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Adsorption properties of zeolites synthesized from coal fly ash for Cu (II)

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Abstract

This study explored the hydrothermal synthesis of zeolites in a homogeneous reactor using coal fly ash (CFA) as a raw material via a two-step method at normal pressure. Fourier transform infrared spectroscopy and X-ray powder diffraction analysis showed that the synthetic products has the basic structural unit of microporous zeolite molecular sieves, and consiste of zeolite 4A and zeolite X. The ability of zeolites synthesized from CFA to adsorb Cu(II) was studied. The optimal conditions for adsorption were as follows: pH 5 and dosage of modified CFA 4g l^{-1}. The isothermal adsorption of zeolites of Cu(II) showed that the maximum adsorption quantity ranged from 69.44 (at 20°C) to 140.85 mg g^{-1} (at 50°C). Adsorption kinetics analysis showed that chemical adsorption was the rate-controlling step. Apparent activation energy data, however, showed that the process of adsorption of Cu(II) had the features of physical adsorption. Thus, the adsorption process included both chemical and physical adsorption.

Key words

Adsorption, Coal fly ash, Copper ions, Zeolite

Introduction

The amount of coal fly ash discharged from thermal power plants worldwide increases every year. CFA contains large amounts of SiO_2 and Al_2O_3, making it compositionally similar to natural zeolites. Because of these similarities, more than 150 zeolites have been synthesized from CFA in the past few years (Kugbe *et al*., 2009). Although synthesizing zeolites from fly ash represents only one way to process CFA, this practice is starting to attract more attention because such zeolites are high-value industrial materials.

Zeolites, which have permanent negative charges, contain interconnected channels and cages that span their secondary structures (Querol *et al*., 2002). Consequently, zeolites offer efficient ion-exchange properties, reportedly having cation-exchange capacities (CECs) up to 3.75-5.50 meq g^{-1} (Tanaka and Fujii, 2009). Zeolites can be applied to environmental technology for ion exchange, soil improvement, and air purification (Juan *et al*., 2002). In addition, zeolites can be used in wastewater purification because they efficiently adsorb positively charged pollutants in wastewater, such as heavy metals (Jamil *et al*. 2010).

Höller and Wirsching (1985) for the first time reported the process to create zeolites from fly ash, many attempts have been made to derive zeolites from CFA using a one-stage hydrothermal method. The main obstacle to synthesize zeolites from CFA is to speed up the reaction, temperatures in the range of 100-200°C must be applied in order to dissolve the silica and alumina (Querol *et al*., 2002; Blissett and Rowson, 2012). Over a decade later, Hollman *et al*. (1999) pioneered the two-stage hydrothermal method, which reportedly yielded very pure zeolite. As a result, the two-stage hydrothermal method gained considerable interest in the following years (Tanaka and Fujii, 2009). The main disadvantage of the two-stage method are fairly long incubations times (<72 hr) and high temperature (>500°C) required to pre-fuse the CFA with a solid alkali (Blissett and Rowson, 2012). Studies in the literature suggest that it is possible to synthesize zeolites from natural materials and industrial residues, but all of these processes employ large quantities of sodium hydroxide (NaOH) and require high temperature for performing alkaline fusion (Ye *et*

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al., 2008). Such processes have significant costs and are not always reproducible (Bieseki *et al*., 2013).

In this study, a homogeneous-phase reactor was explored to reduce the temperature and reaction time required to synthesize zeolites from CFA. After zeolite synthesis, batch adsorption experiments were performed to investigate their adsorption capacities.

Materials and Methods

The main chemical components of CFA (sampled from Taiyuan First Thermal Power Plant) were SiO_2 (51.63%) and Al_2O_3 (35.00%). The main crystal phase of the ash included mullite ($3Al_2O_3 \cdot 2SiO_2$) and quartz (SiO_2).The raw material also included 4.96% Fe_2O_3.

