

Microwave Preparation and Copper Ions Adsorption Properties of Crosslinked Chitosan/ZSM Molecular Sieve Composites

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ABSTRACT: A novel chitosan-based composite (CTS/ZSM) made of chitosan and ZSM molecular sieve was prepared under microwave irradiation and was used for the removal of Cu (II) ions from aqueous solution. The composites were characterized by FTIR spectra, XRD spectra, and thermogravimetric analysis. The effects of the ZSM content, amount of glutaraldehyde and pH value on adsorption properties of Cu (II) ions by CTS/ZSM were discussed in detail. Contrast with crosslinked chitosan (CCTS), the CTS/ZSM had higher adsorption capacity for Cu (II). Kinetic studies showed that the adsorption of Cu (II) onto CTS/ZSM composite had low correlation coefficients for the pseudo-first and -second order model and intraparticle diffusion model. The equilibrium process was better described by the Langmuir than Freundlich isotherm model. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 129: 86–93, 2013

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INTRODUCTION

As a result of today's widely industrialized society, heavy metal contamination of various water resources is becoming of great concern because of the toxic effect to human beings and other animals and plants in the environment.^{1–3} Copper, in particular, is extensively utilized in the electrical plants, and in the manufacture of fungicides and antifouling paints. It could cause harmful, acute and even fatal effect when Copper ions are ingested at high concentration.⁴ Conventional methods that have been employed for the removal of copper ions from industrial effluents usually include chemical precipitation,⁵ membrane separation,^{6,7} adsorption,⁸ ion exchange,^{9,10} and so on. These technologies have distinct limitations and disadvantages, such as being costly or ineffective, especially in removing metal ions from dilute solutions. One of the new developments for metal removal in recent years is to use bio-sorbents^{11–13} that contains effective functional groups to bind metal ions. Biopolymers are potential adsorbents due to their biodegradability, nontoxicity, and high efficiency.

Chitosan (CTS), a polymer made up of glucosamine units, mainly results from deacetylation of chitin,^{14,15} which is the second abundant polymer in nature next to cellulose. CTS have many useful features such as hydrophilicity, biodegradability, biocompatibility, antibacterial property, and the ability to bind

with transition metals. Many metallic ions, such as Cu (II), Cd (II), Cr (III), Cr (VI), U (VI), Pb (II), Hg (II), Co (II), and Ni (II) can be chemically or physically adsorbed by chitosan or chitosan derivatives from aqueous solutions.^{16–22} It was observed that the amino groups on CTS chains serve as the coordination sites to the uptake of transition metal ions.^{15,23–25} The major employment limitation of chitosan is however in their poor acidic resistance and mechanical strength. A number of attempts have been made to enhance the chemical stabilities of the chitosan in acidic conditions through chemical crosslinking reaction with various cross-linking agents,^{26–29} such as glutaraldehyde (GA), ethylene glycol diglycidyl ether (EGDE), epichlorohydrin (ECH) and so on. The fact that crosslinked chitosan (CCTS) become very stable and maintains their strength even in acidic and basic media enlarges application scale of CTS. Compared to pristine CTS, however, the adsorption capacity for metal ions of CCTS generally decreased, mainly due to a reduction of adsorption groups or enhancement of steric hindrance.¹⁵ Various ways have increasingly been used to enhance the adsorption capacity of CTS and CCTS, such as coating CTS on an organic supports^{30–32} or the introduction of inorganic powders or particles^{33–37} to the CTS matrix. This is becoming an important approach to improve the performance of chitosan-based resins.

In this article, we aimed to find an effective and convenient approach to prepare chitosan-based adsorbents using microwave

irradiation. Microwave irradiation has received increasing interest in organic synthesis due to remarkable enhancements of some organic reactions and significant effects over conventional reaction.^{38,39} In this study, the ZSM molecular sieve (ZSM) was used to improve the adsorption capacity of CCTS and the chitosan/ZSM molecular sieve composites (CTS/ZSM) were prepared under microwave irradiation. Copper ions adsorption onto CTS/ZSM from aqueous solution was investigated in detail. The influence of experimental conditions such as ZSM contents and amount of glutaraldehyde were studied. The adsorption rates were determined quantitatively and analyzed by the first-order and second-order kinetic model and intra-particle diffusion model. The Langmuir and Freundlich equations were used to fit the equilibrium isotherm data.

