

Full Length Research Paper

Adsorption of Pb^{2+} ions on diatomite modified by polypropylene acetamide and barium chloride in aqueous solution

Jian Zhu, Ping Wang*, Xiaofu Wu, Wenlian Luo and Mingjing Lei

Institute of Environmental Science and Engineering Research, Central South University of Forestry and Technology, Changsha, Hunan Province, P. R. China.

Accepted 6 April, 2012

In order to increase diatomite adsorption capacity, polypropylene acetamide (PAM) and barium chloride ($BaCl_2$) were employed to modify the diatomite. Experiments were conducted to investigate surface chemistry characterization and adsorption capacity of the diatomite before and after modification, and adsorption capacity of Pb^{2+} onto raw diatomite, PAM modified diatomite, zeolite, vermiculite and red soil. The results obtained show that the best concentrations of PAM and $BaCl_2$ for diatomite modification were $20\text{ g}\cdot\text{L}^{-1}$ and $0.2\text{ mol}\cdot\text{L}^{-1}$, respectively. PAM and $BaCl_2$ removed most of the impurities on the diatomite, improved surface chemistry characterization and porous structure of the diatomite. Experimental data obtained from the present study indicated that the best condition for Pb^{2+} adsorption on the dry diatomite (diatomite dosage) was $50\text{ g}\cdot\text{L}^{-1}$, pH value was 7, adsorption time was 120 min, and initial concentration of Pb^{2+} was $200\text{ mg}\cdot\text{L}^{-1}$. The present data also indicate that adsorption capacity of PAM modified diatomite and $BaCl_2$ modified diatomite increased by percentages of 23.4 and 28.5%, respectively when compared with raw diatomite. PAM modified diatomite was the most effective and available adsorbent for adsorption of Pb^{2+} .

Key words: Diatomite, modification, Pb^{2+} , adsorption capacity.

INTRODUCTION

Inorganic pollutants, in particular heavy metal ions, constitute a major class of water contaminants. Most heavy metals are known to be toxic and carcinogenic agents, and when discharged in wastewater, represent a serious threat to the human population (Mohammad et al., 2004). In recent years, a great deal of industrial wastewater containing heavy metal ions has been discharged into aquatic bodies due to rapid development of mining, smelting, electroplating and other industries (Singh et al., 2003; Sarkar et al., 2011; Aksoy et al., 2011; Wang et al., 2006). The wastewater leads to serious water pollution and threatens drinking water safety (De Castro Dantas et al., 2001). Recently, heavy metal

pollution of water has attracted considerable attention and researchers. How to effectively prevent wide concern of environmental protection agency, control and repair wastewater containing heavy metal ions is an important issue.

The treatment of industry wastewater containing heavy metal ions is subject of great concern due to its harmful effect on human health and environment. Lead is the metal of high concern in water environment protection as that the presence of excess amount of its ions in water streams would endanger ecosystems and ultimately public health. The common commercially available lead removal technologies include membranes separation, ion exchange and colloid precipitation. Slow kinetics, poor selectivity and low loading capacity of these technologies make the lead removal process less efficient and expensive (Wang and Smith 2007). Over the last few years, adsorption technology has gained prominence as

*Corresponding author. E-mail: csfuwp@163.com. Tel: +86 731 85623795. Fax: +86 731 85623795.

high effect and low cost in treatment of industry wastewater containing lead ions, suitable adsorbent has been considered as an important factor for application of adsorption technology, there is growing interest in using low cost, commercially available material for adsorption of heavy metals (Al-Qodah, 2000; Wu et al., 2008).

Due to high adsorption capacity, rich source, low cost and easy regeneration, diatomite has been widely employed in treatment of industry wastewater (Zaitan and Chafik, 2005; Tsai et al., 2006; Yang et al., 2003; Al-Degs et al., 2001; Khraishah et al., 2004). Diatomite is a kind of non-metal that consisted of the remains of diatoms, grew and deposited in the sea or lake, and changed throughout with natural environmental action. Raw diatomite contains a lot of impurities, the impurities is unfavorable for adsorption performance of heavy metal ions on diatomite in aqueous solution, so it is necessary to modify diatomite to get better adsorption capacity. It is well known that the clay mineral can be chemically treated or activated by acid to develop its pore structure and the surface chemistry of solid, but acid activation is a common chemical modification, it cannot enhance clay mineral adsorption capacity significantly.