Zeolites synthesis methods: Based on the optimized experimental conditions determined earlier, the two-step synthesis of zeolites was performed in this study. CFA was processed several times using a permanent magnet (6000 Gs, Ningbo, China) to remove the iron in it. Then, 6 g iron-free CFA was added to reaction tanks in a JBJX-8 homogenous reactor (Jianbang, China) containing 60 ml of 3 mol l^{-1} NaOH solution. After sealing, the reactor was set to operate at 100°C and a rotation speed of 20 r min^{-1}. The self-pressure alkali-leaching reaction was allowed to proceed for 2 hr. The supernatants in the reaction tanks were collected to determine the amount of silicon in the alkaline leaching solution by means of silicon molybdenum yellow spectrophotometry. The aluminum and iron contents in solution were also measured by means of test method for analysis of coal ash (GB/T 1547-2007). Sodium metaaluminate was added to the alkaline leaching solution at a molar ratio of SiO_2/Al_2O_3=2.0. The solution was then placed in the reactor again, and the reaction lasted for 4 hr at 100°C. The crystallized products were filtered and washed until pH was 9-10. The products were dried at 100°C and stored overnight.

Zeolites analysis methods : A small portion of the synthesized sample was taken for particle size analysis using a S/N42027 laser particle size analyzer (Ankersmid Eyetech, Germany); Infrared spectra of zeolites were obtained by pressing potassium bromide troche using a Perkin Elmer FTIR spectrometer (Waltham, MA, USA); A D8 Advance X-ray powder diffractometer (Bruker, Germany) was used to analyze the phase of the zeolites synthesized from CFA.

Adsorption experiments methods: A stock solution of Cu(II) (1000 mg l^{-1}) was prepared in deionized double-distilled sterilized water using copper sulfate pentahydrate ($CuSO_4.5H_2O$; analytical reagent; Guangfu Reagent, China). All working concentrations were obtained by diluting the stock solution with deionized water. Adsorption isotherm experiments were carried at 20, 30 and 50°C. For these experiments, the stock solution of Cu (II) was diluted into six concentrations (40-500 mg l^{-1}). For kinetic experiments, initial Cu(II) solution concentration was set to 80 mg l^{-1}. At predetermined time intervals after exposure to zeolites (5-180 min), 5 ml aliquots of Cu(II) solutions were filtered through 0.22-µm filters and analyzed for the residual concentration of metal ions in solution by TAS-990 atomic absorption spectroscopy (Purkinje General, China). Uptake of Cu(II) q_{eq} (mg g^{-1}) and adsorption yield *Y*(%) were calculated.

Results and Discussion

The particle size analysis through Laser particle size analyzer showed the narrow particle size distribution of zeolites synthesized from CFA. The mean diameter of the zeolis was 1.12 µm and the half-content diameter (D50) was 0.77 um.

It indicated weak and broad bands in the region of 4000-400 cm^{-1}. The peak at 1002 cm^{-1} corresponds to the asymmetric stretching vibrations of Si–O–Si bonds (or Al–O–Al bonds).The peak of near 680 cm^{-1} corresponds to the symmetric stretching vibrations of internal tetrahedral (Al–O–Al bonds or Si–O–Si bonds). Band at 560 cm^{-1} could be ascribed to double ring mode of external linkage of zeolite framework (Fig.1). The bands at about 466 cm^{-1} could be assigned to O–Si–O (or O–Al–O) bending vibration in internal tetrahedral (Titova *et al*., 1995). The three-dimensional (3D) framework of zeolites was made up of tetrahedral $(SiO_4)^{4-}$ and $(AlO_4)^{5-}$ skeleton, which were the basic units of zeolitic materials (Blissett and Rowson, 2012).

The XRD peaks patterns of CFA-derived zeolites, which were regular and of high intensity, coincided well with the characteristic peaks of zeolite 4A (PDF 43-1042) and zeolite X (PDF 39-0218). Therefore, zeolites in the present work primarily consisted of zeolite 4A and zeolite X, whereby the ratio of zeolite 4A to zeolite X was nearly 3:1 (Fig.2).

