Desalination and Water Treatment
www.deswater.com

doi: 10.1080/19443994.2013.769919

51 (2013) 7166–7171
November

Adsorption of Pb^{2+}, Cu^{2+} and Ni^{2+} from aqueous solutions by novel garlic peel adsorbent

Sha Liang, Xueyi Guo*, Qinghua Tian

School of Metallurgical Science and Engineering, Central South University, Changsha 410083, China
Tel./Fax: +86 731 88836207; email: xyguo@mail.csu.edu.cn

Received 11 December 2012; Accepted 18 January 2013

ABSTRACT

The viability of garlic peel (GP) to remove Pb^{2+}, Cu^{2+}, and Ni^{2+} was evaluated in this paper. Characterization of prepared GP adsorbent was performed using scanning electron microscopy and Fourier-transform infrared spectrophotometer. Batch experiments were carried out to investigate the effects of pH, temperature, time, and initial metal ion concentration on the adsorption of single heavy metal ion by GP. Competitive adsorption of binary mixture (Pb^{2+}/Cu^{2+} and Pb^{2+}/Ni^{2+}) by GP was also investigated. The results showed that the adsorption process could attain equilibrium within 20 min, and kinetics was found to fit pseudo-second-order equation. GP had remarkable higher adsorption affinity for Pb^{2+} than Cu^{2+} and Ni^{2+} with the maximum adsorption capacity as 209 mg/g. The adsorption efficiency and uptake capacity of one metal ion were reduced by the presence of the other metal ion. The adsorption mechanism was supposed to be ion exchange between Ca^{2+} of GP with heavy metal ions in the solution.

Keywords: Garlic peel; Heavy metal ions; Competitive adsorption

1. Introduction

Water contamination by toxic heavy metal ions arising from the discharge of untreated metal containing effluent is a major concern. The heavy metal ions are stable and persistent environmental contaminants since they cannot be degraded and destroyed. Although heavy metal removal from inorganic effluent can be achieved by conventional treatments such as chemical precipitation, electrochemical treatment, ion exchange and membrane technologies, each treatment has its inherent limitation. For low concentrations of metal ions, biosorption of heavy metals from wastewater has emerged in response to the shortcomings of the conventional physicochemical treatments, as can be considered a cost-effective and ecological alternative in this field of environmental pollution [1,2].

Agricultural by-products are usually composed of lignin and cellulose as major constituents and may also include other polar functional groups of lignin. These groups, including alcohols, aldehydes, ketones, carboxylic, phenolic, and ether groups, have the ability to bind heavy metal ions through complexation or ion exchange [3]. Garlic peel (GP), low-cost agricultural waste, could be used for the effective removal and recovery of heavy metal ions form wastewater streams. Due to the high consumption of garlic, massive amounts of peels are disposed, causing a severe problem in the community [4]. The aim of this work was to evaluate the potential of GP for the removal of Pb^{2+}, Cu^{2+}, and Ni^{2+} from aqueous solutions.

---

*Corresponding author.

2. Experimental

2.1. Chemicals

All chemicals used in this study were of pure analytical grade. Stock solutions (1.0 g/L) of single heavy metal were prepared by dissolving $CuCl_2 \cdot 2H_2O$, $Pb(NO_3)_2$ and $Ni(NO_3)_2 \cdot 6H_2O$ in double-distilled water, respectively, then diluted to desired concentrations when used. 0.1 mol/L HCl and 0.1 mol/L NaOH were used to adjust the solution pH.

2.2. Preparation and characterization of GP adsorbent

GP used in this study was collected from the vegetable market inside our university, Changsha, China. The sample was sopped in tap water for two days, and then was washed many times to remove mud and some other attachments. After that, the sample was washed with double-distilled water several times and then was freeze dried for 24 h. The dried GP was crushed to obtain the average particle size around 500–800 μm. Surface morphology of GP was studied by scanning electron microscopy (SEM) analysis using a JSM-5600LV scanning electron microscope. Fourier-transform infrared (FTIR) spectrum of GP was taken with a Fourier-transform infrared spectrophotometer (JASCO FT/IR-410, Japan). Pressed pellets were prepared by grinding the powder specimens with spectroscopic grade KBr for FTIR spectra test.