In present study, polypropylene acetamide (PAM) and barium chloride (BaCl_2) was employed to modify the diatomite. The main objective of this work was to illustrate the suitability of an easy and efficient method for modification of the diatomite, and evaluate their adsorption properties for the removal of lead ions (Pb^{2+}) from aqueous solution. The effects of pH value, initial concentration of Pb^{2+} , adsorption time, and diatomite dosage on adsorption of Pb^{2+} onto modified diatomite were tested by single factor experiment to determine the best adsorption conditions. Raw diatomite and modified diatomite was used to adsorb Pb^{2+} under the best adsorption conditions to find out the changes of adsorption capacity before and after modification. Five common adsorbents (PAM modified diatomite, vermiculite, zeolite, raw diatomite and red soil) were selected to adsorb Pb^{2+} in aqueous solution to find out the difference of the five adsorbents' adsorption capacity.

MATERIALS AND METHODS

Materials

The diatomite samples used as adsorbents in this study were obtained from the Mineral Plant of Shengzhou County, Zhejiang province, P. R. China. The characterization of the diatomite were as follows, median particle size was 7.5 μm , bulk density was 0.57 $\text{g}\cdot\text{cm}^{-3}$, surface area ratio was 58.0 $\text{m}^2\cdot\text{g}^{-1}$. Their typical chemical compositions consist of 64.8% SiO_2 , 16.4% Al_2O_3 , and 2.91% Fe_2O_3 . Before using, the diatomite was ground and sieved to produce particles with diameters in the range 30-400 nm, washed several times with distill water, dried in the oven (105°C) at least 2 h, cooled to room temperature, and then stored under dry conditions. polypropylene acetamide (PAM) and barium chloride (BaCl_2), which were purchased from Shanghai Experimental Reagents Ltd. Co. of Shanghai (P. R. China) in the grade for

analysis, was selected as a chemical activator to modified the diatomite samples for the purpose of developing its pore structure and the surface chemistry of solid. The adsorbate used in adsorption experiment was Pb^{2+} , which prepared by $\text{Pb}(\text{NO}_3)_2$ (A. R. grade) in distill water.

Chemical modification

The standard solution of PAM and BaCl_2 were prepared in a concentration range of 1-20 $\text{g}\cdot\text{L}^{-1}$ and 10 -100 $\text{g}\cdot\text{L}^{-1}$. The dried diatomite dosage was 50 g per 200 ml PAM solution and 50 g per 100 ml BaCl_2 solution. The process of chemical modification of the dried diatomite by PAM and BaCl_2 occurred in ground-glass flask with stopper. Therefore, the solution containing diatomite and PAM or BaCl_2 was first prepared in the flask, and then the flask was placed in a shaker bath which was shaken at 200 rpm for 3 h under constant temperature conditions. Afterward, the solution was filtered in a vacuum filter flask and washed several times with distill water to remove the ions and other residues. The resulting samples were finally dried at 105°C for 24 h, and then stored under dry conditions. Chemical modification of the dry diatomite with the BaCl_2 solution should be under the condition of the existence of H_2SO_4 in a constant concentration of 0.5 mol/L. The best concentrations of PAM and BaCl_2 standard solution for modification of the dry diatomite was determined by adsorption capacity of Pb^{2+} onto the resulting samples. Scanning electron microscope (SEM) was employed to find out the changes of pore structure and surface chemistry characterization of the dry diatomite before and after modification.

Equilibrium adsorption

In present study, a concentration range of 5-60 $\text{g}\cdot\text{L}^{-1}$ was employed for the adsorbent (raw diatomite or modified diatomite), and a concentration range of 100-1000 $\text{g}\cdot\text{L}^{-1}$ for the adsorbate (Pb^{2+} ions). The effect of pH was studied by adding accurate amounts of standard HSO_4 and NaOH solution to a sample series of given adsorbate and adsorbent concentrations, whilst that of adsorption time was tested at values of 15, 30, 60, 120 min, respectively. The equilibrium adsorption test was conducted by transferring an accurately weighed amount of the adsorbent and 100 ml of a standard ion solution of different concentrations into a 250 ml ground-glass flask with stopper, and then the flask was shaken at 200 rpm for a certain time under constant temperature. When equilibrium had been attained, the solutions were filtered and the Pb^{2+} ion concentration remaining in the aqueous phase determined by flame atomic adsorption spectroscopy (AAS). The equilibrium adsorption density, q ($\text{mg}\cdot\text{g}^{-1}$) and the ion removal efficiency η (%) were calculated from the relationship:

