A STUDY ON ADSORPTION OF Pb(II), Cr(III) AND Cu(II) FROM AQUEOUS SOLUTION BY PEANUT HUSK

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ABSTRACT. Peanut husk has been used in this work for removing Pb(II), Cr(III) and Cu(II) from aqueous solution. Batch adsorption studies were carried out under different pH, initial concentration of metal ions, interfering metal ions, time and temperature. Adsorption was poor in strongly acidic solution but was improved in alkaline medium and continuously increased with rise in pH. The presence of one metal decreased the removal of the other metal ions. The adsorption processes were more akin towards second-order equation. The suitability of the adsorbent was tested by fitting the adsorption data with Langmuir and Freundlich isotherms, which gave good fits with both isotherms. For an adsorbent amount of 2 g/L and initial metal ions 10 mg/L, the maximum monolayer values of Pb(II), Cr(III) and Cu(II) was 4.59 mg/g, 3.34 mg/g and 2.96 mg/g. The adsorption was in the order Pb(II) > Cu(II) > Cr(III). The values of the thermodynamic parameters, ΔH, ΔS and ΔG, indicated the interactions to be thermodynamically favorable.

KEY WORDS: Peanut husk, Heavy metals, Sorption isotherm, Kinetics

INTRODUCTION

Many toxic heavy metals have been discharged to the environment as industrial wastes, causing serious water and soil pollution [1-3]. Thus, a safe and effective treatment of heavy-metal-bearing wastewater is necessary. Heavy metal waste waters are usually treated by adding alkaline materials such as lime, fly ash, or alkaline industrial wastes to precipitate metals as hydroxides [4, 5]. Major disadvantages of this method are the need for continuous addition of the amendment, low reaction rates, and the production of huge amounts of secondary wastes [6, 7]. The uptake of heavy metals onto low-cost sorbents, such as oak sawdust, is seen as an alternative to the mentioned treatment techniques [8, 9]. Peanut husk is a kind of agriculture waste with large quantities in China. This material causes a significant disposal problem [10, 11].

In the present study, the adsorption of heavy metal ions on peanut husk was evaluated under various conditions such as pH, heavy metal concentrations, and temperature. In addition, a series of tests were conducted to investigate how the presence of other metal ions affected the removal of one metal ion. Finally, the adsorption isotherms and kinetics of heavy metals adsorption on peanut husk were studied.

EXPERIMENTAL

Materials. The peanut husk used in the present work was obtained from the nearby villages of Nanjing, China. The peanut husk was dried at an oven temperature of 40 ºC, and sieved into 40 to 60 mesh (0.45 mm to 0.60 mm). The presence of organic pigments reduces the efficiency of a biomaterial as metal adsorbent and hence, peanut husk was treated with formalin. 10 g peanut husk was mixed with 250 mL of 0.2 M formalin and 1.0 M H_2SO_4, reacted 3 hours at a temperature of 50 ºC. The peanut husk was washed with deionized water to remove residual materials [12]. The peanut husk was oven-dried again and stored in desiccator.

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All chemicals used in the experiment were of 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 $Pb(NO_3)_2$, $Cr(NO_3)_3 \cdot 9H_2O$ and $Cu(NO_3)_2 \cdot 3H_2O$, respectively, using double distilled water and serially diluted to working solutions of varying initial concentration for experimental purposes. 1 M NaOH and HCl were used to adjust the pH of the solutions.

Methods

An aliquot of 100 mL of heavy metal solutions was placed in a 250 mL bottle to start the experiments. The initial metal ion concentration used in the tests ranged between 5 and 50 mg/L. 0.2 g peanut dusk was added to the solutions. Before adding the peanut husk into the solutions, the pH values were adjusted by adding NaOH and HCl solutions, which range from 1.9 to 6.2. Samples were agitated with a speed of 200 rpm at a constant temperature. At preset time intervals of the experiments, the aqueous samples were taken and then filtered. The filtrates were analyzed for heavy metals concentration using an atomic absorption spectrophotometer (Hitachi Z8100, Japan) with an air/acetylene flame.

