SORPTION OF Cu(II) BY CHEMICALLY GRAFTED HYDROXAMIC ACID-ZEOLITE

(Erapan Cu(II) oleh Zeolit Terubahsuai Dengan Asid Hidroksamik)

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Abstract

Sorption of Cu(II) by zeolite sorbent chemically modified with hydroxamic acid (HASiZP) is described. The maximum sorption capacity of Cu(II) occurred at pH 5. Sorption capacity of Cu(II) by HASiZP was doubled compared to the original zeolite. Kinetic study shows that Cu(II) sorption followed by second order kinetic model. The sorption of Cu(II) followed Langmuir isotherm model with maximum capacity of 33.32 mg/g at 25°C and increased to 48.12 mg/g at 70°C. Cu(II) sorption by the HASiZP was endothermic and spontaneous processes with positive values of entropy changes.

Keywords: Hydroxamic acid-grafted zeolite, Cu(II), sorption.

Abstrak

Kertas ini membincangkan erapan Cu(II) oleh zeolit terubahsuai oleh asid hidroksamik (HASiZP). Erapan maksimum Cu(II) berlaku pada pH 5. Muatan erapan Cu(II) oleh HASiZP meningkat dua kali ganda berbanding zeolit asal. Kajian kinetik menunjukkan erapan Cu(II) mengikuti model kinetic order kedua. Erapan Cu(II) mematuhi model isotherma Langmuir dengan muatan maksimum 33.32 mg/g pada 25°C dan meningkat kepada 48.12 mg/g pada 70°C. Erapan Cu(II) oleh HASiZP adalah proses endotherma dan spontan dengan perubahan entropi positif.

Kata kunci: Zeolit terubahsuai oleh asid hidroksamik, Cu(II), erapan

Introduction

Heavy metals are toxic substances and must be removed from wastewater prior to their discharge into receiving waters. Among methods available for heavy metal removal, sorption by ion exchange is an attractive one due to its simplicity and safe which requires only mild operating conditions. Using a low cost exchanger such as zeolite, the method can be made cost-effective. Zeolites either synthetic or natural are hydrated aluminosilicate. The structures of zeolites consist of three dimensional frameworks of SiO₄ and AlO₄ tetrahedra. The isomorphous replacement of Si⁴⁺ by Al³⁺ produces a negative charge in the lattice. The negative charge is balanced by cations such as Na⁺ and K⁺. The cations as well as water molecules occupy the non-framework positions such as the voids and channels, formed by different combination of Si- or Al-tetrahedra in the framework. They are represented by the empirical formula $M^{n+}_{2/n}O$, Al₂O₃, xSiO₂, yH₂O, where M^{n+} is the exchangeable cation of valency n. These cations are exchangeable with certain cations in solutions, such as lead, cadmium, copper, zinc, and manganese [1]

Mining waste and copper mine drainage, fertilizer manufacturing, petroleum refining, paints and pigments, steel works, foundries, electroplating and electrical equipments contribute significant quantities of dissolved copper to receiving water streams. Although copper is an essential element, acute doses cause metabolic disorders. Inhalation of copper produces dermatitis. Chronic copper poisoning among others causes hemolytic anemia, neurological abnormalities and corneal opacity [2]. The maximum acceptable limit of copper ion concentration in drinking water is <3 μ g/l. Copper, along with arsenic and mercury is recognized as exhibiting the highest relative mammalian toxicities such as liver damage, Wilson disease and insomnia. Due to the toxic effect the permissible limit of copper effluent discharge is limited to 0.25 mg/l, as per the Environmental Protection Agency (EPA) USA. However some countries even have lower permissible limit such 0.05–0.1mg/l in Hong Kong and Japan [3,4] and 0.20 mg/l in Malaysia [5].

Zeolite has been used by many workers to adsorbed heavy metals including copper [6]. However one of the drawbacks of zeolite sorbent is generally low sorption capacity [7]. Hence, many attempts were made to enhance the sorption capacity of zeolites towards heavy metals. Moon et al [8] reported that modification of zeolite by polyacrylonitrile enhanced the sorption capacity towards Sr and Cs by 80% to 3.92 and 2.47 meq/g, respectively. The cysteamine treated zeolite was significantly enhanced the binding capacity towards Hg [9]. Zeolite was also modified by treatment with phytic acid and used for sorption of Pb. Phytic acid increased sorption capacity of zeolite for Pb from 0.28 to 1.65 mmol/g [10].