$$q=(C_0-C_e)V/W \quad 1$$

$$\eta=(C_0-C_e)/C_0\times 100\% \quad 2$$

where C_0 ($\text{mg}\cdot\text{L}^{-1}$) represents the initial Pb^{2+} ion concentration, C_e ($\text{mg}\cdot\text{L}^{-1}$) is the equilibrium Pb^{2+} ion concentration, V (mL) is the volume of Pb^{2+} ion solution, W (g) is the adsorbent (raw diatomite or modified diatomite) dosage.

RESULTS AND DISCUSSION

Modification of the dry diatomite

Figure 1A shows that the curve of adsorption capacity of

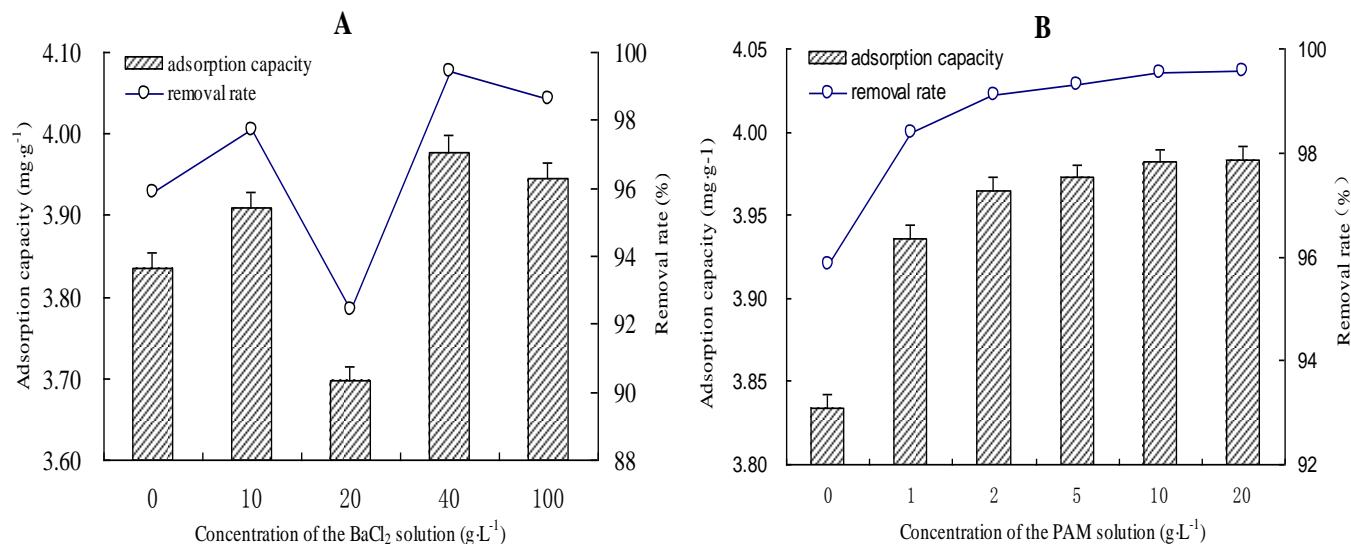


Figure 1. The influence of the PAM and BaCl₂ solution concentration (A. PAM, B. BaCl₂). Significant differences among treatments ($P < 0.05$).

