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Study on the Adsorption Properties of Ni(Ⅱ) by Linde Typr/.ee F(K) Zeolite

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Abstract. The batch experiments were conducted to examine the adsorption properties of Ni(Ⅱ) ions by synthesizing Linde type F(K) zeolite from coal fly ash. Several important parameters were investigated. The adsorption isotherm and kinetics equation were also discussed. The results showed that, the zeolite doses had obvious effect on the adsorption properties of Ni(Ⅱ). With the increasing of zeolite doses, the adsorption efficiency was improved significantly, and the saturated adsorption capacity was decreased continuously. The adsorption efficiency increased from 12% to 92% as pH increased from 2.0 to 7.0. With the increasing of temperature and contact time, the adsorption efficiency of Ni(Ⅱ) ions improved obviously. Langmuir adsorption isotherm and Pseudo- first order model showed better calculation results for the adsorption of Ni(Ⅱ) on Linde type F (K) zeolite.

1. Introduction

Nowadays, heavy metals pollution has become a severe public health problem in the world. Heavy metals in aqueous solution could join the food chain and then has the toxic effects on the environment and human beings [1,2]. Many methods such as adsorption, reverse osmosis, chemical precipitation, ion-exchange could reduce the concentration of heavy metals. In recent years, the method of adsorption to treatment heavy metals wastewater become a hot topic [3]. To remove the heavy metals effectively, the suitable adsorbent was the key technology [4-6]. Fly ash was generated during the combustion of coal for energy production. That was an industrial by-product, and recognized as an environmental pollutant [7]. Because of the environmental problems presented by the fly ash, considerable research has been undertaken on the subject worldwide. The utilization of fly ash as a low-cost adsorbent and zeolite synthesis for the removal of heavy metals has been studied in several

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literatures [8-10]. Fly ash was found to have a higher adsorption capacity for Cd(II), as Fly ash obtained from the combustion of poultry litter was also utilized as an adsorbent for the removal of Cr(III) from aqueous solution [11]. Wang et al. [9] studied the removal of heavy metals (Cu and Zn) from wastewater using zeolites synthesized from fly ash. Hui et al. [12] used the zeolite 4A synthesized by recycled coal fly ash to adsorb mixed heavy metal ions.

Linde type F(K) zeolite was gained from hydrothermal reaction between fly ash and high concentration KOH solution[13]. Chen et al. used the product as an adsorbent to treat the heavy metal of Zn(II)[14] and Cu(II)[15], and got a high removal rate. The present work focused on utilizing the Linde type F (K) zeolite to removal heavy nickle ions in water. The adsorption isotherm and kinetics of the process and the sorption capacity of the adsorbents were determined in relation to the effects of various factors on the adsorption process. The parameters in this study included adsorbent dosage, initial concentration of the heavy metal ions, initial pH of the solution, temperature and contact time.

2. Experimental

The Ni(Ⅱ) solution was prepared for this study by dissolving $Ni(NO_3)_2 \cdot 6H_2O$ in 1L of distilled water to make its synthetic solutions. The initial concentration of Ni^{2+} ions was 50 mg/L and 100 mg/L, respectively. Alkaline solution used for zeolite synthesis is prepared through dissolving KOH in distilled water. The solutions used for adjusting adsorption pH are prepared through dissolving NaOH and HNO_3 in distilled 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%). All chemicals used in our experiment are analytical reagent and bought from China National Pharmaceutical Group Corporation.

The 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: 1.01325×105) for 48h. The obtained products were washed with distilled water and dried at 105˚C.

The batch studies were conducted by mixing zeolite with Ni(II) metallic solutions prepared in the laboratory. The zeolite was mixed with Ni^{2+} solution in 10 ml polypropylene tubes. The pH of solution was adjusted by 0.01 mol/L NaOH and 0.01 mol/L HNO_3 solutions. The tubes with mixtures were fixed in a water bath shaking box and shaken at 150rpm.

The mixtures was filtered through 0.45μm membrane filter using a vacuum pump after adsorption reaction, and the filtrate was, subsequently, analysed for its Ni(II) content using AA240DUO atomic adsorption spectrophotometry (Agilent Technologies, Inc. USA). The pH of solution is determined by a Q/GHSC 1544-2009 pH meter. Following the same procedure, different parameters were studied, such as adsorbent dosage, initial metal concentration, initial pH, reactive temperature and contact time.

3. Results and Discussion

Effect of zeolite dosage on adsorption. The effect of zeolite dosage on the adsorption efficiency of Ni(II) was shown in Fig.1.

