Asian Journal of Chemistry; Vol. 27, No. 5 (2015), 1805-1810

ASIAN JOURNAL OF CHEMISTRY

http://dx.doi.org/10.14233/ajchem.2015.17916

Removal of Aqueous Pb(II) Using Low-Cost Agricultural Wastes Modified by 3-Aminopropyltrimethoxysilane

ZHUHONG DING[1,*], RUI YU[1], XIN HU[2] and YUFENG ZHANG[1]

[1]School of Environment, Nanjing University of Technology, 30 Puzhu Southern Road, Nanjing 211816, P.R. China
[2]State Key Laboratory of Analytical Chemistry for Life Science, Center of Material Analysis, 20 Hankou Road, Nanjing University, Nanjing 210093, P.R. China

*Corresponding author: Tel.: +86 25 58139654; E-mail: dzhuhong@njtech.edu.cn

Received: 29 April 2014; *Accepted*: 2 July 2014; *Published online*: 20 February 2015; AJC-16895

In order to develop the low-cost and high efficient absorbents, agricultural by-products *e.g.*, peanut hulls, soybean shells and grapefruit peels were chemically modified with 3-aminopropyltrimethoxysilane after the saponification using 17.5 % NaOH. Chemical modification was confirmed by infrared spectra and N contents. The optimum adsorption parameters for Pb(II) were around 4.5 for pH and 2 g L^{-1} for ratio of solid to liquid. The kinetic adsorption fitted well with the pseudo-second order kinetic model and the isotherm adsorption fitted well with Langmuir adsorption model. The maximum absorption capacities of chemically-modified peanut hulls, soybean shells and grapefruit peels were 32.9, 75.8 and 154 mg g^{-1}, respectively. More than 90 % Pb(II) can be desorbed from modified biosorbents using 1 mol L^{-1} HCl solution. Chemically-modified grapefruit peels exhibited higher absorption capacities and can be used as potential the low-cost and high efficient absorbents for the removal of Pb(II) from wastewater.

Keywords: Batch adsorption, Kinetics, Isotherm, Peanut hulls, Soybean shells, Grapefruit peels.

INTRODUCTION

Adsorption techniques as well as chemical precipitation, ion exchange, membrane filtration, electrolytic methods, reverse osmosis and solvent extraction have been widely investigated for the removal of metals from wastewater[1,2]. However, most of these techniques have high preparation and/or running costs and thus cost-effective alternative adsorbents have been one of the hot issues of recent researches for environmental protection. The biosorbent is an adsorbent of natural origin such as residuals of agricultural activities and wastes from food industries that are available in large amounts. For example, nutshells, fruit stones, bagasse and agricultural residues from sugarcane, rice and peanut hulls, sawdust, *etc.* have been investigated as potential precursors for adsorption of metal ions from wastewater[3-7]. These agricultural by-products are mainly composed of lignin and cellulose. The polar functional groups of these constituents such as aldehydes, ketones, carboxylic, phenolic and ether groups have the ability to bind heavy metals by replacing hydrogen ions with metal ions in solution or by donating an electron pair from these groups to form complexes with the metal ions in solution[3].

Although these adsorbents are effective in a wide range of solutes, particularly divalent metal cations, they suffer from some drawbacks such as low exchange or sorption capacity, poor physical stability (*i.e.* partial solubility) and discolouration into solution of some agricultural by-products such as peanut hulls and rice shell. In order to overcome these problems, chemical activation and/or modification of the raw adsorbents are required. Chemical activation was carried out using base solutions (sodium hydroxide), mineral and organic acid solutions (nitric acid, sulfuric acid, citric acid, *etc.*) and oxidizing agent (hydrogen peroxide) at various concentrations to remove soluble organic compounds and to enhance adsorption efficiency[8-11]. Now, biosorbents functionalized with coordination ligands like amine, carboxyl, sulphonic, amide and so forth have been investigated to improve the sorption capacity of pollutants from wastewater[12-14]. In particular amino group onto an adsorbent has been found to be one of the most effective groups for adsorption of heavy metals from aqueous solution. For example, triethylamine was introduced into wheat residue to improve the removal of Cr(VI) ions from aqueous solution[15]. The removal of Cu, Co, Ni and Zn from aqueous solution was increased when cellulose modified with 2-aminomethylpyridine[16].

In this study the agricultural by-products-peanut hulls, soybean shells and grapefruit peels were treated with 17.5 % NaOH solution to remove soluble compounds and to reduce

hemicellulose and lignin. The mercerized peanut hulls, soybean shells and grapefruit peels were reacted with 3-aminopropyltrimethoxysilane, a silanization reagent under the catalysis of methylbenzene. 3-Aminopropyltrimethoxysilane-modified peanut hulls, soybean shells and grapefruit peels were used for adsorption of Pb(II) in aqueous solution. The modified adsorbents were characterized by using scanning electron microscopy, elemental analyzer and Fourier-transform infrared spectrometer. Factors affecting the adsorption behaviour of Pb(II), such as pH, ratio of solid to liquid, competitive sorption of various metal ions, initial metal concentration and adsorption time, were then investigated. The adsorption performance of the modified peanut hulls, soybean shells and grapefruit peels was compared.

