

Poly(acrylic acid) modifying bentonite with *in-situ* polymerization for removing lead ions

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ABSTRACT

In this paper, a new kind of poly(acrylic acid) modified clay adsorbent, the poly(acrylic acid)/bentonite composite (PAA/HB) was prepared by *in-situ* polymerization, and utilized to remove lead(II) ions from solutions. The maximum adsorption of adsorbent is at pH 5 for metal ions, whereas the adsorption starts at pH 2. The effects of contact time (5–60 min), initial concentration of metal ions (200–1,000 mg/L) and adsorbent dosage (0.04–0.12 g/100 mL) have been reported in this article. The experimental data were investigated by means of kinetic and equilibrium adsorption isotherms. The kinetic data were analyzed by the pseudo-first-order and pseudo-second-order equation. The experimental data fitted the pseudo-second-order kinetic model very well. Langmuir and Freundlich isotherms were tried for the system to better understand the adsorption isotherm process. The maximal adsorption capacity of the lead(II) ions on the PAA/HB, as calculated from the Langmuir model, was 769.2 mg/g. The results in this study indicated that PAA/HB was an attractive candidate for removing lead(II) (99%).

Key words | adsorption, bentonite adsorbent, isotherm, kinetics, lead ions, poly(acrylic acid)/bentonite composites

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INTRODUCTION

The contamination of ground and surface water caused by hazardous metal ions is becoming a public concern for China. Over recent decades, a remarkable increase of heavy metal contamination has posed many serious environmental problems due to their toxicity to many living forms. Lead(II) is one of the most toxic heavy metal elements. Lead has been introduced into natural waters from a variety of sources such as building construction, lead-acid batteries, lead smelting, mining, plating, ammunition, and the ceramic glass industries. China is the biggest refined lead consumer, 70% of which is used for manufacturing batteries. But the recycling system of lead storage batteries has been imperfect, and has caused tremendous damage to the environment. The cell industry is the main source of lead wastewater. It will lose 4.54–6.81 mg of lead when a battery is manufactured (Xie 2010). The presence of excess lead in drinking water causes diseases such as anemia, encephalopathy, and hepatitis (Ahmad *et al.* 2009). It cannot be broken down but can be converted to other forms (Boudrahem *et al.* 2011). Many treatment processes have been applied for the removal of heavy metals from

wastewater such as: adsorption (Ozcan *et al.* 2009), ion exchange (Medvidovic *et al.* 2007), chemical settling (Banfalvi 2006), electrochemical degradation (Fan *et al.* 2008) and integrated chemical-biological treatment (Sudarjanto *et al.* 2006). Among them, adsorption is a well known equilibrium separation process and an effective method for water decontamination applications (Rafatullah *et al.* 2009). Adsorption has been discovered prior to other processes for water re-use according to first cost, flexibility and simplicity of design. Above all, the adsorption does not produce harmful substances. In order to get high-effective, low-cost and convenient adsorbents, many studies have been carried out (Liu *et al.* 2008).

Numerous sorbents such as synthetic resin (Rajesh *et al.* 2011), activated carbon (Zhang *et al.* 2010), carbon nanotubes (Tian *et al.* 2010), chitosan/natural zeolites (Dragan *et al.* 2010), clay minerals (Zhang & Hou 2008) and biosorbents (Shen *et al.* 2009) have been tested for their potential application to remove heavy metals from wastewater. Bentonite, a kind of cheap natural clay, has been found to be especially useful for removing heavy metal ions by exchangeable metal

cations from wastewater and in reducing the dispersion of pollutants in soil (Caglar *et al.* 2009). However, as the bentonite has highly hydrophilic layers, it cannot effectively remove hydrophobic pollutants. It is also difficult to separate bentonite from wastewater because of high dispersion. To enhance its capability to adsorb heavy metals from aqueous solution, the surface of bentonite needs to be modified. Many modification methods have been used. The most significant mechanism in the activation of natural bentonite was exchange by H^+ ions, which increased the specific surface area of the bentonite. These transformations in bentonite layers can give rise to significant changes in cation exchange capacity (CEC), and the chemical and mineralogical characteristics of bentonite (Ravichandran & Sivasankar 1997). In this work, through *in-situ* polymerization, bentonite treated with acid (HB) was modified by poly(acrylic acid) (PAA). The obtained PAA/HB was used to remove lead ions from aqueous solutions. The influence of the conditions, such as time and initial concentration of lead(II) ions on the PAA/HB was tested and the adsorption process with respect to its kinetic and thermodynamic was also evaluated in this study.