Theoretical basis

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 [13]. An adsorption process is usually described by the following two widely used isotherms [14]:

(a) Langmuir isotherm: $q_e = Q_0 \dfrac{bC_e}{1 + bC_e}$ (1)

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

(b) Freundlich isotherm: $q_e = K_F C_e{}^n$ (2)

where q_e is the amount of metal ions adsorbed per unit mass of the adsorbent, C_e is 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 [15, 16].

Thermodynamics. The thermodynamic parameters, ΔH, ΔS, ΔG, for the adsorption process are calculated using the following equations [17]:

$$\ln K_d = \frac{\Delta S}{R} - \frac{\Delta H}{RT}$$ (3)

$$\Delta G = \Delta H - T\Delta S$$ (4)

where K_d is the equilibrium constant. The values of ΔH and ΔS are determined from the slope and the intercept of the linear plot of $\ln K_d$ versus $1/T$. Putting these values in Eq (4), ΔG can be calculated.

Kinetics. The kinetics of the adsorption process could be studied by carrying out a separate set of adsorption experiments at constant temperature in which the progress of the process is followed with time. Lagergren-first-order and second-order Equations were used to evaluate the adsorption interactions.

(a) Lagergren-first-order equation:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \tag{5}$$

where q_t is the amount of adsorption time t(min); k_1 is the rate constant of the equation; 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 [18, 19].

(b) Second-order equation:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^{\;2}} + \frac{1}{q_e} t \tag{6}$$

where k_2 is the rate constant of the second-order-equation; q_t is the amount of adsorption time t(min) and q_e is the amount of adsorption equilibrium (mg/g) [12, 20-21].

RESULTS AND DISCUSSION

Modification of peanut husk

Peanut husk comprises catechol, pyrogallol and phloroglucinol [22], and the H^+ ions of hydroxyl groups can exchange with metal ions. The low cost and effectiveness make them good biomaterial for heavy metals disposal. But, peanut husk contains soluble organic pigment. Using peanut husk as a sorbent, the filtrate is russet and needs further disposal. So, peanut husk must be modified before it is used.

FT-IR spectrum of unmodified and modified peanut husk showed slight differences (Figure 1). After modification, the 3415.6 cm^{-1} band corresponding to the OH stretching vibration decreased, and the 1737.6 cm^{-1} band of the C=O stretching vibration increased, which mean there was condensation reaction between formaldehyde and OH. The 1510 cm^{-1} band corresponding to the C=C stretching vibration decreased. Formaldehyde can eliminate some unsaturated organic compound from peanut husk during modification.

After modification, percent disposal of Pb(II), Cr(III) and Cu(II) on peanut husk increased by 5.6 %, 11.0 %, 19.8 %.
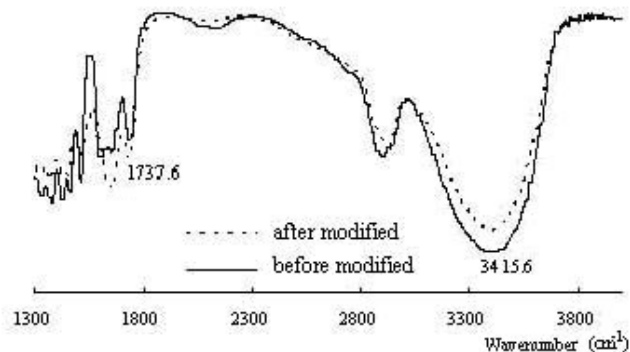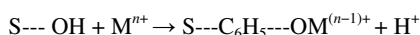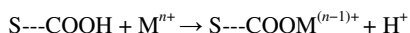

Figure 1. FT IR of unmodified and modified peanut husk.