2.3. Batch adsorption experiment

Batch adsorption experiments were conducted to evaluate the effects of some parameters including solution pH, temperature, time and initial concentration on the adsorption of Pb^{2+}, Cu^{2+}, and Ni^{2+} by GP. A fixed amount of GP (20 mg) was added to 10 mL metal ion solution with various initial pH (1.5, 2.5, 3.5, 4.5, 5.5), temperature (30, 40, 50, 60℃), time (1, 3, 5, 7, 10, 15, 20, 40, 60, 90, 120 min) and initial metal ion concentration (100, 200, 300, 400, 500, 600, 800, 1,000 mg/L). The mixture was shaken at a speed of $100\,\text{min}^{-1}$ in a thermostated shaker. After adsorption, the mixture was filtered and the adsorption efficiency was calculated by analyzing the metal ion concentration in filtrate by using an AA-6650 atomic absorption spectrophotometer (AAS, Shimadzu).

The adsorption efficiency (Adsorption%) and the amount of metal adsorbed at equilibrium (q_e) were determined by using the following equation:

$$\text{Adsorption\%} = \frac{C_0 - C_e}{C_0} \times 100\% \tag{1}$$

$$q_e = \frac{(C_0 - C_e)V}{m} \tag{2}$$

where C_0 and C_e represent the initial and equilibrium metal ions concentrations (mg/L), respectively; V is the volume of the solutions (mL) and m is the amount (mg) of adsorbent. All the adsorption experiments were conducted in duplicate, and the mean values were calculated. The results were reproducible at most 5% error.

3. Results and discussion

3.1. Characterization of the GP adsorbent

SEM is widely used to study the morphological features of the adsorbent. An observation of the SEM micrograph of GP (Fig. 1) indicates the irregular and porous surfaces, which assure that GP has an adequate morphology for binding metal ions. EDAX is usually used to analyze the elemental constitution of solid samples and the results show the principal elements of GP are C, H, O, N, and Ca. The existence of Ca element is due to the calcium component such as calcium pectate in the cell wall of GP.

FTIR spectrum of GP is shown in Fig. 2. The broad and intense absorption peaks at around $3{,}425\,\text{cm}^{-1}$ correspond to the O–H stretching vibrations due to inter- and intra-molecular hydrogen bonding of polymeric compounds (macromolecular associations), such as alcohols, phenols, and carboxylic acids, as in pectin, cellulose and lignin [5], thus, showing the presence of "free" hydroxyl groups on the adsorbent surface. The peaks at $2{,}917\,\text{cm}^{-1}$ are attributed to the symmetric

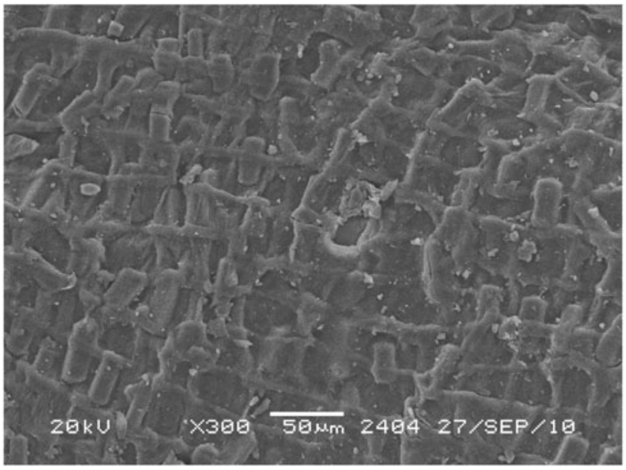

Fig. 1. SEM micrograph of GP (magnification: 300×).

