ELSEVIER

Journal of Hazardous Materials 141 (2007) 163–167

Journal of Hazardous Materials

www.elsevier.com/locate/jhazmat

Kinetic studies of adsorption of Pb(II), Cr(III) and Cu(II) from aqueous solution by sawdust and modified peanut husk

Qin Li, Jianping Zhai *, Wenyi Zhang, Mingmei Wang, Jun Zhou

State Key Laboratory of Pollution Control and Resource Reuse, School of the Environment, Nanjing University, Nanjing 210093, P.R. China

Received 7 May 2006; received in revised form 26 June 2006; accepted 27 June 2006
Available online 1 July 2006

Abstract

Sawdust and modified peanut husk were used as adsorbents to remove Pb(II), Cr(III) and Cu(II) from aqueous solution. Results of kinetic experiments demonstrated that the adsorption was effective and rapid. Three different kinds of kinetic models (i.e., intraparticular diffusion model, Lagergren-first-order and second-order equations) were used to investigate the adsorption mechanisms. The adsorption of heavy metals on sawdust and modified peanut husk is not an intraparticular diffusion control. The kinetic adsorption data can be described by the second-order equation and the adsorption might be a rate-limiting control. The suitability of the adsorbent was tested by fitting the adsorption data with Langmuir and Freundlich isotherms, which gave good fits with both isotherms.

Keywords: Adsorption; Sawdust; Modified peanut husk; Heavy metals; Kinetics; Isotherm

1. Introduction

With the rapid increase in global industrial activities, heavy metal pollution has become serious [1]. Heavy metals may come from various industrial sources such as electroplating, metal finishing, textile, storage batteries, lead smelting, mining, plating, ceramic and glass industries. Lead, chromium and copper are common contaminants of industrial wastewaters. Because they pose serious environmental problems and are dangerous to human health, considerable attention has been paid to methods for their removal from industrial wastewaters [2,3].

There are various methods for removing heavy metals including chemical precipitation, membrane filtration, ion exchange, liquid extraction or electrodialysis [4,5]. However, these methods are not widely used due to their high cost and low feasibility for small-scale industries [6]. In contrast, the adsorption technique is one of the preferred methods for removal of heavy metals because of its efficiency and low cost. Conventional adsorbents such as granular or powdered activated carbon are not always popular as they are not economically viable and technically efficient [7]. Non-conventional materials have been tested in a large scale for this purpose, such as fly ash [8], lignite [9], tree fern [10], etc.

In this research, sawdust and modified peanut husk have been used as adsorbents to remove Pb(II), Cr(III) and Cu(II) from wastewater. Sawdust and peanut husk are often considered as solid wastes of agriculture and widely available [11,12]. These materials cause a significant disposal problem. Efforts have been made to use the cheapest and unconventional adsorbents to adsorb heavy metals from aqueous solution. A series of experiments have been performed to characterize heavy metals adsorption equilibrium on sawdust and modified peanut husk. Three different kinds of kinetic models (Intraparticular diffusion models, Lagergren-first-order and second-order equations) were selected to determine which of these mechanisms predominates in heavy metals adsorption by sawdust and modified peanut husk. The experimental data was compared with Langmuir and Freundlich isotherms. This information will be useful for further application of the treatment system.

2. Materials and methods

2.1. Materials and equipment

The sawdust and peanut husk were applied from the suburb of Nanjing, China. The sawdust is of poplar trees. The sawdust

* Corresponding author. Tel.: +86 25 83592903; fax: +86 25 83592903.
E-mail address: jpzhai@nju.edu.cn (J. Zhai).

0304-3894/$ – see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.jhazmat.2006.06.109

and peanut husk were dried at an oven temperature of 40 °C, and sieved into 40–60 meshes (0.45–0.60 mm). The sawdust was washed with deionized water to remove dust and other materials. The peanut husk was modified with formalin to reduce organic pigment. 10 g peanut husk was mixed with 250 ml 0.2 mol/l formalin and 1.0 mol/l H_2SO_4, reacted 3 h at a temperature of 50 °C. The modified peanut husk was washed with deionized water to remove residual materials. The rinsed sawdust and modified peanut husk were oven-dried again and stored in desicater.

