Desalination and Water Treatment
www.deswater.com

doi: 10.5004/dwt.2018.21990

103 (2018) 216–220
January

Adsorption of heavy metal ions with modified diatomite from effluent

Wangkun Liu[a], Jian Zhang[a,b,*], Na Li[a], Qingwei Ping[a]

[a]*School of Light industry and Chemical Engineering, Dalian Polytechnic University, Dalian, 116034, China, Tel. +86 411 8632 3327, Fax +86 411 8632 3736, email:673170056@qq.com (W. Liu), zhangjian@dlpu.edu.cn (J. Zhang), linda_326@126.com (N. Li), pingqw@dlpu.edu.cn (Q. Ping)*
[b]*State Key Laboratory of Pulp and Paper Engineering, South China University of Technology, Wushan Road 381, Guangzhou, 510640, China*

Received 28 September 2017; Accepted 31 January 2018

ABSTRACT

Heavy metal ions pollution has become one of the most serious environmental problems today. Recently various methods for heavy metal ions removal from wastewater have been extensively investigated. These technologies include chemical precipitation, ion-exchange, adsorption, membrane filtration, coagulation–flocculation, flotation and electrochemical methods. Comparatively speaking, adsorption of inorganic non-metallic materials was recognized as an effective and economic method, such as activated carbon and diatomite. This work mainly discusses the properties of the diatomite and the modified diatomite and their application levels in treatment of wastewater containing heavy metal ions. The operating variables of modified methods and adsorption conditions were studied as well. The equilibrium was investigated as well. Results showed that the diatomite and the modified diatomite can adsorb the heavy metal ions efficiently, especially the modified diatomite. The adsorption of heavy mental ions by the diatomite was restricted by temperature and pH. Currently, the lower temperature and pH were, the less removal efficiency was achieved. After being treated with alkaline, the surface area of the diatomite was improved greatly which achieved better adsorption properties. The isotherms results revealed that the equilibrium data fitted the Langmuir model better. It confirmed the applicability of the diatomite as an efficient adsorbent and provided an attractive and low-cost process to remove hazardous materials.

Keywords: Diatomite; Heavy metal ions; Adsorption; Equilibrium; Modified

1. Introduction

Lead played an important role in industrial activities including the manufacture of paint, printing, battery industries and other fields for its wide distribution and high ductility. But it also brought many more environmental problems with the rapid development of its wide application. Among them, the pollution of water by lead is especially serious [1]. These pollutants could cause serious environmental problems due to their acute toxicity and their accumulation in food chains. It is difficult to metabolize once lead it enters the human body. It especially affects children's growth and development, intelligence, learning, memory and other health functions [2,3]. According to the reports, it revealed that children's blood lead poisoning phenomenon exists generally in some areas of China [4,5] Therefore, the prevention and remediation of lead pollution is of special importance [6].

Physical, chemical and biological methods [7] for heavy metal ions removal have been widely researched recently, such as membrane filtration [8], Ion exchange [9], and adsorption techniques [10]. Adsorption has obvious advantages in removing heavy metal ions in comparison with other methods. Numerous adsorbents such as bentonite [11], textile wastes [12], graphene oxides [13], palm kernel husk carbon [14], and various modified diatomite [15–19] have been investigated for their potential application to lower heavy metal ions concentrations from aqueous solutions. Based on our earlier research works, it found

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*Corresponding author.

the diatomite was a promising adsorbent for the removal of hazardous substance because of its excellent adsorption properties.

Diatomaceous earth, or simply "diatomite" for short, is kind of low-density biogenic sediment, which consists essentially of amorphous silica ($SiO_2{\cdot}nH_2O$) derived from opalescent frustules of diatoms. It consists of a wide variety of shapes and characterized by a high porosity, low density and high surface area. All these properties suggest that the diatomiteis a potential adsorbent for pollutants found in industrial wastewater such as dyes, colloid resin and etc. Based on this fact, in this work, local diatomaceous earth was tested for its potential use as an adsorbent for the removal of Pb(II) ions. Furthermore, the effect of surface modification of diatomite by NaOH on Pb(II) adsorption was investigated as well. The equilibrium studies revealed the adsorption mechanism.

