

## Effects of adsorption of copper-polluted water by Ti-MCM-41

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**Abstract.** Ti-MCM-41 zeolite was hydrothermally synthesized by using tetrabutyl orthotitanate as titanium source and fumed silica as silicon. Powder X-ray diffraction UV-vis diffuse reflectance spectroscopy and inductively coupled plasma were used to characterize the product, results indicated revealed that the Ti-MCM-41 material was synthesized successfully with ordered hexagonal structure. Ti-MCM-41 zeolite was used to investigate the effects of contact time, adsorption temperature, pH value and reusability on the adsorption of Cu(II). The results showed that the optimal adsorption conditions were: contact time was 60 min, adsorption temperature was 333 K and pH value was 6 for the initial Cu(II) concentration of 50 mg/L. The adsorption rate and adsorption capacity of Cu(II) were 90.52% and 45.26 mg/g, respectively. In the meantime, Ti-MCM-41 showed outstanding reusability on adsorption of Cu(II).

### Introduction

In recent years, metal pollution in ground water, mainly with copper, is increasing. The removal of Cu(II) ions in water is currently a strategic issue. Among all the water processing methods, the adsorption method received the most attention because its high-efficiency, versatile, economical and easy operation etc [1,2]. MCM-41 zeolite possess well-ordered, hexagonal array of pore channels and tunable pore size, has attracted considerable attention due to its potential applications in catalysis, separation, and adsorption for heavy metals [3,4]. Unfortunately, MCM-41 zeolite is liable to collapse when exposed to boiling water or mechanically compressed due to the amorphous frameworks and thin walls [5, 6]. The hydrothermal stability of MCM-41 can be enhanced by implanted Ti into the framework [7]. However, the literature studies on the adsorption of Cu(II) with Ti-MCM-41 are very limited.

In this report, Ti-MCM-41 was synthesized by hydrothermal method [8], X-ray diffraction, UV-vis diffuse reflectance spectroscopy and inductively coupled plasma were used to characterize the prepared material. The synthesized Ti-MCM-41 zeolite was used for adsorption of Cu(II) in aqueous solution. The optimum adsorption conditions for the adsorption of Cu(II) have been established and reusability of Ti-MCM-41 was investigated.

### Material and methods

**Synthesis of Ti-MCM-41.** Following previous procedures [8], Ti-MCM-41 was hydrothermally synthesized use cetyltrimethylammonium tosylate (CTATos, 99%) as a structure-directing agent. In a typical synthesis, 3.3 g CTATos was dissolved in 60 mL water and stirred for 2 h at 353 K. 10.43 g tetramethylammonium hydroxide (TMAOH, 25%) aqueous solution was added into 48 mL water, followed by 4.88 g fumed silica under vigorous agitation. The silicate solution was stirred for 2 h at 353 K and cooled to 273 K, then tetrabutyl titanate (TBOT, 98%) isopropanol solution containing 0.92 g TBOT and 2 g isopropanol was added slowly and continued to stir for 50 min at 273 K. Alcohol was removed by stirring at 333 K for 2 h and the water content was adjusted. The above mixture was dropwise added into CTATos solution. The gels with the molar compositions of SiO<sub>2</sub>: 1/30 TiO<sub>2</sub>: 0.09 CTATos: 0.35 TMAOH: 82 H<sub>2</sub>O were stirred continuously for 2 h at 353 K and then heated in

autoclave under static condition at 443 K for 2 days. The product was filtered, washed with amounts of distilled H<sub>2</sub>O, dried at 373 K overnight and finally calcined in air at 823 K for 6 h.

**Recovery of Ti-MCM-41.** The used Ti-MCM-41 zeolite was separated by centrifugation (at 3000 rpm for 5min) and the residual solid was dried at 353 K. Then the zeolite was added to 100 mL of the HCl with the concentration of 1 mol/L, stirred 8 h, filtered, washed with distilled H<sub>2</sub>O, dried at 373 K overnight.