FTIR shows the main functional groups of sawdust are –OH, C=C and –C=O. The main functional groups of modified peanut husk are –OH, C=C and –COOH. To most adsorbents, the sites responsible for the adsorption process are due to the –COOH and –OH groups [13–15].

$$\text{S–COOH} + \text{M}^{n+} \rightarrow \text{S–COOM}^{(n-1)+} + \text{H}^+$$
$$\text{S–OH} + \text{M}^{n+} \rightarrow \text{S–OM}^{(n-1)+} + \text{H}^+$$
$$\text{S–COOH} + \text{M(OH)}^{(n-1)+} \rightarrow \text{S–COOM(OH)}^{(n-2)+} + \text{H}^+$$
$$\text{S–OH} + \text{M(OH)}^{(n-1)+} \rightarrow \text{S–OM(OH)}^{(n-2)} + \text{H}^+$$

where S denotes the polymerized surface.

All chemicals used in experiment were analytical grade, and solutions were prepared with distilled water. The stock solutions of Pb(II), Cr(III) and Cu(II) (1000 mg/l) were prepared from analytical grade $Pb(NO_3)_2$, $Cr(NO_3)_3{\cdot}9H_2O$, $Cu(NO_3)_2{\cdot}3H_2O$ using double distilled water and serially diluted to working solutions of varying initial concentrations for experimental purposes. 1 mol/l NaOH and HCl were used to adjust the pH of the solutions.

2.2. Adsorption experiments

A volume of 100 ml of heavy metal solutions was placed in a 250 ml bottle to start the experiments. The initial metal ion concentrations used in the tests ranged from 5 to 50 mg/l. 0.2 g sawdust or modified peanut husk was added to the solutions. High pH can cause precipitation of some metals, and low pH can cause few or no adsorption. To keep high adsorption amount and free of precipitation effect, using 1 M NaOH or 1 M HCl to adjust the suspension to pH 4.0 ± 0.2. Samples were agitated with a speed of 200 rpm at 25 °C. At present time intervals of the experiments, the aqueous samples were taken and then filtered. The filtrates were analyzed for heavy metals concentration using an atomic adsorption spectrophotometer (Hitachi Z8100, Japan).

2.3. Adsorption kinetic model

In an attempt to present the kinetic equation representing adsorption of heavy metals on sawdust and modified peanut husk, three kinds of kinetic models were used to test the experimental data. These are intraparticular diffusion models, Lagergren-first-order equation and second-order equation.

2.3.1. Intraparticular diffusion model [16,17]

A intraparticular mass transfer diffusion model proposed by Weber and Morris [18] was used in this research. In the model, the fractional approach to the equilibrium changes according to a function of $(Dt/r^2)^{0.5}$, where D is the diffusion coefficient within the solid adsorbent and r is the particle radius.

The intraparticular diffusion rate constant can be determined:

$$q_t = K_{id} t^{1/2} \tag{1}$$

where q_t is the amount of adsorption time t (min) (mg/L) and K_{id} is the rate constant of intraparticular diffusion (mg/g/min).

2.3.2. Lagergren-first-order equation [19,20]

Lagergren-first-order equation is the most popular kinetics equation. The form is

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \tag{2}$$

After definite integration by applying the conditions $q_t = 0$ at $t = 0$ and $q_t = q_t$ at $t = t$, Eq. (2) becomes the following:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \tag{3}$$

where q_t is the amount of adsorption time t (min) (mg/g); k_1 the rate constant of the equation (l/min); q_e is the amount of adsorption equilibrium (mg/g).

The adsorption rate constant, k_1, can be determined experimentally by plotting of $\ln(q_e - q_t)$ against t.