2. Experimental

2.1. Materials

The raw diatomite samples were provided by Jilin Lulin novel materials Co., Ltd., Baishan, Jilin province, China. The morphology features and surface characteristics of the diatomite samples were observed using scanning electron microscopy (JEOL, JSM-6460LV, Japan). The specific surface area was obtained by surface from the linear part of the BET plot (P/P0 = 0.05~0.20) at 77 K using a Quanta chrome autosorb NOVA 2200e volumetric analyzer. Sodium hydroxide, lead nitrate, and other chemical agents were of analytical grade and were purchased from commercial sources in China.

2.2 Surface modification

Naturally occurring diatomaceous earth has been tested as a potential sorbent for Pb(II) ions according to the method of Salman T [20]. The results indicated that the maximum value reached 17.58% when the dosage was 0.06 g. It was not ideal, so NaOH was used as modifier in order to improve the reaction activity of diatomite. 10 g of diatomite were immersed in sufficient 5% sodium hydroxide. The reaction temperature was maintained at 60°C for 90 min. The sample was then washed, dried in an oven at 100°C, desiccated and stored in tightly stoppered glass bottle for the following research.

2.3 Adsorption studies

The adsorption of Pb (II) onto modified diatomite was investigated by using batch mode. The following experiments were conducted by using a range of Pb(II) concentrations (20, 50, 100 mg·L^{-1}). Adsorption experiment was carried out by shaking adsorbent with 20 mL aqueous solution of Pb(II) to determine the effects of various process parameters, different conditions of temperature (25, 35, 45°C), diatomite dosage (0.06 g), contact time (10–180 min), and pH (from 1.0 to 13.0). The system was adjusted to the desired pH varying from 1 to 13 by adding minute volumes of NaOH or HCl. After the suspensions were shaken, the solid and liquid phases were separated through 0.45 µm filter membrane. The concentration of Pb(II) in aqueous solutions was determined by atomic absorption spectrometer (AAS 180-80, JAPAN) [21].

The metal uptake capacity (Q_e) and removal efficiency (R) of Pb(II) onto modified diatomite were calculated according to Eqns. (1) and (2).

$$Q_e = \frac{\left(C_0 - C_e\right) \times V}{M} \tag{1}$$

$$\mathrm{R} = \frac{\left(C_0 - C_e\right) \times 100}{C_0} \tag{2}$$

where Q_e is the adsorption capacity at equilibrium (mg g^{-1}), R is the removal efficiency (%); C_0 is the initial concentration (mg·L^{-1}); C_e is the equilibrium concentration (mg·L^{-1}); V is the volume of solution (L); M is the mass of modified diatomite (g).

3. Results and discussion

3.1. Characterization of diatomite

The morphology of the raw diatomite and the modified diatomite was shown by the scanning electron micrograph (Fig. 1 and Fig 2). It was found that the raw diatomite was not pure enough and most of the holes in the surface were blocked by impurities which reduced the adsorption efficiency. However after the modification, results revealed that the disc surface of the modified diatomite was much cleaner with a clearly identifiable channel structure, which provided a good possibility for Pb(II) to be trapped and adsorbed.

The surface areas and pore-size of diatomite were studied by Brunauer–Emmett–Teller (BET) (Table 1). The surface area, pore volume and the pore diameter were increased greatly after modification. This results are consistent with the front SEM work. It indicated that the modified diatomite showed an excellent surface structure and high specific surface area.

