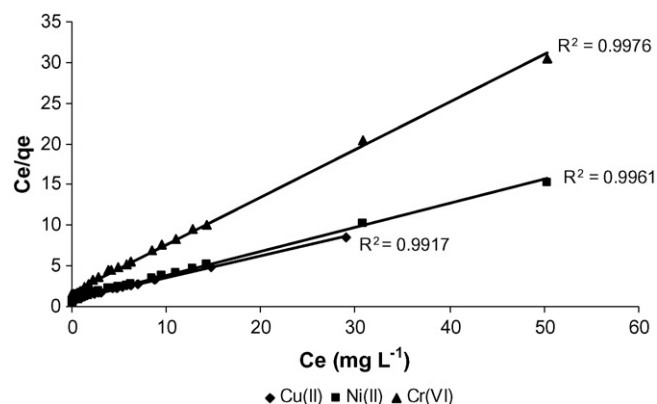


Fig. 6. Linearized Langmuir isotherms for adsorption of Cu(II), Ni(II), and Cr(VI) by modified sawdust (dosage of modified sawdust: 40 g L⁻¹ at pH 4 for Cu(II), 30 g L⁻¹ at pH 8 for Ni(II), and 60 g L⁻¹ at pH 3 for Cr(VI); shaking speed, 250 rpm; temperature, 293 K).

capacities were calculated by means of least-squares regression using Eqs. (5)–(7). The resulting adsorption isotherms for heavy metals used in this study are shown in Figs. 5–7.

The obtained data were applied to the Langmuir adsorption isotherm [26] using the following linear expression of this

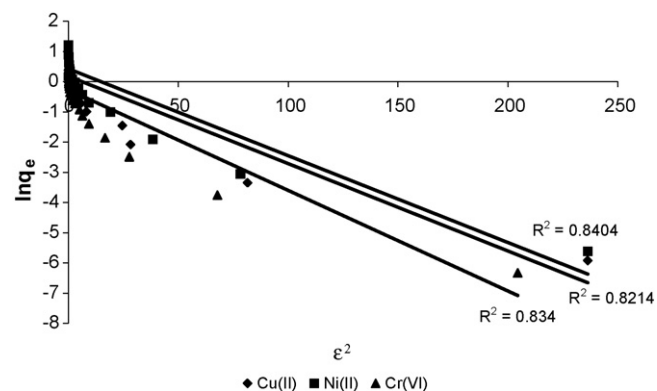


Fig. 7. Linearized D-R isotherms for adsorption of Cu(II), Ni(II), and Cr(VI) by modified sawdust (dosage of modified sawdust: 40 g L⁻¹ at pH 4 for Cu(II), 30 g L⁻¹ at pH 8 for Ni(II), and 60 g L⁻¹ at pH 3 for Cr(VI); shaking speed, 250 rpm; temperature, 293 K).

model:

$$\frac{C_e}{q_e} = (bK)^{-1} + \frac{C_e}{b} \quad (5)$$

where q_e is the metal uptake per unit weight of sawdust (mg g^{-1}) at the equilibrium metal concentration in the aqueous phase, and is expressed as $q_e = [(C_0 - C_e) \times V]/M$; V (L) is the volume of the solution; M (g) the amount of adsorbent added to the solution; C_e (mg L^{-1}) the metal concentration in the aqueous phase; and b (mg g^{-1}) and K (L mg^{-1}) are the Langmuir constants related to the sorption capacity and energy of adsorption, respectively. The Langmuir isotherm assumes a homogeneous surface and a constant sorption potential.

The Dubinin–Radushkevich (D–R) isotherm [27], which assumes a heterogeneous surface, is expressed as follows:

$$q_e = X'_m \exp(-K' \varepsilon^2) \quad (6)$$

where ε (the Polanyi potential) = $RT \ln(1 + 1/C_e)$, q_e is the amount of metal ions adsorbed per unit weight of modified sawdust (mg g^{-1}), X'_m the adsorption capacity of the sorbent (mg g^{-1}), C_e the equilibrium concentration of metal ions in solution (mg L^{-1}), K' is a constant related to the adsorption energy ($\text{mol}^2 \text{kJ}^{-2}$), R the gas constant ($\text{kJ K}^{-1} \text{mol}^{-1}$), and T is the temperature (K).