Fig. 3 showed that the pH of Cu(II) solution (3.5-10.0) had a significant effect on the ability of CFA-derived zeolite to adsorb Cu (II). Although Cu (II) was completely removed from solution in three experiments where pH was above 6, it was concluded that these higher pH conditions caused Cu(II) to precipitate (Cho *et al*., 2005; Hsu *et al*., 2008). Therefore, the pH of initial Cu (II) solution was set to 5.0 in the subsequent experiments.

The adsorption yield of Cu (II) on CFA-derived zeolites increased as the concentration of zeolites increased (from 0.5 to 10 g l^{-1}), as shown in Fig. 4. When the zeolite concentration was greater than 4g l^{-1}, the adsorption yield increased gently, and nearly achieved maximum. Therefore, 4 g l^{-1} was determined to be the optimal zeolites concentration for subsequent experiments, considering both effectiveness and cost efficiency.

In order to study the adsorption properties of CFA-derived zeolites, adsorption isotherms of Cu(II) on zeolites was generated as shown in Fig. 5. The sorption isotherm of Cu(II) was simulated using mathematical equations developed by Langmuir (1918),

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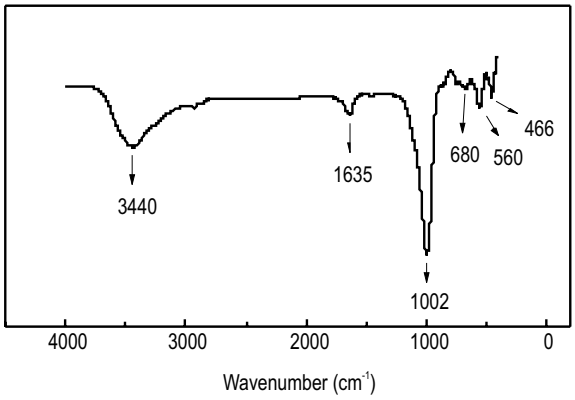

Fig. 1 : FT-IR spectrum of zeolites prepared from CFA

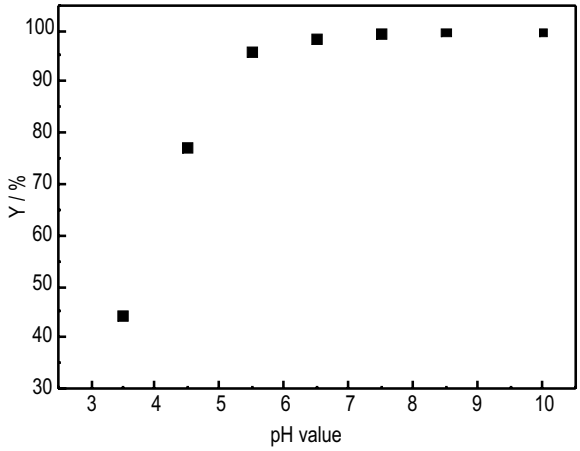

Fig. 3 : The effect of pH value on adsorption yield of Cu (II) on the zeolite prepared from fly ash (zeolites concentration 4 g l^{-1}, 30°C, 60 min, initial Cu(II) concentration 80 mg l^{-1})

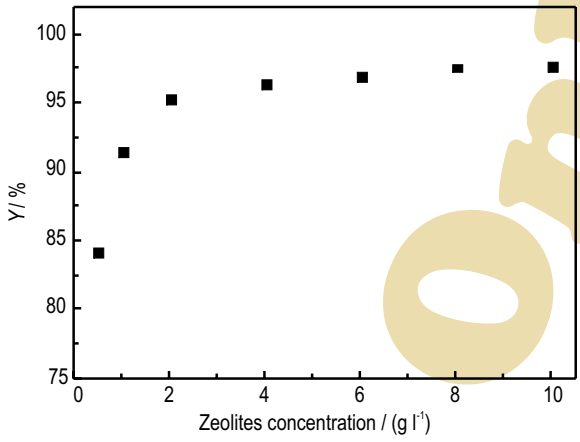

Fig. 4 : The effect of zeolite concentration on adsorption yield of Cu (II) on the zeolites prepared from fly ash (pH 5, 60 min, 30°C, initial Cu (II) concentration 80 mg l^{-1})

