Adsorption of Cu(II) from Aqueous Solution on Fly Ash Based Linde F (K) Zeolite

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ABSTRACT: *The work focuses on the removing of Cu(II) from aqueous solution by Linde F(K) zeolite. The zeolite is synthesized from fly ash by hydrothermal process. The adsorption experiments discuss several factors including the optimal solution pH, zeolite dosage, adsorption temperature, adsorption kinetics and adsorption isotherm equation. The results show that, the optimal solution pH is 6 and the efficient zeolite dosage is 4g/L. Higher reaction temperature could favor the removal of Cu(II). The adsorption of Cu(II) on Linde F (K) zeolite is monolayer adsorption. The experiment data could be calculated by pseudo-second-order model and Langmuir isotherm. The adsorption process is endothermic and spontaneous and the system disorder increases with temperature.*

KEY WORDS: *Fly ash, Cu, Adsorption, Linde F (K), Zeolite.*

INTRODUCTION

Heavy metal effluent could be discharged from many industry branches including metal mining, smelting and electroplating. Because of its toxic effect on organism, heavy metal pollution seriously threatens the environment safety and human healthy all over the world. Therefore, the methods and technologies to treat this harmful effluent become one of research focuses in environment science.

To be an essential trace element for human being, Cu(II) also could cause many serious problems to people's healthy when the concentration is higher than an accepted level [1]. It has been proved that Cu(II) could accumulate in liver if human intakes excess. And then, it would lead to numerous serious consequences including kidney damage, severe headaches, hair loss, hypoglycemia, increased heart rate, nausea, widespread

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Table 1: Chemical composition of fly ash (%).

Oxides	SiO_2	Al_2O_3	CaO	Fe_2O_3	Na_2O	MgO	K_2O	TiO_2	P_2O_5	LOI*
F-Fly ash	56.71	28.9	2.34	4.02	0.46	0.04	1.32	1.07	0.12	4.81

**LOI = loss on ignition at 960 °C.*

capillary damage and central nervous system irritation [2-4]. So, the removal of Cu(II) is very necessary before the effluent discharged to natural environment. Now, the conventional Cu(II) removal technologies include ion exchange, chemical precipitation, membrane filtration, electrolytic methods, solvent extraction and adsorption. Among these technologies, considering the cost and industrial application feasibility, adsorption is regarded as the most competitive one. *Cho* developed a novel chitosan/clay/magnetite composite to adsorb Cu(II) ions [5]. *Lombardo* uses aminopropyl-modified mesoporous silica SBA-15 as agents to treat Cu ions [6]. *Li* discovered that titanate nanofibers after alkali treatment could be used for adsorption of Cu(II) [7]. Among Cu(II) adsorbents, fly ash based zeolite attracted more attentions because of lower cost and sufficient suitability. As we known, fly ash is a solid waste coming from power plant. The zeolite prepared from these recycle industry waste should greatly reduce the cost of adsorption. On the other hand, many scientists have pointed that fly ash based zeolite shows excellent ability for Cu(II) adsorption. Nascimento suggested that a synthetic zeolite produced from fly ash could be used for heavy metal (Zn, Cu, Mn and Pb) adsorption [8]. The pure-form zeolites (A and X) synthesized from fly ash were applied for Zn and Cu adsorption by *Wang* [9]. *Koukouzas* utilized CFB-fly ash as raw materials to synthesis zeolite and it showed remarkable heavy metals adsorption results [10].

As a microporous crystalline hydrated aluminosilicates, zeolite could be considered as inorganic polymers built from an infinitely extending three-dimensional network of tetrahedral units. Different synthesis conditions (alkaline type, alkaline solution concentration, temperature and synthesis procedure) would result in different network. So far, many literatures pay attention to the fly ash based zeolite synthesized from Na-based alkaline solution and moderate alkaline environment [8-10]. Few papers focus on the K-based alkaline solution and high alkaline environment. On 2009, *Miyaji* has successfully synthesized a zeolite called Linde F (K) zeolite by fly ash and implied its adsorption potential. [11]. However, until now, no further results about its adsorption ability have been published. The main objective of this paper is to evaluate the feasibility of removing Cu(II) from aqueous solutions using Linde F (K) zeolite prepared by fly ash. The influence of several important parameters such as solution pH, zeolite dosage, contact time and adsorption temperature are investigated. Adsorption kinetics, adsorption isotherm and adsorption thermodynamic are also discussed.