**Adsorption Experiments.** The Cu(II) adsorption experiments were performed by batch technique to obtain the adsorption rate and adsorption capacity. A fixed amount of Ti-MCM-41 zeolite (0.05 g) was taken in stoppered conical flasks, 50 mL of Cu(II) solutions with concentration of 50 mg/L was added. The solution pH value was adjusted by using 0.1 mol/L HCl and 0.1 mol/L NH<sub>4</sub>OH. The mixture was stirred vigorously by using a magnetic stirrer at 200 rpm for different contact time at different temperatures. After adsorption, the mixture was centrifuged and the amount of Cu(II) ions in the solution was measured by atomic absorption spectroscopy. The adsorption rate (Q) and adsorption capacity ( $q_e$ ) were calculated from the equation 1 and 2, respectively.

$$Q = (c_0 - c_e) / c_0 \times 100\% \quad (1)$$

$$q_e = (c_0 - c_e) / m \times V \times 0.001 \quad (2)$$

Where Q (%) is the the adsorption rate,  $q_e$  (mg/g) is the adsorption capacity,  $c_0$  (mg/L) is the initial concentrations of Cu(II) ions,  $c_e$  (mg/L) represent the equilibrium concentrations of Cu(II) ions,  $m$  (g) is the weight of Ti-MCM-41 and  $V$  (L) is the solution volume.

## Results and discussions

**Characterization of Ti-MCM-41.** The XRD pattern of Ti-MCM-41 is presented in Fig. 1a. There are three well-resolved intense peaks as (100), (110) and (200) [3], confirming well-ordered hexagonal mesoporous structure. This result indicates that the Ti-MCM-41 zeolite as-synthesized was highly crystalline materials with a pure phase. The UV-visible spectra of Ti-MCM-41 is shown in Fig. 1b. The absorption of Ti-MCM-41 exhibits a characteristic main band at 210 nm together with a weak shoulder around 260 nm, which indicates that the Ti atoms are incorporated into the framework of the MCM-41 hexagonal structure and highly dispersed as the isolated tetrahedrally coordinated Ti species [9, 10]. The ICP results revealed that the Si/Ti molar ratio of Ti-MCM-41 was 43.

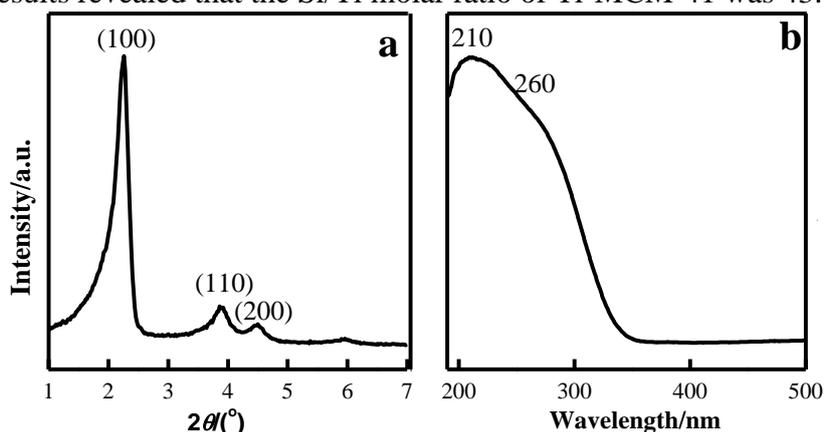


Fig.1 X-Ray diffraction pattern (a) and UV-Vis spectrums (b) of Ti-MCM-41.