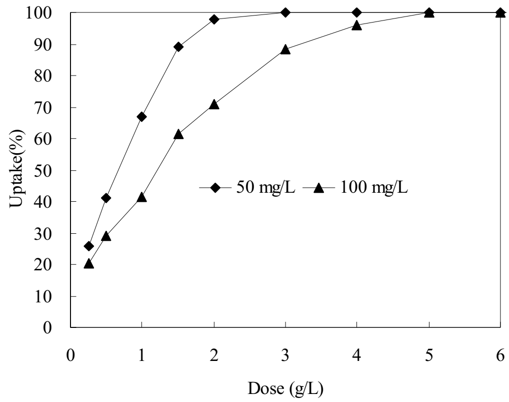

Fig.1 Effect of zeolite dosage on Ni uptake

The zeolite dosage was 0.25, 0.50, 1.00, 2.00, 3.00, 4.00, 5.00 and 6.00 g/L, respectively. The initial concentration of Ni(II) solutions was 50 mg/L and 100 mg/L, respectively. The initial pH of adsorption system was 7, the temperature was 25℃, and the reaction time was 10 hours. It can be seen that, the zeolite dosage had a significant effect on the adsorption removal of Ni(II) ions. When the initial concentration of Ni(II) ions was 100 mg/L, the adsorption efficiency increased from 20% to nearly 95% as the dose increased from 0.25 to 4.00 g/L. It should be resulted from more adsorption sites which are supplied from higher zeolite dosage. However, the adsorption efficiency of Ni(II) ions had a little increase with a continuous increase of zeolite dosage from 4 g/L to 6g/L. Fig.1 also showed that, the adsorption efficiency increased from 26% to nearly 99% as the dose increased from 0.25 to 2.00 g/L when the initial concentration of Ni(II) ions was 50 mg/L. The adsorption system tended to saturate as the further increase of zeolite dosages.

The effect of zeolite dosage on the saturated adsorption capacity was shown in Fig.2. It indicated the saturated adsorption capacity underwent a continuous decrease. When the initial concentration of Ni(II) ions was 100 mg/L, the saturated adsorption capacity decreased from 81 mg/g to 17 mg/g with

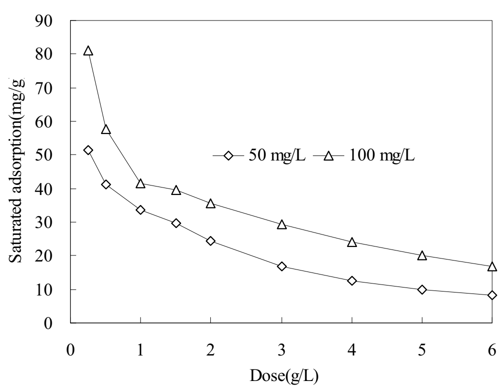

Fig.2 Effect of zeolite dosage on the saturated adsorption capacity

zeolite dosage increasing from 0.25 g/L to 6.00 g/L. When the initial concentration was 50 mg/L, the saturated adsorption capacity decreased from 51 mg/g to 8 mg/g with the same zeolite doses.

Effect of pH on adsorption. The pH of system will not only influence the surface charge of adsorbent, but also the state between the metal ions and adsorbent. The solution pH played an important role in the adsorption process. The effect of pH on metal Ni uptake was shown in Fig.3. The pH was taken from 2.0 to10.0. The zeolite dosage was 2.0g/L, the initial concentration of Ni(II) solutions was 100 mg/L, the temperature was 25℃, and the shaking time was 10 hours. As shown in Fig.3, the adsorption efficiency was improved obviously with the increasing of pH. The adsorption efficiency increased from 12% to 92% as pH increased from 2.0 to 7.0. The adsorption efficiency was nearly 100% with the continuous increasing pH from 8.0 to 10.0. Hui et al.[12] suggested the precipitation pH of Ni(II) ions was 7.77 when the initial concentration of mixed heavy metal ions was 100 mg/L.