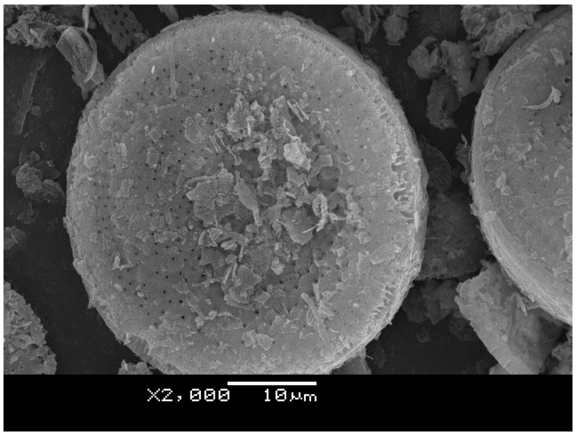

Fig. 1. SEM of the diatomite.

3.2. Effect of pH on the Pb(II) adsorption

The pH of the aqueous solution was a key element affecting the sorption of Pb(II) as it not only influences Pb(II) species in solution, but also affects the surface properties of the adsorbents [22]. Results are shown in Fig. 3.

As shown in Fig. 3, the adsorption capacity revealed that the removal efficiency increases obviously as the pH range of 1–5, the maximum value reached 86.24% at pH 5, and then decreased with further increase in pH values. The effect of pH can be explained by considering that the main difference species of lead in aqueous solution. It showed Pb^{2+} species at pH < 7, $Pb(OH)^+$ species at pH 7.5–9, $Pb(OH)_2$ species at pH 9.5–11 and $Pb(OH)_3^-$ species at pH >11 [23].

The researchers [24,25] found that the enhanced adsorption of Pb(II) at pH 2–5 was owing to the electrostatic attraction between negatively charged diatomite and positively charged Pb(II) species such as Pb^{2+} or $Pb(OH)^+$ species. Due to the electrostatic repulsion between the negatively charged surface of diatomite and negatively charged $Pb(OH)_3^-$ species, the adsorption of Pb(II) could be difficult. Based on the result, the pH 5 was chosen for further adsorption experiments.

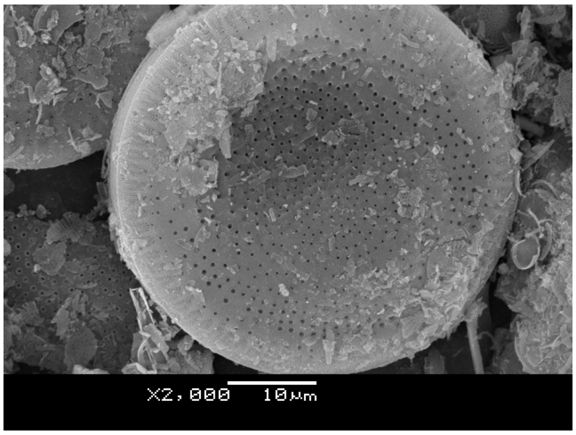

Fig. 2. SEM of the modified diatomite.

Table 1
BET of the diatomite material

	S_{BET} ($m^2 \cdot g^{-1}$)	Pore volume ($cm^3 \cdot g^{-1}$)	Pore diameter (nm)
Diatomite	15.32	0.058	7.356
Modified diatomite	46.90	0.091	12.451

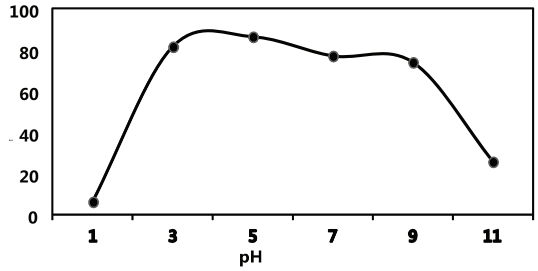

Fig. 3. Effect of pH on Pb(II) adsorption.

3.3 Effect of contact time on the Pb(II) adsorption

The effect of contact time on the Pb(II) was studied at room temperature. Fig. 4 shows that the removal of Pb(II) by adsorption using the modified diatomite was rapid during the initial period of contact time which may be due to the larger surface area of the diatomite. As the surface adsorption sites become exhausted, the uptake rate was controlled by the rate at which the adsorption was transported from the exterior to the interior sites of the absorbent particles.