EXPERIMENTAL

Materials and Instruments

Chitosan (degree of deacetylation: 85%) was purchased from Shandong Ao-Kang biotech. Glutaraldehyde (GLA) 20% water solution was analytical-grade reagents and was obtained from Tianjin North Chemical Reagent Factory. ZSM molecular sieve (SiO₂/Al₂O₃: 30–35) was supplied by Shandong Qi-Lu Huaxin Industry. All other reagents and solvents were used on analytical grade without further purification. All solutions were prepared with distilled water. A microwave oven (MM721AAU-PW) produced by Guangdong Midea microwave oven manufacturing was employed to promote the reaction.

Preparation and Characterization

Preparation of CTS/ZSM Composite Under Microwave Irradiation. About 0.5 g CTS was distilled in 50 mL of 2% acetic acid with magnetic stirring and the ZSM molecular sieve was added. And then the mixed solution was put under ultrasonic radiation for half an hour. Then 20% GLA solution was added to the solution and stirring continued for next 10 min. And the mixed solution was put under microwave irradiation at middle grade for 3 min, so the CTS/ZSM composite was cross-linked. The obtained product was precipitated with 5% NaOH solution and washed with distilled water several times until the washing liquid became neutralized. The composites with different ZSM contents and different crosslinker amount were prepared at the same steps and the products were dried in a vacuum oven at 60°C.

Characterization of the CTS and CTS/ZSM Composites. FTIR spectra of the solid products were recorded on a Nicolet 380 spectrophotometer (Thermo-electron corporation, USA) using KBr pellets. Wide angle X-ray diffraction (XRD) measurements were performed at room temperature with an Ultima IV X-ray diffractometer (Rigaku, Japan) using Cu K α radiation. The surface of CTS/ZSM composites were observed under a VHX-600E Super field depth 3D microscopy (Keyence, Japan). And thermal gravimetric analyses (TGA) were performed on CTS and CTS/ZSM samples using TG/DT6300 (NSK, Japan) in the temperature range of 20–600°C at a heating rate of 10°C per minute.

Adsorption Experiments

All batch adsorption experiments were carried out by mixing 0.2 g sample with 50 mL aqueous solution of copper sulfate

with desired concentration at room temperature for a given time. The pH value of Cu (II) solution was adjusted with acetic acid using a mettler-Toledo 320 pH-meter. The pH dependency of Cu (II) adsorption by CTS/ZSM composites was studied in the pH range of 2.5–8. The initial pH of the Cu (II) solution was adjusted using HCl (or acetic acid) or 0.10 mol L⁻¹ NaOH solutions. A series of adsorption studies were also conducted under the optimum pH value to investigate the effect of ZSM contents and amount of glutaraldehyde.

Batch kinetic experiments were conducted by mixing 0.2 g sample with 50 mL Cu(II) ions solution (C₀: 30 mmol L⁻¹) at room temperature for predetermined intervals of time. For equilibrium adsorption experiments, 50 mL of various initial concentration of Cu (II) solution was added with 0.2 g sample and the adsorption continued until the equilibrium was established. Both the initial and the final concentration of Cu (II) solution were measured by EDTA titrimetric method using a spectrum Lab 54 UV-vis spectrophotometer (Shanghai Lengguang Tech).

The adsorption capacity of the samples for Cu (II) ions was calculated through the following equation:

$$q = (C_0 - C)V/m \quad (1)$$

where q is the amount of Cu (II) adsorbed at time t or at equilibrium (mmol g⁻¹). C_0 is the initial concentration of Cu (II) solution (mmol L⁻¹). C is the liquid-phase Cu (II) concentration at time t or at equilibrium (mmol L⁻¹) and m is the mass of the adsorbent used (g), and V is the volume of Cu (II) solution (L).

Further experiments were proceeded to investigate the regeneration and repeatability of the CTS/ZSM composites. The CTS/ZSM resin adsorbed Cu (II) ions was dipped into 0.10 mol L⁻¹ HCl solution stirring for 5 h at room temperature to remove the Cu (II) ions and then was treated with 0.1 mol L⁻¹ NaOH for 5 h. Finally it was filtered and washed thoroughly with distilled water to neutrality and dried in a vacuum oven at 50°C. The dried resin obtained was used in regeneration adsorption experiment and the process was repeated for five times to observe the reusability of samples.

RESULTS AND DISCUSSION

Characterization of CTS and CTS/ZSM

In this experiment, the ZSM molecular sieve was incorporated to improve the adsorption capacity of crosslinked CTS. Figure 1 showed the FTIR spectra of CTS, CCTS, and CTS/ZSM. It was observed from Figure 1(a–c) that the intense band at around 3445 cm⁻¹ should be assigned to the stretching vibration of O–H and N–H on chitosan chains. The characteristic peaks of amide groups in CTS chain, amide I and amide II bands at 1647 and 1540 cm⁻¹, were observed respectively.