Several researchers have modified zeolite in attempted to increase copper adsorption. Panayotova et al [11] modified the zeolite surface by treatment with acetic acid and found that the treated zeolite increased the copper sorption by 34% to 10.8 mg/g. Recently Panneerselvam et al [12] reported modification of zeolite with phosphoric acid by wet method and used for sorption of Cu(II) ions from aqueous solution. The sorption capacity for Cu(II) ion was increased by about 67% to 2.37 mmol/g compared to unmodified zeolite. Modification of zeolite for Cu(II) adsorption was also reported by Duola and Dimirkou [13]. They described modification of zeolite by ferric nitrate solution in potassium hydroxide. Cu(II) sorption capacity was increased to 37.5 mg g⁻¹ (175%) from 13.6 mg g⁻¹. In addition, Wang et al [14] reported that in the presence of humic acid, the sorption of Cu by zeolite increased by 78% to 34 mg/g. It is known that humic acid possing multiple functional group such as phenolic (—OH) and carboxylic groups (—COOH) that can interact with heavy metals through complex formation or chelation. Cu(II) adsorption is increased in the presence of humic acid can be attributed to this complexion effect.

In the present paper, preparation of chemically modified zeolite with hydroxamic acid functional group is described. Zeolite P was grafted with methyl-3-trichlorosilylpropionate $(Cl_3Si(CH_2)_2COOCH_3)$. The grafted zeolite (symbolized by SiZP) was treated with hydroxylammonium in alkaline medium. The hydroxamic acid functional zeolite (HASiZP) was evaluated for its sorption ability towards copper (II) ions from aqueous solutions. Parameters investigated were the pH, contact time, temperature, initial concentration and sorbent dosage. Hydroxamic acid has long been known to complex heavy metals including Cu(II) [15, 16].

Experimental

Materials and methods

Silica of rice husk ash was denoted by Ibnu Sina Institute, University Technology Malaysia. Zeolite P was prepared from the silica of rice husk using method described elsewhere [17]. Copper sulphate was obtained from BDH. All other chemicals used were of analytical reagent grade were also purchased from BDH.

Preparation of grafted hydroxamic acid-zeolite P

About 5.0 g zeolite P (ZP) was reacted with 1.20 g of methyl-3-trichlorosilylpropionate $(Cl_3Si(CH_2)_2COOCH_3)$ in 25 ml toluene. The solvent was removed under vacuum and the treated zeolite powder obtained (SiZP) was heated for 8 h at 100 °C in an oven. A solution of 1.25 g of sodium hydroxide in 12.5 ml of methanol was added to 12.5 ml solution of 1.75 g of hydroxylammonium chloride in methanol and the precipitate was filtered off. The filtrate was added to the SiZP powder obtained above and the mixture was shaken for overnight at 25°C. The resulting sorbent (HASiZP) was washed with methanol and water and dried at 60°C for 3 h. The treated and untreated zeolites were analysed for functional groups by FTIR using Perkin Elmer 1600 Spectrophotometer using KBR disc. The zeolites were characterized by powder XRD analysis using a Siemens Model D-500 diffractometer. The samples were scanned at 0.003° steps using Ni filtered CuK_{\alpha} radiation.

Sorption of Cu(II) ions by HASiZP

Effect of pH on Cu(II) sorption by HASiZP was carried out as follows. Exactly 1.00 ml of 0.05 M of copper sulphate solution was pipetted and dissolved into a series of 30 ml centrifuge tubes. The pH was adjusted to pH 1 and pH 2 with HCl solution and pH 3 to pH 5 by buffer solution of sodium acetate 0.01M. A 5.0 ml of each solution was taken for the determination of Cu(II) initial concentration. About 0.1 g of HASiZP was added to the other 20 ml Cu(II) solution. The mixture was shaken overnight at room temperature and the sorbent was filtered. The concentration of Cu(II) in the filtrate was analysed using inductively coupled plasma atomic emission spectrometer (ICP-AES) model Perkin Elmer P1000. The method was repeated for the fresh zeolite P.