MATERIALS AND METHODS

Materials

Natural bentonite (NB) was obtained from the Xinjiang of China. Sulfuric acid activation bentonite (HB) was obtained by further treatment with H_2SO_4 . Acrylic acid (AA) was treated by reduced pressure distillation before use. Lead nitrate ($Pb(NO_3)_2$), sulfuric acid (H_2SO_4), *N,N'*-methylenebisacrylamide, ammonium persulfate, nitric acid (HNO_3) and sodium hydroxide (NaOH) were all analytical reagent and commercially available.

Adsorbent

The procedure by which the bentonite was activated by sulfuric acid was guided by the literature (Bhattacharyya & Gupta 2007): 20 g of bentonite was refluxed with 200 mL 0.25 mol L^{-1} of H_2SO_4 for 3 h. The obtained sulfuric acid activated bentonite (HB) was filtrated and washed with distilled water several times until it was free of SO_4^{2-} , then dried at 80°C until a constant weight was attained.

The PAA/HB was prepared as follows: HB (5.0 g) and AA (10.8 g) were dispersed in 30 mL of water, and then were stirred vigorously at room temperature for 2 h. The mixture

was partially neutralized with 15 mL of NaOH solution (9.0 mol L^{-1}), after that, *N,N'*-methylenebisacrylamide (12 mg) was added. The solution was gradually heated to 50°C under the protection of nitrogen for 30 min. Then ammonium persulfate (36 mg) was introduced into the mixture under continuous stirring. After the mixture reacted for 40 min at 70°C under a nitrogen atmosphere, the raw product was obtained. Finally, the raw product was washed with distilled water several times and dried at 80°C in a hot air oven until the weight of the product was constant. The material was sieved with a 100 Mesh and stored in a tight plastic container.

Analysis of the adsorbent sample

By use of an X-ray diffractometer (D/max-2400, Rigaku Corporation, Japan), we got X-ray diffraction (XRD) analysis of the adsorbent, and the phase characterizations of the PAA/HB and its materials were surveyed. Surface morphology was studied by scanning electron micrographs (SEM) (JSM-6701F, Japan Electron Optics Laboratory Corporation, Japan). For the main functional groups that might be involved in metal adsorption, a Fourier Transform Infrared (FTIR, FTS3000, Digilab Corporation, USA) analysis was performed by analyzing the HB, PAA/HB and PAA/HB-Pb, with the spectral wavelength from $4,000$ to 400 cm^{-1} .

Adsorption experiments

Batch experiments on adsorption were carried out by agitating 0.1 g of PAA/HB in 100 mL of lead(II) ion solution in a 250 mL stoppered conical flask, which was done at 120 rpm, in a thermostatted water bath shaker at 20°C . The lead(II) ions solution was separated from the adsorbent by filtering the mixture with a vacuum pump. The effect of adsorbent dosage (0.04 – $0.12 \text{ g } 100 \text{ mL}^{-1}$), contact time (5–60 min), solution pH (2.0–7.0) and initial concentration of lead (200 – $1,000 \text{ mg L}^{-1}$) was studied. The concentration of lead(II) ions in the supernatant solution was measured by flame atomic absorption spectrophotometer. The removal efficiency and adsorption capacity were computed in the following equations:

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

$$\text{Adsorption capacity} = \frac{(C_0 - C_e)V}{m} \quad (2)$$

where C_0 and C_e are the initial and equilibrium

concentration of metal ions (mg/L) in the solution. V is the volume of metal ions solution (L) and m is the weight of the adsorbent (g).

Regeneration

In many cycles of adsorption/desorption, the repeated availability of PAA/HB in lead(II) ions adsorption is quite crucial for the application of PAA/HB in the removal of lead(II) ions from wastewater in real work. The desorption for lead(II) ions from the PAA/HB was carried out by shaking them in HNO_3 solution of 100 mL, $10^{-4} \text{ mol L}^{-1}$ with a temperature of 20°C for 1 h and then filtered. The concentration of desorbed lead(II) in the filtrate was determined. Following each desorption step, the adsorbent was washed with distilled water, dried to constant weight, and reloaded with lead(II).