**Effect of contact time.** Fig. 2 shows the effect of contact time intervals ranging from 0 to 80 min on the adsorption of Cu(II) by Ti-MCM-41 zeolite. It is apparent that contact time has significant influence on the adsorption efficiency. The experiments showed (Fig. 2) rapid adsorption of Cu(II) within the initial 50 min and the equilibrium was observed at 60 min with the adsorption rate and adsorption capacity reaching 90.52% and 45.26 mg/g. A further increase in contact time to 80 min had a slightly effect on the Cu(II) removal. At the beginning of adsorption, plenty of available vacant adsorption sites on the surface of Ti-MCM-41 were gradually decreased. Cu(II) was not strongly adsorbed by adsorbent due to the repulsive forces between inside the aqueous phase and solute

molecules on the surface. Therefore, the minimum contact time of 60 min could be considered for optimum adsorption of Cu(II) on Ti-MCM-41.

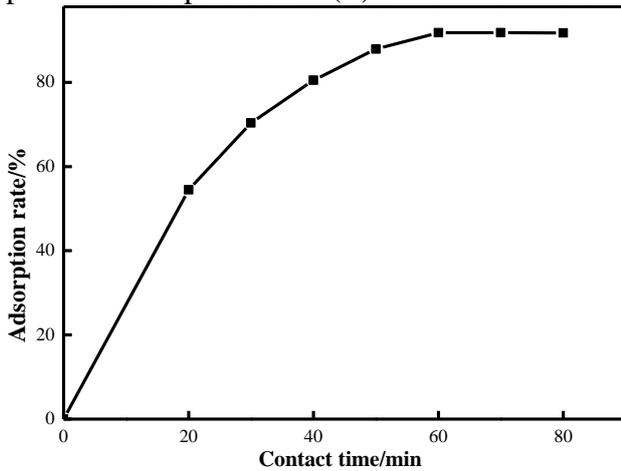


Fig. 2 Effect of contact time on the adsorption of Cu(II).

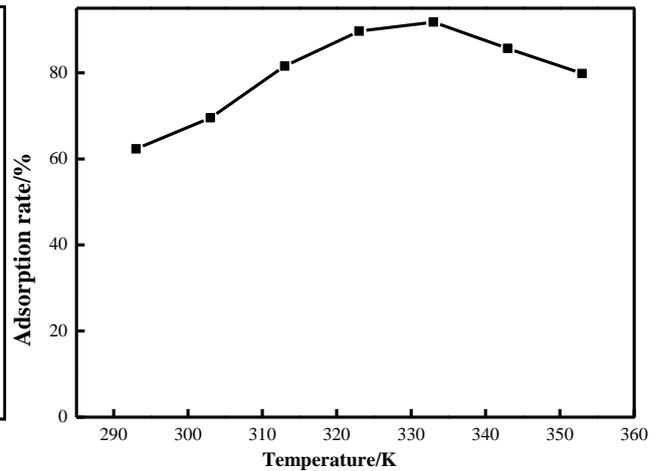


Fig. 3 Effect of temperature on the adsorption of Cu(II).

**Effect of adsorption temperature.** The adsorption of Cu(II) on Ti-MCM-41 was studied at temperatures of 293, 303, 313, 323, 333 and 343K. As shown in Fig. 3, the adsorption of Cu(II) significantly increased with rise in temperature from 293 to 333 K. The increased adsorption may be attributed to enhanced rate of intraparticle diffusion [11], which indicated that adsorption of Cu(II) on Ti-MCM-41 was an endothermic process. However, when the temperature was further increased (> 333 K), the adsorption of Cu(II) decreased slowly. As the temperature increased, the mobility of Cu(II) increased causing the ions to escape from Ti-MCM-41 zeolite to the liquid phase. Therefore, the desorption of Cu(II) occupied a leading position. Hence, we chose 333 K as the suitable adsorption temperature.