EXPERIMENTSAL SECTION

Chemicals

The aqueous solution of Cu(II) is prepared through dissolving $Cu(NO_3)_3$ in DI water. 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 HCl in DI water. All chemicals used in the experiment are analytical reagent and bought from China National Pharmaceutical Group Corporation.

Zeolite synthesis and character

The Linde F (K) zeolite is synthesized through fly ash reacted with KOH solution. The original fly ash is gained from Taicang harbour golden concord electric-power generation Co. Ltd (Taicang, Jiangsu province). The chemical composition is showed in Table 1. The zeolite synthesis procedures are as follow: Firstly, in order to get rid of un-burned carbon and other impurities, the original fly ash is mixed with DI water (liquid/solid=5, 200rpm and room temperature) and then the mixture is left to stand. After the mixture liquid is separated into solid and liquid, the supernatant solution is abandoned and the deposit sediment is filtered with 0.45μm membrane. The solid is dry to constant weight under 150˚C. Secondly, the dry fly ash is mixed with 8M KOH solution for 5h (liquid/solid=5, 200rpm and 95˚C). After reaction, the mixture is also filtered with 0.45μm membrane. During the filtering, huge amount of DI water is used to wash the zeolite particles to clean the residue alkali until the pH of filtrate reach about 7. Finally, the filter solid is also dry to constant weight under 150˚C.

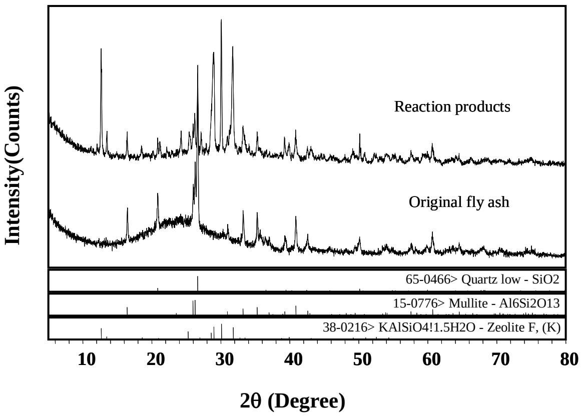

Fig. 1: XRD patterns of original fly ash and reaction products.

To reduce the cost of zeolite synthesis, the alkaline solution is recycle used for about 50 times.

The zeolite is character by XRD and the X-ray diffraction patterns for the powder samples are taken on a Shimadzu XD- 3A diffractometer, using Cu-Kα radiation (λ = 1.54056Å).

Adsorption experiments

The adsorption experiments are conducted as typical batch studies. The zeolite is mixed with 10mL Cu(II) solution in 20ml Teflon bottles. The bottles with mixtures are fixed in a water bath shaking box and shaken at 200rpm. After adsorption, the mixtures are filtered with 0.45μm membrane and then the concentration of Cu(II) in solution is measured by AA240FS atomic adsorption spectrophotometry.

According to the unit procedure, the effect of solution pH on adsorption is conducted as 2-10 of pH, 4h contact time, 0.04g zeolite and 40˚C. The pH of solution is adjusted by 0.01mol/L NaOH and 0.01mol/L HCl solution. The pH of solution is determined by a Q/GHSC 1544-2009 pH meter.

The effect of zeolite dosage on adsorption is carried out as 0.005g to 0.08g zeolite, 6 of pH, 4h contact time and 40˚C. The effect of contact time and temperature on adsorption is run as 0.5 to 7h contact time, 20 to 60˚C, 6 of pH and 0.04g zeolite.

RESULTS AND DISCUSSIONS

XRD

Fig. 1 shows the XRD patterns of original fly ash and products after reaction. Only peaks due to quartz (2θ: 26.74˚, 20.96˚, 50.26˚ etc.), mullite (2θ: 26.20˚, 25.80˚, 16.5˚ etc.) as well a small 'halo' peak (2θ: range from 20˚ to 30˚) which corresponds to the amorphous phase in the original fly ash could be observed on the XRD patterns. After reaction with alkaline solution, the peaks of quartz and mullite are still observed while the 'halo' nearly disappear, indicating that the main reaction of zeolite synthesis occurs between amorphous phase and alkaline solution. Besides these, it could be found that many new crystalline peaks belong to Linde type F (K) zeolite (2θ: 32.14˚, 30.34˚, 29.01˚, etc, PDF No. 38-0216) appears on the XRD pattern of product. This results present that the new Linde type F (K) zeolite is successfully synthesized.