RESULTS AND DISCUSSION

Characterization of adsorbents

XRD analysis

XRD patterns of HB, PAA/HB and PAA/HB-Pb were recorded. For the XRD pattern of HB, one reflection was observed at $2\theta = 5.06^\circ$, the interlamellar distance (d_{001} values) was found to be 1.75 nm. Compared with HB, the position of the d_{001} peak of the PAA/HB sample shifted from 1.75 to 2.03 nm, which indicated that interlamellar expansion and interlayer polymerization were formed. According to the formula $\Delta d = d - 0.96 \text{ nm}$, where d is the basal spacing of the PAA/HB, 0.96 nm is the thickness of

a clay layer. The estimated basal spacing value theoretically is 1.07 nm and the dimension of AA is 0.52 nm. This result suggested that AA intercalated into the interlayers of bentonite.

SEM analysis

SEM images of HB (a), PAA/HB (b) and PAA/HB-Pb (c) are shown in Figure 1. Obviously, a stripping, sheet morphology and varied depth surface-breaking crack merged on the surface of HB. In other words, the channel in the structure of HB was opened. This meant that the acid activation enhanced the adsorption capacity of bentonite due to the increased surface area and pore volume. Furthermore, the sample of PAA/HB presented that stripping, layered-structure and smooth surface, which meant composite was formed between HB and AA monomer, which might be convenient for the penetration of solutions into the polymeric network, and beneficial to the adsorption of heavy metals (Zhang et al. 2007). PAA/HB-Pb displayed similar morphology with PAA/HB.

FT-IR analysis

The FT-IR spectra of HB, PAA/HB and PAA/HB-Pb were measured. The spectra displayed a number of absorption peaks, indicating the complex nature of adsorbents. Compared with the IR spectrum of HB, the peak at $1,707 \text{ cm}^{-1}$ represented the $\text{C}=\text{O}$ stretching vibration of the carboxylic group of PAA/HB, and the peak at $1,572 \text{ cm}^{-1}$ indicated the presence of $-\text{COO}^-$ asymmetric stretching vibration of PAA/HB. The appearance of the peaks at 1,454 and $1,411 \text{ cm}^{-1}$ indicated the presence of $-\text{COO}^-$ symmetric stretching vibration of PAA/HB. Compared with the curve

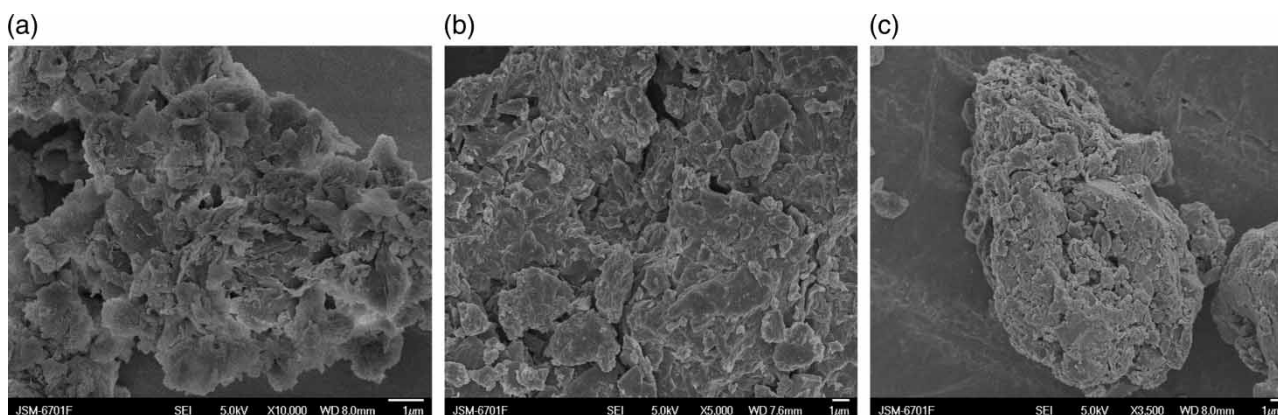


Figure 1 | Scanning electron micrographs for HB (a), PAA/HB (b) and PAA/HB-Pb (c).

of PAA/HB, the absorption bands of C=O of carboxylic group and -COO^- group were shifted from 1,707, 1,572, 1,454 and $1,411\text{ cm}^{-1}$ to 1,698, 1,522, 1,448 and $1,398\text{ cm}^{-1}$, respectively. These results showed that the reaction of bentonite and AA monomer took place during the polymerization process and the complexes were formed between -COO^- and lead(II) ions.