Effect of pH

The effect of pH can be explained in terms of pH_{zpc} (zero point of charge) of the adsorbent. Liao and Liao measured the pH_{zpc} of peanut husk and it is at 5.4 [23]. When pH is below 5.4, the surface charge of the adsorbent is positive. On the other hand, at pH less than pH_{zpc}, the predominant metal species [M^{n+} and $M(OH)^{(n-1)+}$] are positively charged, therefore, uptake of metals in the pH range of 2-5.4 is a H^+–M^{n+} exchange process. The possible sites on peanut husk for specific adsorption includes H^+ ions in ---OH and ---COOH functional groups in which H^+ ions can be exchanged for cations in solution [24]:

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

$$S\text{--- }OH + M^{n+} \rightarrow S\text{---}C_6H_5\text{---}OM^{(n-1)+} + H^+$$

where S denotes the polymerized surface.

Decrease in removal of metal ions at lower pH was apparently due to the higher concentration of H^+ ions present in the reaction mixture which compete with the M^{2+} ions for the adsorption sites of peanut husk [25]. An increase in pH above pH_{zpc} showed a slight increase in adsorption in which the surface of the adsorbent was negatively charged and the sorbate species were still positively charged. And the increasing of pH resulted in precipitation of many metals. The results are shown in Figure 2.
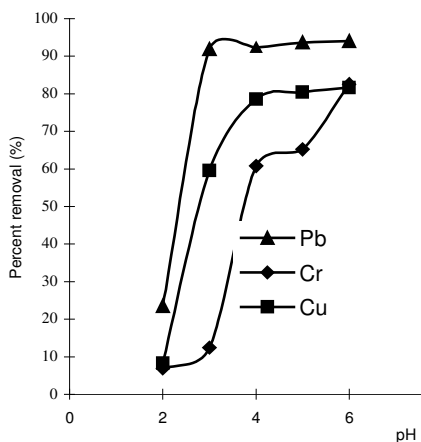

Figure 2. Effect of pH on removal of Pb(II), Cr(Ш) and Cu(II).

Effect of initial metal ions concentration

The adsorption experiments were carried out with metal ions concentrations of 5, 10, 20, 30, 40, 50 mg/L with a constant modified peanut husk amount of 2 g/L, time 3 h, pH 4 at 298 K. The amount of metal ions adsorbed per unit mass at different concentrations is shown in Figure 3. The amount increased almost with an increase in metal ions concentration. At low metal ion loads, adsorption involved the high energy sites. Under these conditions, the ratio of number of moles of metal ion to the available adsorption sites was low, and therefore, the amount adsorbed per unit mass increased slowly [24]. With an increase in metal ion load, the higher energy sites would be rapidly saturated and the metal ions would gradually occupy the lower energy sites, resulting in a continuous increase in the amount adsorbed per unit mass. Then a plateau was

seen which indicated unavailability of further adsorption of heavy metals onto modified peanut husk on account of metal ions saturated surfaces.
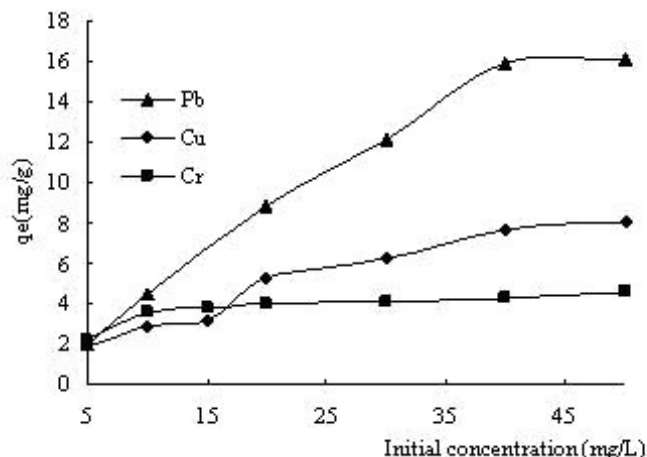

Figure 3. Amount of metal ions adsorbed per unit mass (q_e) for different initial concentrations (5, 10, 20, 30, 40 and 50 mg/L) at 298 K (modified peanut husk 2 g/L, pH 4, time 3 h).