modified diatomite and removal rates of Pb²⁺ with increasing of the BaCl₂ solution concentration was just like "M". This indicated that modification of the dry diatomite by BaCl₂ included four stages. The first stage was that deposition of BaSO₄, which was obtained from the reaction of BaCl₂ and H₂SO₄, improved pore structure of the diatomite, the impurities on the diatomite surface were eliminated by rubbing of BaSO₄, and the inner-channels in the diatomite were under-propped by BaSO₄, this was favorable for adsorption of Pb²⁺ onto the diatomite, hence adsorption capacity of the diatomite against Pb²⁺ and removal rates of Pb²⁺ increased. The second stage was that, excessive deposition of BaSO₄ restrained adsorption of Pb²⁺ on the diatomite due to its block, this led to decrease of the diatomite adsorption capacity against Pb²⁺ and removal rates of Pb²⁺. The three stage was that, SO₄²⁻ dissolved from BaSO₄ combined with Pb²⁺ to generate precipitation (PbSO₄), simultaneously, the adsorption of Pb²⁺ on diatomite kept on. Hence, adsorption capacity of the diatomite and removal rates of Pb²⁺ got enhancement again. The last stage was that, adsorption of Pb²⁺ onto surface of the diatomite got equilibrium. The results showed that the best concentration of the BaCl₂ solution for the diatomite chemical modification was 40 g·L⁻¹.

The effects of the PAM solution concentration on adsorption capacity of the diatomite and removal rate of Pb²⁺ in aqueous solution were shown in Figure 1B. Figure 1B illustrated that adsorption capacity of the diatomite and removal rates of Pb²⁺ were both promoted by the PAM solution significantly ($P < 0.05$) in a concentration range of 0-5 g·L⁻¹. When the PAM solution concentration varied from 5 to 10 g·L⁻¹, the increase degree of adsorption capacity of the diatomite and removal rate of Pb²⁺ was weak. The results indicated that the PAM

solution had the most efficient affect on the development of pores structure of the diatomite; it can be further confirmed from scanning electron microscope (SEM) of the diatomite pores structure shown in Figure 3. Two reasons could explain this phenomenon, one was that the diatomite surface and pores was covered by PAM, this could improve pore structure of the diatomite. The other was that PAM could be hydrolyzed to CO-NH₂ and other hydrolyzates in the aqueous solution. -NH₂ of CO-NH₂ could be replaced by -OH of H₂O, this made the diatomite surface bring with more negative charge. In short, good pore structure and more negative charge could improve adsorption capacity of the diatomite and removal rate of Pb²⁺. The results revealed that the best concentration of the PAM solution for the diatomite chemical modification was 20 g·L⁻¹.

Characterization of modified diatomite

Figure 2 shows scanning electron microscope (SEM) of the dry diatomite particle before and after modification by the PAM solution. Figure 2 shows that the diatomite covered with a layer of PAM. PAM covered on the diatomite's surface as well as its pores and channels, improved its surface chemistry characterization and pore structure, and enhanced its surface negative charges. All of those were favorable for adsorption of Pb²⁺ on the diatomite. Figure 3 shows scanning electron microscope (SEM) of the dry diatomite particle before and after modification by the BaCl₂ solution. Figure 3 shows that raw diatomite surface was rough, and its pores were blocked by impurities. After modification by the solution containing BaCl₂ and H₂SO₄, impurities were eliminated, modified diatomite surface was smooth, and its pores

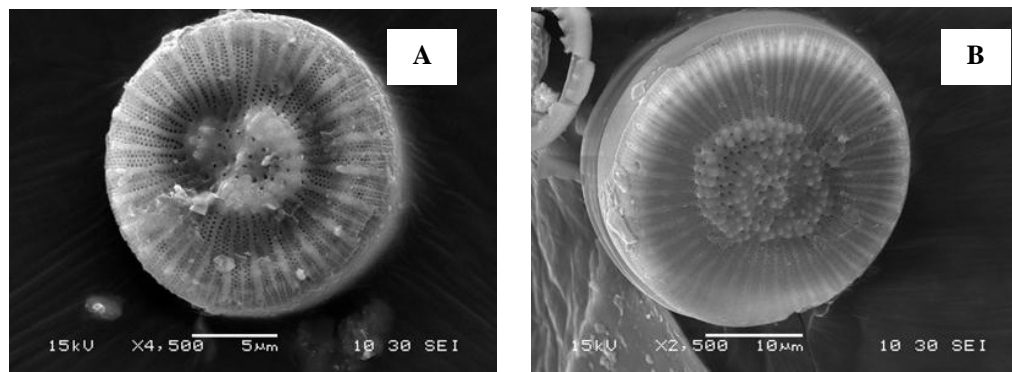


Figure 2. Scanning electron microscope (SEM) of diatomite particles before and after modification by the PAM solution (A. Before, B. After).