Comparing with the pristine CTS, the new peak in CCTS and CTS/ZSM composite at 1640 cm⁻¹ represented the formation of the imine (C=N) linkage which confirmed that cross-linking reaction had taken place. The absorption band at about 470 cm⁻¹ in Figure 1(c) should be assigned to the bending vibration

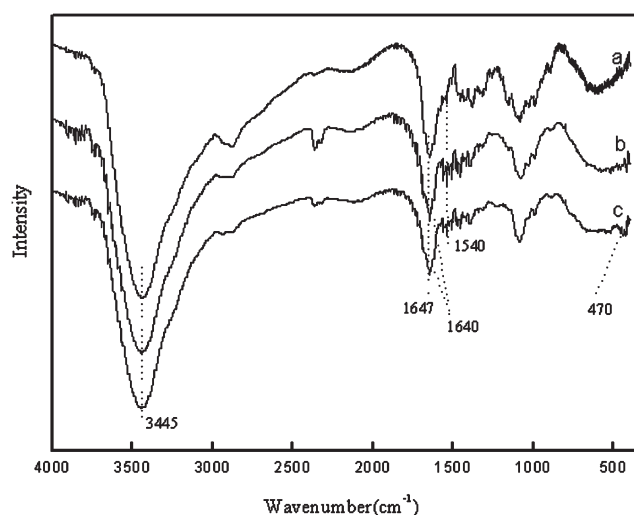


Figure 1. FTIR spectra of CTS (a), CCTS (b), and CTS/ZSM (c).

of Si—O groups in ZSM molecular sieve. So the crosslinked CTS/ZSM composites were successfully prepared under microwave irradiation and the reaction time could be shortened compared to conventional methods.^{26–29}

Figure 2 depicted the XRD spectra of CTS and CTS/ZSM. The XRD patterns of CTS represented the distinct crystalline peaks at angles of $2\theta = 10^\circ$ and 20° . This was due to plenty of hydroxyl and amino groups existed in the chitosan chains, which can form stronger intermolecular and intramolecular hydrogen bonds.^{23,40} In addition, the structure of chitosan molecules had certain regularity. As a result, chitosan molecules can form crystalline regions easily. However, as regards CTS, the characteristic peak at angle of $2\theta = 10^\circ$ in CTS/ZSM disappeared, and the characteristic peak at angle of $2\theta = 20^\circ$ decreased obviously. And new peaks at angles of $2\theta = 22^\circ$ and 30° should be characteristic of ZSM molecular sieves. So it can be inferred that the introduction of ZSM and crosslinking resulted in the decrease of crystallinity caused by CTS chains.

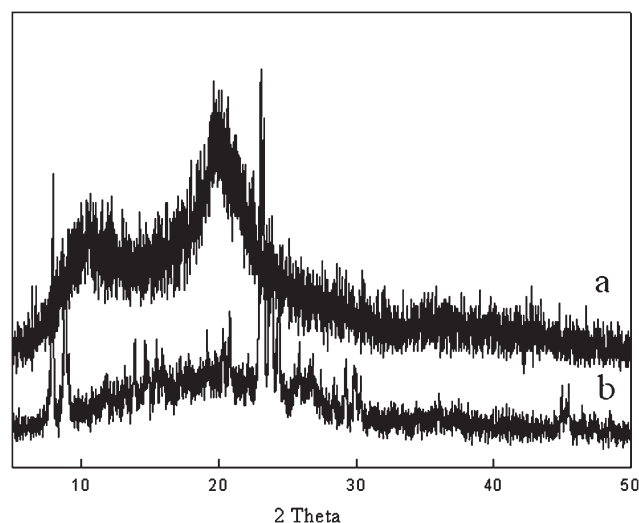


Figure 2. XRD spectra of CTS (a) and CTS/ZSM (b).

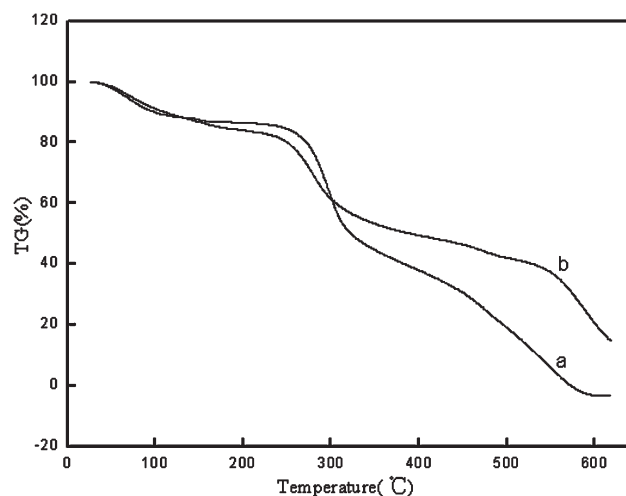


Figure 3. TGA curve of CTS (a) and CTS/ZSM (b).