Adsorption Isotherm

The adsorption data follow the empirical Freundlich isotherm (Table 1), which is applicable to non-specific adsorption on heterogeneous solid surfaces. 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 indicated the favorable nature of adsorption of metal ions on peanut husk. The adsorption intensity given by the Freundlich coefficient, *n* was less than 1, in all cases, which means the adsorption of Pb(II), Cr(III) and Cu(II) on peanut husk are favorable adsorption.

Table 1. Freundlich and Langmuir adsorption parameters at 298 K. (adsorbate 2 g/L, initial metal ions 10, 20, 30, 40, 50 mg/L, pH 4, time 3 h).

Adsorbate	Freundlich coefficient			Langmuir coefficient		
	K_F	n	R^2	Q_0 (mmol/g)	b	R^2
Pb^{2+}	0.3405	0.4685	0.9773	0.1408	32.55	0.9570
Cr^{3+}	0.1834	0.4369	0.9804	0.1475	58.18	0.9625
Cu^2	0.0860	0.1707	0.9748	0.1597	31.91	0.9716

Effect of temperature and thermodynamic

The initial metal ion concentration used in the tests was 10 mg/L and the pH values were adjusted to 4. Samples were agitated for 3 hours at a constant temperature range from 10 ^{o}C to 60 ^{o}C. The dependence of the amount adsorbed on temperature is given in Figure 4. The temperature had a dramatic effect on the adsorption metal ions on peanut husk. As the temperature increased the adsorption capacity rose at the beginning and then came down. The process is controlled by the adsorbate-adsorbent interactive forces [26]. The results indicate that chemical adsorption becomes stronger in comparison to physical adsorption as the temperature

increases [27]. Thus, although the process as a whole is endothermic in low temperature, it shows the tendency to become exothermic as the temperature increases. Therefore, higher temperature is not favorable for the adsorption process.
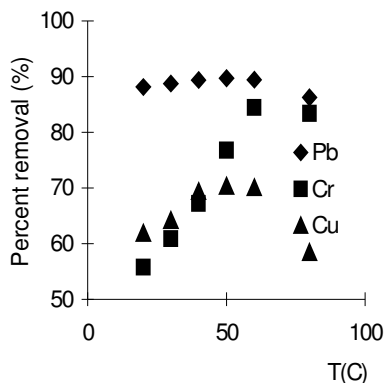

Figure 4. Effect of temperature on amount of Pb(II), Cr(Ⅲ) and Cu(II) adsorbed per unit mass (peanut 2 g/L, initial metal ions 10 mg/L, pH 4, time 3 h).

Table 2. Thermodynamic data for the adsorption of Pb(II) , Cr(Ⅲ) and Cu(II) (peanut 2 g/L, initial Pb(II), Cr(Ⅲ) and Cu(II) 10 mg/L, pH 5, time 3 h).

Adsorbate	q_e (mmol/g)	ΔH (kJ/mol)	ΔG (kJ/mol)			ΔS(J/mol•K)		
			298K	308K	323K	298K	308K	323K
Pb^{2+}	0.1930	17.42	-5.29	-5.30	-7.10	76.21	73.79	75.93
Cr^{3+}	0.3846	12.82	-5.67	-7.83	-8.30	62.05	67.05	65.40
Cu^{2+}	0.3147	30.89	-4.35	-7.31	-8.63	118.25	124.02	122.35

ΔH, ΔS and ΔG for the adsorption process are computed from the plots of $\ln K_d$ versus $1/T$ (Table 2). ΔH is in the range of 12.82 to 30.89 kJ/mol indicating the endothermic nature of the interactions.

ΔS lies in the range of 62.05 to 152.35 J/mol.K. Entropy increase accompanying the process illustrates increased randomness at the solid-solution interface supporting strong affinity of the adsorbent for heavy metals [28].