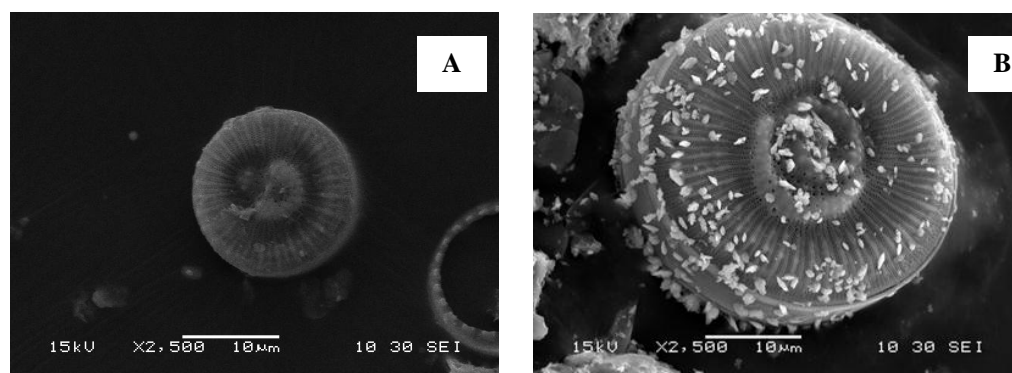


Figure 3. Scanning electron microscope (SEM) of diatomite particles before and after modification by the solution containing BaCl_2 and H_2SO_4 (A. Before, B. After).

structure improved. There was much BaSO_4 crystal separated out on diatomite surface and its pores. These phenomena indicated that there were two processes of modification for the diatomite by the solution containing BaCl_2 and H_2SO_4 , one was that BaSO_4 deposited on diatomite surface and rubbed its surface, this could removed impurities of the diatomite. The other process was that, BaSO_4 crystal was absorbed on surface of the diatomite; it could underprop the inner-channels in the diatomite.

Adsorption of Pb^{2+} on the dry diatomite

The effect of diatomite dosage, the value of pH, adsorption time, and initial ions concentration on the adsorption process of Pb^{2+} on the dry diatomite were displayed in Figure 4, adsorption capacity of the dry diatomite increased with increasing of diatomite dosage, pH value, adsorption time and initial concentration of Pb^{2+} , removal rates of Pb^{2+} increased with increasing of diatomite dosage, pH value, adsorption time while decreased with increasing of Pb^{2+} ions initial concentration. As shown in Figure 4A, there was obvious

relationship between adsorption capacity and diatomite dosage; this may be due to the fact that the increase of diatomite dosage can provide more effective surface area, pores, inner-channels, hydroxyl and negative charges for adsorption of Pb^{2+} on the diatomite in aqueous solution (Al-Degs et al., 2001). The adsorption capacity increased with increasing diatomite dosage up to $60 \text{ g}\cdot\text{L}^{-1}$, having a value of $4.97 \text{ mg}\cdot\text{L}^{-1}$, and then remained constant, therefore, a diatomite dosage of $60 \text{ g}\cdot\text{L}^{-1}$, or above, ensured full coverage of all adsorption site. As shown in Figure 4B, adsorption capacity increased with increasing of pH value, it can be attributed to the relationship between the value of pH and the diatomite specific surface characterization (Bayat, 2002). Varying of the pH value can change the diatomite surface electric potential (ζ). Hydroxyl ($-\text{OH}$) of the diatomite surface was difficult to dissociation in a low value of pH in aqueous solution, this reduced diatomite surface negative charges. Furthermore, when the value of pH was low, concentration of H^+ was higher in aqueous solution; H^+ competed with Pb^{2+} to get adsorption sites. The best value of pH for diatomite absorbing Pb^{2+} got from this test was 7. As shown in Figure 4C, extending adsorption time was favorable for adsorption of Pb^{2+} on the diatomite.

