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Adsorption of Lead Ions by Linde type F(K) Zeolite

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Abstract. The Test was to examine the adsorption property of Pb(Ⅱ) irons by Linde type F (K) zeolite. The zeolite was synthesized by fly ash. The adsorbent dosage, pH, reaction temperature and reaction time were investigated. The adsorption isotherm and adsorption kinetics equation were studied. The results showed the adsorbent dosage, pH, reaction temperature and reaction time had significant effects on the adsorption of Pb(Ⅱ) irons. The removal rate was improved with the increasing of zeolite dosage. The saturated adsorption capacity was decreased gradually. The adsorption of Pb(Ⅱ) irons tended to saturate when initial pH was 6. With the increasing of temperature, the equilibration time of adsorption was shorter. Langmuir isotherm was more applicable to explain the monolayer adsorption procedure of Pb(Ⅱ) on Linde type F(K) zeolite. For adsorption kinetics, pseudo-second order model showed better calculation results.

1. Introduction

Heavy metals are nowadays among the most important pollutants in source and treated water, are becoming a severe public health problem, can be toxic to aquatic life and cause natural waters to be unsuitable as potable water sources [1]. The adsorption with the selection of a suitable adsorbent can be an effective technique for the removal of heavy metals from wastewater [2]. Over recent years, the production of low cost adsorbents has prompted a growing research interest [3]. Fly ash, one of the most abundant waste materials, was formed by the combustion of powdered coal. The amount of fly ash released by factories and thermal power plants has been increased throughout the world. Efficient disposal of fly ash is a worldwide issue because of its massive volume and harmful effects on the environment [4]. The major components of fly ash make it a potential agent for the adsorption of heavy metal contaminants in water and wastewaters [3,5]. Fly ash has potential use in wastewater treatment because of its major chemical components, which are alumina, silica, ferric oxide, calcium oxide, magnesium oxide and carbon, and its physical properties such as porosity,

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particle size distribution and surface area. As a technique for recycling fly ash, synthesis of zeolite from coal fly ash has attracted a great deal of attention [6,7]. Therefore, the synthesis of zeolite will be a successful alternative to deal with fly ash waste, resulting in low-cost and environmentally friendly materials.

Linde F (K) type zeolite is a product gained from hydrothermal reaction between fly ash and high concentration KOH solution. Miyaji had successfully used fly ash to synthesize the zeolite and implied its potential for adsorption [8]. This work is to synthesize Linde F (K) type zeolite from fly ash, and to use it as an adsorbent for removal of Pb(II) from aqueous solution. Chen et al. treated Zn(II) and Cu(II) using Linde F (K) zeolite as an adsorbent, and got a high removal effect[9,10]. In this research several important parameters, including zeolite dosage, pH, temperature and contact time were studied. Adsorption isotherm and kinetics equation were also discussed.

2. Experimental

The Pb（Ⅱ)aqueous solution is prepared through dissolving $Pb(NO_3)_2$ in DI water and the concentration is 150 mg/L. Alkaline solution used for zeolite synthesis is prepared through dissolving KOH in DI water. The solutions used for adjusting adsorption pH are prepared through dissolving NaOH and HNO_3 in DI water. The original fly ash is gained from Taicang Harbour Golden Concord Electric-Power Generation Co. Ltd. (Taicang, Jiangsu Province). The main chemical composition are SiO_2 (51.06%), Al_2O_3 (32.36%), CaO (2.91%), Fe_2O_3 (4.68%), Na_2O (0.45%), MgO (0.90%), K_2O (1.00%) and TiO_2 (1.17%).

Linde type F (K) zeolite is synthesized through fly ash reacted with KOH solution. The zeolite synthesis procedures are as follow. The KOH aqueous solution (8 mol/L) was added to fly ash (2g) in a separable flask and the solution was refluxed with stirring at 95˚C under the opened system (atmosphere pressure: 1.01325×10^5) for 48h. The obtained products were washed with distilled water and dried at 105˚C.