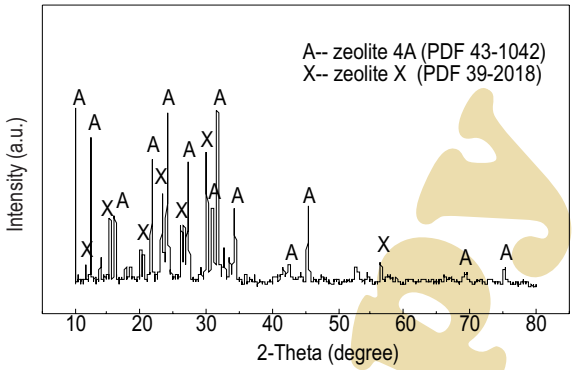

Fig. 2 : XRD patterns of zeolites prepared from CFA

which assumed that the removal of metal ions occurs on a homogenous surface by monolayer sorption. The high correlation coefficients as shown in Fig. 6 and Table 1 indicated that the adsorption of Cu(II) on these zeolites at 20, 30, 50°C fit the Langmuir model well. This suggested that the adsorption procedure was consistent with a monolayer adsorption model, meaning that one adsorption site only adsorbs one Cu (II) ion, and when all adsorption sites were occupied, the adsorption reached dynamic equilibrium (Chen *et al*., 2009). Our CFA-derived zeolites in this study showed better adsorption capacities than some other similar type materials (Nascimento *et al*., 2009), and that higher temperature improved adsorption.

The Langmuir equilibrium constant Q^0 became greater when temperature was increased. This clearly indicated that absorption was endothermic. In order to determine the thermodynamic feasibility and the thermal effects of sorption, Gibbs free energy (ΔG°), entropy (ΔS°), and enthalpy (ΔH°) associated with the process was calculated. The sorption process was determined to be energetically favorable and spontaneous according to negative ΔG° value shown in Table 1. The decrease of ΔG° that occurred as the temperature increased indicates that the sorption process was favored at high temperature. ΔS° and ΔH° values were calculated and shown in Fig. 7 (Gupta and Ali 2004). The value of ΔH° was found to be positive, indicating that the adsorption of Cu(II) onto zeolites was endothermic, but also explaining the rate of Cu(II) adsorption increased with increasing temperature. ΔS° value was also found to be positive, which reflects an irregular increase in randomness at the composite material–solution interface during adsorption (Ma *et al*., 2011).

Fig. 8 showed the adsorption yield of Cu(II) by CFA-derived zeolites as a function of contact time and temperature. These plots indicated that sorption progressed in two steps. The first step was rapid sorption of the metal ion within 60 min, followed by a slower second step during which equilibrium was attained. This behavior, characterized by an initial rapid and quantitatively predominant sorption followed by a slower and quantitatively insignificant sorption, has been extensively

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Table 1 : Adsorption isotherms analysis and the model parameters

T(°C)	Langmuir model and thermodynamics parameters					
	Q^o (mg g^{-1})	b (L mg^{-1})	R^2	ΔG° (kJ mol^{-1})	ΔH° (kJ mol^{-1})	ΔS° (J $(mol.K)^{-1}$)
20	69.444	0.0141	0.9968	-6.4551		
30	90.909	0.0616	0.9942	-10.3853	200.7498	51.6557
50	140.850	0.1158	0.9850	-12.7672		

Table 2 : Adsorption kinetic analysis and the model parameters

T(°C)	The pseudo-second-order rate model parameters			
	k_2 (g (mg.min)$^{-1}$)	q_{eq} (mg g^{-1})	R^2	E_a (kJ mol^{-1})
20	0.0187	15.8983	0.9997	26.9374
30	0.0244	20.0401	0.9998	
50	0.0513	20.3666	1.0	