The D–R isotherm can be expressed in linear form as follows:

$$\ln q_e = \ln X'_m - K' \varepsilon^2 \quad (7)$$

The regression parameters and correlation coefficients (R^2) presented in Table 5, Figs. 6 and 7 indicate that the adsorption data best fitted the Langmuir adsorption isotherm for all three metals. However, under industrial conditions, mixing of the adsorbent and the wastewater solution would be imperfect, thus the adsorbent surface is less likely to be homogeneous and the assumptions required by the Langmuir isotherm would be less likely to be correct. The good fit of the Dubinin–Radushkevich (D–R) isotherm (all R^2 values >0.82) suggest that these isotherms could be more appropriate under industrial conditions. At 293 K, the values of the adsorption capacity (b) in the Langmuir isotherm were 3.22, 3.29, 1.70 mg g^{-1} for Cu(II), Ni(II), and Cr(VI), respectively, and the corresponding values of adsorption capacity (X'_m) in the D–R isotherm were 1.31, 1.54, 1.21 mg g^{-1} . Table 5 also shows that

the adsorption capacities increased with increasing temperature for both isotherms. This change occurs because of increasing kinetic energy of the sorbent particles, which increases the frequency of collisions between the adsorbent and metal ions and thus enhances adsorption of metals on the surface of the sorbent.

A comparison of the sorbent capacity of modified sawdust with that of other available adsorbents is summarized in Table 1. Although modified oak sawdust has a lower adsorption capacity per unit mass, its lower cost and greater availability mean that it provides a comparable adsorption capacity per unit cost. The mean adsorption energy (E , kJ mol^{-1}) can be obtained from the K' values of the D–R isotherms [27] using the following equation:

$$E = (-2K')^{-1/2} \quad (8)$$

The Langmuir isotherm constants do not explain the chemical or physical properties of the adsorption process. However, the mean adsorption energy (E) calculated from the D–R isotherm provides important information about these properties [27]. For $E < 8 \text{ kJ mol}^{-1}$, physisorption dominates the sorption mechanism. If E is between 8 and 16 kJ mol^{-1} , ion-exchange is the dominant factor. If $E > 16 \text{ kJ mol}^{-1}$, sorption is dominated by particle diffusion. The adsorption energies were 3.87, 4.43, and 4.26 kJ mol^{-1} for Cu(II), Ni(II), and Cr(VI), respectively, at a temperature of 293 K (Table 5), suggesting that the sorption process was dominated by physical forces at all studied temperatures and that these forces were more important than ion-exchange and particle diffusion.

3.6. Adsorption thermodynamics

The changes in Gibbs free energy (ΔG), enthalpy (ΔH), and entropy (ΔS) for the adsorption process were obtained using the following equations [28]:

$$\Delta G = -RT \ln b \quad (9)$$

$$\ln b = (\Delta S/R) - (\Delta H/RT) \quad (10)$$

where R is the ideal gas constant ($\text{kJ mol}^{-1} \text{K}^{-1}$) and T is the temperature (K). The enthalpy change (ΔH) and the entropy change (ΔS) are calculated from a plot of $\ln b$ (from the Langmuir isotherm) versus $1/T$ (Fig. 8). The results of these thermodynamic calculations are shown in Table 6. The negative value for

Table 5

Regression parameters for the Langmuir and D–R adsorption isotherms for solutions of Cu(II), Ni(II), and Cr(VI) at different temperatures