The sorption rate was measured by shaking 0.1 g of the HASiZP in 20 ml of a 100 ppm Cu(II) solution at pH 5 for different time periods (15, 30, 60, 120, 240, 360, 480 and 1440 minutes) at 25, 50 and 70 °C. The Cu(II) concentration was determined as above. The sorption isotherm was studied by shaking 0.1 g of the HASiZP in 20 ml of Cu(II) solutions of various concentrations (50, 100, 150, 200, 250 and 300 ppm) for 16 h at pH 5 at room temperature. The experiment was repeated at 50 and 70 °C. The initial and residual Cu(II) concentrations were analysed as above.

The removal efficiency (%) and the sorption capacity, q (mg/g) of Cu(II) by the virgin and modified zeolites were computed using the following equations.

Removal efficiency % =
$$100 \left(\frac{C_0 - C_e}{C_0} \right)$$
 (1)

$$q = V\left(\frac{C_0 - C_e}{m}\right) \tag{2}$$

where q is the amount of sorbed Cu(II) ions (mg/g), C_0 and C_e are the initial and equilibrium concentration of Cu(II) ion in solution (mg/l), respectively, V (liter) is the solution volume and m is mass of the sorbent (g). Experiments involving Cu(II) sorption were done in triplicates and the average values with standard deviations of less than 10% were reported.

Results and Discussion Synthesis and characterization of grafted hydroxamic acid-zeolite P

The grafted hydroxamic acid zeolite P was synthesized according to the following scheme:



The FTIR spectrum of zeolite treated with Cl₃Si(CH₂)₂COOCH₃ shows an intense absorption band at 1740 cm⁻¹ which is due to C=O vibrations in the grafted ester. After hydroxylamine treatment, a new band appear at 1640 cm⁻¹ region related to C=O starching vibrations in hydroxamic acids [18]. The XRD pattern ZP and HASiZP are given in Figure 1. Both spectra show nearly similar patterns illustrating absence of structural change in the zeolite modification.

Sorption of copper (II) by HASiZP

The effect of pH on Cu(II) removal was studied by performing equilibrium sorption experiments at different pH values 1-5. Lower pH was not investigated due to dissolution of zeolite while higher pH caused the Cu(II) to precipitate. The results of Cu(II) uptake by the zeolites are illustrated in Figure 2. For both zeolites the uptake efficiency gradually increases as the pH increases and maximum at pH 5. The graphs show that the uptake of Cu(II) is about two times higher for HASiZP compared to ZP. The high sorption capacity is due to the presence of hydroxamic acid group which form complex with copper ion [15].



Figure 1: XRD pattern of zeolite p (ZP) before and after modification with hydroxamic acid (HASiZP).



Figure 2: Sorption capacity of Cu(II) by ZP and HASiZP. Cu(II) 200 mg/L, 20 ml, sorbent dosage 0.1 g.

Kinetic studies of Cu(II) sorption by HASiZP

Figure 3 shows the amount of copper ions sorbed at various interval times, for a fixed concentration of 100 mg/l at different temperatures. The Figure shows, at the initial stage the rate of Cu(II) sorption by the HASiZP was rapid and with more than 90% sorption occurred within the first 15 min of contact time. This is followed by a slow phase sorption process and saturation is reached in about 480 min. The amount of Cu(II) sorbed increases with the increase in temperature indicating an endothermic nature of the sorption process. The rapid Cu(II) sorption by HASiZP in the initial stage could be due to complex formation of Cu ion with hydroxamic acid functional group [15] while the slow phase could be due to exchange of Cu(II) with sodium ion in inner zeolite pores [19]. The rate constant for the Cu(II) ion removal from the solution was determined using pseudo-first-order and pseudo-second-order rate models. The Lagergren first-order rate expression [20] is written as:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \tag{3}$$

where q_e and q_t are the amount of metal ion (mg/g) sorbed by HASiZP at equilibrium and at time *t*, respectively, and k_1 is the rate constant of the first-order adsorption (min⁻¹). The slope and intercept of the linear plots of $\ln(q_e - q_t)$ versus *t* are shown in Figure 4. It was observed that the sorption followed the pseudo-first-order-equation over the entire range of the experimental shaking time but with low correlation coefficient and the values of the first-order rate constants did not change with temperature as shown in Table 1. In many cases, the first-order equation of Lagergren does not fit well with the whole range of contact time and is generally applicable over the initial stage of the sorption processes [21].