EXPERIMENTAL

Preparation of chemically-modified biosorbents: Peanut hulls, soybean shells and grapefruit peels were collected from local farmers' market. They were washed in running tap water and then transferred to an oven set at 65 °C to dry. The dried raw biomass were milled by a universal high-speed smashing machine (FW80, Tianjin Taisite Instrument Co., Ltd., China) and sieved by using an 80-mesh sieve. The raw powders were washed several times with distilled water (18.2 MO) (Milli Q Advantage A10 System,, Millipore China Ltd.) to remove adhering colouration and impurities and then dried at 65 °C. The raw powders of peanut hulls, soybean shells and grapefruit peels were treated with 17.5 % NaOH for 72 h to remove soluble compounds and to reduce hemicellulose and lignin and then washed several times with distilled water near neutral pH and dried.

The dose of the 3-aminopropyltrimethoxysilane, reaction temperature and time were optimized using orthogonal experiments in pre-experiment for the modified reaction and they were 3 mL 3-aminopropyltrimethoxysilane at 100 °C for 10 h for mercerized soybean shells (6 g) and for 6 h for the mercerized peanut hulls and grapefruit peels and (6 g), respectively. Under the catalysis of methylbenzene, 3-aminopropyltrimethoxysilane was reacted with mercerized peanut hulls, soybean shells and grapefruit peels under the optimized parameters. After filtering and washing, the 3-aminopropyltrimethoxysilane modified biosorbents were obtained and they were abbreviated as AP, AS and AG, respectively.

Properties of chemically-modified biosorbents: The contents of N in the mercerized and the chemically-modified peanut hulls, soybean shells and grapefruit peels were determined using an elemental analyzer (EA) (Vario MICRO, Elementar) *via* high-temperature catalyzed combustion followed by thermal conductivity detection of the resulting N_2 gases.

Morphological analyses of the mercerized and the chemically-modified peanut hulls, soybean shells and grapefruit peels were performed using scanning electron microscopy (SEM) (model S-3400N II, Hitachi Co., Tokyo, Japan) with an accelerating voltage of 20 kV. The sample was fixed on an aluminum holder and sputtered with platinum. Representative micrographs of the raw biomass and chemically-modified biosorbents were obtained at 500 × magnification with a secondary electron detector.

Infrared spectra of the mercerized and the chemically-modified peanut hulls, soybean shells and grapefruit peels were recorded using a fourier-transform infrared spectrometer (FT-IR, NEXUS870, NICOLET Co., USA) in the range 4000-500 cm^{-1}, using a KBr disc containing 1 % of finely ground sample produced using a bench press.

Batch adsorption experiments: Batch adsorption experiments were carried out at a room temperature (20 ± 2 ºC) by adding 0.1 g adsorbent to 100 mL polyethylene centrifuge tubes containing 50 mL Pb(II) solution of desired concentrations. The solution pH was adjusted using 0.01 mol L^{-1} NaOH and 0.01mol L^{-1} HCl. After equilibration by shaking for a certain contact time in a rotary shaker, the mixture was centrifuged at 4000 rpm for 10 min. Then Pb(II) in the supernatant was determined using inductively coupled plasma optical spectrometry (ICP-OES, Optima 5300, Perkin-Elmer SCIEX) as soon as possible. The adsorption percentage (Q%) and the amount of adsorbed Pb(II) (q_t) per unit adsorbent mass were calculated were calculated using the following equations[17]:

$$Q\ (\%) = [(C_0\text{-}C_t)/C_0] \times 100$$

$$q_t = [(C_0\text{-}C_t)\ V]/m$$

where C_0 and C_t are the initial and equilibrium concentration of Pb(II) at time 0 and *t* (mg L^{-1}), respectively; q_t is the amount adsorbed (mg g^{-1}) at time *t*; V is the volume of the solution (L); and m is the mass of the adsorbent (g).

Influence of biosorbents' dose was carried out using 100 mg L^{-1} Pb(II) solution with 3 h at pH 4.6 under different solid/liquid ratios (20, 10, 4, 2 and 1 g L^{-1}). The effects of solution pH (from pH 2 to pH 7) on the equilibrium adsorption of Pb(II) were investigated using 100 mg L^{-1} Pb(II) solution with 3 h under the solid/liquid ratios of 2 g L^{-1}. In the kinetic tests, 0.1 g of adsorbent was added to 50 mL of 100 mg L^{-1} Pb(II) solution with the contact time between 1 and 360 min. In the isotherm experiments, 0.1 g of adsorbent was added to 50 mL of Pb(II) solution of concentrations between 1 and 300 mg L^{-1}. The simultaneous sorption of Cd (5 mg L^{-1}), Cr (20 mg L^{-1}), Cu (20 mg L^{-1}), Ni (20 mg L^{-1}), Pb (20 mg L^{-1}) and Zn (20 mg L^{-1}) was investigated with 3 h at pH 4.6 under the solid/liquid ratios of 2g L^{-1}. All the adsorption experiments were conducted in duplicate and the mean values are reported.