Heavy metals	T (K)	Langmuir isotherm			D–R isotherm			
		b (mg g^{-1})	K (L mg^{-1})	R^2	X'_m (mg g^{-1})	K' ($\text{mol}^2 \text{kJ}^{-2}$)	E (kJ mol^{-1})	R^2
Cu(II)	293	3.22	1.01	0.99	1.31	0.03	3.87	0.83
	303	3.38	1.34	0.99	1.40	0.03	3.84	0.79
	313	3.60	1.79	0.98	1.47	0.04	3.60	0.77
Ni(II)	293	3.29	0.21	0.99	1.54	0.03	4.43	0.84
	303	3.34	0.28	0.99	1.47	0.03	4.13	0.82
	313	3.37	0.36	0.99	1.41	0.03	3.99	0.80
Cr(VI)	293	1.70	0.30	0.99	1.21	0.03	4.26	0.82
	303	1.72	0.37	0.99	1.13	0.03	4.06	0.79
	313	1.74	0.26	0.92	1.07	0.03	4.08	0.73

Table 6
Thermodynamic constants for the adsorption of Cu(II), Ni(II), and Cr(VI) on the modified sawdust at various temperatures

Heavy metals	T (K)	$\ln b$	ΔG (kJ mol ⁻¹)	ΔH (kJ mol ⁻¹)	ΔS (kJ mol ⁻¹ K ⁻¹)	R (kJ mol ⁻¹ K ⁻¹)
Cu(II)	293	1.168	-2.840	4.331	0.024	8.3×10^{-3}
	303	1.218	-3.064			
	313	1.282	-3.330			
Ni(II)	293	1.192	-2.898	0.876	0.013	8.3×10^{-3}
	303	1.205	-3.030			
	313	1.215	-3.156			
Cr(VI)	293	0.533	-1.295	0.908	0.008	8.3×10^{-3}
	303	0.540	-1.359			
	313	0.557	-1.446			

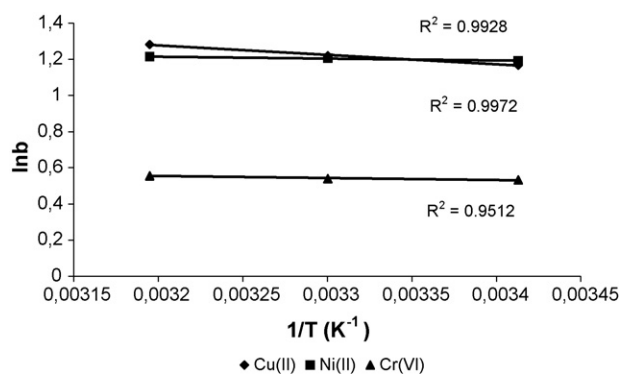


Fig. 8. Plot of the Langmuir isotherm constant ($\ln b$) vs. temperature ($1/T$). The thermodynamic parameters in Table 6 are determined from this graph.

the Gibbs free energy for all three metals shows that the adsorption process is spontaneous and that the degree of spontaneity of the reaction increases with increasing temperature. The overall adsorption process seems to be endothermic ($\Delta H = 4.33$, 0.88 , and 0.91 kJ mol⁻¹ for Cu, Ni, and Cr, respectively). This result also supports the suggestion that the adsorption capacity of modified sawdust for all metals increases with increasing temperature. Table 6 also shows that the ΔS values were positive (i.e., that entropy increases as a result of adsorption). This occurs as a result of redistribution of energy between the adsorbate and the adsorbent. Before adsorption occurs, the heavy metal ions near the surface of the adsorbent will be more ordered than in the subsequent adsorbed state and the ratio of free heavy metal ions to ions interacting with the adsorbent will be higher than in the adsorbed state. As a result, the distribution of rotational and translational energy among a small number of molecules will increase with increasing adsorption by producing a positive value of ΔS and randomness will increase at the solid–solution interface during the process of adsorption. Adsorption is thus

likely to occur spontaneously at normal and high temperatures because $\Delta H > 0$ and $\Delta S > 0$.