ΔG is in the range of -5.29 to -14.51 kJ/mol. The decrease in Gibbs energy is significant as it shows the interactions to be spontaneous. It is also observed that the decrease was more at higher temperatures indicating that the interactions were favored by an increase in temperature in agreement with the endothermic nature of metal ions adsorption on peanut husk [29].

Effect of time and kinetics of adsorption

The initial metal ion concentration used in the tests was 10 mg/L and the pH values were adjusted to 4. Samples were agitated 5 min to 3 h at 25 °C. The removal of Pb(II), Cr(Ⅲ) and Cu(II) increased with time and attained saturation in about 180 min, shown in Figure 5. Basically, the removal of sorbate is rapid but it gradually decreases with time until it reaches equilibrium. For an adsorbent amount of 2 g/L and initial metal ions 10 mg/L, the adsorption of Pb(II), Cr(Ⅲ) and Cu(II) was 45.7 %, 28.65 % and 37.25 %. The adsorption was in the order Pb(II) > Cu(II) > Cr(Ⅲ).
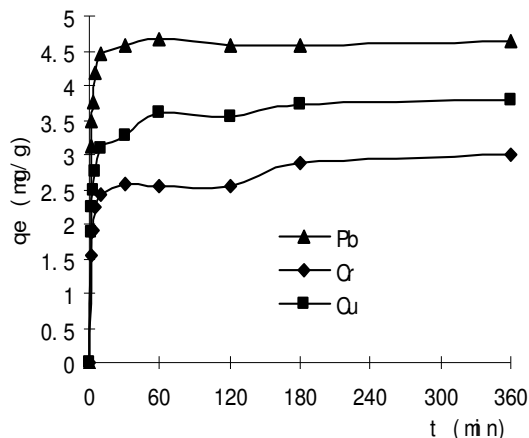
Figure 5. Variation of amount of Pb(II) , Cr(III) and Cu(II) adsorbed per unit mass of modified peanut husk (qe) with time at 298 K (peanut 2 g/L, initial metal ions 10 mg/L, pH 4, time 3 h).

Using Lagergren-first-order and second-order equations to investigate the adsorption of Pb(II), Cr(III) and Cu(II) on modified peanut husk, 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 3.

Table 3. Lagergren-first-order and Second-order rate parameters for Pb(II) , Cr(III) and Cu(II) adsorption on modified peanut husk (peanut 2 g/L, initial Pb(II), Cr(III) and Cu(II) 10 mg/L, pH 4, time 3 h)

Adsorbate	q_e (mg/g)	Lagergren-first-order			Second-order		
		$k^1 (10^{-2} min^{-1})$	$q_{e,c}$ (mg/g)	R^2	$k^1 (10^{-2} min^{-1})$	$q_{e,c}$ (mg/g)	R^2
Pb^{2+}	4.59	4.66	10.62	1.47462	2.948	4.6425	0.9999
Cr^{3+}	3.34	3.02	1.32	1.115497	0.674	2.9922	0.9966
Cu^{2+}	2.96	3.80	37.91	5.504137	4.026	3.8066	0.9996

The second-order equation appears 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 modified peanut husk might be a rate-limiting control [30, 31]. The adsorption of Cu(II) on modified peanut husk is faster.

CONCLUSIONS

The uptake of heavy metals on the peanut husk is influenced by pH and the amount adsorbed increases with gradually decreasing acidity. The adsorption is supported by Langmuir and Freundlich isotherms and the adsorption coefficients indicate favorable adsorption. Adsorption of heavy metals on the peanut husk takes place through sufficiently strong endothermic interactions accompanied by thermodynamically favorable entropy and Gibbs energy changes. The adsorption kinetics shows better agreement with the second-order equation.

