

## Adsorption of Copper ions by Montmorillonite/Sodium Humate/N-Isopropyl Acrylamide composite

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The montmorillonite-based composites can be used to adsorb copper ions to relieve contamination. The montmorillonite/sodium humate/copper ion complex, which can be obtained by mixing montmorillonite, sodium humate (surface modification of montmorillonite), and N-isopropyl acrylamide, is ideal candidate for adsorption of copper ions. First, the modified montmorillonite-based adsorbents were characterized by infrared spectroscopy and scanning electron microscopy. Then, effects of incubation time and initial concentration of copper ions on adsorption of copper ion by modified montmorillonite were investigated. The results revealed that modification by (3-acrylamidopropyl) trimethylammonium chloride, N-isopropyl acrylamide, or sodium humate can significantly improve the adsorption capability of montmorillonite. The adsorption rates at initial concentration of 1000 mg/L can be up to 96.98% and 95.02%. In summary, the montmorillonite/sodium humate/N-isopropyl acrylamide composite shows great adsorption capability towards copper ions.

**Keywords:** montmorillonite modification; humic acid sodium; Acrylamide; copper ion; waste water treatment

### INTRODUCTION

Owing to its severe toxicity, concentration along the food chain upwards, and absence of effective separation approaches, heavy metals in natural water bodies has been a global environment issue. Over the past decades, contamination of water bodies in domestic cities caused by long-term, considerable discharge of municipal and industrial waste water has been a significant issue [1]. To make it worse, contamination of water bodies may lead to significant soil contamination due to sewage flow and sewage irrigation. Therefore, a cost-effective and efficient sewage treatment approach has been urgently needed [2].

Montmorillonite ( $\text{Al}_2(\text{OH})_2\text{Si}_4\text{O}_{10}$ ) is a lamellar aluminosilicate with considerable reserve. This substance is characterized by large inner surface area and inter-layer domain adjustability. Hence, montmorillonite-based materials for effective, low-cost, and facile water treatment have gain increasing popularity. Consisting of  $\text{Al}_2\text{O}_3$ ,  $\text{SiO}_2$ , and several ions (e.g.,  $\text{Ca}^{2+}$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Na}^+$ ), montmorillonite has a octahedron crystal structure ( $\text{SiO}_2:\text{Al}_2\text{O}_3 = 2:1$ ). As is known, aluminum ions and silicon ions can substitute each other. As a result, the montmorillonite crystal cell is negatively charged and can adsorb certain cations, although the interaction is so weak that the cations are readily exposed to substitution by other low-valence ions. As the ion substitutions take

place in the inter-layer space, the structure of montmorillonite is relatively stable. However, the ion substitutions have a significant effect on the physical and chemical properties of montmorillonite.

Montmorillonite swells significantly in water as the inter-layer space can adsorb considerable amount of water molecules. The fine crystal grains of montmorillonite lead to large specific surface area, while the weak inter-layer interactions result in easy expansions and separations of montmorillonite crystal layers in solvent [3]. As a result, montmorillonite has relatively large inner surface area. Nevertheless, the adsorption capability of montmorillonite is not outstanding. For instance, the Langmuir adsorption capacities of untreated and acid activated bentonite for copper have been demonstrated to be 42.41 mg/g and 32.17 mg/g [4], respectively. Hence, the adsorption capability of montmorillonite needs to be further improved. Owing to loose aromatic ring structure and the pores with varying sizes, humics can interact with heavy metals via complexation. Additionally, high contents of carboxyl, hydroxyl, and carbonyl functional groups were observed in humic acid. Therefore, humic acid can easily adsorb on soil minerals in natural environment. The humic acid in sodium humate can interact with active surface of clay via complexation [5]. Also, sodium humate can increase the density of complexation sites and generate ligands on the surface of montmorillonite [6]. In this article, montmorillonite/sodium humate/n-isopropyl acrylamide complex was prepared and used for adsorption of copper ions.

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This study provides references for treatment of copper ion containing wastewater.

## SAMPLE PREPARATION

### *Equipment and materials*

Equipment: 50 mL beaker, 2000 mL beaker, balance (graduated value = 0.1 mg), glass rod, 2000 mL measuring flask, filter paper, oven, three-neck bottle, nitrogen bottle, water bath container, polyethylene tube, and shaking incubator.