3.7. Adsorption kinetics

In order to define the adsorption kinetics of heavy metal ions, the kinetic parameters for the adsorption process were studied for contact times ranging between 1 and 720 min by monitoring the percent removal of the heavy metals by the adsorbent. The data were then regressed against the Lagergren equation, which represents a first-order kinetic equation, Eq. (11); [29] and against a pseudo-second-order kinetic equation Eq. (12); [16]:

$$\log(q_e - q_t) = (\log q_e) - k_1 t \quad (11)$$

$$(t/q_t) = (1/[k_2 q_e^2]) + (1/q_e)t \quad (12)$$

where q_t is the metal uptake per unit weight of sawdust (mg g⁻¹) at time t , q_e is the metal uptake per unit weight of sawdust (mg g⁻¹) at equilibrium, and k_1 (min⁻¹) and k_2 (g mg⁻¹ min⁻¹) are the rate constants of the first-order and pseudo-second-order kinetics equations, respectively. The slopes and intercepts of these curves were used to determine the values of k_1 and k_2 , as well as the equilibrium capacity (q_e). The calculated (cal) value of q_e (Table 7) from the first-order kinetics model was dramatically lower than the experimental (exp) value. However, the linearized pseudo-second-order kinetics model (Fig. 9 and Table 7), provided much better R^2 values (all values greater than or equal to 0.99) than those for the first-order model (0.37, 0.64, and 0.49), even though the calculated values did not closely approximate the measured experimental values. As a result, the sorption system appears to follow pseudo-second-order reaction kinetics. The first- and pseudo-second-order kinetics rate constants for the adsorption of Cu(II), Ni(II), and Cr(VI) ions on modified saw-

Table 7
Kinetics parameters for the adsorption of Cu(II), Ni(II), and Cr(VI) on the modified sawdust at 293 K

Heavy metal ions	First-order					Pseudo-second-order			
	$q_{e,exp}$ (mg g ⁻¹)	$q_{e,cal}$ (mg g ⁻¹)	k_1 ($\times 10^{-4}$ min ⁻¹)	Δq_e (%)	R^2	$q_{e,cal}$ (mg g ⁻¹)	k_2 (g mg ⁻¹ min ⁻¹)	Δq_e (%)	R^2
Cu(II)	3.22	2.29	2.0	28.67	0.373	1.391	0.031	56.81	0.989
Ni(II)	3.29	1.23	8.0	62.75	0.637	2.915	0.919	11.38	0.998
Cr(VI)	1.70	0.86	2.0	49.26	0.488	1.045	0.115	38.50	0.997

exp: experimental result; cal: calculated result.

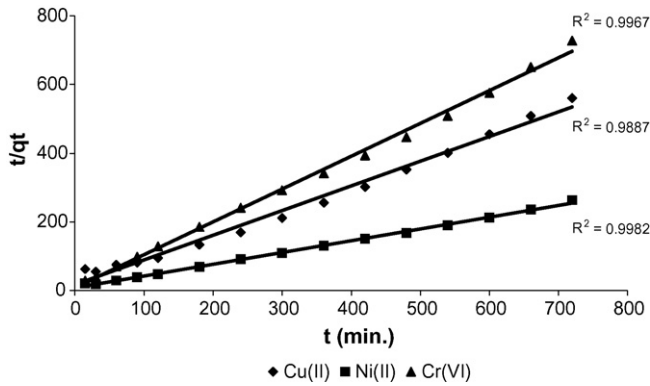


Fig. 9. Linearized pseudo-second-order kinetics plots for adsorption of Cu(II), Ni(II), and Cr(VI) by modified sawdust (dosage of modified sawdust: 40 g L⁻¹ at pH 4 for Cu(II), 30 g L⁻¹ at pH 8 for Ni(II), and 60 g L⁻¹ at pH 3 for Cr(VI); shaking speed, 250 rpm; temperature, 293 K).

dust were $k_1 = 2.0 \times 10^{-4}$, 8.0×10^{-4} , and $2.0 \times 10^{-4} \text{ min}^{-1}$, respectively, and $k_2 = 0.031$, 0.919, and $0.115 \text{ g mg}^{-1} \text{ min}^{-1}$, respectively.