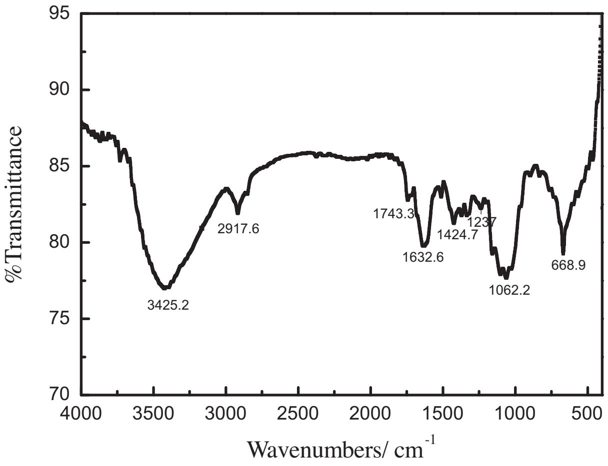

Fig. 2. FTIR spectra of GP.

and asymmetric C–H stretching vibration of aliphatic acids [6]. The peak observed at 1,743 cm^{-1} is the stretching vibration of bond due to non-ionic carboxyl groups (–COOH, –COOCH$_3$), and may be assigned to carboxylic acids or their esters [6]. The peaks at 1,632 and 1,424 cm^{-1} are due to asymmetric and symmetric stretching vibrations of C=O in ionic carboxylic groups (–COO$^-$), respectively [7]. Aliphatic acid group vibration at 1,237 cm^{-1} may be assigned to deformation vibration of C=O and stretching formation of –OH of carboxylic acids and phenols [8]. Peaks at 1,062 cm^{-1} may be due to stretching vibration of C–OH of alcoholic groups and carboxylic acids.

3.2. Effect of equilibrium pH

Solution pH is the most important parameter that affects the surface charge of the adsorbent and metal speciation. The influence of equilibrium pH on the adsorption of Pb^{2+}, by GP is shown in Fig. 3. It can be seen that pH has strong effect on the adsorption efficiency, which increased with the increasing pH and achieved maximum value at equilibrium pH around 5.5. Lower adsorption at lower pH is probably due to the presence of excess of H$^+$ ions competing with the metal ions for adsorption sites. At higher pH values, the lower number of H$^+$ and greater number of ligands with negatives charges result in greater metal ion adsorption [9]. Obviously, GP has higher affinity for Pb^{2+} than Cu^{2+} and Ni^{2+}.

3.3. Effect of temperature

Fig. 4 shows the effect of temperature on the adsorption of Pb^{2+}, Cu^{2+}, and Ni^{2+}. It turns out that temperature had different effects on the adsorption for different metal ions. The adsorption efficiency for Pb^{2+} kept high values above 99% under tested temperatures, but for Cu^{2+} and Ni^{2+}, temperature had negative effect.

3.4. Adsorption kinetics

The adsorption kinetics was investigated for better understanding of the dynamics of adsorption of Pb^{2+}, Cu^{2+} and Ni^{2+} onto GP. Effect of adsorption time is shown in Fig. 5. It can be concluded that all the adsorption process proceeded rapidly and could attain equilibrium within 20 min. The fast adsorption rate reflects good accessibility of the binding sites of the GP to metal ions. This has practical advantages in terms of reducing reactor volumes and time.