The removal efficiency reached equilibrium at 150 min with 86.02% adsorption capacity. Thus the contact time of 150 min was chosen in subsequent sorption experiments to guarantee the optimum Pb(II) absorption.

3.4. Adsorption isotherms study

The effect of temperature on Pb(II) removal was studied by using a solution pH of 5, with a contact time of 150 min in each batch equilibrium adsorption. The effect of Pb(II) equilibrium concentration on the adsorption capacity of the modified diatomite was carried out at 25°C, 35°C and 45°C as shown in Fig.5.

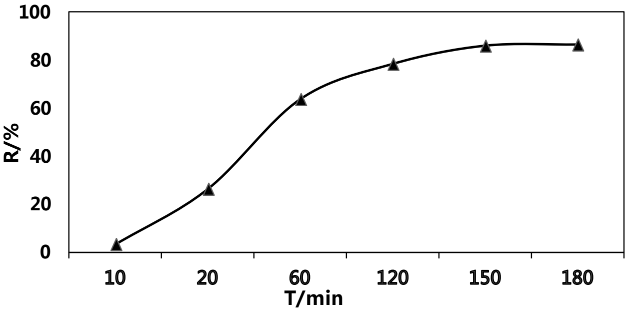

Fig. 4. Effect of contact time on Pb(II) adsorption.

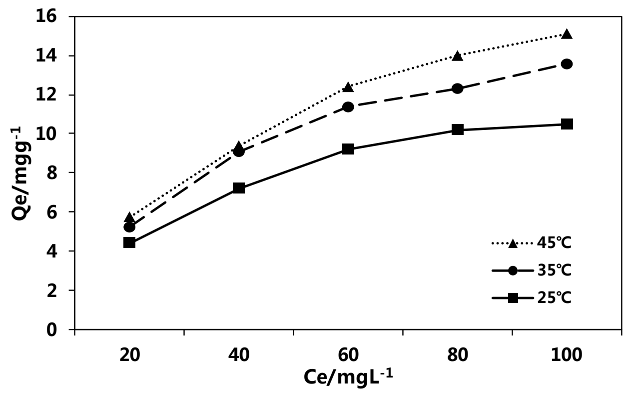

Fig. 5. Adsorption isotherms of Pb(II) on modified diatomite.

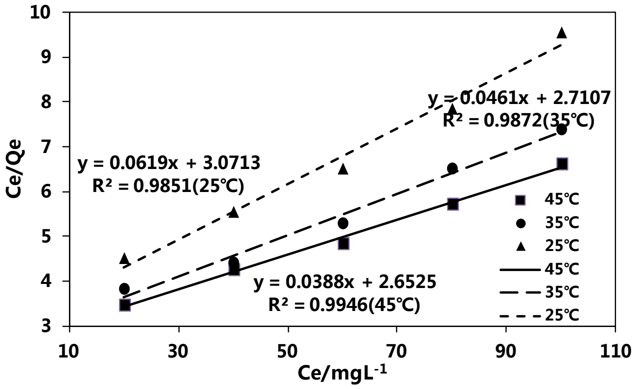

Fig. 6. Langmuir isotherms for Pb(II) adsorption on modified diatomite.

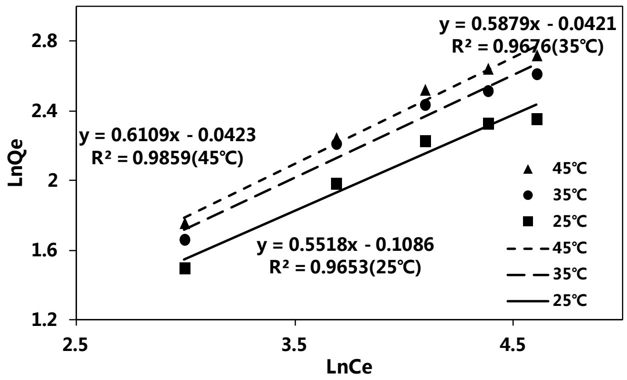

Fig. 7. Freundlich isotherms for Pb(II) adsorption on modified diatomite.