The external mass-transfer constant (k_s) was calculated from the initial slope of the curve for C_t/C_0 versus time [30]. Intraparticle diffusion was characterized using the relationship between specific sorption (q_t) and the square root of time ($t^{1/2}$). This relation is expressed as follows [30]:

$$q_t = k_d t^{1/2} + C \quad (13)$$

where q_t is the quantity of metal ions adsorbed at time t (mg g^{-1}), k_d the initial rate of intraparticle diffusion ($\text{mg L}^{-1} \text{ min}^{-1/2}$), and C is the y -intercept. When the metal ion solution is mixed with the adsorbent, transport of the metal ions from the solution through the interface between the solution and the adsorbent occurs into pores in the particles. There are four main stages in the process of adsorption by porous adsorbents [31]: (i) solute transfer from the bulk solution to the boundary film that surrounds the adsorbent's surface, (ii) solute transport from the boundary film to the adsorbent's surface, (iii) solute transfer from the adsorbent's surface to active intraparticle sites, and (iv) interactions between the solute molecules and the available adsorption sites on the internal surfaces of the adsorbent. One or more of these four steps controls the rate at which solute is adsorbed. The first and second steps were very slow and were found to be the rate-determining step. Fig. 10 illustrates the diffusion of the heavy metal ions within modified sawdust as a function of time and shows that intraparticle diffusion occurred in three stages for Ni(II) ions and two stages for the Cu(II) and Cr(VI) ions. The intraparticle diffusion constants for all three stages (k_{d1} , k_{d2} , k_{d3}) are given in Table 4. Table 4 shows that the heavy metal ions diffused quickly among the particles at the beginning of the adsorption process, then intraparticle diffusion slowed down and stabilized. The deviation of these lines from the origin (i.e., a y -intercept other than 0) indicates that intraparticle transport is not the only rate-limiting step. It can be assumed that external mass transfer controls the rate of adsorption because of the very slow transfer speeds. The external mass transfer constants (k_s) were 4×10^{-4} , 5×10^{-4} , and $3 \times 10^{-4} \text{ min}^{-1}$ for

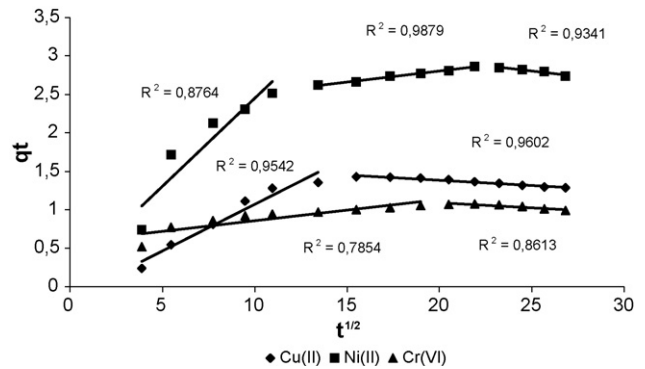


Fig. 10. Plot of the intraparticle diffusion kinetics for the three heavy metal ions (shaking speed, 250 rpm; temperature, 293 K).

Cu(II), Ni(II), and Cr(VI) ions, respectively, at a shaking speed of 250 rpm.

4. Conclusions

This paper presented the results of a detailed study of the adsorption process that removed Cu(II), Ni(II), and Cr(VI) ions from aqueous solution using a common, naturally occurring material: oak sawdust. Acid-modified sawdust was suitable for the removal of heavy metals from artificial wastewater, and although its adsorption capacity per unit mass was lower than that of competing substances such as ion-exchange resins and activated carbon, its high adsorption capacity per unit cost makes this material a promising and economical alternative. For example, the capacities were 2450 mg Cu(II) (US\$)⁻¹ for sawdust, 99 mg Cu(II) (US\$)⁻¹ for NaOH precipitation, 608 mg Cu(II) (US\$)⁻¹ for ion-exchange, and 15 mg Cu(II) (US\$)⁻¹ for activated carbon. It is also possible to recover the adsorbed metals by burning the sawdust in an energy cogeneration plant equipped with suitable scrubbers to recover the metals, and this may become an important source of recycled metals (all three metals in our study are important natural resources). The maximum removal efficiencies were 93% for Cu at pH 4 > 84% for Cr at pH 3 > 82% for Ni at pH 8. Operational parameters such as the shaking speed, amount of adsorbent, contact time, initial heavy metal concentrations, and solution pH all clearly affected the removal efficiency. The results in this paper provide a good indication of the different operating conditions that would be required for efficient removal of each heavy metal from aqueous solution. We also found that the Langmuir and D–R isotherms could both be used to model isothermal sorption of heavy metals on modified sawdust, and that the kinetics data were best modeled by a pseudo-second-order kinetics equation. Based on the results of this analysis, external mass transfer appears to control the rate of adsorption. The adsorption process was also thermodynamically spontaneous under natural conditions.