The results from TGA analysis were presented in Figure 3. As shown in Figure 3, chitosan which had two main decomposition stages with one starting at 260°C and another starting at around 330°C completely burnt out at 600°C . The TGA curve of CTS/ZSM which showed similar decomposition stages of CTS with a relatively less weight loss indicated that the thermal property of CTS was enhanced through cross-linking and adding of ZSM molecular sieve.

Figure 4 showed the micrograph of CTS/ZSM and it was indicated that the surface were porous and rough.

Effect of ZSM Content on Cu (II) Adsorption

Figure 5 showed the variation of ZSM molecular sieve content (wt %) on Cu(II) adsorption capacity of CTS/ZSM composites. From Figure 5, it can be observed that the ZSM amounts significantly affected the adsorption performance though the ZSM molecular sieve had little adsorption for Cu (II) ions while used alone. The adsorption uptake of ZSM/CTS for Cu (II) showed maximum adsorption capacity at 4 wt % ZSM content, and then decreased with further addition of the ZSM. When the

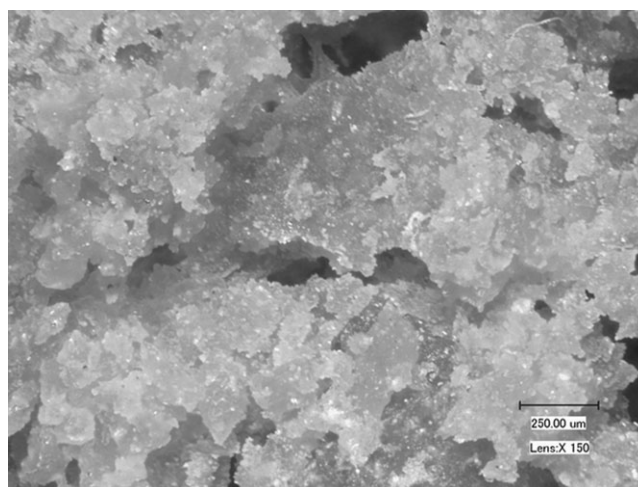


Figure 4. Micrograph of CTS/ZSM composite.

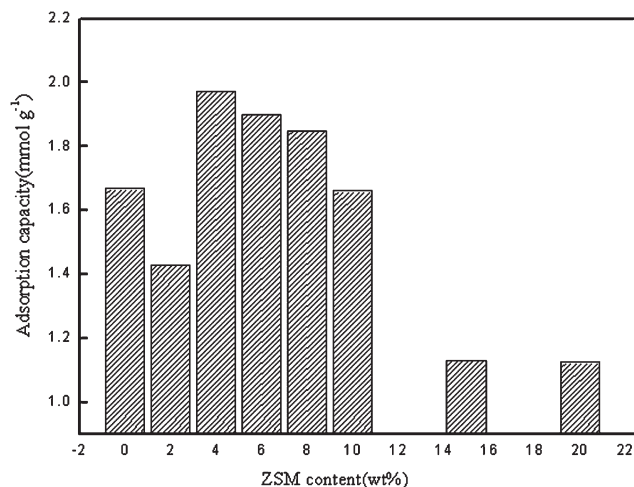


Figure 5. Effect of ZSM contents on Cu (II) adsorption.

ZSM ratio was <10 wt %, ZSM molecular sieve could act as physical crosslinking points which made the chitosan more regularly arrangement in the crosslinked chitosan network.⁴¹ So the more adsorption sites could be exposed to make the adsorption capacity larger than CCTS. Once the ZSM content exceeded 10 wt %, instead of providing physical cross-linking, excess ZSM component acted as filler in the polymeric network of the composite. Because the adsorption capacity of ZSM for Cu (II) was much low, the filled ZSM may greatly decrease the adsorption capacity of the CTS/ZSM composites.

