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Original Research

A New Montmorillonite/Humic Acid Complex Prepared in Alkaline Condition to Remove Cadmium in Waste Water

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Abstract

A new montmorillonite/humic acid complex preparation method in the alkaline environment was studied by experiment, and the complex effect on remediation of heavy metal pollution was verified. The best technological condition of the montmorillonite/humic acid complex preparation in alkaline environment was that the mass ratio between montmorillonite and humic acid was 100:3, the reaction solution was 0.01 mol/L sodium nitrate solution, the pH value of the reaction solution was 8.5, and the reaction time was 24 hours. The complex has better remediation effect on cadmium waste water. The cadmium adsorption capacity of the complex was 18.96 mg/g, and the pH value ranges of cadmium waste water suited for the complex was from 5 to 9.

Keywords: montmorillonite/humic acid complex, alkaline environment, removal effect, cadmium waste water

Introduction

Clay minerals, as an aggregate of minerals and colloidal substances, are hydrous aluminosilicate minerals that dominantly make up the colloid fraction (<200nm) of soils, sediments, rocks, and water beings [1-3]. The large surface area, cation exchange capacity (CEC), high abundance and local availability, non toxicity, chemical and mechanical stability, Brønsted and Lewis acidity, low costs, ability to be recycled, layered structure, etc., determine the usefulness of clays as a natural cleaning agent [4-6]. Montmorillonite, one of the most widely used clays, has been proven efficient in removal of heavy metals, including Cd, which is of great concern because of the increasing trend in discharge, non-degradation in nature, and high toxicity to plants, animals, and human beings [1, 7, 8].

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There is growing interest in research on improving the removal of heavy metal ions from industrial wastewaters [9, 10]. Various attempts have been made to improve the quality and characteristics of the clays such as using acid activation under high temperature, and replacing the interlayer inorganic cations with Fe(III) nitrate, aliphatic, and aromatic ammonium bromide [11-13]. Some researchers have reported that modification by humic acid could enhance the adsorption capacities of the clays [14]. In fact, humic acid with a negative charge has high cation exchange capacity and good complex performance and has a significant role in adsorption of heavy metals, and clay minerals can combine with humic acids to form organic/inorganic complex, and the complex can react with pollutants in the environment [14, 15].

At present, most organic/inorganic complexes were obtained and used to remove the heavy metals in neutral-acid condition. Arias et al. studied the characteristics of copper and cadmium on kaolin by the presence of humic acids and the selected experimental pH values ranging from 4 to 7 [14]; Belghiti et al. selected pH values ranging from 4 to 7 as the experimental condition to study the pH effect on imazethapyr adsorption onto montmorillonite (M), Cu-montmorillonite (Cu-M), and Cu humicacid-montmorillonite (Cu-HA-M) [16]. Other authors' experimental pH conditions were similar to bromide [17-20]. However, very few studies have investigated preparation of complexes in an alkaline environment. There also is no information on effects of the complex on remediation of heavy metals in alkaline environment. The objective of this study was to:

(1) Prepare a new montmorillonite/humic acid complex preparation method in alkaline environment
(2) Use it to remove cadmium from wastewater

Experiments

Chemicals

Montmorillonite, Cadmium nitrate, and humic acid were purchased from Sigma-Aldrich (St. Louis, MO). Potassium chloride, sodium hydroxide, and nitric acid were purchased from Lach Ner (Brno, Czech Republic). All chemicals were of analytical reagent grade. Deionized water was supplied from a Milli-Q water purification system (Millipore, Bedford, MA).

Montmorillonite/Humic Acid Complex Preparation Technological Parameters Selection

Reaction Time

Put 0.2 g montmorillonite each into nine Erlenmeyer flasks and pour 20 mL quality concentration 300 mg/L humic sodium solutions into each flask in which the pH values of the solutions were 8.5, make the reaction in constant temperature oscillator at 298K, set reaction time to 10 min, 30 min, 1 h, 2 h, 3 h, 4 h, 6 h, 12 h, 24 h, 36 h, respectively. When time's out, centrifuge the flasks and collect the supernatant and analyze the concentration of humic acid by spectrophotometer.

Mass Ratio between Montmorillonite and Humic Acid

Put 0.2 g montmorillonite each into 6 Erlenmeyer flasks, pour 20 mL humic sodium solutions into each flask and the humic acid quality concentration of solutions was 10, 50, 100, 200, 300, and 500 mg/L, respectively, in which the pH values of the solutions were 8.5, set the reaction time 24 h. When time's out, centrifuge the flasks and collect the supernatant and analyze the concentration of humic acid by spectrophotometer.