**Effect of pH value.** The soluble copper is in favor of Cu(II) ions (blue) at lower pH but it shifts to Cu(OH)<sub>2</sub> (dark brown) when the pH is more than 7 [12]. In order to determine the effect of pH value on the adsorption capacity of Ti-MCM-41, solutions were prepared at various pH values ranging from 2.0 to 6.0 (Fig. 4). It is found that the adsorption of Cu(II) obvious increased from pH=2 to pH=6. This attribute to high concentrations of H<sup>+</sup> could bonding with Si-OH and Ti-OH groups, which decreased the number of charged sites (such as Si-OH and Ti-OH groups) and reduces the attraction between Cu(II) and adsorbent surface [13]. The strong pH dependent adsorption of Cu(II) on Ti-MCM-41 indicated that the process is dominated by surface complexation.

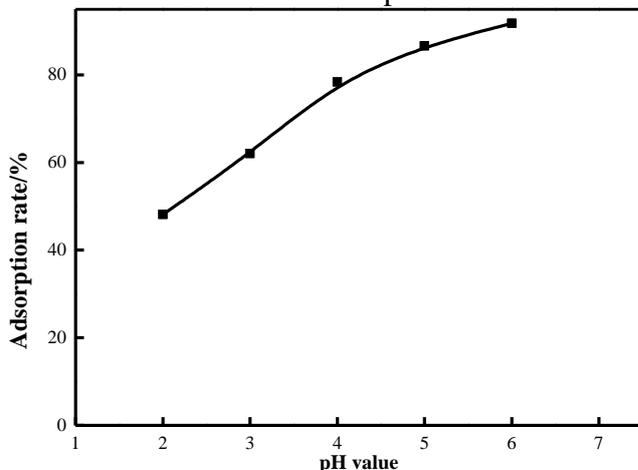


Fig. 4 Effect of pH value on the adsorption of Cu(II).

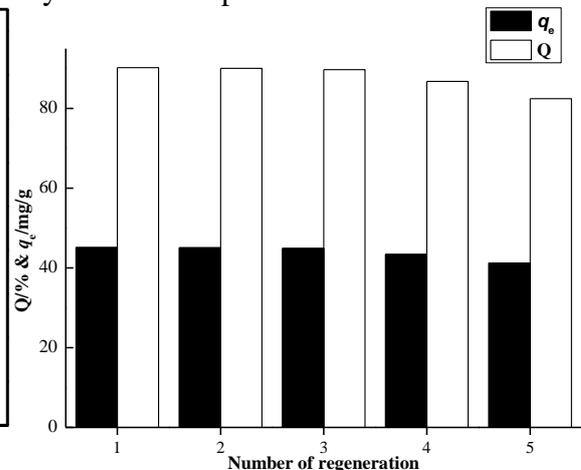


Fig. 5 The adsorption-regeneration cycles of Ti-MCM-41.

**Reusability of Ti-MCM-41.** In addition to adsorption capacity, the applicability of sorbents depends also on their reusability. Ti-MCM-41 was first reused on the adsorption of Cu(II). The experiments were initiated with an enlarged adsorbent dosage of 1 g, the Cu(II) ions adsorbed onto

Ti-MCM-41 were eluted out by HCl. Then, it was subjected to a repeated process at a constant ratio of absorbent-adsorbate. The adsorption-desorption cycle (Fig. 5) results indicated that the Ti-MCM-41 could be reused up to 6 times without a significant decrease in the adsorption of Cu(II), the adsorption rate and adsorption capacity maintained as 82.42% and 41.21 mg/g, respectively. Therefore, Ti-MCM-41 have potential practical application prospect for the removal of Cu(II) from water and wastewater.

## Conclusion

The results suggest that the adsorption of Cu(II) is influenced by the contact time, the adsorption temperature and the solution pH value. The adsorption reached the equilibrium when contact time was 60 min, the optimized adsorption temperature was 333 K and the best pH value was 6. The maximum adsorption rate and adsorption capacity of Cu(II) ions with Ti-MCM-41 90.52% and 45.26 mg/g, respectively. Furthermore, Ti-MCM-41 possessed excellent reusability on the adsorption of Cu(II), which have good prospects for the removal of Cu(II) from water and wastewater in practical application.

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