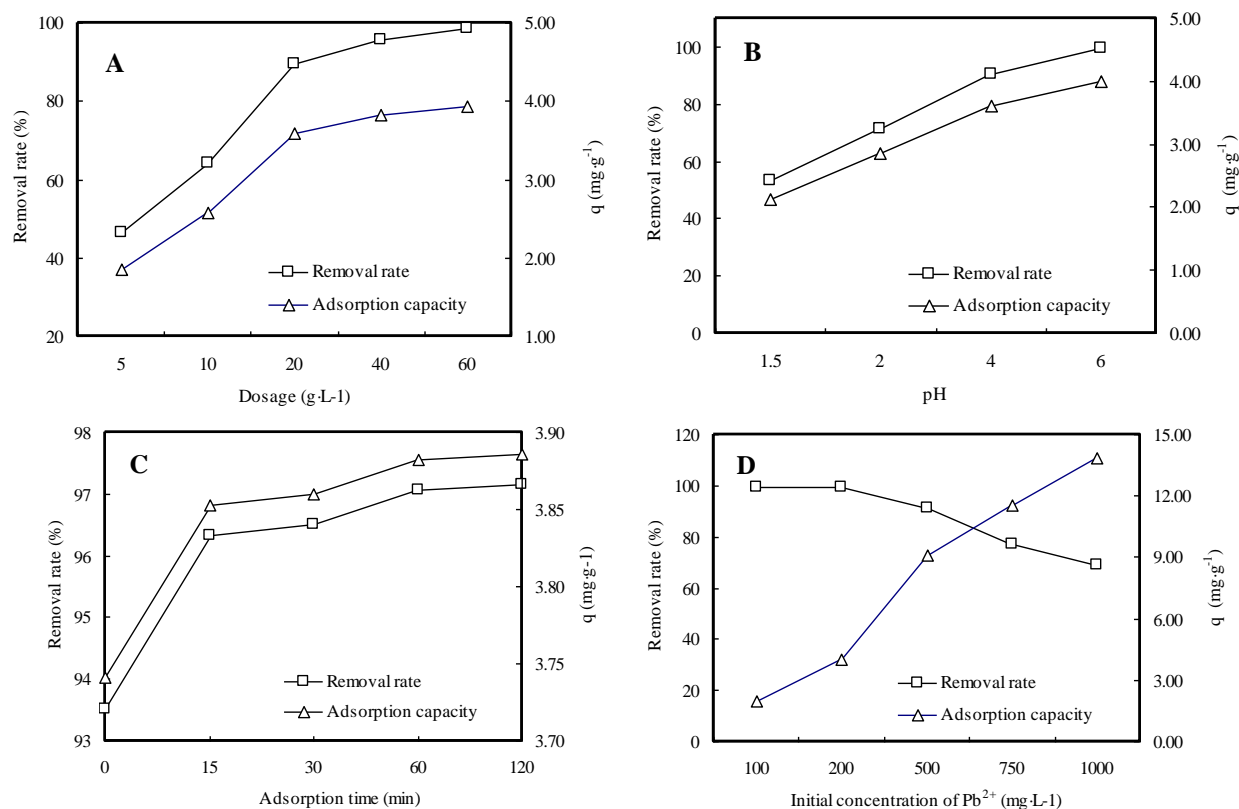


Figure 4. The effect of diatomite dosage, pH value, adsorption time and initial Pb²⁺ concentration on adsorption of Pb²⁺ on the dry diatomite. Significant differences among treatments ($P < 0.05$).

This was due to the fact that lead ions (Pb²⁺) could get more and more adsorption sites with extending of adsorption time. The adsorption equilibrium was obtained after 120 min. Diatomite dosage, the value of pH, adsorption time were maintained constant, as shown in Figure 4D, the lead (Pb²⁺) adsorption characterization were dependent on initial concentration of Pb²⁺. Adsorption capacity decreased with increasing of initial concentration of Pb²⁺, this can be explained by the fact that limited adsorbent cannot provided extra available surface area and inner-channels for increasing lead ions (Pb²⁺), the dry diatomite had the best adsorption capacity of Pb²⁺ while the value of Pb²⁺ initial concentration was 200 mg·L⁻¹. Therefore, the best condition for adsorption of Pb²⁺ on the diatomite was that, the dosage of diatomite was 50 g·L⁻¹, the value of pH was 7, adsorption time was 120 min, initial concentration of Pb²⁺ was 200 mg·L⁻¹.

Adsorption capacity comparison

A study of adsorption capacity of lead ions (Pb²⁺) on the raw diatomite and the modified diatomite under the best condition in aqueous solution was conducted; the results are shown in Table 1. As shown in Table 1, the

Table 1. Adsorption capacity of Pb²⁺ onto raw diatomite (DE), PAM modified diatomite (PAM-DE) and the BaCl₂ modified diatomite (Ba-DE) under the best adsorption condition.