Materials: distilled water, 0.1 mol/L HCl and NaOH solution, 2-acrylamido-2-methylpropane sulfonic acid (purchased from Shanghai Macklin Biochemical Co., Ltd.), ammonia sulfate, N-isopropyl acrylamide (purchased from Shanghai Saen Chemical Co., Ltd.), (3-acrylamidopropyl) trimethylammonium chloride (purchased from Shanghai Saen Chemical Co., Ltd.), Ca-based montmorillonite (Ca-MMT, purchased from Linyi Luse Chemical Co., Ltd.), sodium humate (SH, purchased from Linyi Luse Chemical Co., Ltd.). All chemicals used were analytical grade.

### *Preparation of composite adsorbent*

a) 11.39 g 2-acrylamido-2-methylpropane sulfonic acid was added into a three-neck flask equipped with thermometer and condenser and stirred at room temperature, followed by addition of 3.3 g Ca-MMT and 5 g SH. Then, nitrogen was injected and kept for 30 min, followed by heating to 40~50 °C in water bath.

b) 96 mg ammonia sulfate was added into 2.5 mL of water and kept for 10 min. Then, the solution was heated up to 80 °C and kept for 3 h. Herein,  $w(\text{Ca-MMT}) = 20\%$  and  $w(\text{SH}) = 30\%$ .

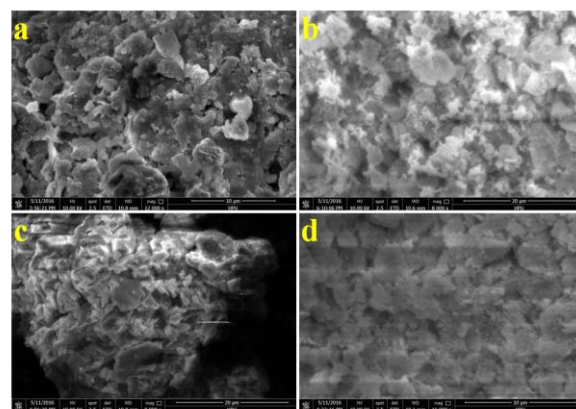
c) The product was collected and dried at 70 °C until no weight loss was observed; the product was then sieved using a 200-mesh sieve.

d) 2-acrylamido-2-methylpropane sulfonic acid was replaced by 6.22 g of N-isopropyl acrylamide and 15.2 g of (3-acrylamidopropyl) trimethylammonium chloride. Adsorbents were prepared by following the steps mentioned above and labelled appropriately.

### *Sample characterization*

#### *Characterization by scanning electron microscopy*

The scanning electron microscope used was Quanta 250 FEG-SEM field emission scanning electron microscope (FESEM) purchased from FEI Corp., USA. The scanning was conducted under low vacuum mode and 10 kV voltage and the resolution was 2.5 nm.



**Fig. 1.** The SEM photos of sample a, b, c and d represent sample 1, 2, 3 and MMT

Fig. 1 a, b, c, and d shows FESEM images of (3-acrylamidopropyl) trimethylammonium chloride/sodium humate/montmorillonite (Sample A), N-isopropyl acrylamide/sodium humate/montmorillonite (Sample B), 2-acrylamido-2-methylpropane sulfonic acid/sodium humate/montmorillonite (Sample C), and montmorillonite (Sample D), respectively. Herein, Sample D shows typical properties of montmorillonite: the particles were coarse, clusters with varying sizes, large thicknesses, and irregular shapes [7]. As observed, modified and unmodified samples exhibited similar structures, while Sample A and B showed relatively loose structures (original size of montmorillonite particles varies from 3  $\mu\text{m}$  ~ 4  $\mu\text{m}$ ). Sample A showed in homogeneous particle size with average size of 1  $\mu\text{m}$ , while Sample B showed clustered surface particles, indicating that the presence of adsorbents increased the specific surface area of montmorillonite and exposure of increasing metal ions. As a result, the adsorbing capability was enhanced. In Fig. 1 c, agglomeration was observed and the internal channels were blocked, resulting in reduced adsorbing capability.

#### 3.2 Characterization by Fourier Transform infrared spectroscopy

The FTS-40 Fourier Transform infrared spectroscopy (FTIR) was purchased from BIO-RAD Co. Ltd., USA. Samples were prepared accordingly and characterized using FTIR. The resolution is 16  $\text{cm}^{-1}$ , the scanning wave number ranges from 4000  $\text{cm}^{-1}$  to 300  $\text{cm}^{-1}$ , and the scanning lasts for 16 cycles for each sample.