Effect of Amount of Glutaraldehyde on Cu (II) Adsorption

In the experiment when the amount of 20% GLA solution reached at least 0.6 mL, the composite can form effective and adequate strength. The influence of amount of GLA on Cu (II) adsorption was shown in Figure 6. When the amount of the cross-linker increased, the uptake of the Cu (II) on CTS/ZSM first increased and then decreased. The increase in Cu (II) adsorption was mainly attributed to the low levels of crosslinking agent in the complex preventing the formation of closely packed chain arrangements. The next decrease in the adsorption

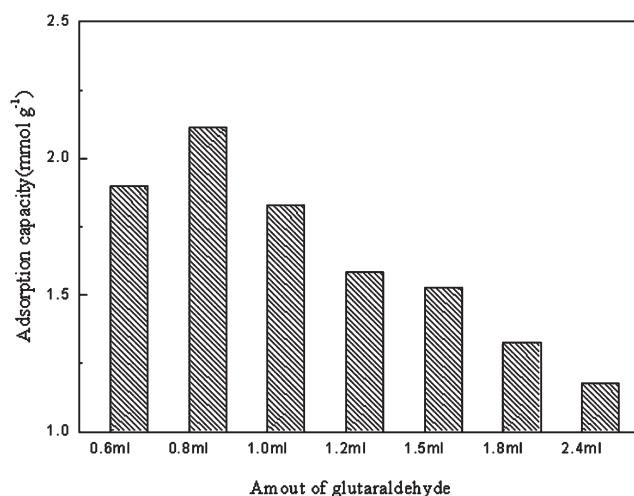


Figure 6. Effect of amount of glutaraldehyde on Cu (II) adsorption.

owned to the decrease of amine group because of the crosslinking reaction and at higher levels of crosslinkers the products had lower swelling capacities because of the more extensive three-dimensional network.¹⁵

Effect of pH Value on Cu (II) Adsorption

The pH value of the metal ion solution played an important role on the adsorption capacity in the whole adsorption process. Figure 7 showed the influence of pH₀ of Cu (II) ion solution on the adsorption capacity of CTS/ZSM composites. It can be seen from Figure 7 that the adsorption capacity increased sharply when pH₀ of Cu (II) solution increased from 2.5 to 5.2, and then decreased a little with the increase of pH₀ from 5.2 to 8.0. At low pH₀, most of the amino groups of CTS in the composite were ionized and presented in the form of NH₃⁺, electrostatic repulsion between Cu (II) and NH₃⁺ ions may prevent the adsorption of Cu (II) ions onto the composite.¹¹ When pH₀ value raised, more amino groups could chelate and adsorb Cu (II) ions and adsorption capacity increased. Considering the precipitation formation of Copper when the pH value of Cu (II) solution exceeds 8.0, the pH₀ of 5.2 was selected as the initial pH value of Cu (II) solution for other adsorption experiments.

Adsorption Kinetics

The adsorption kinetics of Cu (II) was illustrated in Figure 8. The adsorption capacity increased with time during the initial 5 h of the sorption process. After that, the uptakes increased slowly and reached equilibrium value.

To obtain further insight into the mechanism of the adsorption of Cu (II) on CTS/ZSM, a pseudo-first order and pseudo-second order kinetic models were cited to evaluate the experimental data. The pseudo-first order kinetic model⁴² can be formulated as:

$$\log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \quad (2)$$

The pseudo-second order kinetic model⁴³ can be expressed as:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (3)$$

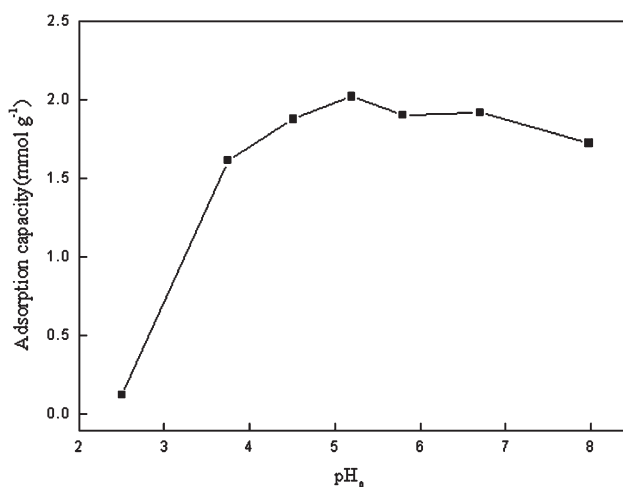


Figure 7. Effect of pH value on Cu (II) adsorption.