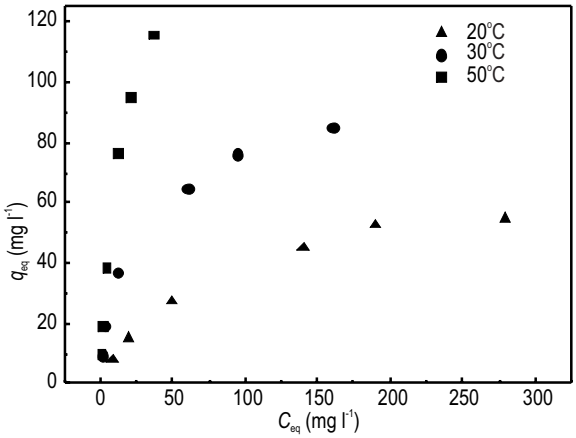

Fig. 5 : Adsorption isotherms of Cu(II) on zeolites at various temperature (zeolites concentration 4g l^{-1}, pH 5, 60 min)

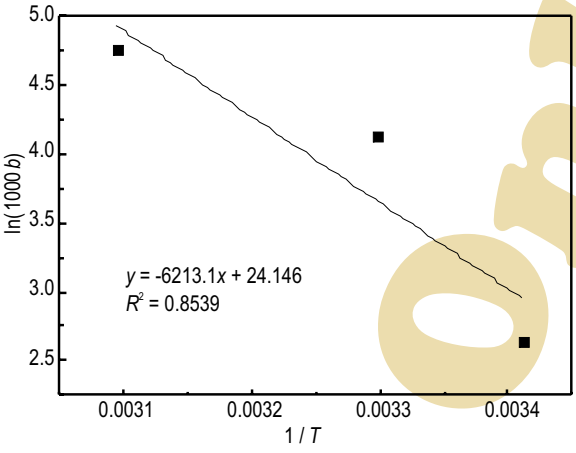

Fig. 7 : Relationship between the adsorption constant from Langmuir model and temperature

reported (Nouri *et al*., 2007). The rapid step was thought to arise because of the abundant availability of active sites on zeolite. As these sites became increasingly occupied, the sorption became less efficient and therefore slower (Chang and Jiang, 2004).

In order to investigate the rate law describing Cu (II) sorption, the kinetic data obtained from the batch experiments

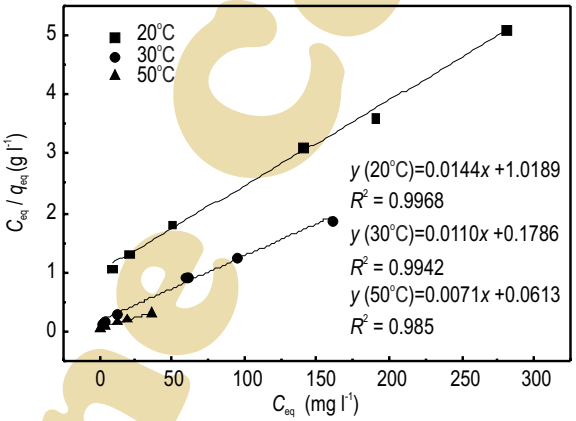

Fig. 6 : Plots of Langmuir model for Cu(II) adsorption on the zeolites prepared from fly ash (Solid lines represent predicted data obtained from Langmuir equation; Solid dot represent the data obtained from the batch experiments)

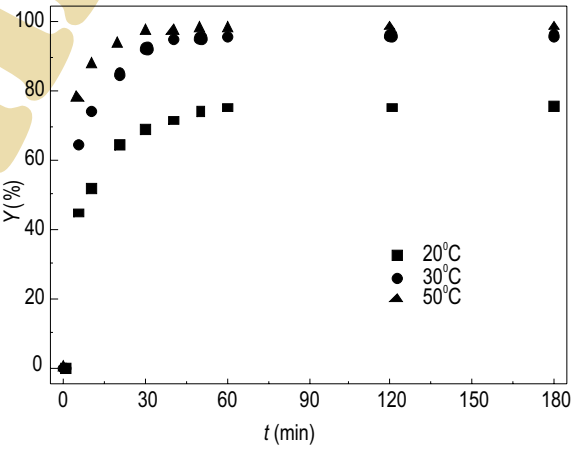

Fig. 8 : The effect of adsorption time on adsorption yield of Cu(II) on the zeolite prepared from fly ash (zeolites concentration 4g l^{-1}, pH 5, T 30°C, initial Cu(II) concentration 80 mg l^{-1})