Adsorption of lead(II) ions

From the above analysis, it was suggested that AA molecules were intercalated into the sheets of HB, and then polymerized. Therefore, HB may play an important role in immobilization of AA. Their adsorption properties of removal of lead(II) ions from aqueous solutions were evaluated. The respective adsorption ability of natural bentonite (NB), HB, PAA and PAA/HB in the removal of lead(II) ions is shown in Table 1. The removal efficiency of lead(II) ions by PAA/HB was approximately twice that by NB and PAA. This finding meant that PAA/HB was an effective adsorbent.

Effect of pH on lead(II) ions adsorption

The pH value of the solution is the most important parameter affecting metal ion adsorption because hydrogen ions compete with the positively charged metal ions on the active sites of the adsorbent. Thus, adsorption experiments were carried out in the pH range of 2.0–7.0. The results are shown in Figure 2. The percentage of lead(II) adsorption on PAA/HB increased with increasing pH and reached a plateau value at pH = 5.0. At low pH, adsorption efficiency might decrease, due to the occupation by lots of H^+ ions of the adsorption activity sites on the surface of PAA/HB, which hindered the adsorption of lead(II) ions. However, with increasing pH, the adsorption efficiency might decrease due to the formation of Pb(OH)_2 , which was weakly adsorbed compared with PAA/HB's adsorption

Table 1 | Adsorption ability of different adsorbents in the removal of lead(II) ions

Adsorbent	$[\text{Pb}^{2+}]_{\text{Residual}}$ (mol L^{-1})	Pb^{2+} removal (%)	Adsorption capacity (mg g^{-1})
NB	257.0	48.6	243.0
HB	183.6	63.3	316.4
PAA	254.0	49.2	246.0
PAA/HB	0.6	99.9	499.4

Cond: $[\text{Pb}^{2+}]_{\text{Initial}} = 500\text{ mg L}^{-1}$; $[\text{Adsorbent}] = 0.1\text{ g } 100\text{ mL}^{-1}$; pH = 5.0; Time: 1 h.

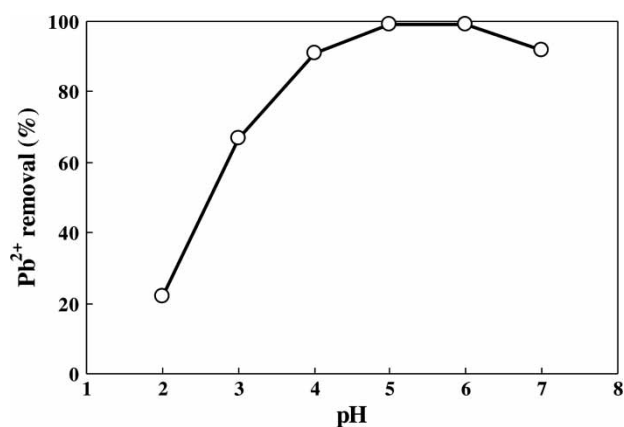


Figure 2 | Effect of pH value on the removal of lead(II) ions.

of lead(II) ions. So pH = 5.0 was considered the optimum condition and was used in following study.

Effect of adsorbent dosage

The optimum adsorbent dosage was determined by varying from 0.04 to $0.12\text{ g } 100\text{ mL}^{-1}$. As shown in Figure 3, the increase of removal efficiency could be explained by the increasing surface area on which the adsorption took place. The adsorption efficiency decreased when the adsorbent dosage was more than $0.1\text{ g } 100\text{ mL}^{-1}$. This situation may be due to overlapping of adsorption sites as a result of over-crowding of adsorbent particles (Namasivayam et al. 1998). The optimum adsorbent dosage in removal of lead(II) ions was $0.1\text{ g } 100\text{ mL}^{-1}$.