The pseudo-second-order rate model [22] is expressed as:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{4}$$

where k_2 (g/mg min) is the rate constant of pseudo-second-order kinetic model. The kinetic plot of t/q_t versus t for Cu(II) removal at different temperatures is presented in Figure 5. The relationship is linear, and the high correlations coefficient of the plots (Table 1) shows that the process of Cu(II) sorption follows pseudo-second-order kinetics. The k_2 and the initial sorption rate represented as $h = k_2 q_e^2$ were calculated and are given in Table 1. The data show that the values of the initial sorption rate, h and rate constant, k_2 increase with increase in temperature. The correlation coefficient R^2 are higher compared to Largergren model, and the calculated equilibrium sorption capacity q_e (Table 1) is more consistent with the experimental data. The results suggest that the pseudo-second-order sorption mechanism is predominant and that the over all rate constant appears to be controlled by the chemisorption process [21, 22].

It is known that at an intensive stirring in the sorption experiment, the intraparticle diffusion of solute from the solution into the sorbent pores could be a limiting step. The Morris–Weber equation for intraparticle diffusion [23] is written as;

$$q_t = K_{id} t^{1/2} \tag{5}$$

where K_{id} is the diffusion rate constant of the intraparticle transport (mg/g min^{1/2}). According to this model, if a straight line passing through the origin is obtained by plotting a graphic of q_t versus $t^{1/2}$, it can be assumed that the mechanism for the sorption process is diffusion based. Figure 6 shows the Morris–Weber plots of q_t versus $t^{1/2}$ are straight lines but with low correlation coefficient of R² about 0.8 and did not pass through origin. The result shows that the sorption of Cu(II) by HASiZP only partly controlled by intraparticle diffusion mechanism. The rate constant of intrapartical diffusion, K_{id} at various temperatures were calculated from the slope of the linear plots obtained, and are presented in Table 1.

Sorption isotherms

The sorption isotherms for the removal of Cu(II) were studied at three different temperatures, 25, 50 and 70°C. Figure 7 shows that the sorption capacity of Cu(II) increased with respect to the increase of initial concentration and

then reach a plateau value. The uptakes of the Cu(II) also increase with the increase in temperature thus indicating that the process is endothermic. The isotherm parameters were evaluated using Langmuir model, which equation can be written as [24]:

$$\frac{C_e}{q_e} = \frac{1}{K_L b_L} + \frac{C_e}{K_L} \tag{6}$$

where q_e is the amount of solute sorbed per unit weight of the sorbent (mg/g), C_e the equilibrium concentration of the solute (mg/l), K_L the monolayer adsorption capacity (mg/g) and b_L the constant related to the free energy of adsorption (L/mg).



Figure 3: Sorption of Cu(II) by HASiZP at various time periods. Cu(II) 100 mg/L, dosage 0.1 g



Figure 4: Pseudo-first-order kinetic plots for sorption of Cu(II) onto HASiZP at various temperatures

The Langmuir isotherm plots for the sorption of the Cu(II) ion on the HASiZP are shown in Figure 8. The straight lines with a high correlation coefficient obtained shows that the sorption followed Langmuir isotherm. The isotherms constants presented in Table 2 shows that the theoretical Langmuir sorption capacity (K_L) was found to be 33.32 mg/g at 25°C and increased to 48.12 at 70°C. These values were comparable with other modified zeolites [13,14]. The Langmuir constants, K_L and b_L increase with the increase in temperature showing that the sorption capacity and intensity of the sorption are enhanced at higher temperatures. Higher temperature could increase zeolite pore size that resulted in enhancement of the rate of intraparticle diffusion of the solute [25].