The pseudo-second-order kinetic model (3), which assumes the rate is proportional to the square of the

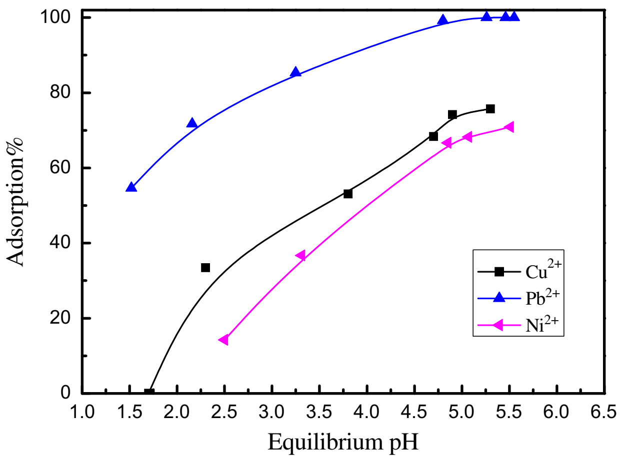

Fig. 3. Effect of equilibrium pH on the adsorption of Pb^{2+}, Cu^{2+} and Ni^{2+} by GP (C$_0$: Pb^{2+} 100 mg/L, Cu^{2+} or Ni^{2+} 50 mg/L; 30°C, 1.5 h).

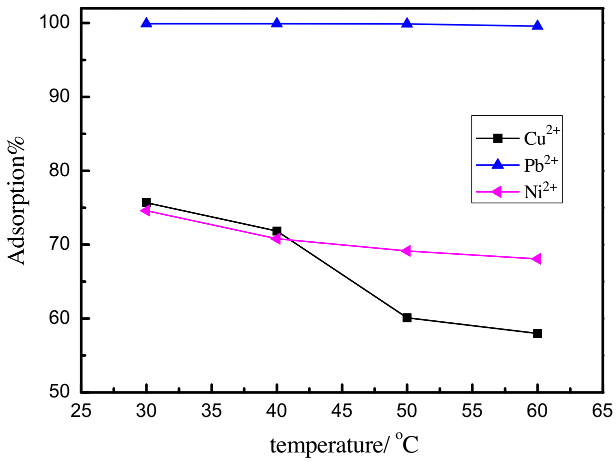

Fig. 4. Effect of temperature on the adsorption of Pb^{2+}, Cu^{2+} and Ni^{2+} by GP (C$_0$: Pb^{2+} 100 mg/L, Cu^{2+} or Ni^{2+} 50 mg/L; pH 5.5, 1.5 h).

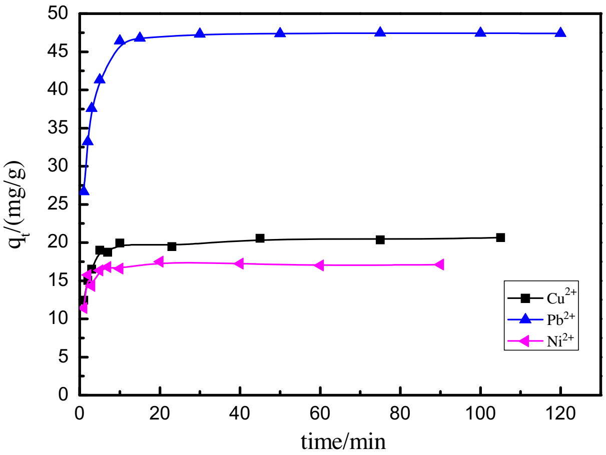

Fig. 5. Effect of adsorption time on the adsorption of Pb^{2+} Cu^{2+} and Ni^{2+} by GP (C_0: Pb^{2+} 100 mg/L, Cu^{2+} or Ni^{2+} 50 mg/L; pH 5.5; 30°C).

Table 1
Kinetics parameters of the pseudo-second-order rate equation for metal ions adsorption

Metal ion	$q_{e.exp}$ (mg/g)	$q_{e.cal}$ (mg/g)	k_2(g/(mg·min))	R^2
Pb^{2+}	47.4	47.7	0.036	0.9999
Cu^{2+}	20.5	20.7	0.067	0.9997
Ni^{2+}	17.1	17.2	0.235	0.9997

number of remaining free surface sites was used to model the data in Fig. 5 [10].