Results indicated that the Pb(II) adsorption on modified diatomite increased with the increase of Pb(II) concentration and temperature. The increase was obvious as the temperature increased from 25°C to 35°C. However the increase was slow from 35°C to 45°C. It suggested that the adsorption of Pb(II) on the diatomite is endothermic, indicating that the adsorption was favorable at higher temperature.

The Langmuir model [26] and Freundlish model [27] were expressed as follows:

$$\frac{C_e}{Q_e} = \frac{C_e}{Q_{\max}} + \frac{1}{Q_{\max} K_L} \tag{3}$$

$$\ln Q_e = \ln K_F + \frac{1}{n} \ln C_e \tag{4}$$

where Q_{max} is the maximum value of metal ion adsorption per unit weight of adsorbent that is related to the monolayer adsorption capacity (mg·g^{-1}), K_L is a Langmuir constant relate to the affinity of the binding sites and energy of adsorption (L·g^{-1}), k_F (L·g^{-1}) and n is Freundlich parameter which correspond to adsorption capacity and adsorption intensity, respectively.

The results are shown in Fig. 6 and Fig. 7.

Table 2
Langmuir and Freundlich parameters for Pb(II) adsorption on modified diatomite

	Langmuir			Freundlich		
T(°C)	Q_{max} (mg.g^{-1})	K_L	R^2	K_F	$1/n$	R^2
25	16.16	0.0202	0.9851	0.9586	0.6109	0.9859
35	21.69	0.0170	0.9872	0.9588	0.5879	0.9676
45	25.77	0.0146	0.9946	0.8971	0.5518	0.9653

The calculated results of Langmuir and Freundlich isothermal adsorption parameters are summarized in Table 2.

Table 2 shows that the maximum monolayer capacity obtained from Langmuir was 25.77mg·g^{-1} at 45°C. It revealed that the diatomite exhibited better ability to remove Pb(II) from aqueous solution. However, by comparing the coefficient of determination (R^2) values, it was found that the adsorbent systems are well described by the Langmuir isotherm model. The $(1/n)$ value indicates the degree of nonlinearity between solution concentration and adsorption as follows: when $1/n < 1$, then adsorption is a physical process. when $1/n > 1$, then adsorption is a chemical process. The $(1/n)$ value in Freundlich equation was found to be 0.55–0.62, (Table 2). The situation is most common and maybe due to a distribution of surface sites or any factor that causes a decrease in adsorbent-adsorbate interaction with increasing surface density and the values of $(1/n)$ within the range of 0–1 represent good adsorption [28]. In the present study, it indicated the adsorption of the heavy metal ions onto modified diatomite was physical process.

4. Conclusion

The modified diatomite used in this study was superior to the raw diatomite. The high increase in adsorption efficiency of the modified diatomite was attributed to the increase in surface area, pore volume and electronegativity. The adsorption of Pb(II) on modified diatomite is strongly dependent on pH. When pH was 5, the removal efficiency reached the maximum value at 150 min with 86.51% adsorption capacity. The adsorption is endothermic and favorable at high temperature. By comparing the coefficient of determination (R^2) values, the adsorption isotherms of Pb(II) on modified diatomite can be described well by the Langmuir model and the adsorption of Pb(II) onto modified diatomite was a physical process. The researchers also confirmed the applicability ofthe modified diatomite as an efficient adsorbent and provided an attractive and low-cost process to remove hazardous materials.

Acknowledgements

Authors are grateful to the Fund of state key laboratory of pulp and paper engineering (No. 201523)

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