Sample	W ₀ (g·L ⁻¹)	pH	C ₀ (mg·L ⁻¹)	t (min)	q (mg·g ⁻¹)
DE	50	7	200	120	6.52
PAM-DE	50	7	200	120	9.12
Ba-DE	50	7	200	120	8.51

W₀, dosage of samples; C₀, initial concentration of Pb²⁺; t, adsorption time; q, adsorption capacity of samples. Significant differences among treatments ($P < 0.05$).

adsorption capacity of Pb²⁺ on the PAM modified diatomite (PAM-DE) was found to be higher than that on the raw diatomite (DE) or the BaCl₂ modified diatomite (Ba-DE), with the relative adsorption capacity following the sequence: PAM-DE > Ba-DE > DE. This was attributed to the fact that adsorption capacity of adsorbent was governed by its surface characterization and pores structure, PAM-DE and Ba-DE had more effective surface area, pores, inner-channels, hydroxyl and negative charges than DE, hence the adsorption capacity of PAM-DE and Ba-DE increased by percentage of 23.4 and 28.5% compared with DE, respectively. This indicated

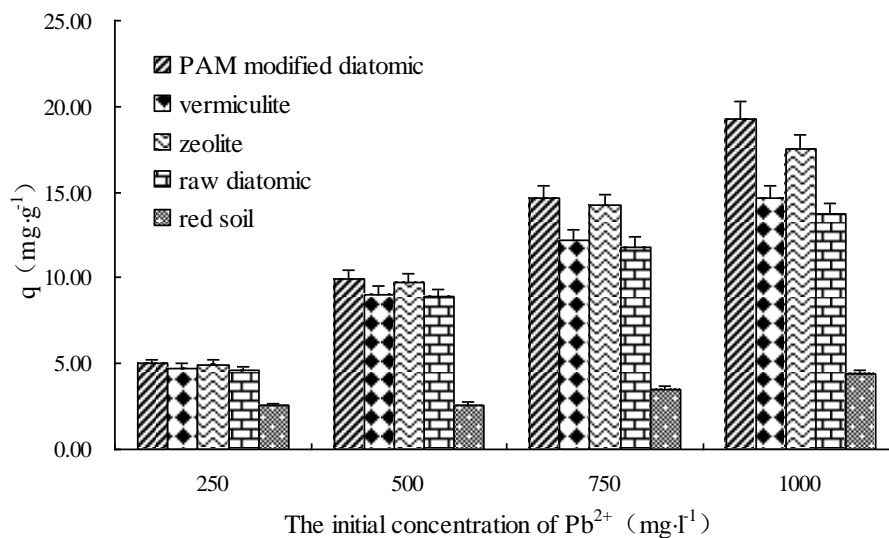


Figure 5. Adsorption capacity of Pb²⁺ onto the five adsorbents under different initial concentration of Pb²⁺. Significant differences among treatments ($P < 0.05$).

that PAM and BaCl₂ could improve surface characterization and pores structure of diatomite effectively.

A study of adsorption capacity of Pb²⁺ onto the five adsorbents (PAM modified diatomite, zeolite, vermiculite, raw diatomite, red soil) in aqueous was undertaken in this work. As shown in Figure 5, the relative adsorption capacity of lead ions (Pb²⁺) onto the five adsorbents followed the sequence: PAM modified diatomite > zeolite > vermiculite > raw diatomite > red soil, this indicated that PAM modified diatomite is the most effective and available adsorbent for adsorption of Pb²⁺. The adsorption capacity of Pb²⁺ onto PAM modified diatomite was found to be affected by initial Pb²⁺ concentration significantly ($P < 0.05$), with its value increasing from 9.84 to 19.30 mg·g⁻¹ as the initial Pb²⁺ concentration changed from 250 to 1000 mg·L⁻¹, this can be explained by the fact that the PAM modified diatomite have better surface characterization than other adsorbents.

Conclusion

PAM and BaCl₂ eliminated most of the impurities on the diatomite effectively, improved its special surface characterization and pores structure significantly, and thus, increased its adsorption capacity against Pb²⁺. The best concentration of the BaCl₂ and PAM solution for chemical modification of the diatomite was 40 and 20 g·L⁻¹, respectively.