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{3}$$

where q_t and q_e are the amounts of ion adsorbed at time t and at equilibrium (mg/g), respectively, and k_2 is the constant of pseudo-second-order rate (g/(mg·min)). The modeled results are shown in Table 1, from which it can be seen that the adsorption process fitted well to the pseudo-second-order equation with $R^2 > 0.999$.

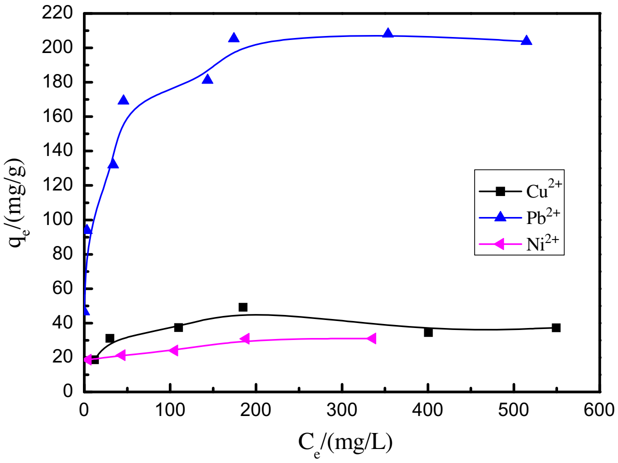

Fig. 6. Adsorption isotherm of adsorption of Pb^{2+}, Cu^{2+} and Ni^{2+} by GP (pH 5.5, 1.5 h, 30 ℃).

3.5. Adsorption isotherms

The equilibrium adsorption isotherm experiments were performed by plotting metal ions adsorbed (q_e) against the equilibrium concentration of metal ions (C_e) in solution (Fig. 6). It can be seen from Fig. 6 that adsorption capacity increased with the increasing metal ion concentration until adsorption saturation was reached. GP showed remarkable high adsorption ability for Pb^{2+} ions compared with Cu^{2+} and Ni^{2+} ions.

The analysis of the isotherm data by fitting them to different isotherm model is an important step to find the suitable model that can be used for design purpose. Both Langmuir (4) and Freundlich (5) models were used to analyze the isotherm data [11,12]:

$$\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{1}{q_m} C_e \tag{4}$$

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \tag{5}$$

where q_m is the maximum amount of adsorption (mg/g), K_L the adsorption constant (L/mg), K_F the constant representing the adsorption capacity, and n is the constant depicting the adsorption intensity.

Table 2
A comparison of Langmuir and Freudlich isotherm model

Metal ion	Langmuir model			Freundlich model		
	q_m (mg/g)	K_L (L/mg)	R^2	K_F	$1/n$	R^2
Pb^{2+}	209	0.112	0.998	80.85	0.163	0.927
Cu^{2+}	37	0.129	0.996	16.02	0.143	0.659
Ni^{2+}	32	0.564	0.987	14.70	0.123	0.849

Table 3
Lead adsorption capacity of some natural agricultural by-product reported in literatures

Adsorbent	q_m(mg/g)	References
Garlic peel	209	This study
Orange peel	90	[14]
Tea waste	65	[15]
Wheat bran	64	[16]
Mango peel waste	99	[17]
Maize bran	143	[18]
Sago waste	47	[19]
Grape bagasse	42	[7]

Table 2 shows the applicability of Langmuir and Freundlich models for Pb^{2+}, Cu^{2+} and Ni^{2+} adsorption by GP. It can be concluded that the isotherm data were better fitted Langmuir model, which assumes that all adsorption sites are equivalent and adsorption in active sites is independent of whether the adjacent is occupied. Both Langmuir isotherm and pseudo-second-order kinetic model assume that the surface of GP is homogenous and the operating adsorption mechanism is chemisorption involving valency forces through sharing or exchange of electrons between ions and GP [13]. The maximum Langmuir adsorption capacities of Pb^{2+}, Cu^{2+} and Ni^{2+} on GP were calculated as 209, 37 and 32 mg/g, respectively. A comparison of adsorption capacity of Pb^{2+} by some other biosorbents reported in the literatures is listed in Table 3. It can be seen that without any chemical modification, raw GP exhibits excellent adsorption ability for Pb^{2+} ions.