2.3.3. Second-order equation [21–23]

The second-order equation is in the following form:

$$\frac{dq}{dt} = k_2(q_e - q_t)^2 \tag{4}$$

After definite integration by applying the conditions $q_t = 0$ at $t = 0$ and $q_t = q_t$ at $t = t$, Eq. (4) becomes the following:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \tag{5}$$

where k_2 is the rate constant of the second-order equation (g/mg/min); q_t the amount of adsorption time t (min)(mg/g); q_e is the amount of adsorption equilibrium (mg/g).

2.4. Adsorption isotherms

The adsorption isotherm is based on the assumptions that every adsorption site is equivalent and that the ability of a particle to bind there is independent of whether or not adjacent sites are occupied [24]. An adsorption process is usually described by the following two widely used isotherms [25]:

(a) Langmuir isotherm:

$$q_e = Q_0 \frac{bC_e}{1 + bC_e} \tag{6}$$

where q_e is the amount of metal ions adsorbed per unit mass of the adsorbent, C_e the equilibrium solution concentration, Q_0 and b are the Langmuir equilibrium coefficients.

(b) Freundlich isotherm:

$$q_e = K_F C_e^n \quad (7)$$

where q_e is the amount of metal ions adsorbed per unit mass of the adsorbent, C_e the equilibrium solution concentration, K_F and n are Freundlich equilibrium coefficients. For favorable adsorption, $0 < n < 1$, while $n > 1$ represents unfavorable adsorption, and $n = 1$ indicates linear adsorption. If $n = 0$, the adsorption process is irreversible [26,27].

3. Results and discussion

3.1. Effects of adsorption time

Fig. 1 shows the time profiles of sawdust and modified peanut husk adsorption of different heavy metals. Adsorption of Pb(II), Cr(III) and Cu(II) showed an increasing trend up to a reaction time of 1 h beyond which adsorption appeared to have approached equilibrium. After 1 h, the adsorption capacity of Cr(III) by sawdust was still increasing. The others became constant. After 6 h, all got equilibrium. The rate of uptake of heavy metals by modified peanut husk was faster than sawdust.

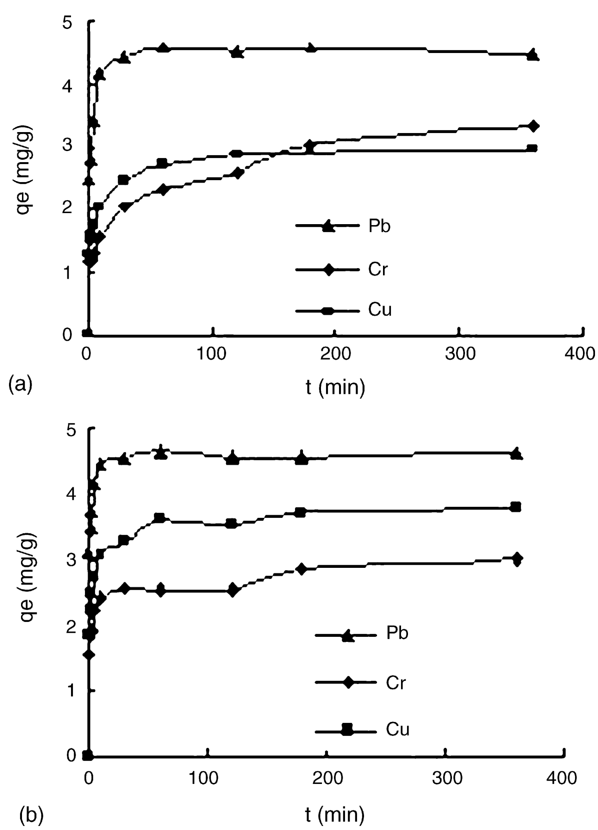

Fig. 1. Amount adsorbed of (a) sawdust and (b) modified peanut husk at different adsorption time (modified peanut husk 2 g/l, initial metal ions 10 mg/l, pH 4).