Effect of solution pH

The solution pH has a significant effect on the adsorption of Cu(II) on zeolite. Fig. 2 shows the effect of pH on Cu(II) removal. It could be seen that the removal percentage of Cu increases with the rise of pH and it is maximum to about 100% when pH is higher than 7. Based on the understanding of basic chemistry knowledge, we know that the precipitation of $Cu(OH)_2$ would occur when pH higher than about 6-7. A simple calculation tells us that the Cu(II) would precipitate after pH higher than 6.8 in our systems. So, in our opinion, the removal of Cu(II) from solution after pH of 6 should be effected together with adsorption of zeolite and precipitation. To study the true adsorption ability of zeolite on Cu(II), the other disturbing factor must be eliminated and so, pH of 6 is considered as the optimal pH and applied for all other experiments.

Effect of zeolite dosage on adsorption

The effect of zeolite dosage on adsorption of Cu(II) is depicted in Fig. 3 when the pH of 6 is used. It could be seen that the adsorption result increases with the rise of zeolite dosage. But the major increase is found when zeolite dosage ranges from 0.5g/L to 4g/L. The Cu(II) removal increases from about 25% to 98% under this range. In contrast, the saturated adsorption amount is observed to decrease with zeolite dosage. When the zeolite dosage increases from 0.5g/L to 8g/L, saturated adsorption amount continuous decrease from about 49.5 mg/L to 12.5 mg/L. It could be easily explained that more reactive adsorption surfaces are supplied when zeolite dosage increasing. Considering the adsorption efficiency, the most efficient zeolite dosage is chosen as 4g/L.

Effect of contact time and adsorption temperature on adsorption

To carry out kinetics analysis, some basic experiment data is need. For this paper, preliminary kinetics experiments are conducted as the effect of contact time and adsorption temperature. The results are presented in Fig. 4. As Fig. 4 shows that, the removal rate of Cu(II) increases sharply with the adsorption temperature. Under 20˚C, the Cu(II) removal rate reaches only 88% after 7h, while about 90% Cu(II) removal is obtained after only 1h under 60˚C. Then, as a result of adsorption rate increasing, the required contact time for adsorption saturation decreases. It could be seen that required contact time for adsorption saturation is about 7h for 20˚C, 5h for 40˚C and 2h for 60˚C.

Adsorption kinetics

For studying the adsorption kinetics, the Lagergren pseudo-first-order model [12] and Blanchard pseudo-second-order model [13] is widely used. The equations of two models are as follow:

The Lagergren pseudo-first-order model

$$\mathrm{Ln}(q_e - q) = \mathrm{Ln}q_e - k_1 t \tag{1}$$

where q_e is equilibrium adsorption amount of Cu(II) on zeolite (mg/g), q is adsorption amount of Cu(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

$$\frac{t}{q} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{2}$$

where k_2 is rate constant of second-order model.

The data in Fig. 4 is plot as these two models and the results are showed in Fig. 5, Fig. 6 and Table 2. From the parameters in Table 2, it could be seen that the R^2 value (correlation coefficient) of pseudo-second-order model ranges from 0.993 to 0.999, which is much higher than first-order model (0.82 to 0.97). The observation reveals that pseudo-second-order model is more suitable for explaining the adsorption procedure of Cu(II) on zeolite. On the other hand, the optimal model could be chosen

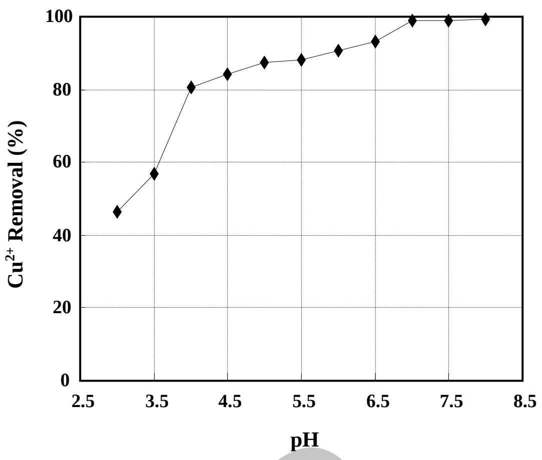

Fig. 2: Effect of pH on removal efficient of Cu(II).