3.6. Adsorption of ions from binary metal solutions

Although the adsorption capacity for Pb^{2+} by GP is relatively high in single lead solution, practical industrial wastewater always contains several heavy metal ions rather than target metal ion. In order to test the adsorption ability for Pb^{2+} by GP in mixture solutions, effects of the presence of Cu^{2+} and Ni^{2+} ions on the adsorption of Pb^{2+} ions were investigated in terms of adsorption efficiency and equilibrium isotherm.

Fig. 7(a) shows the effect of Cu^{2+} and Ni^{2+} ions with increasing concentrations on the adsorption efficiency of 100 mg/L of Pb^{2+} ions at pH 5.5. As showed in Fig. 7(a), the results indicated that the equilibrium uptake of Pb^{2+} decreased with the concentration of Cu^{2+} or Ni^{2+} kept increasing. Ni^{2+} ion in the binary solution did not affect Pb^{2+} uptake as much as Cu^{2+} ion. Analogously, the effect of Pb^{2+} ions on the Cu^{2+} and Ni^{2+}adsorption on GP is shown in Fig. 7(b). The uptake of both Cu^{2+} and Ni^{2+} ions, especially for Ni^{2+}, dropped quickly when Pb^{2+} ions coexisted in the solution.

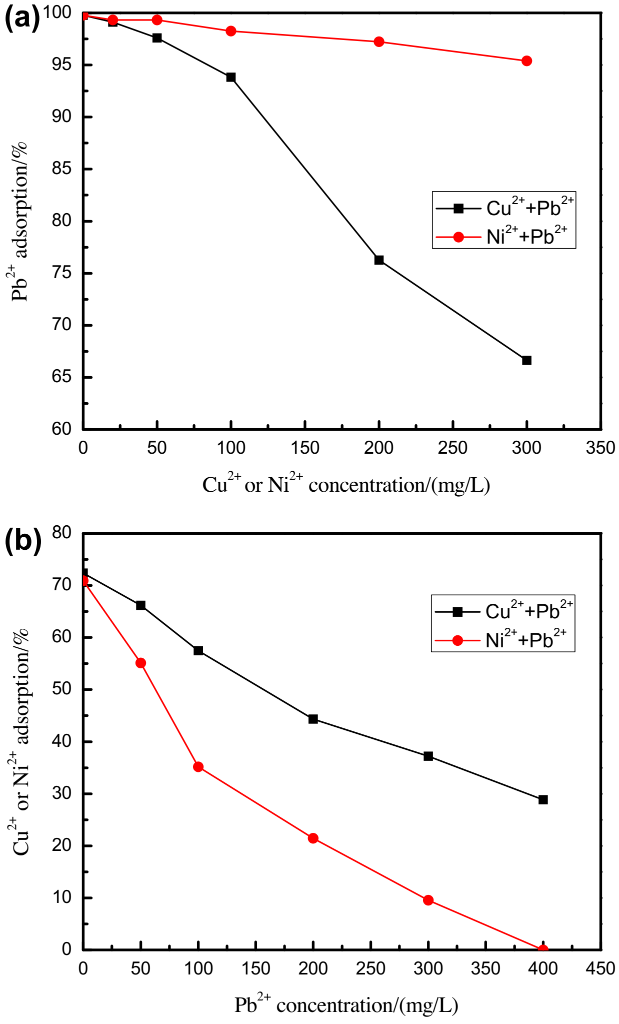

Fig. 7. (a) Effect of Cu^{2+} and Ni^{2+} on Pb^{2+} adsorption by GP; (b) Effect of Pb^{2+} on Cu^{2+} and Ni^{2+} adsorption by GP.