Effect of initial lead(II) ion concentration

Optimum concentration was determined after experimental studies with lead(II) ion concentrations ranging from 200 to

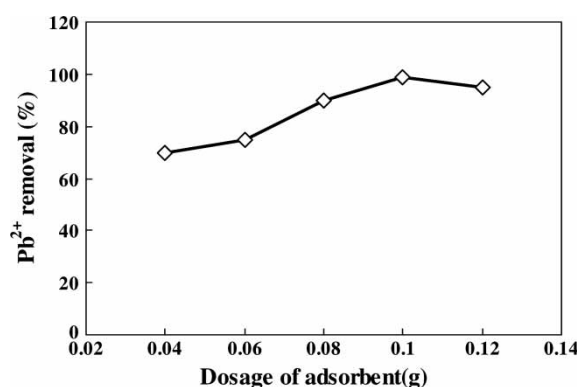


Figure 3 | Effect of adsorbent dosage on the removal of lead(II) ions. Cond: pH = 5.0; Temp: 20 °C; Time: 1 h.

1,000 mg L⁻¹. It was found that the removal rate of lead(II) by PAA/HB was dependent on the initial concentration (Figure 4). The optimum initial metal concentration was 500 mg L⁻¹, at which the amount of metal ions in effluent met class I of the National Integrated Wastewater Discharge Standard of China. At low concentration, the ratio of available surface to initial lead(II) concentration is larger, so the removal is higher. In the case of higher concentrations this ratio is low; hence the percentage removal is less.

Effect of contact time

The contact time was also evaluated as one of the most important factors affecting the adsorption efficiency. With the previous optimum values of pH, adsorbent dosage and metal concentration, the effect of time on removal efficiency was measured (Figure 5). It revealed that the rate of removal of lead(II) ions was initially high, which was

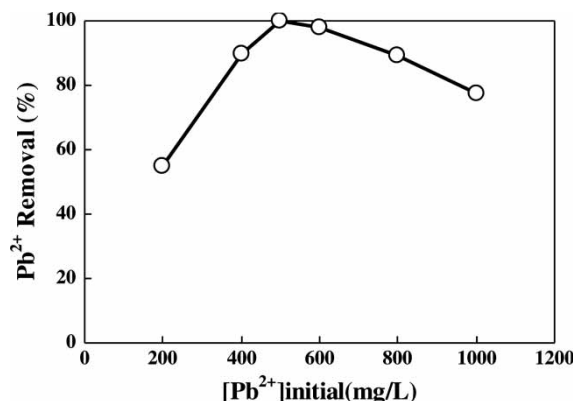


Figure 4 | Effect of different initial concentrations of lead(II) ions. Cond: [PAA/HB] = 0.1 g 100 mL⁻¹; pH = 5.0; 20 °C; Time: 1 h.

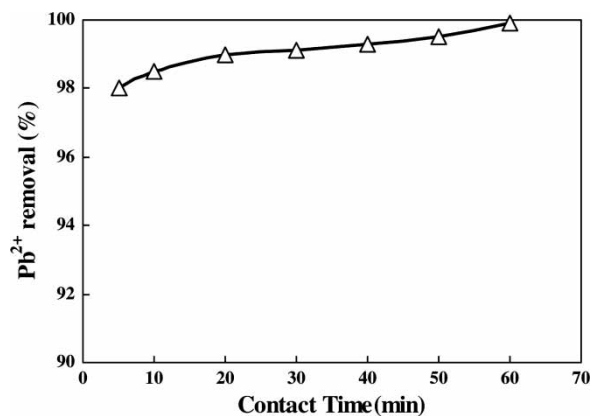


Figure 5 | The influence of time in adsorption of lead(II) ions. Cond: [Pb²⁺]_{initial} = 500 mg L⁻¹; [PAA/HB] = 0.1 g 100 mL⁻¹; pH = 5.0; 20 °C.

probably due to the availability of active sites of the adsorbent for the adsorption of these ions. As the surface adsorption sites became exhausted, the rate of uptake was controlled by that of transport from the exterior sites to the interior of the adsorbent particles (Ahmad et al. 2009). The maximum adsorption capacity was observed at 60 min.