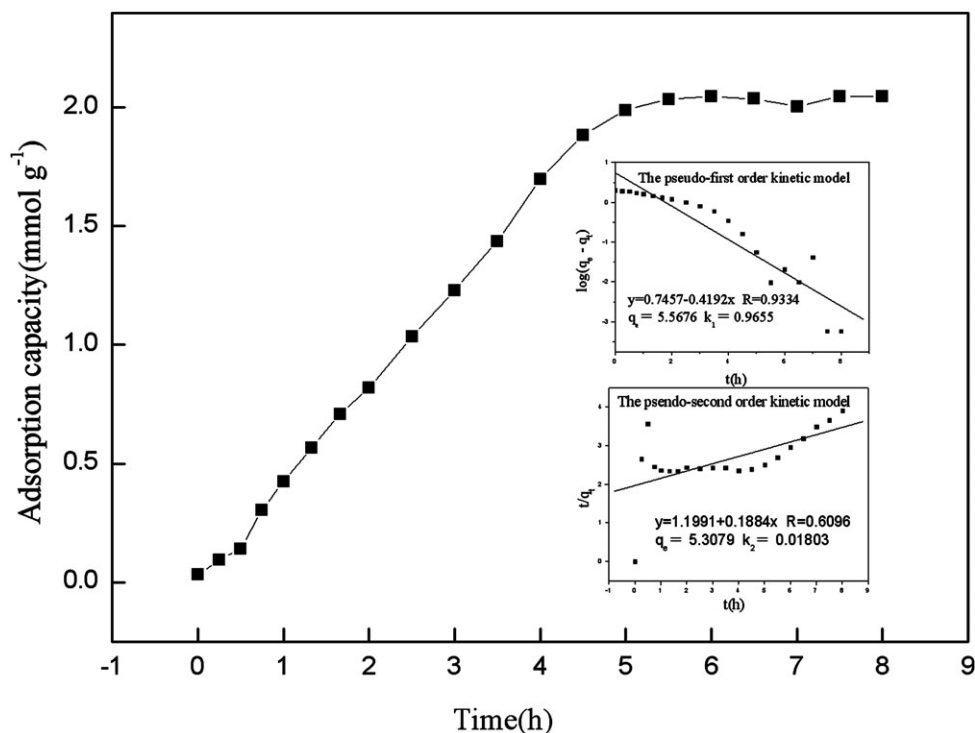


Figure 8. Adsorption kinetics of Cu(II) on CTS/ZSM.

q_e and q_t (mmol g⁻¹) are the adsorption capacities at equilibrium and at time t , respectively. k_1 (min⁻¹) is the rate constant of the pseudo-first order adsorption and k_2 (gmmol⁻¹ min⁻¹) is the rate constant of the pseudo-second order adsorption. All the corresponding parameters obtained from the linear plots of $\log(q_e - q_t)$ versus t and t/q_t versus t was also listed in Figure 8.

It can be seen that the linear correlation coefficient (R) for the pseudo-first order kinetic model and pseudo-second order model were 0.9334 and 0.6096, respectively. Their calculated equilibrium adsorption capacities $q_{e,cal}$ (5.5676 and 5.3079 mmol g⁻¹) were vary greatly with the experimental data (2.0454 mmol g⁻¹). It can be inferred that the pseudo-first and pseudo-second order model could not explain the adsorption of Cu (II) onto CTS/ZSM composites.

The adsorption kinetics results were also analyzed in terms of intraparticle diffusion model to investigate whether the intraparticle diffusion was the rate controlling step in adsorption of Cu (II) on CTS/ZSM composite. The model proposed by Weber and Morris⁴⁴ can be written as follows

$$q_t = k_p t^{1/2} + C \quad (4)$$

where k_p (mmol g⁻¹ h^{1/2}) was the rate constant of intraparticle diffusion.

Weber–Morris fitting curve using plots of q_t versus $t^{1/2}$ was given in Figure 9. If the intraparticle diffusion was the sole rate determining step, the plots of q^t vs. $t^{1/2}$ should be linear and pass through the origin. It was observed that the fitting curve in the Figure 9 was not through the origin and can distinguish

two distinct regions. The initial curved region corresponded to the external surface uptake, the second stage related the gradual uptake reflecting intra-particle diffusion as the rate limiting step and final plateau region indicated.³⁰ Based on the results it may be concluded that intraparticle diffusion is not only the rate determining factor. The external surface uptake and equilibrium uptake had also some influences in the adsorption process.

Adsorption Isotherm Study

Figure 10 showed the adsorption isotherms of Cu (II) on the CTS/ZSM at room temperature. It was observed that the adsorption capacity increased with increase in equilibrium concentration and attained a saturated value.