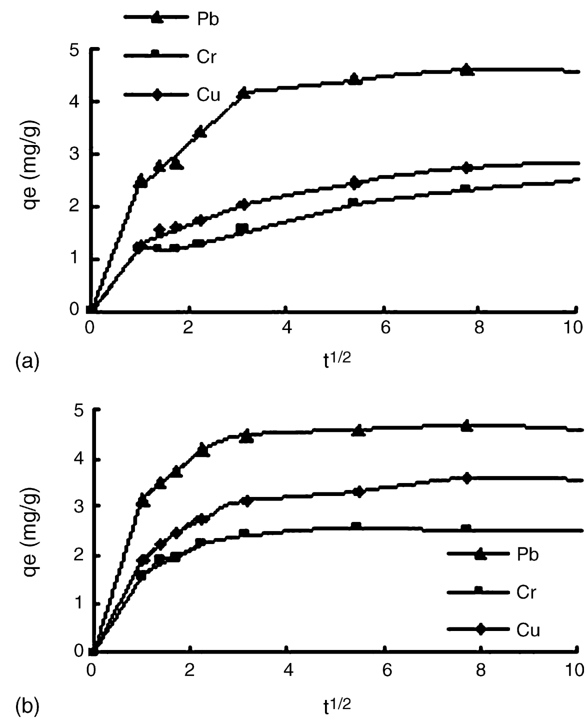

Fig. 2. Relation plots of q_t and $t^{1/2}$ for adsorption of Pb(II), Cr(III) and Cu(II) by (a) sawdust and (b) modified peanut husk at 298 K (modified peanut husk 2 g/l, initial metal ions 10 mg/l, pH 4).

3.2. Intraparticular diffusion model

The relation plots of q_t and $t^{1/2}$ are shown in Fig. 2. The plots do not go through origin. The adsorption of heavy metals on sawdust and modified peanut husk is not intraparticular diffusion control. Rengarajd [28,29] found membrane diffusion is the main control of phenol adsorption on activated carbon. The rate constant of intraparticular diffusion on sawdust and modified peanut husk increased Pb(II)> Cu(II) > Cr(III).

3.3. Lagergren-first-order equation

The amount of adsorption equilibrium, q_e, the rate constant of the equation (l/min), k_1, the calculated amount of adsorption

Table 1
Lagergren-first-order rate parameters for Pb(II), Cr(III) and Cu(II) adsorption on sawdust and modified peanut husk

Adsorbent	Adsorbate	q_e (mg/g)	k^1 ($\times 10^{-2}$ min^{-1})	$q_{e,c}$ (mg/g)	R^2
Sawdust	Pb^{2+}	4.59	2.86	1.3958	0.9037
	Cr^{3+}	3.34	1.11	2.2517	0.8506
	Cu^{2+}	2.96	2.30	1.4499	0.9386
Modified peanut husk	Pb^{2+}	4.66	10.62	1.4746	0.9445
	Cr^{3+}	3.02	1.32	1.1155	0.7629
	Cu^{3+}	3.80	37.91	5.5041	0.9233

Table 2
Second-order rate parameters for Pb(II), Cr(III) and Cu (II) adsorption on sawdust and modified peanut husk

Adsorbent	Adsorbate	q_e (mg/g)	k_1 ($\times 10^{-2}$ min^{-1})	$q_{e,c}$ (mg/g)	R^2
Sawdust	Pb^{2+}	4.59	4.244	4.5126	0.9998
	Cr^{3+}	3.34	0.23	3.3490	0.9907
	Cu^{2+}	2.96	0.903	2.9806	0.9998
Modified peanut husk	Pb^{2+}	4.66	2.948	4.6425	0.9999
	Cr^{3+}	3.02	0.674	2.9922	0.9966
	Cu^{2+}	3.80	4.026	3.8066	0.9996

Table 3
Freundlich and Langmuir absorption parameters at 298 K (absorbate 2 g/l, initial metal ions 10, 20, 30, 40, 50 mg/l, pH 4, time 3 h)