Kinetics of adsorption

Adsorption kinetics was used in order to explain the adsorption mechanism and adsorption characteristics. In this study, pseudo-first-order and pseudo-second-order kinetic equations were used to test the experimental data. The adsorption rate constant is shown as below (Veli & Alyuz 2007), which was proposed by Lagergren and Ho using pseudo-first-order reaction kinetics:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \quad (3)$$

where k_1 is the adsorption rate constant for the first-order adsorption, q_t (mg g⁻¹) is the amount of heavy metal adsorbed at time t and q_e (mg g⁻¹) is the amount of heavy metal adsorbed at saturation.

In order to calculate the adsorption rate constant of lead (II) ions, pseudo-first-order reaction kinetics was applied for the lead(II) ion adsorption. It was seen that the curve was nonlinear in the plots of $\ln(q_e - q_t)$ against time, which meant pseudo-first-order reaction kinetics could not identify the diffusion mechanism.

Adsorption data were further evaluated according to the pseudo-second-order reaction kinetics proposed by Ho and McKay (Veli & Alyuz 2007).

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (4)$$

where k_2 is the second order reaction constant.

The curve in the plot of t/q_t against t is linear and k_2 rate constants can be calculated from the slope of the curve (Figure 6). The k_2 , calculated q_e value and the corresponding linear regression correlation coefficient R were 500.0 mg g⁻¹, 0.004 g mg⁻¹ min⁻¹ and 0.9999, respectively. Moreover, the values of q_e calculated from pseudo-second order kinetics were in agreement with the experimental values of q_e . These results indicated that PAA/HB's adsorption for lead(II) ions accords with pseudo-second order kinetics and is mainly controlled by the film diffusion mechanism.

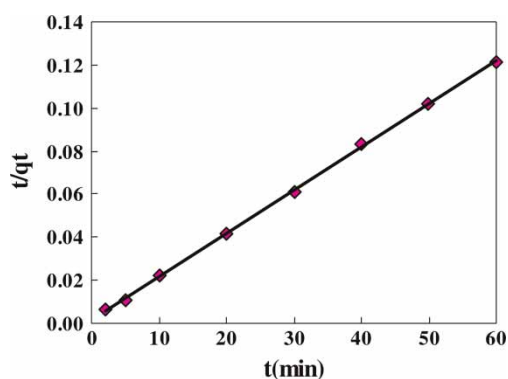


Figure 6 | Kinetic models for lead(II) ions.

Adsorption isotherm

The process of the removal of lead(II) ions by PAA/HB was carried out using the Langmuir (Gok *et al.* 2008) and Freundlich (Pehlivan & Arslan 2007) isotherm models of equilibrium modeling. The linear forms of the Langmuir and Freundlich isotherm equations are represented by the following equations:

$$\text{Langmuir: } \frac{C_e}{q_e} = \frac{1}{q_{\max} K_L} + \frac{C_e}{q_{\max}} \quad (5)$$

$$\text{Freundlich: } \lg q_e = \lg K_F + \frac{1}{n} \lg C_e \quad (6)$$

where q_e is the equilibrium lead(II) ion concentration on the adsorbent (mg g^{-1}), C_e is the equilibrium lead(II) ion concentration in solution (mg L^{-1}), q_{\max} is the maximum adsorption capacity (mg g^{-1}) and K_L is the Langmuir constant (L mg^{-1}), which is related to the free energy of adsorption. K_F ($\text{dm}^3 \text{g}^{-1}$) is the Freundlich constant and

n (dimensionless) is the heterogeneity factor, which has a lower value for more heterogeneous surfaces.

The plots of Langmuir and Freundlich for the adsorption of lead(II) ions by the composite are shown in Figure 7. As the figures show, the Langmuir model fits the equilibrium data better than the Freundlich model. The volume of remaining liquid was reduced because the composite adsorbed water mainly at low initial lead(II) ions concentration. Thus, lead(II) ions concentration between 500 to 1,000 mg L^{-1} was considered as optimum condition and used in Langmuir and Freundlich models. The K_L , q_{\max} and R^2 were 0.0765 L mg^{-1} , 769.2 mg g^{-1} and 0.9839.

A comparison of the adsorption capacity of other adsorbents for removing lead(II) is presented in Table 2. Aside from the differences in experimental conditions, differences also exist in the properties of each adsorbent such as structure, functional groups, and surface area. However, qualitatively, it is evident that the adsorption capacity of PAA/HB, in general, exceeds or is comparable to those for other adsorbents. So, the PAA/HB can be used to treat the contaminated water that contains lead.