Desorption tests: They were performed in an identical manner to the sorption tests. The pellets obtained by centrifugation in the sorption stage were dried at 65 ºC, weighed and resuspended in 1 mol L^{-1} HCl with 3 h under the solid/liquid ratios of 2 g L^{-1} at room temperature in a rotary shaker. After equilibration the mixture was centrifuged at 4000 rpm for 10 min. Then Pb(II) in the supernatants was determined using ICP-OES.

RESULTS AND DISCUSSION

Properties of chemically-modified biosorbents

SEM images of the mercerized biomass and chemically-modified peanut hulls, soybean shells and grapefruit peels were shown in Fig. 1. As can be seen from the Fig. 1, the mercerized peanut hulls, soybean shells and grapefruit peels had large particles, a compacter configuration and a low porosity. Chemically-modified biosorbents had a rougher surface, a looser structure and higher porosity. Therefore, the chemically-modification might increase the binding sites of Pb(II).

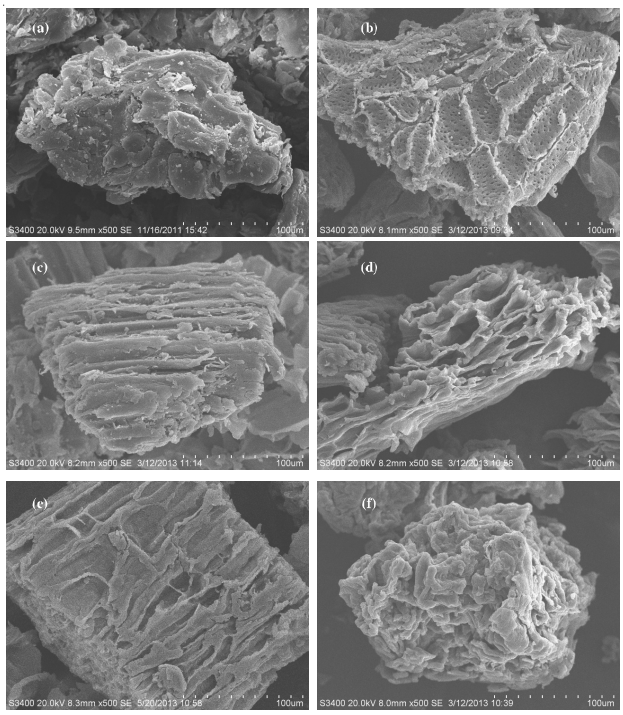

Fig. 1. SEM images of raw and modified peanut hulls (a and b), soybean shells (c and d) and grapefruit peels (e and f)

FTIR spectra of the mercerized biomass and chemically-modified peanut hulls, soybean shells and grapefruit peels were shown in Fig. 2. As shown in Fig. 2, the broad and intense absorption peak around 3400 cm^{-1} can be attributed to hydroxyl OH (alcohols, phenols and carboxylic acids) group stretching vibration absorption peak; the peak observed around 2920 cm^{-1} corresponds to the C-H stretching vibration of the CH, CH_2 and CH_3 bond; the peak observed at 1730 cm^{-1} is the stretching vibration of the C=O bonds from non-ionic carboxyl groups (-COOH, -$OOCH_3$) and may be from carboxylic acids or their esters[18]; 1370 cm^{-1} is carbonyl vibration of C=O (-COOH, -$COOCH_3$) absorption peak; the peak around 1370 cm^{-1} is ascribed to C-H deformation vibration absorption peak in the cellulose and hemicellulose[19].

Compared with the mercerized biomass, the C=O vibration peak in the vicinity of 1730 cm^{-1} disappeared, indicating the C=O bond of the mercerized peanut shells, soybean hulls and grapefruit peels may be involved in the reaction; the C-H deformation vibration absorption peak in cellulose and hemicellulose in the vicinity of 1370 cm^{-1} decreased. While apparent peak at 897.4, 896.3 and 895.5 cm^{-1} for non-plane rocking vibration peaks of -NH_2 improved. These changes indicated the successful chemical modification.

The nitrogen contents of the mercerized biomass and chemically-modified biosorbents were 0.80 and 1.12 % for peanut hulls, 0.82 and 1.23 % for soybean shells and 0.85 and 1.26 % for grapefruit peels, respectively. The nitrogen contents N contents in modified biosorbents were all higher than that in the mercerized biomass, indicating that amino group successfully grafted onto the peanut shell, soybean hull and grapefruit peel powders.