Absorbent	Adsorbate	Freundlich coefficient			Langmuir coefficient		
		K_F	n	R^2	q_e (mg/g)	b	R^2
Sawdust	Pb^{2+}	0.1734	0.3166	0.9898	21.05	45.34	0.9692
	Cr^{3+}	0.0908	0.2525	0.9981	5.52	51.44	0.9881
	Cu^2	0.0663	0.1380	0.9862	6.585	52.58	0.9912
Modified peanut husk	Pb^{2+}	0.3405	0.4685	0.9773	29.14	32.55	0.9570
	Cr^{3+}	0.1834	0.4370	0.9804	7.67	58.18	0.9625
	Cu^2	0.0860	0.1707	0.9748	10.15	31.91	0.9716

equilibrium, $q_{e,c}$, and the coefficient of determination, R^2 are shown in Table 1. Except the R^2 of Cr(III) adsorption on modified peanut husk is 0.7629, others are all larger than 0.85. But the calculated amount of adsorption equilibrium ($q_{e,c}$) is far form the actual amount of adsorption equilibrium (q_e). So, the Lagergren-first-order equation is not suitable for heavy metals adsorption on sawdust and modified peanut husk.

3.4. Second-order equation

The second-order equation for Pb(II), Cr(III) and Cu(II) adsorption on sawdust and modified peanut husk is shown in Fig. 3. The amount of adsorption equilibrium, q_e, the rate constant of the equation (l/min), k_1, the calculated amount of adsorption equilibrium, $q_{e,c}$, and the coefficient of determination, R^2 are shown in Table 2. The second-order equation appeared to be the better-fitting model than Lagergren-first-order equation because it has the higher R^2. The calculated amount of adsorption equilibrium ($q_{e,c}$) is similar to the actual amount of adsorption equilibrium (q_e). The adsorption rate is related to the concentration of the activated sites on the surface of adsorbent. The adsorption of heavy metals on sawdust and modified peanut husk might be a rate-limiting control. The Pb(II) adsorption on sawdust and Cu(II) adsorption on modified peanut husk were faster. The Cr(III) adsorption on sawdust was the slowest, which is in accordance with Fig. 1.

3.5. Asorption isotherm

Fig. 3 shows the adsorption isotherm of Pb(II), Cr(III) and Cu(II) on sawdust and modified peanut husk at 298 K. The adsorption data follow the empirical Freundlich isotherm (Table 3), which is applicable to non-specific adsorption on heterogeneous solid surfaces. In order to ascertain whether the adsorption is chemisorptive in nature with chemical forces metal ions to the surface of sawdust and modified peanut husk, the experimental data are also tested with respect to Langmuir isotherm. The plots have good linearity in both the cases at 298 K. The values of the coefficients indicate the favorable nature of adsorption of metal ions on the sawdust and modified peanut husk. The adsorption intensity given by the Freundlich coefficient, n, is <1 in all cases.

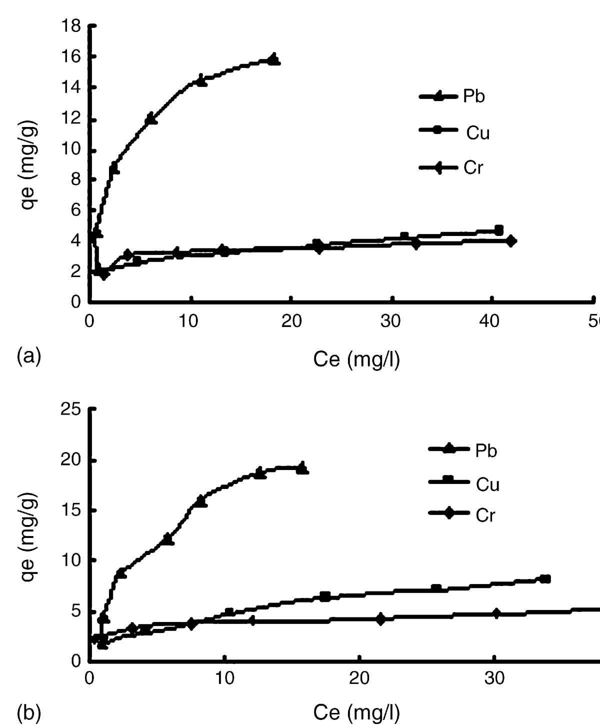

Fig. 3. Adsorption isotherm of Pb(II), Cr(III) and Cu(II) on (a) sawdust and (b) modified peanut husk at 298 K (modified peanut husk 2 g/l, pH 4, time 3 h).