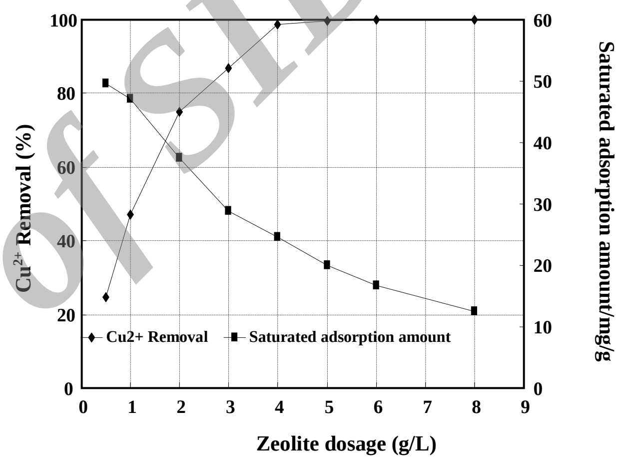

Fig. 3: Effect of zeolite dosage on removal efficient and saturated adsorption amount of Cu(II).

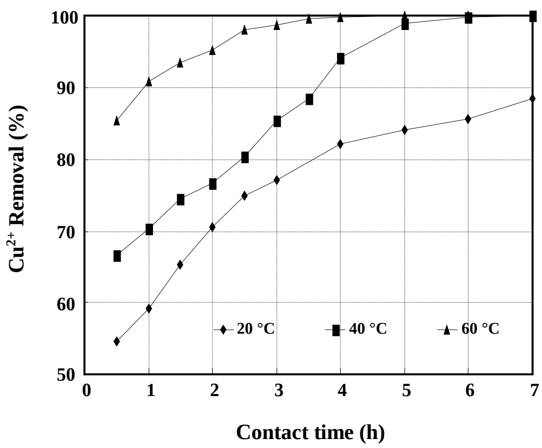

Fig. 4: Effect of contact time and adsorption temperature on removal efficient.

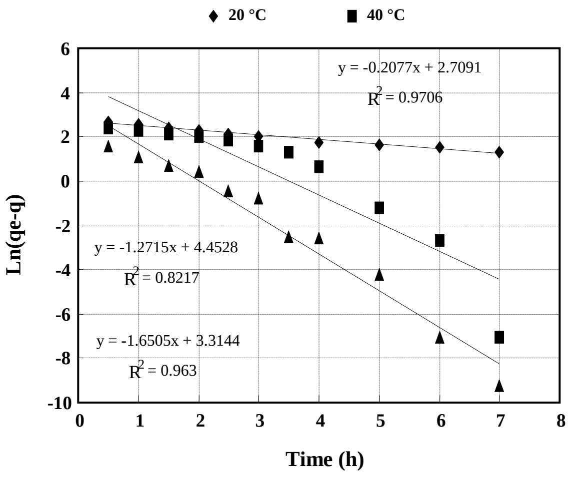

Fig. 5: Pseudo-first-order kinetics plot for adsorption of Cu(II).

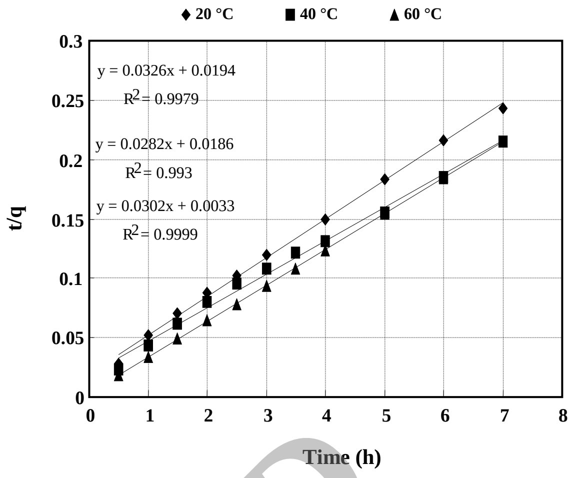

Fig. 6: Pseudo-second-order kinetics plot for adsorption of Cu (II).

based on root mean square error (RMSE) [14], which is defined as follow:

$$RMSE = \sqrt{\frac{\sum_{1}^{N}(q_{exp} - q_{cal})^2}{N}} \quad (3)$$

where q_{exp} and q_{cal} is equilibrium adsorption amount of Cu on zeolite (mg/g) gained from experiments and model calculation.