Operating variables influenced Pb(II) adsorption onto modified biosorbents: Lead(II) adsorption efficiency increases with the increase of solution pH from 2 to 7, indicating that the initial pH has great effects on Pb(II) adsorption [Fig. 3 (a)]. For example, the removal rates were 7.01 % for AP, 33.3 % for AS and 67.1 % for AG at pH of 2, respectively [Fig. 3 (a)]. The removal rates increased with the increasing pH and arrived at a relatively stable level (about 100 %) [Fig. 3 (a)]. The pH has effects on the protonation of the functional groups on the biosorbent surface, such as carboxyl, phosphate and amino groups, as well as the chemical characteristics of the metal ions, such as solubility. For example, Pb(II) will be formed $Pb(OH)^+$, $Pb(OH)_2$ at higher pH values[17]. The optimum pH value for Pb(II) removal using different biosorbents was generally in the range of pH 4-5[20,21]. Hence a pH about 4.6 was used for the batch experiments.

The solid to liquid ratios have less impact on adsorption efficiency of Pb(II) onto chemically-modified peanut hulls, soybean shells and grapefruit peels (Fig. 3 (b)). For example, when the solid to liquid ratios were above 2 g L^{-1}, the percentage removal of Pb(II) would arrive at 100 % for three biosorbents [Fig. 3 (b)]. In view of the adsorption efficiency and the cost, the optimum adsorbent dosage was recommended as 2 g L^{-1} of the solid to liquid ratio.

The simultaneous sorption of Cd, Cr, Cu, Ni, Pb and Zn onto modified peanut hulls, soybean shells and grapefruit peels was shown in Fig. 4. AG has the better adsorption performance for all studied elements than AS and AP (Fig. 4). The adsorption capacity of chemically-modified biosorbents is in the order of AG > AS > AP for all studied elements (Fig. 4). Lead(II) can be preferentially removed from solution by the modified peanuts hulls, soybean shells and grapefruit peels, then Cu(II) and Cr(III). The selective adsorption of metal ions by those biosorbents wa snot clear.

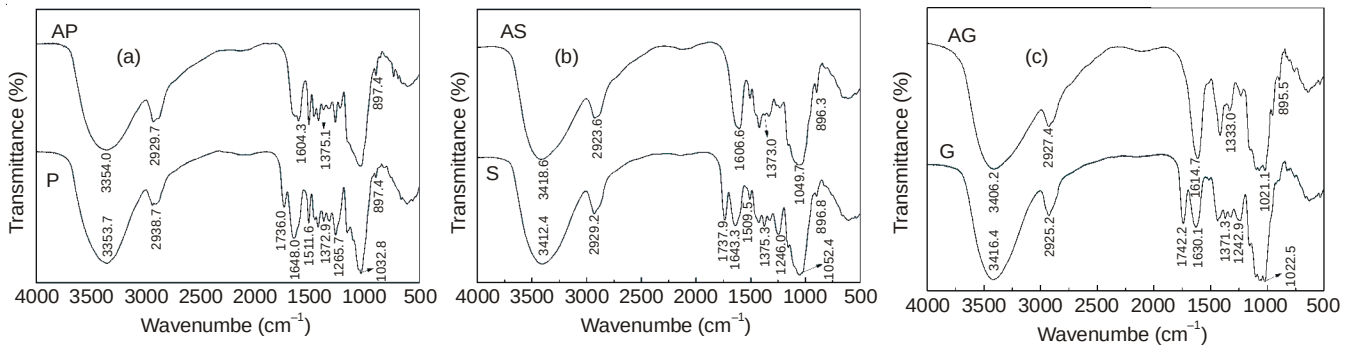

Fig. 2. FTIR spectra of raw and modified peanut hulls (a), soybean shells (b) and grapefruit peels (c)