4. Conclusion

The capacity of sawdust and modified peanut husk in adsorption of Pb(II), Cr(III) and Cu(II) has been investigated, and the experimental data demonstrate that sawdust and modified peanut husk are two effective adsorbents of heavy metals in solutions. Intraparticular diffusion models, Lagergren-first-order and second-order equations were selected to determine which of these mechanisms predominates in heavy metals adsorption by sawdust and modified peanut husk. The following conclusion can be made from this study:

(1) Adsorption of Pb(II), Cr(III) and Cu(II) showed an increasing trend up to a reaction time of 1 h beyond which adsorption appeared to have approached equilibrium. After 1 h, the adsorption of heavy metals reached equilibrium except Cr(III) adsorption on sawdust. After 6 h, all reached equilibrium.
(2) The adsorption of heavy metals on sawdust and modified peanut husk is not intraparticular diffusion control. The rate constant of intraparticular diffusion on sawdust and modified peanut husk increased Pb(II) > Cu(II) > Cr(III).
(3) The second-order equation appears to be the better-fitting model than Lagergren-first-order equation. The calculated amount of adsorption equilibrium ($q_{e,c}$) by second-order equation is similar to the actual amount of adsorption equilibrium (q_e). The adsorption of heavy metals on sawdust and modified peanut husk might be a rate-limiting control.
(4) The adsorption data follow both Freundlich and Langmuir isotherm. The adsorption of Pb(II), Cr(III) and Cu(II) on sawdust and modified peanut husk are favorable adsorption.

Acknowledgments

This work was supported by the Analysis and Measure Foundation of Nanjing University (06HK10). We also thank two anonymous reviewers and the associate editor whose thoughtful comments helped to improve the clarity of the manuscript.