Thermodynamic parameters

Thermodynamic parameters such as enthalpy change (ΔH°), free energy change (ΔG°) and entropy change (ΔS°) can be estimated using experimental equilibrium constants. The free energy change of the sorption reaction is given by the following equations:



Figure 5: Pseudo-second-order kinetic plots for sorption of Cu(II) onto HASiZP at various temperatures



Figure 6: Morris-Weber plots for sorption of Cu(II) onto HASiZP.

Tem °C	Exp. Cap.	Pseudo-first-order			Ps	Pseudo-second-order				Intra- particle	
	q _e (mg/g)	$k_1 \pmod{(\min^{-1})}$	q _e (mg/g)	R^2	k ₂ (g/mg min)	h (mg/g min)	q _e (mg/g)	R ²	K _{id} mg/g min ^{1/2}	R ²	
25	8.72	0.0039	1.84	0.929	0.033	2.54	8.73	1	0.0176	0.755	
50	9.03	0.0046	1.72	0.980	0.035	2.84	9.04	1	0.0178	0.808	
70	9.19	0.0045	1.86	0.963	0.036	3.06	9.20	1	0.0171	0.795	

Table 1 Parameters of the pseudo-first-order, pseudo-second-order kinetic and intraparticle diffusion models of Cu(II) sorption by HASiZP



Figure 7: Effect of initial Cu(II) concentrations on sorption capacity by HASiZP.



Figure 8: Langmuir isotherm plots for Cu(II) sorption by HASiZP at various temperatures.

Temperature	Exp. capacity	Langmui isotherm			
°C	q _e	K_L	$b_{\rm L}$	\mathbb{R}^2	
	mg/g	mg/g	L/mg		
25	33.32	41.15	0.033	0.949	
50	39.44	47.16	0.054	0.943	
70	48.12	53.76	0.145	0.965	

Table 2. Langmuir and Freundlich isotherms constants for the sorption of Cu(II) ions from aqueous solutions onto HASiZP

$$\Delta G_{\circ} = \Delta H_{\circ} - T \Delta S_{\circ} \tag{7}$$

$$\Delta G^{\circ} = -RT \ln K_{\rm D} \tag{8}$$

and

$$K_{D} = \frac{Amount \ of \ sorbate \ in \ adsorbent \ (mg / g)}{Amount \ of \ sorbate \ in \ solution \ (mg / ml)}$$
(9)

where *R* is the universal gas constant, 8.314 J mol⁻¹ K⁻¹ and T is temperature in Kelvin. The distribution coefficient, (K_D) was found increased with the increase of temperature, indicating the endothermic nature of adsorption. Figure 9 shows that the plots of ΔG° versus temperature are linear. The value of ΔH° and ΔS° were determined from the intercept and slope of the plots and shown in Table 3. The negative values of ΔG° at various temperatures indicate the spontaneous nature of the adsorption processes. The positive value of ΔS° indicates an increase in the randomness of the system after the sorption process. One of the processes could be the release of 6 moles of hydrated water molecules into solution for each mole of copper ion sorbed into zeolite [26]. In addition, the positive value of ΔH° confirms that the adsorption is endothermic which in agreement with the results reported by other workers [12].



Figure 9: Plots of ΔG° versus temperature.

Temperature (K)	ΔG° (kJ/mol)	∆H° (kJ/mol)	ΔS° (J/mol K)
298	-17.37	39.29	188.6
323	-20.57		
343	-25.98		

Table 3. Thermodynamic parameter for sorption of Cu(II)

Conclusions

Hydroxamic acid functional group was grafted onto zeolite P. The modified zeolite (HASiZP) enhanced the sorption of Cu(II) by 100% compared to the original zeolite. The XRD patterns of HASiZP and ZP were almost similar showing that the modification did not affect its crystallinity. Cu(II) sorption by HASiZP followed second order kinetic model. Isotherm study showed that the sorption followed Langmuir model with maximum capacity of 33.32 mg/g at 25°C and increased to 48.12 at 70°C. The Cu(II) sorption was endothermic as shown by the negative value of Δ H°. The negative free energy showed that the sorption process was spontaneous. The positive value of Δ S° showed that Cu(II) sorption increased the randomness of the system. The modified zeolite may be used to improved sorption capacity of other types of heavy metal ions which can form complex with hydroxamic acid and could be useful for wastewater treatment and control of environmental pollution.

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