Table 2 | Comparison of adsorption capacity of other adsorbents

Adsorbents	q_{\max} (mg/g)	References
Graphene nanosheets	22.4	Huang <i>et al.</i> (2011)
Activated carbon	51.8	Mohammadi <i>et al.</i> (2010)
Tourmaline	200.0	Wang <i>et al.</i> (2011)
Meranti sawdust	34.3	Rafatullah <i>et al.</i> (2009)
Aminated polyacrylonitrile nanofiber mats	60.6	Kampalanonwat & Supaphol (2010)
PAA/HB	769.2	Present study

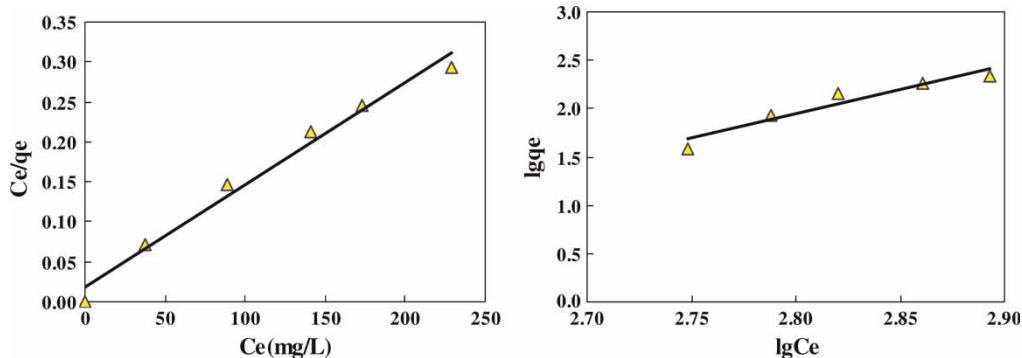


Figure 7 | Isotherm for lead(II) ions.

Adsorption mechanism

The highest value of q_{\max} obtained was 769.2 mg g^{-1} . This value was found to be higher than those of many corresponding adsorbents reported in the literature (Singh et al. 2007; Jang et al. 2008). According to the values of q_{\max} , a chelation model could be the dominating adsorption mechanism. It might be related to the fact that $-\text{COO}^-$ groups could easily form a more stable group with lead(II) ions than ion exchange. The possible mechanism of lead(II) ions adsorption on the composite is schematically presented in Figure 8. The molecular chain might tend to extend because of the interaction between hydrophilic groups of complex and water molecules in lead nitrate solutions. Then, chelation was formed between carboxyl groups of the PAA/HB and the lead(II) ions, which increased the degree of cross linking of the composite. When cross linking points increased, they were enough to resist the elastic repulsion among the polymer chains, thus the water absorbency reached a maximum. Subsequently, with the continual increase in the complex degree of carboxylate groups and lead(II) ions, the adsorbent collapsed and the initially absorbed water was squeezed out of the adsorbent network. After lead(II) ions adsorption, the IR spectra showed the change of the chemical environment of $-\text{COO}^-$ of the PAA/HB in lead nitrate solutions. It was considered that the degree of polymerization of PAA would influence its chelating activity. However, the degree of polymerization was difficult to control under free radical polymerization. Based on the above analysis, the chelation model may be the dominating adsorption mechanism for lead(II) ions by the composite.