References

[1] J.P. Chen, L. Wang, Characterization of metal adsorption kinetic properties in batch and fixed-bed reactors, Chemosphere 54 (2004) 397–404.
[2] O. Keskinkan, M.Z.L. Goksu, A. Yuceer, M. Basibuyuk, C.F. Forster, Heavy metal adsorption characteristics of a submerged aquatic plant (Myriophyllum spicatum), Process Biochem. 39 (2003) 179–183.
[3] K.A. Matis, A.I. Zouboulis, N.K. Lazaridis, Removal and recovery of metals from dilute solutions: applications of flotation techniques, in: G.P. Gallios, K.A. Watis (Eds.), Mineral Processing and the Environment, Kluwer Academic Publishers, Dordrecht, The Netherlands, 1998, pp. 165–196.
[4] M. Sitting, Handbook of Toxic and Hazardous Chemicals, Noyes Publications, Park Ridge, NJ, 1981.
[5] J.W. Patterson, Industrial Wastewater Treatment Technology, 2nd ed., Butterworth-Heinemann, London, 1985.
[6] A. Sohail, S.I. Ali, N.A. Khan, R.A.K. Rao, Removal of chromium from wastewater by adsorption, Environ. J. Pollut. Contr. 2 (1999) 27–31.
[7] S.S. Gupta, K.G. Bhattacharyya, Removal of Cd(II) from aqueous solution by kaolinite, montmorillonite and their poly(oxo zirconium) and tetrabutylammonium derivatives, J. Hazard. Mater. B 128 (2006) 247–257.
[8] A. Mathur, D.C. Rupainwar, Asian Environ. 10 (1988) 19.
[9] N. Balasubramanaian, A. Jafar Ahamed, Pollut. Res. 17 (1998) 341.
[10] Y.S. Ho, Water Res. 37 (2003) 2323.
[11] W.J. Chen, X.G. Cheng, Using sulfuric acid to measure the lignin of peanut husk, Minjiang University 23 (2) (2002) 72–76.
[12] L.J. Yu, S.S. Shukla, K.L. Dorris, Adsorption of chromium from aqueous solutions by maple sawdust, J. Hazard. Mater. 100 (2003) 53–63.
[13] L.J. Yu, S.S. Shukla, K.L. Dorris, A. Shukla, J.L. Margrave, Adsorption of chromium from aqueous solutions by maple sawdust, J. Hazard. Mater. 100 (1–3) (2003) 53–63.
[14] R. Zacaria, G. Claire, A. Yves, L.C. Pierre, Modeling of single and competitive metal adsorption onto a natural polysaccharide, Environ. Sci. Technol. 36 (10) (2002) 2242–2248.
[15] C. Jeon, J.Y. Park, Y.J. Yoo, Biosorption model for binary adsorption sites, J. Microbiol. Biotechnol. 11 (5) (2001) 781–787.
[16] W.J. Weber, J.C. Morris, Advances in water pollution research: removal of biologically-resistant pollutions from waste waters by adsorption, in: Proceedings of the International Conference on Water Pollution Symposium, vol. 2, Pergamon Press, Oxford, 1996, pp. 231–266.
[17] J.S. Sun, Z.Q. Zhang, Y. Liu, The sorption of aniline from aniline-contanining wastewater by CTMAB-rectorite, Ion Exchange Adsorption 18 (2) (2002) 223–231.
[18] E. Tiitem, R. Apak, C.F. Unal, Adsorptive removal of chlorphenols from water by bituminous shale, Water Res. 32 (8) (1998) 2315–2324.
[19] C. Namasivayam, D. Kavitha, Adsorptive removal of 2-chlorophenol by low-cost coirpitch, J. Hazard. Mater. B 98 (2003) 257–274.
[20] C.Y. Chen, Y.Y. Zhuang, Adsorption equilibrium and kinetic of dyes on dried activated sludge, J. Safety Environ. 3 (3) (2003) 46–50.
[21] M. Otero, F. Rozada, L.F. Calvo, A.I. Garcia, A. Mordn, Kinetic and equilibrium modeling of the methylene blue removal from solution by adsorbent materials produced from sewage sludges, Biochem. Eng. J. 15 (2003) 59–68.
[22] X.J. Zhang, H.Y. Land, Synthesis and adsorption kinetics of the chelate compound of chitosan with ferrous ions, Chin. J. Appl. Chem. 20 (8) (2003) 749–753.
[23] C.Y. Lin, L. Li, Kinetics of phenol sorption to organobentonite from water, Acta Sci. Circumstantiae 23 (6) (2003) 738–741.
[24] S. Ahmed, S. Chughtai, M.A. Keane, The removal of cadmium and lead from aqueous solution by ion exchange with Na–Y zeolite, Sep. Purif. Technol. 13 (1998) 57–64.
[25] S.H. Gharaibeh, W.Y. Abu-el-sha'r, M.M. Al-Kofahi, Removal of selected heavy metals from aqueous solutions using processed solid residue of olive mill products, Water Res. 25 (1991) 499–528.
[26] G. McKay, H.S. Blair, J.R. Gardner, Adsorption of dyes on chitin-1. equilibrium, J. Appl. Polym. Sci. 27 (1982) 3043–3057.
[27] D. Ghosh, K.G. Bhattacharyya, Adsorption of methylene blue on kaolinite, Appl. Clay Sci. 20 (2002) 295–300.
[28] S. Rengaraj, S.H. Moon, R. Sivabalan, B. Arabindoo, V. Murugesan, Agricultural solid waste for the removal of organics:adsorption of phenol from water and wastewater by palm seed coat activated carbon, Waste Manage. 22 (2002) 543–548.
[29] S. Rengaraj, S.H. Moon, R. Sivabalan, B. Arabindoo, V. Murugesan, Removal of phenol from aqueous solution and resin manufacturing industry wastewater using an agricultural waste: rubber seed coat, J. Hazard. Mater. B 89 (2002) 185–196.