In Fig. 8, the adsorption isotherm of Pb^{2+} in the presence of Cu^{2+} and Ni^{2+} with various concentrations as 50 and 100 mg/L was compared with the results in the single-ion situation. As shown in Fig. 8, the adsorption of Pb^{2+} by GP in the binary system followed the same adsorption isotherm pattern, with the equilibrium capacity lower than that for the single Pb^{2+} ions. The maximum Langmuir adsorption capacities calculated for Pb^{2+} present in binary mixture were 126 mg/g (with 50 mg/L of Cu^{2+}), 123 mg/g (with 100 mg/L of Cu^{2+}), 150 mg/g (with 50 mg/L of Ni^{2+}), 142 mg/g (with 100 mg/L of Ni^{2+}) compared with 209 mg/g in single Pb^{2+} solution. A fixed quantity of GP could only offer a finite number of surface binding sites, some of which would be expected to be saturated by the competing metal ions, especially at relatively high concentration of them, and this was indeed observed.

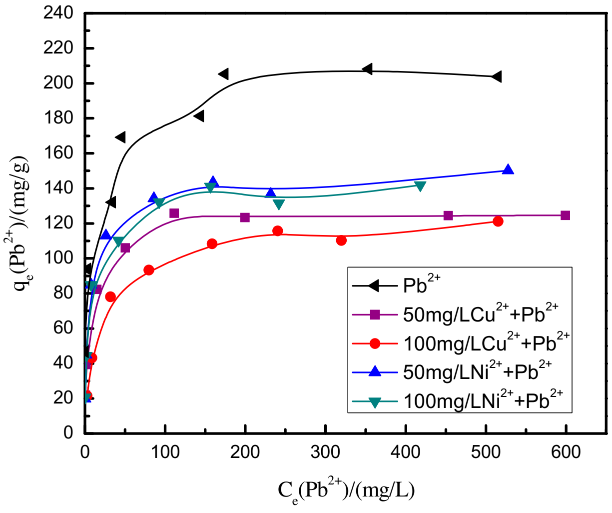

Fig. 8. Adsorption isotherm of Pb^{2+} by GP in single and binary solutions.

3.7. Adsorption mechanism

In the literatures, different mechanism for the adsorption of heavy metal ions onto biosorbents has been proposed. These include physical attraction, ion-exchange, complexation, and oxidation-reduction. It is commonly believed that ion-exchange is the most prevalent mechanism. In our experiments, under certain experiment conditions (C_0: Pb^{2+} 100 mg/L, Cu^{2+} or Ni^{2+} 50 mg/L; pH 5.5; 100 mg/20 mL; 30°C; 2 h), the released amount of Ca^{2+} was detected in the filtrate after adsorption of heavy metal ions by AAS. The results showed that the equivalent concentrations of Pb^{2+}, Cu^{2+}, Ni^{2+} absorbed onto GP were calculated as 0.179, 0.253 and 0.255 meq/g and the equivalent concentrations of Ca^{2+} released into the solution were 0.302, 0.472 and 0.433 meq/g, respectively. This means Ca^{2+} in the GP was replaced with M^{2+} (Pb^{2+}, Cu^{2+}, Ni^{2+}), moreover, some other calcium components were decomposed and released into the solution.

4. Conclusions

GP, an inexpensive and easily available material, was used to remove Pb^{2+}, Cu^{2+} and Ni^{2+} from aqueous solutions. Solution pH had great influence on the adsorption efficiency. The effect of temperature was insignificant except for Cu^{2+}. The adsorption kinetics was found to fit pseudo-second-order equation. The maximum adsorption capacity of Pb^{2+} by GP was 209 mg/g, which is much higher than many raw natural materials reported in literatures. Competitive adsorption was conducted in binary mixture and the results showed that the uptake capacity of one metal ion was reduced by the presence of the other metal ion. Adsorption mechanism was supposed to be ion exchange.

Acknowledgment

This work was financially supported by grant 50774100 of the National Natural Science Foundations (NNSF) of China and China Scholarship Council (2011).