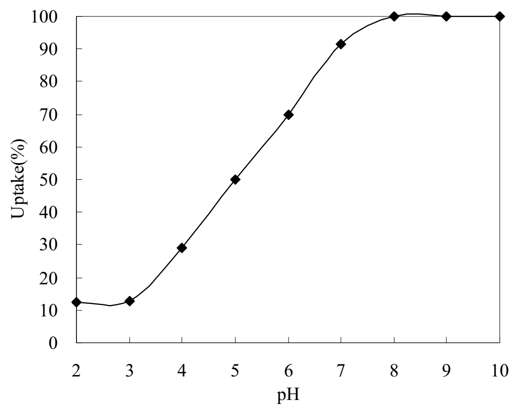

Fig.3 Effect of pH on Ni uptake

Effect of temperature and contact time on adsorption. The effect of temperature and contact time on the adsorption percentage was shown in Fig.4. The temperature was taken of 25℃, 35℃, and 45℃. The adsorption time was 7 hours. The initial concentration of Ni(II) ions was 100 mg/L, the zeolite dosage was 2.00 g/L, and the initial pH was 7. Fig.4 showed that with the increasing of temperature and contact time, the adsorption of Ni(II) metal ions on zeolite increased rapidly. When the temperature was 25℃, the adsorption efficiency increased from 28% to 67% as the contact time increased from 0.5h to 7h, respectively. The adsorption efficiency improved obviously when the temperature increased to 35℃. The Ni uptake percentage increased from 39% to 76% as the contact time increased from 0.5h to 7h, respectively. Compared to the temperature of 25℃ and 35℃, the adsorption efficiency further improved with the temperature increased to 45℃. The adsorption efficiency was 62% when the contact time was 0.5h. The adsorption efficiency was up to 99% with the contact time extended to 7h. The results showed that, the higher of reaction temperature, the shorter of equilibration time for adsorption.

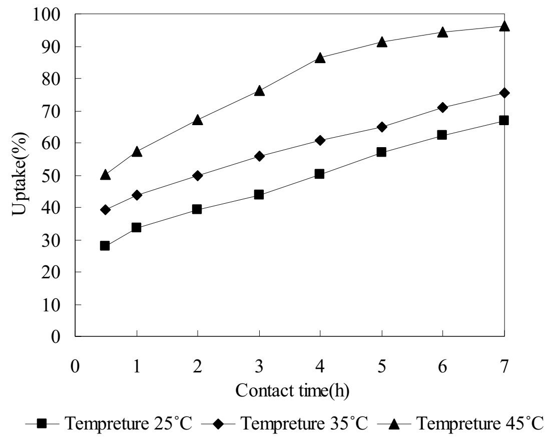

Fig.4 Effect of temperature and contact time on Ni uptake

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 FOR NI(II) ADSORPTION

Initial concentration of Ni^{2+} (mg/L)	Langmuir				Freundlich			
	The linear equation	R^2	Q_m(mg/g)	b(L/mg)	The linear equation	R^2	1/n	K
50 mg/L	y=0.0024x+0.041	0.9809	41.67	0.5839	y=0.1058x+3.274	0.8826	0.1058	26.4168
100 mg/L	y=0.0212x+0.102	0.9884	47.17	0.2078	y=0.1253x+3.1877	0.8713	0.1253	24.2326

Table.1 showed the calculation results of Langmuir and Freundlich isotherm for Ni(II) adsorption. It suggested Langmuir isotherm given better calculation results for Ni(II) adsorption. The R^2 of Langmuir isotherm (0.9809 and 0.9884 when the concentration was 50 mg/L and 100 mg/L, respectively) were higher than the value of Freundlich isotherm (0.8826 and 0.8713 with the same concentration). The Ni(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:

$$\log(Q_e - Q_t) = \log Q_e - (K_1 / 2.303)t \quad (3)$$

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

The Blanchard pseudo-second order model:

$$t / Q_t = 1/(K_2 Q_e^2) + (t / Q_e) \quad (4)$$

where K_2 is rate constant of second order model.

The two models were used to plot the data in Fig. 4, and the results were showed in Tab. 2. According to references, R^2 value was always used to evaluate the rationality of the model. where $Q_{e,\exp}$ and $Q_{e,\mathrm{cal}}$ is equilibrium adsorption amount of Ni(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		38.46	0.2681	0.9938	38.17	0.01691	0.9582
35	50	32.93	0.3132	0.9923	40.98	0.02344	0.9776
45		22.30	0.7238	0.9996	50.25	0.04889	0.9848

Table.2 showed pseudo-first order model could give higher R^2 value (0.9923-0.9996) than second order model (R^2 value was 0.9582-0.9848). This indicated pseudo-first order model was more applicable to the adsorption kinetics of Ni(II) on Linde type F (K) zeolite.

4. Summary

The important parameters, including adsorbent dosage, initial concentration, pH, temperature and contact time, all had obvious effect on the adsorption of Ni(II) ions. With the increasing of adsorbent dosage, the adsorption efficiency of Ni(II) ions was improved significantly. The adsorption system tended to saturate as the further increase of zeolite dosages. However, the saturated adsorption capacity was decreased gradually. The adsorption efficiency of Ni(II) ion was 92% when the initial pH was 7. The equilibration time of adsorption was shorter with the increasing of reaction temperature. The adsorption process of Ni(II) ion accorded with Langmuir adsorption isotherm. In addition, the reaction of adsorption on Linde type F(K) zeolite to Ni(II) ion matched to the pseudo-first class reaction kinetics model.

5. Acknowledgements

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