Ionic Concentration in Reaction Solution

Put 0.2 g montmorillonite into 7 Erlenmeyer flasks respectively, pour 20 mL quality concentration 300 mg/L humic sodium solutions in which the pH values of the solutions were 8.5 and the ion concentrations of sodium nitrate in the reaction solutions were 0, 0.005, 0.01, 0.025, 0.05, 0.1, 0.5 mol/L, respectively, and make the reactions in constant temperature oscillator at 298 K and set reaction time to 24 hours.

pH Value Selection

Put 0.2 g montmorillonite each into Erlenmeyer flasks pour 20 mL quality concentration 300 mg/L humic sodium solutions in which the pH values of the solutions were 2.5, 3, 3.5, 4, 4.5, 5, 6, 7, 8, 8.5, 9, and 10, and make the reactions in constant temperature oscillator at 298K and set reaction time to 24 hours.

Remediation Effect Verification to Cadmium Waste Water by the Complex

The Time to Achieve Best Remediation Effect

Put 0.2 g of the complex into 50ml Erlenmeyer flask and pour 20 mL quality concentration 60 mg·L^{-1} cadmium waste water into the flask, and the pH value of the solution was 8. Make the reactions in constant temperature oscillator at 298K and set reaction time to 10 min, 30 min, 1 h, 2 h, 4 h, 8 h, and 16 h. When time's out, centrifuge the flasks and collect the supernatant and analyze the concentration of cadmium by ICP-MS. The removal ratio of cadmium in waste water is calculated as follows:

$$Q=(M_0-CV)/M_0\times 100\%$$

...where Q is removal ratio of Cd [%], M_0 is Cd initiate concentration [mg·L^{-1}], C is the quality concentration of cadmium in the supernatant after reaction [mg·L^{-1}], and V is volumes [L].

Adsorption Capacity

Put 0.2 g of the complex into each 50ml Erlenmeyer flask and pour 20 mL cadmium quality concentration 7.5 mg·L^{-1}, 15 mg·L^{-1}, 30 mg·L^{-1}, 60 mg·L^{-1}, 120 mg·L^{-1}, and 240 mg·L^{-1} waste water into the flasks and the pH value of the solutions was 8. Make the reactions in constant temperature oscillator at 298K and set reaction time 2h. When time's out, centrifuge the flasks and collect the supernatant and analyze the concentration of cadmium by ICP-MS.

The Removal Effect of Cadmium in Waste Water with Different pH Values

Put 0.2 g the complex into each 50 ml Erlenmeyer flask and pour 20 mL quality concentration 60 mg·L^{-1} cadmium waste water into the flasks in which the pH values of the solutions were 5, 6, 7, 8, 9, make the reactions in constant temperature oscillator at 298K and set reaction time to 2h.

Results and Discussion

Best Complex Preparation Technological Parameters

Best Technological Parameters

- Best Reaction Time

The change of humic acid adsorption by montmorillonite was shown in Fig. 1. The equilibrium time of humic acid adsorption on montmorillonite was about 24 h and the adsorption was 27 mg/g. The best reaction time was selected for 24 hours during complex preparation in the experiment.

- Best Mass Ratio between Montmorillonite and Humic Acid

The influence of humic acid concentration in initiative solutions on mintmorillonite adsorption humic acid was shown in Fig. 2.

The adsorption of humic acid on montmorillonite gradually increased with the increase of initial concentration of humic acid and when the concentration of humic acid was 300 ppm, the montmorillonite adsorption reached saturation. Mass ratio between montmorillonite and humic acid was selected for 100:3 during complex preparation in the experiment.

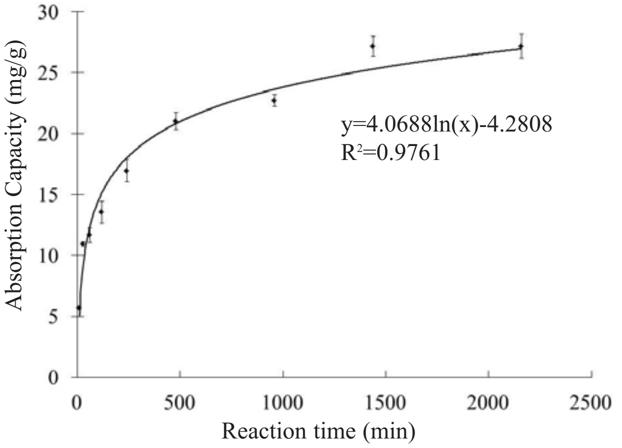

Fig. 1. Humic acid adsorption on mintmorillonite changed with reaction time.