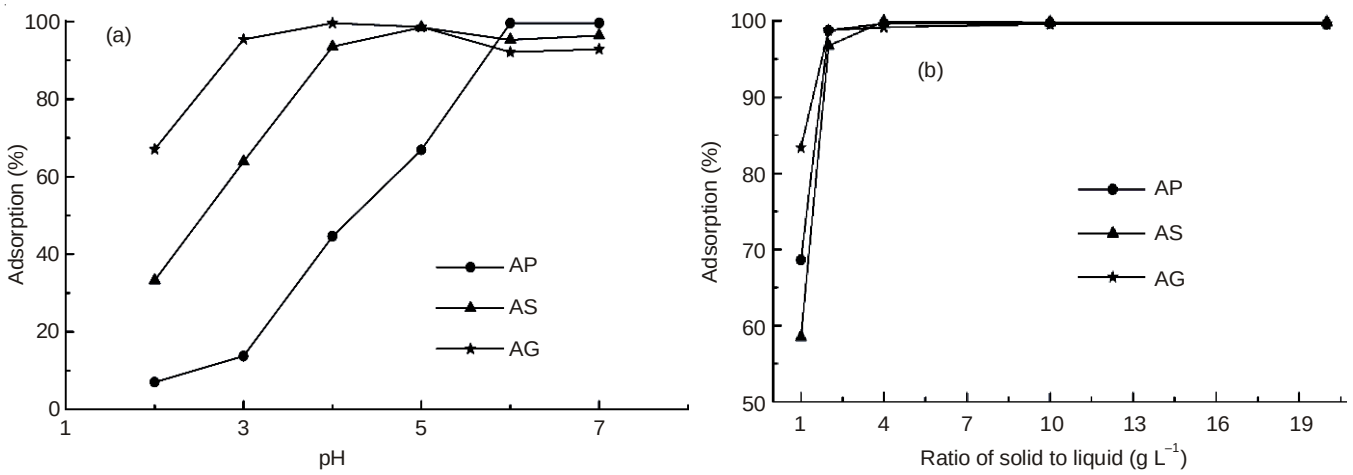

Fig. 3. Absorption of Pb(II) onto modified peanut hulls, soybean shells and grapefruit peels under different pH values (a) and solid to liquid ratios (b)

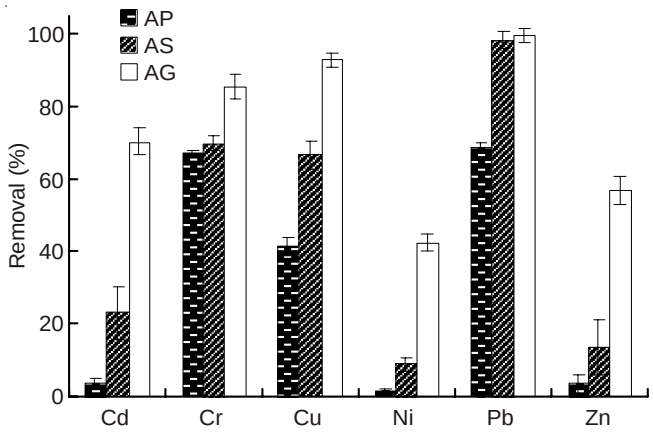

Fig. 4. Simultaneous adsorption of various metal ions onto modified peanut hulls, soybean shells and grapefruit peels

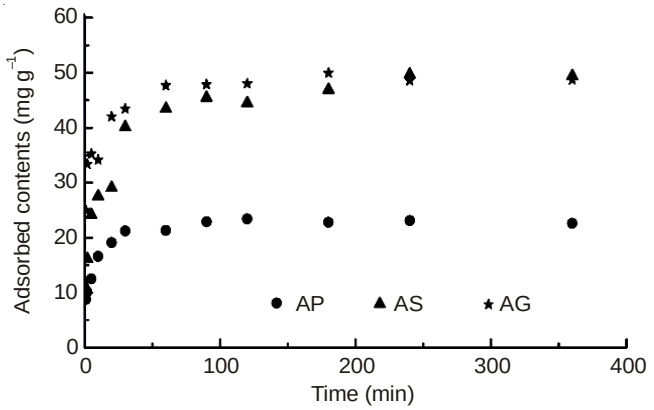

Fig. 5. Adsorption kinetics of Pb(II) onto modified peanut hulls, soybean shells and grapefruit peels

Adsorption kinetics of Pb(II) onto modified biosorbents: The adsorption process was shown in Fig. 5, which showed the equilibrium time varied with chemically-modified biosorbents. The equilibrium time was about 30 min for AP, 180 min for AS and 60 min for AG, respectively. Physisorption is usually very fast, while chemisorption is slow. The equilibrium time indicated the different sorption mechanism of Pb(II) onto these modified biosorbents. Previous studies on the removal of Pb(II) from solutions find that the equilibrium time was approximately 90 min for *Parmelina tiliaceae*[21], 60 min for *Lactarius scrobiculatus*[22] and 10 min for bentonite[23]. Comparing the adsorption capacity of Pb(II) by AP, AS and AG, the adsorption capacity at equilibrium was about 50 mg g^{-1} for AS and AG and about 20 mg g^{-1} for AP, respectively. Obviously, the adsorption capacity of AS and AG was higher than that of AP.

The pseudo-first-order and the pseudo-second-order rate models, which are semi-mechanistic models based on the mono-nuclear and binuclear adsorption mechanisms, respectively[24], are used to fit the experimental data to predict the Pb(II) adsorption process in the present study. They can be expressed as follows:

$$\frac{1}{q_t} = \frac{1}{q_e} + \frac{k_1}{q_e t}$$

$$\frac{t}{q_t} = \frac{1}{(q_e)^2 k_2} + \frac{t}{q_e}$$

where q_t and q_e are the amount of Pb(II) adsorbed at time *t* and at equilibrium, respectively (mg/g) and k_1 and k_2 are the first-order and second-order apparent adsorption rate constants (min^{-1} and mg g^{-1} min^{-1}), respectively.