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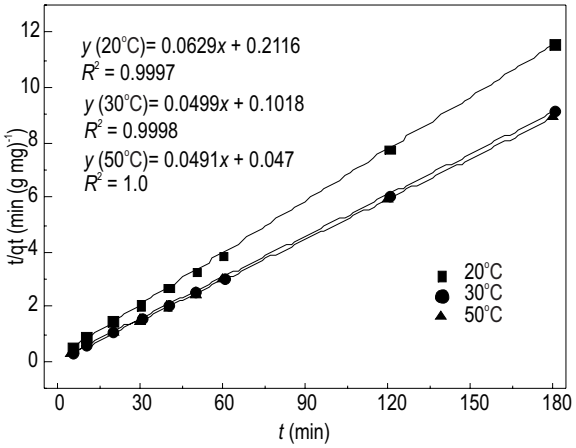

Fig. 9 : Plots of the pseudo-second-order kinetics for Cu(II) adsorption on the zeolites from fly ash (Solid lines represent predicted data obtained from the pseudo-second order model. Solid dot represent the data obtained from the batch experiments)

were analyzed using a kinetic equation. For these types of studies, the pseudo-second-order rate equation was frequently used because it was well equipped to predict behavior over the whole range of adsorption, including external liquid film diffusion, surface absorption, and internal diffusion (Wang *et al*., 2008). The correlation coefficients (R^2) were all greater than 0.999, indicating that the pseudo-second-order equation (Fig. 9 and Table 2) was a suitable model to describe this adsorption procedure. As the pseudo-second-order equation is usually used to describe chemical adsorption processes, the adsorption procedure examined in the present study was primarily chemical adsorption (Ho, 2006). Several other studies on the sorption of divalent metals on heterogeneous sorbents had found that adsorption kinetics generally follow a pseudo-second-order rate law (Reddad *et al*., 2002).

The apparent activation energy (E_a) could be calculated from the slope of linear ln*k* versus 1/*T* plot. R^2 value (0.9904) indicated that the relationship between temperature and adsorption rate obey Arrhenius equation. In general, the value of E_a directed the type of sorption process that would occur. The activation energy for a physical adsorption process was usually less than 40 kJ mol^{-1} because physical adsorption only requires weak forces (Horsfall *et al*., 2004). In contrast, the activation energy for chemical adsorption was usually 84-420 kJ mol^{-1}, on the same order of magnitude as chemical reaction heat. According to Arrhenius equation, E_a was 26.9374 kJ mol^{-1} in this study, indicating that physical sorption played a role in the adsorption of Cu (II) onto zeolites (Aksu, 2002). On the other hand, as mentioned above, the kinetics of this adsorption process agreed with pseudo-second-order kinetics, suggesting that the rate-controlling step in this adsorption process involves chemical sorption. The adsorption process of Cu(II) onto CFA-derived zeolites include both chemical and physical sorption. Zhu *et al*. (2012) made the similar results in the adsorption of metal with inorganic sorbents.

In this study, zeolites 4A/X (about in proportion of 3:1) were synthesized using CFA as raw material *via* a two-step method, at normal pressure. The CFA-derived zeolites were good adsorbents for Cu(II)-containing wastewater. The optimal conditions for adsorption were as follows: pH 5 and dosage of modified CFA 4g l^{-1}. Adsorption of Cu (II) on the CFA-derived zeolites is spontaneous and endothermic process, and the maximum adsorption quantity ranged from 69.44 (at 20°C) to 140.85 mg g^{-1} (at 50°C). Although the synthesis of zeolites constitutes only one small way to repurpose fly ash, these final products may have a higher added value than other CFA-derived materials used for construction applications. Zeolites synthesized from fly ash are potentially useful commercial materials owing to their high cation exchange capacity. There are at least two important applications for these zeolite molecular sieves: Water decontamination and gas purification.

Acknowledgments

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