The adsorption experiments are conducted as typical batch studies. The zeolite is mixed with Pb(II) solution in 10ml polypropylene tubes. The tubes with mixtures are fixed in a water bath shaking box and shaken at 150rpm. After adsorption reaction, the mixtures are filtered with 0.45μm membrane and then the concentration of Pb(II) in solution is measured by AA240DUO atomic adsorption spectrophotometry (Agilent Technologies, Inc. USA). The pH of solution is determined by a Q/GHSC 1544-2009 pH meter.

3. Results and Discussion

Effect of zeolite dosage on adsorption. The effect of zeolite dosage on the adsorption of Pb(II) was shown in Fig.1. The zeolite dosage was taken from 0.25 to 6.00 g/L. The initial concentration of Pb(II) solutions was 150 mg/L, initial pH was 7, the temperature was 25℃, and the shaking time was 12h. For each dose, equilibrium concentration was measured and the uptake percentage and adsorption capacity were calculated. The adsorbent dosage is an important parameter because it determines the capacity of an adsorbent for a given initial concentration of the adsorbed material. The results showed that the zeolite dosage had the significant effect on the adsorption of Pb(II) ions. The adsorption efficiency increased from 46% to nearly 100% as the dose increased from 0.25 to 2.00 g/L. This increase was explained by the increase in the surface area and the available adsorption sites of zeolite samples. With increasing of zeolite content, the available sites for binding Pb(II) increased and thereby enhanced the adsorption from solution to zeolite. Fig.1 also showed the saturated adsorption capacity underwent a continuous decrease from 278 mg/g to 25 mg/g with zeolite dosage increasing from 0.25 g/L to 6.00 g/L. This implied the zeolite dosage should be chosen in a reasonable range.

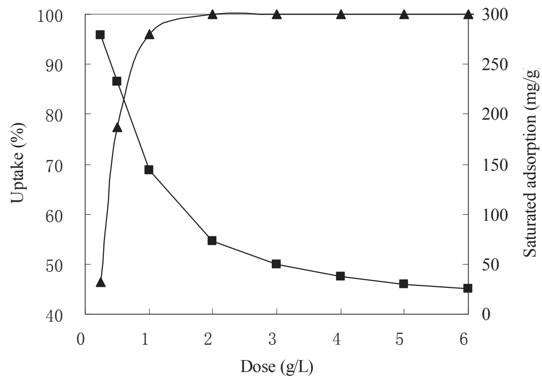

Fig.1 Effect of zeolite dosage on Pb uptake and saturated adsorption capacity

Effect of pH on adsorption. The effect of pH on metal Pb(II) uptake was shown in Fig.2. The experiments were carried out in the pH range of 3.0 to 10.0. The zeolite dosage was 1.00 g/L, the initial concentration of Pb(II) solutions was 150 mg/L, the temperature was 25℃, and the shaking time was 12 hours. As shown in Fig.2, the adsorption efficiency increased from 18% to 97% as pH increased from 3 to 6. The adsorption efficiency was nearly 100% when the pH was 7. It could be seen that the low pH was disadvantage to the adsorption of Pb(II) ions. At low pH values, there was an excess of H_3O^+ ions in the solution, which made a competition between the positively charged hydrogen ions and Pb(II) ions for the available adsorption sites on the negatively charged zeolite surface. As the pH increased, the competition between protons and Pb(II) for surface sites would decrease and Pb(II) ion was the predominating species, which would attract to the surface of zeolite by columbic forces.