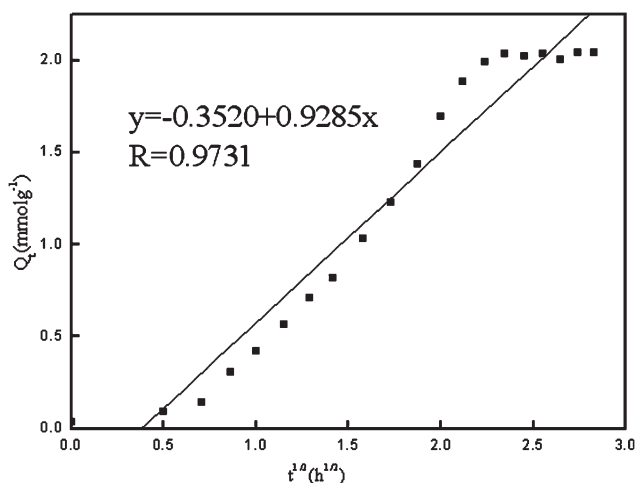


Figure 9. Weber–Morris fitting curve of adsorption data.

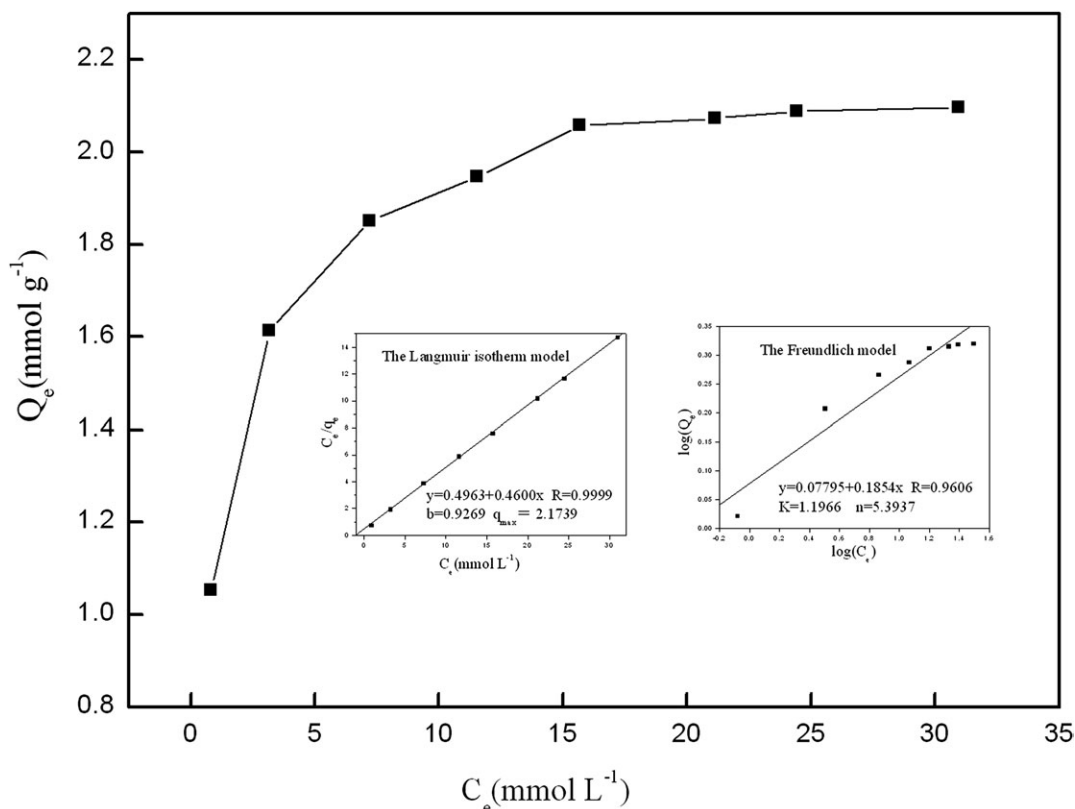


Figure 10. Adsorption isotherm of Cu (II) on CTS/ZSM.

Adsorption isotherms were important for the description of how molecules of adsorbate interact with adsorbent surface. The adsorption curves were analyzed to fit to both the Langmuir and Freundlich equations. The Langmuir isotherm model assumed monolayer adsorption on a surface with a finite number of identical sites, so that all sites were energetically equivalent and there was no interaction between the adsorbed molecules. The Freundlich expression was an empirical equation for

adsorption on heterogeneous surface with a non-uniform distribution of adsorption sites.