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References

- [1] M. Ajmal, A.H. Khan, S. Ahmad, A. Ahmad, Role of sawdust in the removal of copper(II) from industrial wastes, *Water Res.* 32 (1998) 3085–3091.
- [2] M.A. Oliver, Soil and human health: a review, *Eur. J. Soil Sci.* 48 (1997) 573–592.
- [3] S.K. Ouki, R.D. Neufeld, Use of activated carbon for the recovery of chromium from industrial wastewater, *J. Chem. Tech. Biotechnol.* 70 (1997) 3–8.
- [4] C. Özdemir, M. Karatas, S. Dursun, M.E. Argun, S. Dogan, Effect of $MnSO_4$ on the chromium removal from leather industry wastewater, *Environ. Technol.* 26 (2005) 397–400.
- [5] N. Meunier, P. Drogui, C. Montané, R. Hausler, G. Mercier, J.-F. Blais, Comparison between electrocoagulation and chemical precipitation for metals removal from acidic soil leachate, *J. Hazard. Mater.* 137 (2006) 581–590.
- [6] E. Pehlivan, T. Altun, The study of various parameters affecting the ion-exchange of Cu^{2+} , Zn^{2+} , Ni^{2+} , Cd^{2+} , and Pb^{2+} from aqueous solution on Dowex50W synthetic resin, *J. Hazard. Mater.* B134 (2006) 149–156.
- [7] O. Keskinan, M.Z.L. Goksu, M. Basibuyuk, C.F. Forster, Heavy metal adsorption properties of a submerged aquatic plant (*Ceratophyllum demersum*), *Bioresour. Technol.* 92 (2004) 197–200.
- [8] N.R. Axtell, S.P.K. Sternberg, K. Claussen, Lead and nickel removal using *Microspora* and *Lemna minor*, *Bioresour. Technol.* 89 (2003) 41–48.
- [9] A. Shukla, Y.H. Zang, P. Dubey, J.L. Margrave, S.S. Shukla, The role of sawdust in the removal of unwanted materials from water, *J. Hazard. Mater.* 95 (2002) 137–152.
- [10] M.E. Argun, S. Dursun, K. Gür, C. Özdemir, M. Karatas, S. Dogan, Nickel adsorption on the modified pine tree materials, *Environ. Technol.* 26 (2005) 479–488.
- [11] M.E. Argun, Removal of heavy metal ions using chemically modified adsorbents, PhD Thesis, Selçuk University Graduate School of Natural and Applied Science, Selçuklu-Konya, Turkey, 2006.
- [12] T.G. Chuah, A. Jumariah, I. Azni, S. Katayon, S.Y. Thomas Choong, Rice husk as a potentially low-cost biosorbent for heavy metal and dye removal: an overview, *Desalination* 175 (2005) 305–316.
- [13] G.E. Márquez, M.J.P. Ribeiro, J.M. Ventura, J.A. Labrincha, Removal of nickel from aqueous solutions by clay-based beds, *Ceram. Int.* 30 (2004) 111–119.
- [14] E. Erdem, N. Karapinar, R. Donat, The removal of heavy metal cations by natural zeolites, *J. Colloid Interf. Sci.* 280 (2004) 309–314.
- [15] I. Twardowska, J. Kyzioł, Sorption of metals onto natural organic matter as a function of complexation and adsorbent–adsorbate contact mode, *Environ. Int.* 28 (2003) 783–791.
- [16] Y.S. Ho, D.A.J. Wase, C.F. Forster, Batch nickel removal from aqueous solution by sphagnum moss peat, *Water Res.* 29 (1995) 1327–1332.