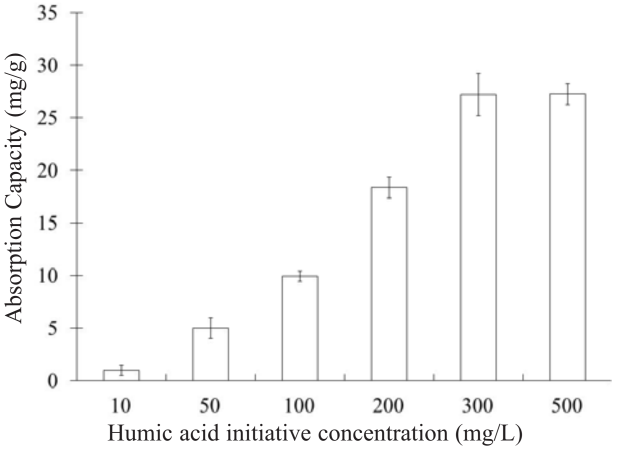

Fig. 2. The influence of humic acid initiative concentration.

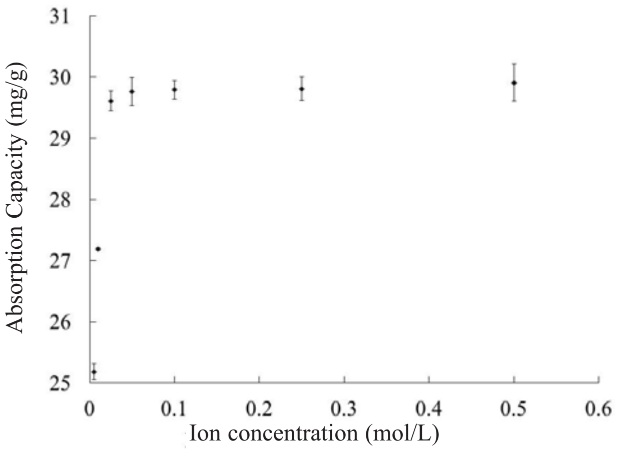

Fig. 3. Influence of Ionic concentration on reaction solution.

- Best Ionic Concentration

The influence of Ion concentration in reaction solution on montmorillonite-adsorbing humic acid was shown in Fig. 3.

The adsorption of humic acid on montmorillonite gradually increased with the increase of the ion concentration in reaction solution at the range of 0 to 0.025 mol/L, and the adsorption did not change after the ion concentration in reaction solution was over 0.025 mol/L. The ion concentration 0.025 mol/L in reaction solution was selected during complex preparation.

- Best pH Value in the Solution

The influence of pH value on adsorption of humic acid by montmorillonite is shown in Table 1.

The adsorption of humic acid on montmorillonite in acid condition was high, but the adsorption decreased as pH value increased. When the pH value was at the range of 7 to 8.5, the adsorption of humic acid on montmorillonite increased and the adsorption of humic acid on montmorillonite was highest when the pH value was 8.5 in alkaline condition. Because the experiment studies the montmorillonite/humic acid complex preparation method in alkaline conditions, 8.5 was selected as the pH value.

The Montmorillonite/Humic Acid Complex Preparation

Based on the experiment, the montmorillonite/ humic acid complex preparation method in alkaline condition was determined as follows:

Put 0.2 g montmorillonite into the Erlenmeyer flask and pour 20 mL quality concentration 300 mg/L humic sodium solutions in which the pH value of the solutions was 8.5,

Table 1. The influence of pH value on adsorption of humic acid by montmorillonite.

pH		2.5	3	3.5	4	4.5	5	6	7	8	8.5	9	10
Adsorption Capacity (mg/g)	Max-value	26.30	25.80	26.22	26.14	26.22	26.08	23.11	18.82	23.66	27.11	26.27	21.18
	Min-value	26.44	25.59	26.58	26.28	26.31	26.15	23.21	19.07	23.82	27.23	26.35	21.44
	Mean-value	26.32	25.7	26.32	26.24	26.17	26.02	23.15	18.99	23.74	27.18	26.35	21.38
	Standard errors	0.020	0.51	0.05	7.33	0.10	0.14	0.029	0.58	0.17	4.59	0.16	0.31

Table 2. The removal effect of the complex in different pH value ranges.

pH		5	6	7	8	9
Removal Ratio (%)	Max-value	96.08	96.89	96.13	99.18	99.29
	Min-value	96.25	97.02	96.27	99.29	99.44
	Mean-value	96.20	96.98	96.21	99.22	99.34
	Standard Errors	0.11	1.51	0.62	0.43	0.98

and the ion concentrations of sodium nitrate in the reaction solutions was 0.01mol/L. Make the reactions start in a constant temperature oscillator at 298K and set reaction time to 24 hours. The solid particle was gained after the Erlenmeyer flask was centrifuged. The montmorillonite/humic acid complex was gained after the solid particle was washed and air-dried.