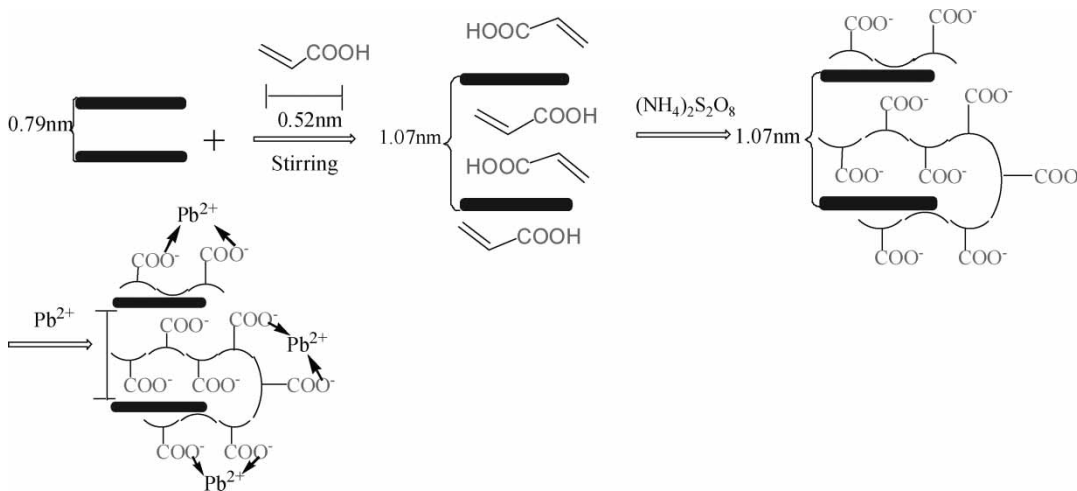


Figure 8 | The suggested mechanism for the adsorption of lead(II) ions onto PAA/Bent.

Regeneration

Desorption studies help to elucidate the mechanisms of adsorption and recovery of the adsorbate and recycling of the adsorbent. The desorption ratio was calculated from the amount of lead(II) ions initially adsorbed by the adsorbent and the final concentration in the desorption medium. The results are illustrated in Figure 9. For five adsorption/desorption cycles, the lead(II) adsorption capacity of the PAA/HB decreased from 99% (cycle 1) to 52% (cycle 5). The reduction in lead(II) uptake in five

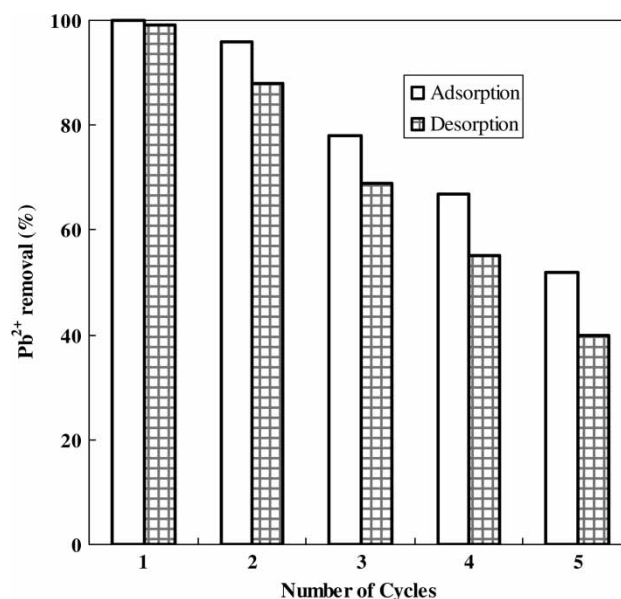


Figure 9 | The performance of PAA/Bent by five cycles of regeneration.

cycles of adsorption/desorption indicates that the binding sites on the surface of the adsorbent were destroyed or morphologically altered upon repeated exposure to a strong acid environment.

CONCLUSION

The obtained poly(acrylic acid) modified bentonite (PAA/HB) is an effective adsorbent for the removal of lead(II) ions from aqueous solutions. PAA/HB's removal efficiency reached 99.9% and the adsorption capacity reached 499.4 mg g^{-1} with 500 mg L^{-1} lead(II) ions solution at 20°C . Kinetic and isotherm studies were carried out. The experimental data fitted the pseudo-second-order kinetic model very well. The adsorption isotherms of PAA/HB for lead(II) ions could be described well by the Langmuir model. Desorption studies showed that PAA/HB can be regenerated effectively, easily for further use. The PAA/HB maximum sorption capacity (evaluated based on Langmuir fit) was higher than other treated residues such as graphene nanosheet, tourmaline, etc. The high adsorption capacity of PAA/HB makes it a suitable material in the removal of heavy metals from solutions for practical application in wastewater treatment.

ACKNOWLEDGEMENTS

The project was supported by NSFC (No. 20964002), the Gansu Sci & Techn Support Project (1011GKCA017), the Funda Res Funds Gansu Univ (2010-176).

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First received 2 May 2011; accepted in revised form 22 November 2011