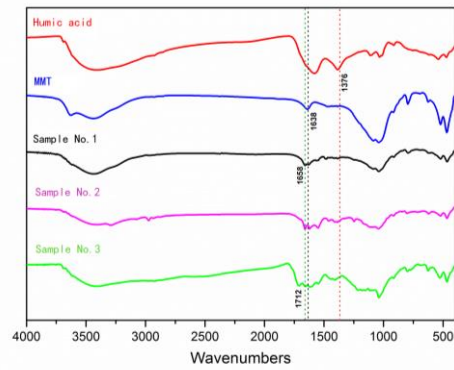


Fig. 2. FTIR curves of samples

Fig. 2 a, b, c, and d show FTIR curves of Sample A, B, C, and D, respectively. As shown in Fig. 2a, the strong and relatively broad peak at 3440  $\text{cm}^{-1}$  corresponds to the stretching vibration absorption of aliphatic and aromatic -OH groups or -NH groups [8] and the peak at 1658  $\text{cm}^{-1}$  corresponds to the (-CONH-)II band in secondary amide. As shown in Fig. 2a, the peak at 3000~2800  $\text{cm}^{-1}$  corresponds to the stretching vibration absorption of aliphatic C-H, and the adsorption peaks at 1612  $\text{cm}^{-1}$  and 1545  $\text{cm}^{-1}$  correspond to the pyridine in the aromatic ring, which can be regarded a compound that is generated by replacing a -CH group in benzene molecule using -N group or the product of reaction between sodium humate and isopropyl acrylamide. As shown in Fig. 2d, the double peak at 1033  $\text{cm}^{-1}$  corresponds to stretching vibration of Si-O-Si, while the peak at 500( $\pm$ 50)  $\text{cm}^{-1}$  is shoulder-shaped, which may be a result of flexural vibration of Si-O-Mg. This was observed in Fig. 2 a, b, and c, especially in Fig. 2 a and b. Therefore, it is deduced that the adsorption valleys were caused by the presence of humic acid [9]. As shown in Fig. 2c, the intensity of the adsorption peak at 3500~1850  $\text{cm}^{-1}$  degraded significantly, indicating decomposition of organic components in the composites.

### ADSORPTION OF COPPER IONS BY COMPLEX ADDITIVE

#### Effects of initial concentration on adsorption capability

0.1g of each composite adsorbent was add in a separate centrifuge tube (50 ml) containing 20 ml of copper ions with different concentrations (50 mg/L, 100 mg/L, 200 mg/L, 500 mg/L, and 1000 mg/L), followed by 10 min vibration at room temperature and 20 min centrifugation (4000 rpm). 10 ml of supernatant was collected and the concentration of residual copper ions was

determined using the spectrophotometry. The adsorption capability and the removal ratio of heavy metal can be calculated using the following equation:

$$Q = V(C_0 - C) / m \quad RE = C_0 - C / C_0 * 100\%$$

where Q is the adsorption capability of montmorillonite towards copper ions at equilibrium, V is the volume of adsorbed solution,  $C_0$  is the initial concentration of copper ions, C is the concentration of copper ions at equilibrium, m is the quantity of complex additive used, and RE is the removal ratio of copper ions at equilibrium [10].

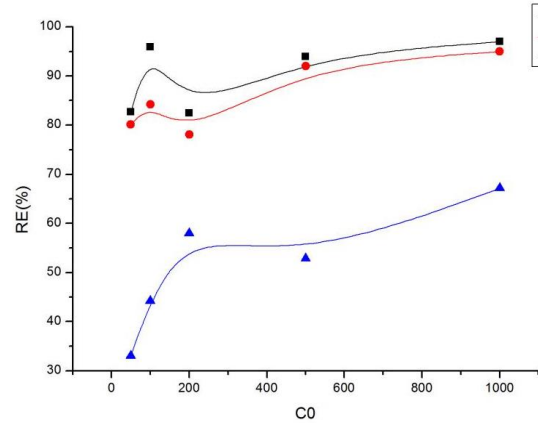


Fig. 3. The removal curve of ratio of copper.

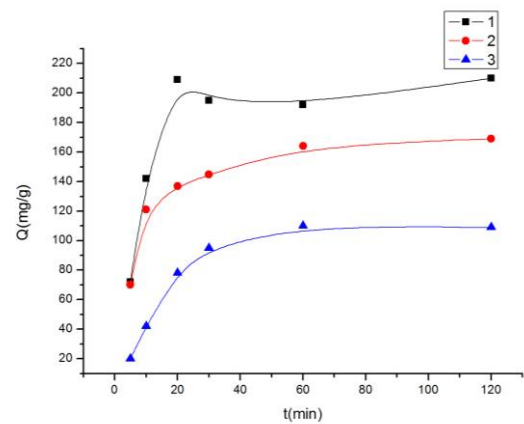


Fig. 4. The relationship between adsorption ability and time.