The Langmuir isotherm model⁴⁵ is represented as follows:

$$\frac{C_e}{q_e} = \frac{1}{Q_{max} \times b} + \frac{C_e}{Q_{max}} \quad (5)$$

The Freundlich model⁴⁶ is expressed as follows:

Table I. Cu (II) Adsorption Capacity and Langmuir Adsorption Constant of Different Chitosan-Based Adsorbents from Literatures

No.	Adsorbent	Q_{max} (mmol g ⁻¹)	b (L mmol ⁻¹)	Reference
1	Chitosan-GLA beads	0.94	0.308	26
2	Chitosan-ECH beads	0.98	0.144	26
3	Chitosan-EGDE beads	0.72	0.137	26
4	Chitosan-alginate beads	1.06	0.04258	29
5	Chitosan-H ₂ fmbme	1.79	0.004	42
6	CCTSL	1.30	24.59	20
7	Chitosan coated PVC	1.38	0.699	30
8	Chitosan coated perlite beads	1.59	1.095	33
9	chitosan-g-poly(acrylic acid)/50%attapulgit	3.15	1.20	41
10	chitosan-tripolyphosphate beads	0.41	3.03	36
11	chitosan-cellulose beads	0.57		11
12	chitosan/PVA beads	0.75	128.93	12
13	CTS/ZSM	2.17	0.9269	This work

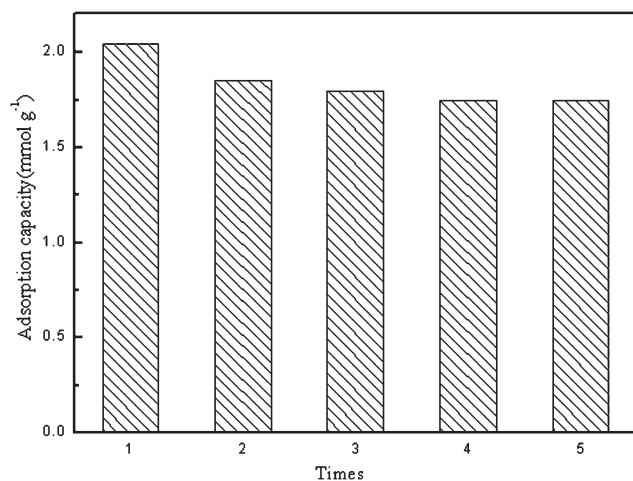


Figure 11. Regeneration of CTS/ZSM composites.

$$q_e = K_F C_e^{1/n} \quad (6)$$

where q_e (mmol g⁻¹) is the amount of Cu (II) adsorbed at equilibrium, C_e (mmol L⁻¹) is the liquid-phase Cu (II) concentration at equilibrium, Q_{\max} (mmol g⁻¹) is the maximum adsorption capacity of the adsorbents, and b (L mmol⁻¹) is the Langmuir adsorption constant, K_F (L g⁻¹) is the Freundlich isotherm constant and $1/n$ (dimensionless) is the heterogeneity factor.

The Langmuir and Freundlich parameters obtained from the plots of C_e/q_e versus C_e and $\log(q_e)$ versus $\log(C_e)$ were also listed in Figure 10. The correlation coefficients of the linear form of the Langmuir model ($R = 0.9999$) were closer to 1 than that of the Freundlich model ($R = 0.9606$). In addition, the Q_{\max} values (2.1739 mmol g⁻¹) for the adsorption of Cu (II) onto the CTS/ZSM calculated from the Langmuir model were consistent with the experimental data. It was inferred that the Langmuir isotherm model gave better fits than the Freundlich isotherm model. This revealed the monolayer coverage of Cu (II) on the surface of the CTS/ZSM composites. Several studies had also shown that the Langmuir isotherm model gave the better fit for the experimental data.^{33,35,47}

Cu (II) ions adsorption onto CTS and its derivatives from literatures were compiled in Table I. The adsorption capacity observed in this study was superior to most of the other adsorbents.

Regeneration of CTS/ZSM Composites

Figure 11 showed the adsorption capacities of the CTS/ZSM resin for Cu (II) ions after reuse for five times. It was observed that the adsorption capacities of Cu (II) ions dropped slightly after each cycle. The results indicated that the CTS/ZSM samples had a good reusability.

CONCLUSIONS

The CTS/ZSM composites were successfully prepared under microwave irradiation. It was showed that the introduction of ZSM improve the Cu (II) ions adsorption capacity of CCTS. Ki-

netic studies showed that the pseudo-first and second order model could not explain the adsorption of Cu (II) onto CTS/ZSM and intraparticle diffusion was not only the rate determining factor. Cu (II) adsorption on CTS/ZSM was better fitted with the Langmuir adsorption isotherm model and monolayer adsorption was formed between the resin and adsorbate.

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