The parameters of the pseudo-first-order and pseudo-second-order kinetic equations were listed in Table-1. For the pseudo-first-order model (Table-1), the correlation coefficient (R^2) was 0.892 for AP, 0.970 for AS and 0.867 for AG,

TABLE-1
MODEL PARAMETERS FOR Pb(II) KINETIC ADSORPTION

	Experimental	Pseudo-first-order			Pseudo-second-order		
	q_{exp} (mg g^{-1})	q_e (mg g^{-1})	k_1 (min^{-1})	R^2	q_e (mg g^{-1})	k_2 (mg g^{-1} min^{-1})	R^2
AP	21.2	21.1	1.60	0.892	23.0	0.017	1.00
AS	46.9	42.6	3.00	0.970	50.2	0.002	1.00
AG	47.7	45.7	0.85	0.867	49.3	0.009	1.00

respectively. The R^2 obtained from the pseudo-second-order kinetic model (Table-1) were close to or equal to 1, higher than corresponding pseudo-first-order model values (Table-1). Previous literatures also reported the faultless matching (R^2 = 1)[25,26]. The calculated q_e values were close to the experimental q_{exp} values, which agreed with previous studies[20,22,27]. Therefore, the adsorption process of AP, AS and AG followed the pseudo-second-order kinetic equation better than pseudo-first-order kinetic equation based on relevant parameters, implying the boundary layer controlling the beginning of the adsorption process[28].

Adsorption isotherm of Pb(II) onto chemically-modified biosorbents: The effect of initial concentration on the adsorption of Pb(II) onto modified biosorbents was shown in Fig. 6. The adsorption capacities increased with the increase of initial Pb(II) concentration and then became stable. The adsorption capacity of the three biosorbents was similar at low concentrations of Pb(II), but with the increase of Pb(II) concentration, the adsorption capacity of the biosorbents differed greatly. Obviously, AG exhibited the highest adsorption capacity for Pb(II), while AP has lowest adsorption capacity (Fig. 6).

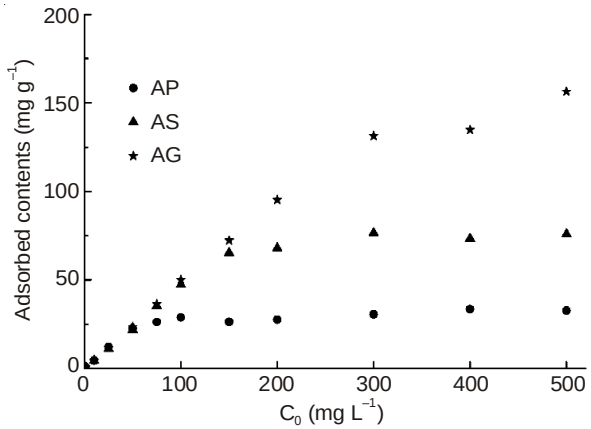

Fig. 6. Effects of initial concentrations of Pb(II) on the adsorption of Pb(II) onto modified peanut hulls, soybean shells and grapefruit peels

Langmuir and Freundlich isotherm models were used to fit the isotherm experimental data in the present study. The Langmuir isotherm assumes monolayer coverage of adsorbent over a homogeneous sorbent surface composed of a finite number of identical sites with equal adsorption activation energies. The Freundlich isotherm model is an empirical equation used to describe the adsorption on a heterogeneous surface and multilayer adsorption of the adsorbent and assumes that different sites with several adsorption energies are involved[29]. Their linear forms are usually written as follows:

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{bq_m}$$

$$\log\ q_e = \log\ K_f + \frac{1}{n}\log\ C_e$$

where C_e is the equilibrium concentration of Pb(II) (mg L^{-1}), q_m is the maximum adsorption capacity of the adsorbent when the surface is completely covered with Pb(II) (mg g^{-1}) and b is the adsorption constant, indicating the affinity between the adsorbent and Pb(II) ions (mg g^{-1}), K_f is a constant related to the adsorption capacity (mg g^{-1}) and 1/n is an empirical parameter related to the adsorption intensity.

The correlation coefficients (R^2) indicate that Langmuir model fitted the experimental data better than Freundlich model (Table-2), suggesting the monolayer adsorption. The experimental adsorption capacities were 33.4, 76.6 and 156 mg g^{-1} for AP, AS and AG, respectively (Table-2). The q_{max} values calculated by Langmuir isotherm model were very important to predict whether the material was suited to adsorption as they give an indication of the total number of available binding sites. The maximum adsorption capacities obtained from Langmuir model were 32.9, 75.8 and 154 mg g^{-1} for AP, AS and AG, respectively (Table-2). The adsorption capacities revealed the stronger binding of Pb(II) ions onto the surface of AG and then AS. The values of 1/*n* in the Freundlich isotherm model were all between 0.1 and 1 (0.25, 0.34 and 0.45 for AP, AS and AG, respectively), suggesting the favorability of the adsorption process for these biosorbents[30].