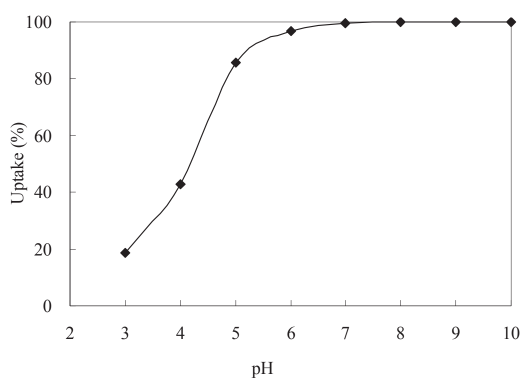

Fig.2 Effect of pH on Pb uptake

Effect of temperature and contact time. The effect of temperature and contact time on the Pb(II) adsorption was shown in Fig.3. The temperature was 25℃, 35℃, and 45℃, respectively. The adsorption time was 12 hours, and the Pb(II) concentration was 150 mg/L. The zeolite dosage wes fixed at 1.00 g/L, and initial pH was 6.0. It could be noticed that the adsorption of Pb(II) ions on zeolite increased with the increase of temperature and contact time. When the temperature was 25℃, the adsorption efficiency increased from 18% to 85%

as the contact time increased from 0.5h to 12h, respectively. With the temperature increased to 35℃, the Pb(II) uptake percentage increased from 41% to 99% as the contact time increased from 0.5h to 12h, respectively. In addition, the adsorption efficiency was improved significantly as the temperature increased to 45℃. The Pb(II) uptake percentage was 86% when the adsorption time was only 0.5h. As shown in Fig.3, the temperature and contact time had significant effects on the Pb(II)adsorption. With the increasing of reaction temperature, the adsorption efficiency of Pb(II) ions was higher, and the equilibration time of adsorption was shorter.

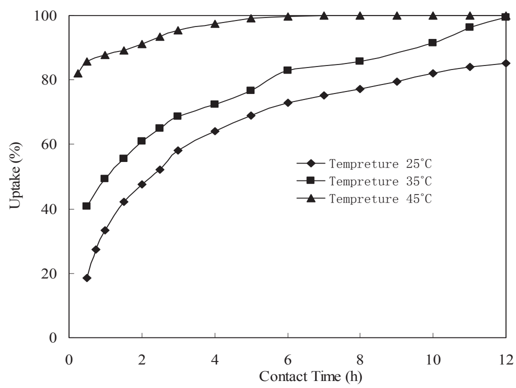

Fig.3 Effect of temperature and contact time on Pb uptake

Adsorption isotherm. For adsorption isotherm, Freundlich isotherm and Langmuir isotherm are usually applied. The equations are as follows.Langmuir isotherm :

$$C_e / Q_e = 1/(bQ_m) + C_e / Q_m \tag{1}$$

where Q_e and C_e are the amount adsorbed (mg/g) and the adsorbate concentration on solution (mg/L), both at equilibrium; b (L/mg) is the Langmuir constant related to the energy of adsorption; and Q_m (mg/g) is the maximum adsorption capacity. Freundlich isotherm :

$$\lg Q_e = \lg K + \frac{1}{n} \lg C_e \tag{2}$$

where K and n are constants for the Freundlich isotherm, they are indicative of the adsorption capacity (mg/g) and adsorption intensity.

Table.1 The Calculation Results Of Langmuir And Freundlich Isotherm

Langmuir				Freundlich			
The linear equation	R^2	Q_m(mg/g)	B(L/mg)	The linear equation	R^2	1/n	K
y=0.0036x+0.0073	0.9831	277.77	0.4932	y=0.3739x+4.076	0.8984	0.3739	58.91

Table1 showed calculation results of Langmuir and Freundlich isotherm. It suggested Langmuir isotherm given better calculation results. The R^2 of Langmuir isotherm (0.9831) was higher than the value of Freundlich isotherm (0.8984). It indicated Pb(Ⅱ) adsorption on Linde F (K) zeolite was a monolayer adsorption procedure.

Adsorption kinetics. The Lagergren pseudo-first order model and Blanchard pseudo-second order model are used to analyze adsorption kinetics. The equations of two models are showed below. The Lagergren pseudo-first order model

$$\log(Q_e - Q_t) = \log Q_e - (K_1/2.303)t \tag{3}$$

where Q_e is equilibrium adsorption amount of Pb on zeolite (mg/g), Q_t is adsorption amount of Pb(Ⅱ) on zeolite at time t (mg/g), K_1 is rate constant of first order model and t is contact time.