References

[1] S.S. Ahluwalia, D. Goyal, Microbial and plant derived biomass for removal of heavy metals from wastewater, Bioresour. Technol. 98 (2007) 2243–2257.
[2] T.A. Kurniawan, G.Y.S. Chan, W. Lo, S. Babel, Comparison of low-cost adsorbents for treating wastewaters laden with heavy metals, Sci. Total Environ. 366 (2006) 409–426.
[3] S.E. Bailey, T.J. Olin, R.M. Bricka, D.D. Adrian, A review of potentially low-cost sorbents for heavy metals, Water Res. 33 (1999) 2469–2479.
[4] B.H. Hameed, A.A. Ahmad, Batch adsorption of methylene blue from aqueous solution by garlic peel, an agricultural waste biomass, J. Harzard. Mater. 164 (2009) 870–875.
[5] R. Gnanasambandam, A. Protor, Determination of pectin degree of esterification by diffuse reflectance Fourier transform infrared spectroscopy, Food Chem. 68 (2000) 327–332.
[6] F.T. Li, H. Yang, Y. Zhao, R. Xu, Novel modification pectin for heavy metal adsorption, Chin. Chem. Lett. 18 (2007) 325–328.
[7] N.V. Farinella, G.D. Matos, M.A.Z. Arruda, Grape bagasse as a potential biosorbent of metals in effluent treatments, Bioresour. Technol. 98 (2007) 1940–1946.
[8] G. Guibavd, N. Tixier, A. Bouju, M. Baudu, Relation between extracellular polymer's composition and its ability to complex Cd, Cu and Pb, Chemosphere 52 (2003) 701–1710.
[9] M. Khormaei, B. Nasernejad, M. Edrisi, T. Eslamzadeh, Copper biosorption from aqueous solutions by sour orange residues, J. Harzard. Mater. 149 (2007) 269–274.
[10] Y.S. Ho, G. Mckay, The kinetics of sorption of basic dyes from aqueous solution by sphagnum moss peat, Can. J. Chem. Eng. 76 (1998) 822–827.
[11] H.M.F. Freundlich, Uber die adsorption in Losungen, Z. Phys. Chem. 57 (1906) 385–470.
[12] I. Langmuir, The adsorption of gases on plane surfaces of glass, mica and platinum, J. Am. Chem. Soc. 40 (1918) 1361–1403.
[13] İ.A. Şengil, M. Özacar, Competitive biosorption of Pb^{2+}, Cu^{2+} and Zn^{2+} ions from aqueous solutions onto valonia tannin resin, J. Hazard. Mater. 166 (2009) 1488–1494.
[14] S. Liang, X.Y. Guo, N.C. Feng, Q.H. Tian, Application of orange peel xanthate for the adsorption of Pb^{2+} from aqueous solutions, J. Hazard. Mater. 170 (2009) 425–429.
[15] B.M.W.P.K. Amarasinghe, R.A. Williams, Tea waste as a low cost adsorbent for the removal of Cu and Pb from wastewater, Chem. Eng. J. 132 (2007) 299–309.
[16] M.A. Farajzadeh, A.B. Monji, Adsorption characteristics of wheat bran towards heavy metal cations, Sep. Purif. Technol. 138 (2004) 197–207.
[17] M. Iqbal, A. Saeed, S. Iqbal Zafar, FTIR spectrophotometry, kinetics and adsorption isotherms modeling, ion exchange, and EDX analysis for understanding the mechanism of Cd^{2+} and Pb^{2+} removal by mango peel waste, J. Hazard. Mater. 164 (2009) 161–171.
[18] K.K. Singh, M. Talat, S.H. Hasan, Removal of lead from aqueous solutions by agricultural waste maize bran, Bioresour. Technol. 97 (2006) 2124–2130.
[19] S.Y. Quek, D.A.J. Waste, C.F. Forster, The use of sago waste for the sorption of lead and copper, Water SA 24(3) (1998) 251–256.