The best condition for adsorption of Pb²⁺ onto the diatomite was that, the dosage of the diatomite was 50 g·L⁻¹, the value of pH was 7, adsorption time was 120

min, initial concentration of Pb²⁺ was 200 mg·L⁻¹. The relative adsorption capacity of Pb²⁺ onto PAM modified diatomite (PAM-DE), BaCl₂ modified diatomite (Ba-DE) and raw diatomite (DE) followed the sequence: PAM-DE > Ba-DE > DE. The relative adsorption capacity of lead ions (Pb²⁺) onto the five adsorbents followed the sequence: PAM modified diatomite > zeolite > vermiculite > raw diatomite > red soil.

ACKNOWLEDGEMENTS

This work was financially supported by the Special Fund of Environmental Public Welfare Industry Research (200909066), Key Program of Changsha Science and Technology Agency (k1001108-31) and Hunan Key Discipline Construction Found of Environmental Science (2006180).

REFERENCES

- Aksoy A, Leblebici Z, Bağcı Y (2011). Determination of heavy metal pollution in some honey samples from Yozgat Province, Turkey. *Environ. Earth Sci.*, 7: 1037-1043.
- Al-Degs Y, Khraisheh MAM, Tutunji MF (2001). Sorption of lead ions on diatomite and manganese oxides modified diatomite. *Water Research*, 35(15): 3724-3728.
- Al-Qodah Z (2000). Adsorption of dyes using shale oil ash. *Water Research*, 34(17): 4295-4303.
- Bayat B (2002). Combined removal of zinc(II) and cadmium(II) from aqueous solution by adsorption onto high-calcium trukish fly ash. *Water Air and Soil Pollut.*, 136(1/4): 69-92.
- De Castro Dantas TN, Neto AA, Moura MC (2001). Removal of cadmium from aqueous solutions by diatomite with micro-emulsion. *Water Research*, 35(9): 2219-2224.
- Khraisheh MMA, Al-Ghouti MA, Allen SJ, Ahmad MNM (2004). The effect of pH, temperature and molecular size on the removal of dyes

- from textile effluent using manganese oxides-modified diatomite. *Water Environ. Res.*, 76(6): 51-59.
- Mohammad A, Al-Ghoutia, Majeda AM, Khraishehb, Maha T (2004). Flow injection potentiometric stripping analysis for study of adsorption of heavy metal ions onto modified diatomite. *Chem. Engr. J.*, 104: 83-91.
- Sarkar S, Ghosh PB, Sil AK, Saha T (2011). Heavy metal pollution assessment through comparison of different indices in sewage-fed fishery pond sediments at East Kolkata Wetland, India. *Environ. Earth Sci.*, 63: 915-924.
- Singh OV, Labana S, Pandey G, Budhiraja R; Jain RK (2003). An overview of metallic ion decontamination from soil. *Appl. Microbiol. Biotechnol.*, 61: 405-412.
- Tsai WT, Lai CW, Hsien KJ (2006). Characterization and adsorption properties of diatomaceous earth modified by hydrofluoric acid etching. *J. Colloid and Interface Sci.*, 297: 749-754.
- Wang B, Smith TR (2007). Performance of a diatomite-based sorbent in removing mercury from aqueous and oil matrices. *J. Environ. Eng. Sci.*, 6(5): 469-476.
- Wang XS, Qin Y, Chen YK (2006). Heavy metals in urban roadside soils part 1: effect of particle size fractions on heavy metals partitioning. *Environ. Geol.*, 50: 1061-1066.
- Wu XF, Zhao F, Chen ML, Zhang YL, Zhao C, Zhou HL (2008). Factors affecting the adsorption of Zn^{2+} and Cd^{2+} ions from aqueous solution onto vermiculite. *Adsorpt. Sci. Technol.*, 26(3): 146-155.
- Yang YX, Zhang JiB, Yang WM, Wu JD, Chen RS (2003). Adsorption properties for urokinase on local diatomite surface. *Appl. Surf. Sci.*, 206:20-28.
- Zaitan H, Chafik T (2005). FTIR determination of adsorption characteristics for volatile organic compounds removal on diatomite mineral compared to commercial silica. *Comptfs Rendus Chimie* 8: 1701-1708.