The comparison of the adsorption capacities obtained from this study to the previous reports was carried out (Table-3). The adsorption capacities of the agricultural and forest waste for Pb(II) differed greatly with the agricultural and forest waste adsorbents[4]. The adsorption capacities were 16.58, 26.94 and 30.46 mg g^{-1} for granular activated carbon, powdered activated carbon and activated carbon fibers, respectively[31]. Agricultural waste adsorbents have equal or greater adsorption capacities than activated carbon[4]. The maximum adsorption capacities for raw peanut hulls, soybean shells and grapefruit peels were 23.8, 45.5 and 76.9 mg g^{-1} [32], respectively. Therefore, chemically-modification improves greatly the adsorption capacities. Therefore, 3-aminopropyltrimethoxysilane-modified grapefruit peels can be used for the effective removal and recovery of lead ions from wastewater.

Desorption tests: Lead(II) absorbed onto AG, AS and AP was desorbed by 1 mol L^{-1} HCl and the average desorption rates were 98.2 % for AP, 95.8 % for AS and 92.2 for AG, respectively. All these were beyond 90 %, suggesting easy treatment of biosorbents contained metal ions and the potential reuse of these chemically-modified biosorbents.

Conclusion

In order to develop the low-cost and high efficient absorbents, agricultural by-products-peanut hulls, soybean shells and grapefruit peels were chemically modified with

TABLE-2
MODEL PARAMETERS FOR Pb(II) ISOTHERM ADSORPTION

	Experiment	Langmuir coefficient			Freundlich coefficient		
	$q_{m(exp)}$ (mg g^{-1})	b (L mg^{-1})	q_m (mg g^{-1})	R^2	K_f (mg g^{-1})	1/n	R^2
AP	33.4	0.15	32.9	0.996	9.39	0.25	0.649
AS	76.6	0.44	75.8	0.999	16.32	0.34	0.652
AG	156.4	0.21	153.8	0.989	26.02	0.45	0.558

TABLE-3
COMPARISON OF THE ADSORPTION CAPACITY FOR Pb(II)

Adsorbents	pH	T (°C)	t(min)	q(mg g^{-1})	[Ref.]
AP	4.6	20	180	33.4	This study
AS	4.6	20	180	76.6	This study
AG	4.6	20	180	156	This study
Lactarius scrobiculatus	5.5	20	60	56.2	22
Amanita rubescens	5	20	30	38.4	33
Cephalosporium aphidicola	5	30	30	36.9	27
Bentonite clay	3.4	25 ± 2	10	52.6	23
lichen	5	20	90	75.8	21
Olive tree pruning waste	5	25	120	26.24	8
Maize stalk sponge	6 ± 0.2	RM*	24 h	80	34
Peanut shells	4.0-4.5	20	200	33.2-41.4	35
Sugarcane bagasse	4	30	24 h	327.4	36

*:Room temperature

3-aminopropyltrimethoxysilane after the saponification using 17.5 % NaOH. Chemical modification was confirmed by infrared spectra and N contents. Factors affecting the adsorption behaviour of Pb(II), such as pH, ratio of solid to liquid, competitive sorption of various metal ions, initial metal concentration and adsorption time, were investigated. Compared with the mercerized biomass, C=O vibration peaks in chemically-modified peanut hulls, soybean shells and grapefruit peels disappeared, while the non-planar rocking vibration peaks of -NH_2 appeared. The N contents increased in the modified bio adsorbents. The adsorption equilibrium could be obtained at 180 min and the kinetic adsorption fitted well with the pseudo-second order kinetic model. The isotherm adsorption data fitted well with Langmuir adsorption model and the maximum absorption capacities of chemically-modified peanut hulls, soybean shells and grapefruit peels were 32.9, 75.8 and 154 mg g^{-1}, respectively. The competitive adsorption of mixed metals solution demonstrates that Pb(II) can be preferentially removed from solution by the modified peanuts shells, soybean hulls and grapefruit peels, than Cu(II) and Cr(III). The desorption rate of Pb(II) from chemically-modified peanut shells, soybean shells and grapefruit peels using 1 mol L^{-1} HCl solution were beyond 90 %. Chemically-modified grapefruit peels exhibited higher absorption capacities than chemically-modified soybean shells and peanut shells and can be used as potential the low-cost and high efficient absorbents for the removal of Pb(II) in wastewater.

ACKNOWLEDGEMENTS

The work was supported by the Natural Science Foundation of China (NSFC) (Grant No. 21007026).