It is easy to understand that lower RMSE means the model is more close to actual experiment. Similar with R^2, the RMSE of pseudo-first-order model is higher which means that pseudo-second-order model is more applicable to the adsorption kinetics of Cu(Ⅱ) on zeolite.

Adsorption isotherm

In order to study the Cu(Ⅱ) adsorption isotherm, Freundlich isotherm and Langmuir isotherm [15-17] are applied. The equation of Langmuir isotherm is as follow:

$$\frac{C_e}{q_e} = \frac{1}{k_L q_m} + \frac{C_e}{q_m} \quad (4)$$

where q_e and C_e are the amount adsorbed (mg/g) and the adsorbate concentration on solution (mg/L), both at equilibrium; k_L (L/mg) is the Langmuir constant related to the energy of adsorption; and q_m (mg/g) is the maximum adsorption capacity.

The equation of Freundlich isotherm is as follow:

$$Ln(q_e) = Ln(k_F) + \frac{1}{n} Ln(C_e) \quad (5)$$

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

Table 3 shows adsorption isotherm after Langmuir and Freundlich calculation. It shows that better calculation results could be gained from Langmuir isotherm and implies that the Cu(Ⅱ) adsorption on Linde F (K) zeolite is a monolayer adsorption procedure.

Adsorption thermodynamic

Adsorption thermodynamic is studied as follow:

$$\Delta G = -RTLn(k_L) \quad (6)$$

$$Ln(k_L) = -\frac{\Delta H}{RT} + \frac{\Delta S}{R} \quad (7)$$

$$\Delta G = \Delta H - T\Delta S \quad (8)$$

where k_L is the Langmuir constant (L/g). ΔG, ΔH and ΔS are Gibbs free energy, enthalpy and entropy, respectively (kJ/mol). R is the gas constant, and T is the absolute temperature.

Because more suitable adsorption data could be gained form Langmuir isotherm, we use equilibrium constant of Langmuir isotherm (k_L) for adsorption study and the results are showed in Table 4. As Table 4, the negative values of ΔG (-15.951 to -19.765 kJ/mol) give

Table 2: Pseudo-first-order and pseudo-second-order rate constants calculated from experiment data.

Temperature/°C	Pseudo-first-order			Pseudo-second-order		
	k_1(/h)	q_{cal} (mg/g)	R^2	k_2(g/mg·h)	q_{cal} (mg/g)	R^2
20	0.2077	15.01	0.9706	0.0488	30.67	0.9979
40	1.2715	85.87	0.8217	0.0509	35.46	0.993
60	1.6505	27.51	0.963	0.2868	33.11	0.9999
q_{exp} (mg/g)	RMSE					
32.5	17.49			1.83		
	53.37			2.96		
	4.99			0.61		

Table 3: Adsorption isotherms constants calculated from experiment data.

Temperature (K)	Langmuir			Freundlich		
	q_m(mg/g)	k_L(L/mg)	R^2	k_f	n	R^2
293	48.3	0.696	0.9837	22.15	5.79	0.8711
313	52.7	0.943	0.9956	29.45	4.38	0.8945
333	53.9	1.27	0.9789	34.57	5.12	0.8827

Table 4: Adsorption thermodynamic constants calculated from experiment data.

Temperature (K)	ΔG (kJ/mol)	ΔH (kJ/mol)	ΔS (kJ/mol K)
293.15	-15.952	12.002	0.0953
313.15	-17.831		
333.15	-19.765		

us that the adsorption of Cu on Linde F (K) zeolite is spontaneous under temperature from 20-60°C and the adsorption become more spontaneous at higher temperatures. Then the positive ΔH (12.002 kJ/mol) and ΔS (0.0953 kJ/mol) value implies that endothermic adsorption and the disorder increasing in the system.

CONCLUSIONS

The Linde F (K) zeolite is successfully synthesized by hydrothermal process using fly ash as raw materials. The optimal solution pH is 6. The most efficient zeolite dosage is 4g/L. Higher experiment temperature could increase adsorption rate and decrease required contact time for adsorption saturation. Pseudo-second-order model and Langmuir isotherm are more applicable to explain the adsorption procedure of Cu(II) on Linde F (K) zeolite. The adsorption process is endothermic and spontaneous. The system disorder increases with temperature.

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