The Remediation Effect to the Cadmium Waste Water by the Complex

The Time to Achieve Best Remediation Effect

The removal effect of the complex to cadmium in different times was shown in Fig. 4. The cadmium removeal effect of the complex was better in 2 hours, and the removal ratio of cadmium was over 99%.

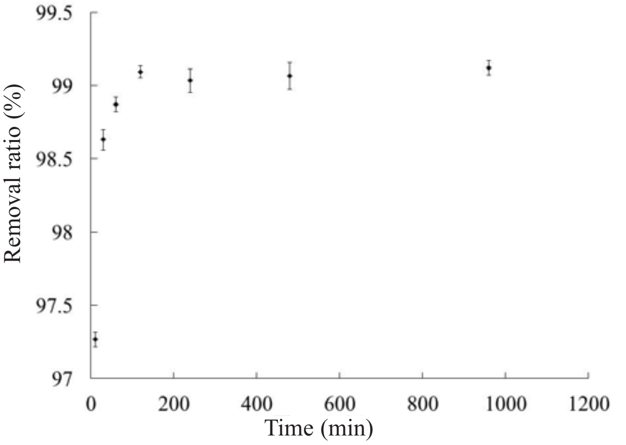

Fig. 4. Cadmium removal effect by the complex with time.

The Removal Ratios of Cadmium in Waste Water in Different Initial Concentrations

The removal ratios of cadmium in waste water in different initial concentrations were calculated, and the result was shown in Fig. 5.

The removal ratios of cadmium in waste water was higher than 99.5%, when cadmium initial concentration in the waste water was 60 mg·L^{-1}. The cadmium adsorption capacity by the complex can be 18.96 mg/g, in which the cadmium initial concentration was 120 mg·L^{-1}.

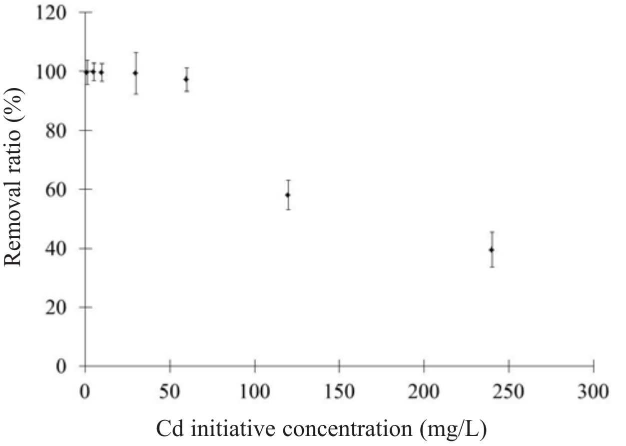

Fig. 5. Influence of cadmium initial concentration on the removal ratio by the complex.

The Removal Effect of Cadmium in Waste Water with Different pH Values

The removal ratio of cadmium by the complex in waste water of different pH values was shown in Table 2. The removal ratios of cadmium in different pH values were higher, and the effect was obvious when the pH value of the waste water was higher than 8. There is wider pH value range that the complex can use to remove cadmium from the waste water.

The Benefit of the Method

To compare with other complexes, the cadmium adsorption capacity of the complex was three times other complexes (cadmium adsorption capacity ranging from 6 to 7 mg/g), the pH value ranges from 5 to 9, which was wider than other complexes (pH value ranging from 4 to 6) and can be used in alkaline environment.

Conclusions

The best technological condition of montmorillonite/ humic acid complex preparation was that the mass ratio between montmorillonite and humic acid was 100:3, the reaction solution was 0.01 mol/L sodium nitrate solution, pH value of the reaction solution was 8.5, and the reaction time was 24 hours.

The complex has a better remediation effect to cadmium in waste water and it can be used in wide pH value ranges from 5 to 9. The cadmium adsorption capacity of the complex was 18.96 mg/g.

To compare with other complexes, the cadmium adsorption capacity of the complex was three times other complexes (cadmium adsorption capacity ranging from 6 to 7 mg/g), the pH value ranges from 5 to 9, which was wider than other complexes (pH value ranging from 4 to 6) and can be used in an alkaline environment.

Acknowledgements

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