- [17] R.S. Bai, T.E. Abraham, Studies on enhancement of Cr(VI) biosorption by chemically modified biomass of *Rhizopus nigricans*, *Water Res.* 36 (2002) 1224–1236.
- [18] Y. Nuhoglu, E. Oguz, Removal of copper(II) from aqueous solutions by biosorption on the cone biomass of *Thuja orientalis*, *Process Biochem.* 38 (2003) 1627–1631.
- [19] N. Tewari, P. Vasudevan, B.K. Guha, Study on biosorption of Cr(VI) by *Mucor hiemalis*, *Biochem. Eng. J.* 23 (2005) 185–192.
- [20] M. Dakiky, M. Khamis, A. Manassra, M. Mer'eb, Selective adsorption of chromium(VI) in industrial wastewater using low-cost abundantly available adsorbents, *Adv. Environ. Res.* 6 (2002) 533–540.
- [21] <https://www1.fishersci.com>.
- [22] P.J. Van Soest, Use of detergents in the analysis of fibrous feeds. Preparation of fiber residues of low nitrogen content, *J. O. A. C.* 46 (1963) 825–829.
- [23] I. Gaballah, G. Kilbertus, Recovery of heavy metal ions through decontamination of synthetic solutions and industrial effluents using modified barks, *J. Geochem. Explor.* 62 (1998) 241–286.
- [24] American Society for Testing and Materials, Method D4749, 1994, Standard Test Method for Performing the Sieve Analysis of Coal and Designating Coal Size, USA.
- [25] P. Brown, I.A. Jefcoat, D. Parrish, S. Gill, E. Graham, Evaluation of the adsorptive capacity of peanut hull pellets for heavy metals in solution, *Adv. Environ. Res.* 4 (2000) 19–29.
- [26] O. Altin, H.O. Ozelge, T. Dogu, Use of general-purpose adsorption isotherms for heavy metal-clay mineral interactions, *J. Colloid Interf. Sci.* 198 (1998) 130–140.
- [27] B.P. Bering, M.M. Dubinin, V.V. Serpinsky, On thermodynamics of adsorption in micropores, *J. Colloid Interf. Sci.* 38 (1972) 185–194.
- [28] D. Mohan, K.P. Singh, Single- and multi-component adsorption of cadmium and zinc using activated carbon derived from bagasse: an agricultural waste, *Water Res.* 36 (2002) 2304–2318.
- [29] C. Namasivayam, R.T. Yamuna, Adsorption of chromium(VI) by a low-cost adsorbent: biogas residual slurry, *Chemosphere* 30 (3) (1995) 561–578.
- [30] G. McKay, The adsorption of basic dye onto silica from aqueous solution—solid diffusion model, *Chem. Eng. Sci.* 39 (1984) 129–138.
- [31] Y.S. Ho, D.A.J. Wase, C.F. Forster, Kinetic studies of competitive heavy metal adsorption by sphagnum moss peat, *Environ. Technol.* 17 (1996) 71–77.
- [32] A. Üçer, A. Uyanik, Ş.F. Aygün, Adsorption of Cu(II), Cd(II), Zn(II), Mn(II) and Fe(III) ions by tannic acid immobilised activated carbon, *Sep. Purif. Technol.* 47 (2006) 113–118.
- [33] B. Yu, Y. Zhang, A. Shukla, S.S. Shukla, K.L. Dorris, The removal of heavy metals from aqueous solutions by sawdust adsorption—removal of lead and comparison of its adsorption with copper, *J. Hazard. Mater.* B84 (2001) 83–94.
- [34] Y.S. Ho, G. McKay, The kinetics of sorption of divalent metal ions onto sphagnum moss peat, *Water Res.* 34 (2000) 735–742.