REFERENCES

1. Li, Y.S.; Liu, C.C.; Chiou, C.S. *Water Environ. Res.* **2003**, 78, 263.
2. Wang, W.X.; Rainbow, P.S. *Ecotox. Environ. Saf.* **2005**, 61, 145.
3. Rainbow, P.S.; Amiard-Triquet, C.; Amiard, J.C.; Smith, B.D.; Best, S. L. *Mar. Eco-Pro. Ser.* **1999**, 183, 189.
4. Doye, I.; Duchesne, J. *Appl. Geochem.* **2003**, 18, 1197.
5. Moreno, N.; Querol, X.; Ayora, C.; Fernández-Pereira, C.; Janssen-Jurkovicová, M. *Environ. Sci. Technol.* **2001**, 35, 3526.
6. Lottermoser, B. *Mine Wastes-Characterization, Treatment and Environmental Impacts*; Springer: Berlin, **2003**.
7. Ziemkiewicz, P.F.; Skousen, J.G.; Simmons, J. *Mine Water Environ.* **2003**, 22, 118.
8. Methmet E.A.; Sukre D.; Celalettin O.; Mustafa K. *J. Hazard. Mater.* **2007**, 141, 77.
9. Katsuya, K.; Keiji, H.; Hiromasa, S.; Rabindra P.D.; Yoshinari, B. *Bioresource Tech.* **2007**, 98, 2787.
10. Shi, Q.; Zhou, R.; Jiao, H.X.; Li, M.J.; Liu, X.H. *J. Henan Univ.* **2004**, 2, 44.
11. Ricordel, S. *Sep. Purif. Technol.* **2001**, 24, 389.
12. Liao, C.D.; Liao, Z.F. *J. Guangxi Teachers College* **2004**, 1, 17.
13. Lin, C.Y.; Li, L. *Acta Sci. Circumstantiae* **2003**, 23, 738.
14. Ahmed, S.; Chughtai, S.; Keane, M. *Sep. Purif. Technol.* **1998**, 13, 57.
15. Gharaibeh, S.H.; Abu-el-sha'r, W. Y.; Al-Kofahi, M.M. *Water Res.* **1991**, 25, 499.
16. McKay, G.; Blair, H.S.; Gardner, J.R. *J. Appl. Polym. Sci.* **1982**, 27, 3043.
17. Khan, S.A.; Rehman, R.; Khan, M.A. *Waste Manage.* **1995**, 15, 271.
18. Namasivayam, C.; Kavitha, D. *J Hazard. Mater.* **2003**, B98, 257.
19. Chen, C.Y.; Zhuang, Y.Y. *J. Saf. Environ.* **2003**, 3, 46.
20. Otero, M.; Rozada, F.; Calvo, L.F.; Garcia, A.I.; Mordn, A. *Biochem. Engineer. J.* **2003**, 15, 59.
21. Zhang, X.J.; Land, H.Y. *Chinese J. Appl. Chem.* **2003**, 20, 749.
22. Browna, P. *Adv. Environ. Res.* **2000**, 4, 19.
23. Yu, L.J.; Shukla, S. S.; Dorris, K.L.; Shukla, A.; Margrave, J.L. *J. Hazard. Mater.* **2003**, 100, 53.
24. Mohan, D.; Gupta, V.K.; Srivastava, S.K.; Chander, S. *Colloid Surfaces A* **2001**, 177, 169.
25. Liao, C.D.; Liao, Z.F. *J. Guangxi Teachers Educ. University* **2004**, 21, 68.
26. Juang, R.S.; Shiau, J.Y.; Shao, H.J. *Sep. Sci. Technol.* **1999**, 34, 1819.
27. Azmal, M.; Mohammad, A.; Yousuf, R.; Ahmed, A. *Indian J. Environ. Health* **1998**, 40, 15.
28. Weber Jr., J.; McGinley, P.M.; Katz, L.E. *Water Res.* **1991**, 25, 499.
29. Cho, H.D.; Kim, Oh, K. *J. Hazard. Mater.* **2005**, B127, 187.
30. Ho, Y.S.; Mckay, G. *Water Res.* **2000**, 34, 735.
31. Panayotova, M.; Velikov, B. *J. Environ. Sci. Health A* **2002**, 37, 139.