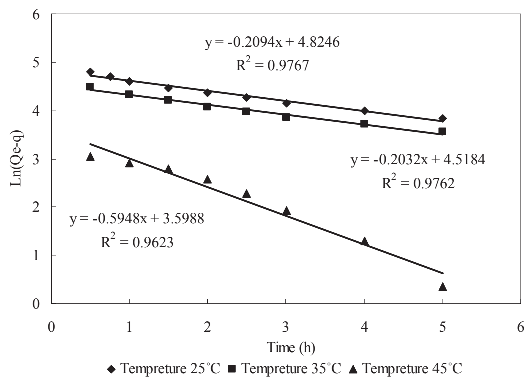

Fig.4 Pseudo-first order kinetics plot for adsorption of Pb

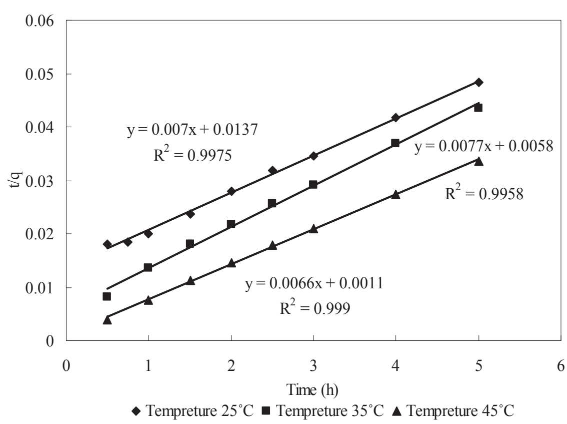

Fig.5 Pseudo-second order kinetics plot for adsorption of Pb

The Blanchard pseudo-second order model:

$$t/Q_t = 1/(K_2 Q_e^{\ 2}) + (t/Q_e) \tag{4}$$

where K_2 is rate constant of second order model.

The two models were used to plot the data in Fig. 3, and the results were showed in Fig. 4, Fig. 5 and Tab. 2. R^2 value (correlation coefficient) was always used to evaluate the rationality of the model. where $Q_{e,\exp}$ and $Q_{e,\mathrm{cal}}$ is equilibrium adsorption amount of Pb(Ⅱ) on zeolite (mg/g) gained from experiments and model calculation.

Table.2 Pseudo-First Order And Pseudo-Second Order Rate Constants

Temperature (℃)	$Q_{e,\,exp}$ (mg/g)	pseudo-first order kinetics			pseudo-second order kinetics		
		$Q_{e,\,cal}$ (mg/g)	K_1	R^2	$Q_{e,\,cal}$ (mg/g)	K_2	R^2
25		124.54	0.4822	0.9767	142.86	0.0036	0.9975
35	150	91.69	0.4680	0.9762	129.87	0.0102	0.9958
45		36.55	1.3698	0.9623	151.52	0.0396	0.9990

As shown in Fig. 4, Fig. 5 and Table. 2, it was obviously found that pseudo-second order model could give higher R^2 value (R^2>0.99) than first order model. This indicated that pseudo-second order model was more applicable to the adsorption kinetics of Pb(Ⅱ) on Linde type F (K) zeolite.

4. Conclusions

The zeolite dosage had significant effect on the adsorption of metal Pb(Ⅱ) irons. The uptake percentage was improved with the increasing of zeolite dosage. The adsorption efficiency increased from 46% to nearly 100% as the dose increased from 0.25 to 2.00 g/L. The saturated adsorption capacity decreased from 278 mg/g to 25 mg/g as zeolite dosage increasing from 0.25 g/L to 6.00 g/L. The adsorption efficiency was nearly 100% when the pH was 7. The low pH was disadvantage to the adsorption of lead ions. With the increasing of temperature and extension of contact time, the adsorption efficiency of Pb(Ⅱ) ions improved obviously. The adsorption process of Pb(Ⅱ) irons on Linde type F(K) zeolite was accorded with Langmuir adsorption isotherm. The adsorption reaction was matched to the pseudo-second class reaction kinetics model.

5. Acknowledgements

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