REFERENCES

1. T.A. Kurniawan, G.Y.S. Chan, W.H. Lo and S. Babel, *Chem. Eng. J.*, **118**, 83 (2006).
2. F.L. Fu and Q. Wang, *J. Environ. Manage.*, **92**, 407 (2011).
3. A. Bhatnagar and M. Sillanpaa, *Chem. Eng. J.*, **157**, 277 (2010).
4. C. Saka, O. Sahin and M.M. Kucuk, *Int. J. Environ. Sci. Technol.*, **9**, 379 (2012).
5. P.C. Mishra and R.K. Patel, *J. Hazard. Mater.*, **168**, 319 (2009).
6. W. Cao, Z. Dang and G.N. Lu, *Environ. Eng. Sci.*, **30**, 672 (2013).
7. R. Rehman, U. Shafique, J. Anwar and S. Ghafoor, *Asian J. Chem.*, **25**, 8285 (2013).
8. G. Blazquez, M.A. Martin-Lara, G. Tenorio and M. Calero, *Chem. Eng. J.*, **168**, 170 (2011).
9. W.S. Wan Ngah and M.A.K.M. Hanafiah, *Bioresour. Technol.*, **99**, 3935 (2008).
10. T. Fatima, R. Nadeem, A. Masood, R. Saeed and M. Ashraf, *Int. J. Environ. Sci. Technol.*, **10**, 1255 (2013).
11. M. Riaz, R. Nadeem, M.A. Hanif, N. Rasool, R. Saeed and I. Muhammad, *Asian J. Chem.*, **25**, 1111 (2013).
12. M.A. Barakat, *Arab J. Chem.*, **4**, 361 (2011).
13. E.C. Silva Filho, L.C.B. Lima, F.C. Silva, K.S. Sousa, M.G. Fonseca and S.A.A. Santana, *Carbohydr. Polym.*, **92**, 1203 (2013).
14. R. Rehman and T. Mahmud, *Asian J. Chem.*, **25**, 8285 (2013).
15. S.H. Chen, Q.Y. Yue, B.Y. Gao and X. Xu, *J. Colloid Interf. Sci.*, **349**, 256 (2010).
16. E.C.S. Filho, L.S. Santos Jr., M.M.F. Silva, M.G. Fonseca, S.A.A. Santana and C. Airoldi, *Mater. Res.-Ibero-Am. J.*, **16**, 79 (2013).
17. K.G. Bhattacharyya and A. Sharma, *J. Hazard. Mater.*, **113**, 97 (2004).
18. F.T. Li, H. Yang, Y. Zhao and R. Xu, *Chin. Chem. Lett.*, **18**, 325 (2007).
19. A. Saeed, M. Sharif and M. Iqbal, *J. Hazard. Mater.*, **179**, 564 (2010).
20. D. Ozdes, C. Duran and H.B. Senturk, *J. Environ. Manage.*, **92**, 3082 (2011).
21. O.D. Uluozlu, A. Sari, M. Tuzen and M. Soylak, *Bioresour. Technol.*, **99**, 2972 (2008).
22. R.A. Anayurt, A. Sari and M. Tuzen, *Chem. Eng. J.*, **151**, 255 (2009).
23. R. Naseem and S.S. Tahir, *Water Res.*, **35**, 3982 (2001).
24. H. Aydin, Y. Bulut and Ç. Yerlikaya, J. Environ. Manage., 87, 37 (2008).
25. L. Semerjian, *J. Hazard. Mater.*, **173**, 236 (2010).
26. Y.S. Ho and G. McKay, *Water Res.*, **33**, 578 (1999).
27. S. Tunali, T. Akar, A.S. Ozcan, I. Kiran and A. Ozcan, *Sep. Purif. Techmol.*, **47**, 105 (2006).
28. G. McKay, Y.S. Ho and J.C.Y. Ng, *Sep. Purif. Methods*, **28**, 87 (1999).
29. E.L. Cochrane, S. Lu, S.W. Gibb and I. Villaescusa, *J. Hazard. Mater.*, **137**, 198 (2006).
30. L. Deng, Y. Su, H. Su, X. Wang and X. Zhu, *Adsorption*, **12**, 267 (2006).
31. Z. Reddad, C. Gerente, Y. Andres and P. Le Cloirec, *Environ. Sci. Technol.*, **36**, 2067 (2002).
32. Y. Rui, X. Hu, Z. Ding and Y. Zhang, *Environ. Eng. Manage. J.*, (Accepted).
33. A. Sari and M. Tuzen, *J. Hazard. Mater.*, **164**, 1004 (2009).
34. G. García-Rosales and A. Colín-Cruz, *J. Environ. Manage.*, **91**, 2079 (2010).
35. F.D. Oliveira, J.H. Paula, O.M. Freitas and S.A. Figueiredo, *Desalination*, **248**, 931 (2009).
36. P.L. Homagai, K.N. Ghimire and K. Inoue, *Bioresour. Technol.*, **101**, 2067 (2010).