Fig.4 shows adsorption curves of Sample 1, 2, and 3 under different initial concentrations of copper ions. As observed in Fig. 3, all composite samples exhibited improved adsorption capability (193.95 mg/g, 190.01 mg/g, and 136.33 mg/g for Sample 1, 2, and 3, respectively), as compared with 42.41 mg/g for montmorillonite [11]. The results are consistent with those of structural characterization mentioned above. With initial concentration of 1000 mg/L, the adsorption rate of Sample 1 and 2 reached 96.98% and 95.02%, respectively. This can be attributed to the 3D

networked structures of Sample 1 and 2 [12]. Specifically, the 3D networked structures allow presence of a significant quantity of anion functional groups from N-isopropyl acrylamide and sodium humate and these anions can attract and retain  $\text{Cu}^{2+}$  by electrostatic interaction and complexation. Hence, the adsorption capability of Sample C was limited by its relatively small inner surface area. Additionally, the adsorption capabilities of these samples increased with the initial concentration of  $\text{Cu}^{2+}$ . The optimized quantity of adsorbent bentonite varies with the initial concentration of  $\text{Cu}^{2+}$  and the adsorbent used and the adsorption capability degrades once the bentonite quantity exceeds the critical value. For Sample 1 and 2, 0.1 g/L composite adsorbent is ideal for initial concentrations below 1000 mg/L.

#### Effects of incubation time on adsorption capability

0.1g of each composite adsorbent was add in a separate centrifuge tube (50 ml) containing 20 mL of 500 mg/L copper ions and kept for 5 min, 10 min, 20 min, 30 min, 1 h, and 2 h, respectively. Fig. 4 summarizes the concentration of copper ions in solution samples collected at different time. As observed, Sample 1 reached equilibrium at 30 min, Sample 2 and 3 reached equilibrium at 1 h, Sample C reached equilibrium at 4 h [13]. Additionally, Sample 1 and 2 follow the secondary adsorption dynamic model ( $dp/dt=k(q_e-q)^2$ ). In other words, adsorptions of copper ions by these adsorbents were related to the concentration of copper ions and the density of surface active sites.

#### CONCLUSIONS

The adsorption capabilities of (3-acrylamidopropyl) trimethylammonium chloride/sodium humate/montmorillonite and N-isopropyl acrylamide/sodium humate/montmorillonite adsorbents towards copper ions were significantly higher than that of 2-acrylamido-2-methylpropane sulfonic acid/sodium humate/montmorillonite adsorbent. The saturated adsorption rates of (3-acrylamidopropyl) trimethylammonium chloride/sodium humate/montmorillonite and N-isopropyl acrylamide/sodium humate/montmorillonite adsorbents reached 193.95 mg/L and 190.01 mg/L, respectively; the saturated removal rates of (3-acrylamidopropyl) trimethylammonium chloride/sodium humate/montmorillonite and N-isopropyl acrylamide/sodium humate/montmorillonite adsorbents reached 96.98% and 95.02%,

respectively. The saturated adsorption rate and removal rate of 2-acrylamido-2-methylpropane sulfonic acid/sodium humate/montmorillonite adsorbent were 136.33 mg/L and 68.17%, respectively. Nevertheless, the adsorption capabilities of all montmorillonite-based composites were significantly improved compared with that of montmorillonite. This can be attributed to the presence of anion functional groups in the composites.

The adsorption efficiencies of composite adsorbents were relatively high. (3-acrylamidopropyl) trimethylammonium chloride/sodium humate/montmorillonite adsorbent reached maximum adsorption capability after 30 min, while 2-acrylamido-2-methylpropane sulfonic acid/sodium humate/montmorillonite and N-isopropyl acrylamide/sodium humate/montmorillonite adsorbents reached maximum adsorption capability after 1 h.

Owing to the gelation nature of 2-acrylamido-2-methylpropane sulfonic acid, the adsorption capability of 2-acrylamido-2-methylpropane sulfonic acid/sodium humate/montmorillonite adsorbent was significantly limited as some channels were blocked.

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**АДСОРБЦИЯ НА МЕДНИ ЙОНИ ОТ КОМПОЗИТ ОТ МОНТМОРИЛОНИТ/НАТРИЕВ ХУМАТ/N-ИЗОПРОПИЛ-АКРИЛАМИД**

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(Резюме)

Композитите на основа монтморилонит може да се използват за адсорбцията на медни йони за намаляване на замърсяванията. Комплексът от монтморилонит/натриев хумат/меден йон, който може да бъде получен при смесване на монтморилонит с натриев хумат (повърхностна модификация на монтморилонита и n-изопропил-акриламид е отлична възможност за адсорбция на медни йони.