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# Preparation and Adsorption Properties of Bentonite Composite Flocculant†

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In this paper, by using the orthogonal analysis method, by simulating the adsorption performance of various pollutants in industrial wastewater, to ascertain the optimum process conditions on sodium bentonite modified by cetyltrimethyl ammonium bromide (CTMAB). Based on this technology, prepare cationic polyacrylamide (CPAM) organic intercalation of bentonite and Ni/Si-CTMAB inorganic organic pillared bentonite and got the optimal experiment preparation scheme as well.

**Keywords: Bentonite, Pillared bentonite, Flocculant.**

## INTRODUCTION

Bentonite is the natural non metallic minerals mainly composed of montmorillonite. With proportion 2:1 and structure of 2-8 hedron with monoclinic system. It is a kind of layered and hydrous aluminum silicate minerals. It has a large specific surface area. It has a good adsorption ability and high exchange ability with cation[1]. But because of the surface of bentonite Si-O structure has strong hydrophilicity and interlayer cation hydrolysis, it's easy to form a thin water film on the surface. Thus organic pollutants can not be effectively adsorbed hydrophobically and restrict the application of bentonite. Bentonite with inorganic organic modification, by using the properties of montmorillonite with layered structure and using intercalation method to insert inorganic-organic to its interlamination. Thus it made its hydrophilic layer hydrated, magnifing its interlayer[2-4]. So it has higher adsorption ability and cation change ability.

In this paper, we use sodium bentonite as raw material, first make its organic modification by using CTMAB, CPAM-CTMAB. Then use Ni-Si to organic bentonite with composite intercalated modification, thus prepared inorganic organic pillared bentonite composite flocculant. Through the simulation of organic dyes in industrial wastewater, insoluble solid particles, potassium phthalate and studied with adsorption for $Cr^{6+}$ and to determine the optimal preparation conditions.

## EXPERIMENTAL

**Preparation of CTMAB modified bentonite:** Weigh a certain amount of sodium bentonite to the flask, according to orthogonal experimental conditions $L^9$ ($3^4$ ) with the corresponding concentration of seriflux adding the appropriate proportions of the CTMAB modifier. Setting the experimental temperature, stir it and let it react in a certain time. After reaction, cool it and subjected to vacuum filtration, dried at a temperature 85 ºC and porphyrize, it form CTMAB modified bentonite.

**Preparation of secondary intercalation CPAM organo-bentonite:** Taking a certain proportion of CTMAB modified bentonite and CPAM to the flask. With the corresponding concentration of seriflux, adding evocating agent ammonium persulfate, crosslinking agent N-N methylene bisacrylamide. Under the atmosphere of $N_2$, pH 6, stirring at 80 ºC for two hours and cool it.After sucking filtration, dried at a temperature 85 ºC and porphyrize it. Then we can get CPAM modified bentonite.

**Preparation of Ni/Si-CTMAB inorganic organic pillared bentonite:** Weigh 78.846 g of nickel sulfate and prepare it for 0.3 mol/L solution. Slowly add 90 mL of 1 mol/L NaOH to the solution of nickel sulphate with a speed of 15 mL/min. Stir it at room temperature for 2 h and get the solution A.Taking 45 mL concentrated sulfuric acid with dilution of 1:1. Add

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slowly to the 52.7 g of sodium silicate solution, to obtain solution B. Left the solutions for 12 h. Under stirring, mix solution A with different amount of solution B. Then we obtained Ni-Si crosslinking agent with different proportion.

Take three samples of the same quantity of CTMAB modified bentonite, make of 3 % seriflux at 60 ºC, in the stirring condition, put Ni-Si crosslinking agent to the solution with a speed of 15 mL/min and add NaOH solution. Make the pH 6, thermostatic reaction for 5 h, vacuum filtration. Drying at 85 ºC and porphyrize it. Then we obtained Ni/Si-CTMAB inorganic organic pillared bentonite.

## RESULTS AND DISCUSSION

**Best preparation process conditions of CTMAB modified bentonite:** To study the preparation process of CTMAB modified bentonite, collocate seriflux concentration A, modified dose, (CTMAB) cation exchange capacity of bentonite CEC (modifier ratio B), reaction temperature (C, ºC), reaction time (D, h) is influencing factor, design the $L^9$ ($3^4$) orthogonal experiment. In order to simulate the industrial wastewater as object, research on the removal rate of organic dye colour, removal rate of turbidity solid insoluble substance, removal rate of potassium acid phthalate COD and removal rate of $Cr^{6+}$ (Tables 1 and 2).

Through Table-2, for colour removal rate, removal rate of turbidity, removal rate of COD, removal rate of $Cr^{6+}$, Effects of sequence is A > B > C > D, C > A > D > B, B > C > A > D, A > B > D > C. Optimization of the process conditions is $A_1B_1C_2D_3$, $A_3B_1C_1D_1$, $A_1B_1C_2D_3$, $A_1B_1C_3D_1$. And according to Table-1 with 9 groups of experimental data comparison, we can get conditions of optimization, ascertain it as $A_1B_1C_2D_1$. And the optimal process conditions we need: seriflux concentration of 3 %, modifier rater is 1.0:1, the reaction temperature is 65 ºC and reaction time for 4 h.

**Comparison of modified bentonite flocculation:** In the same condition of flocculation, comparing the flocculation effect with different kinds of modified bentonite (Table-3).

From Table-3, we can get all the modified bentonites have better flocculation effect than sodium bentonite. CPAM-CTMAB intercalated bentonite has great flocculation effect on insoluble solid waste. Ni/Si-CTMAB inorganic organic pillared bentonite has strong flocculation effect on other items.

**Comparison of the decolorization setting rate with CTMAB modified organic bentonite and CPAM second intercalated bentonite:** For further comparison of the decolorization with CTMAB modified bentonite and CPAM second intercalation organobentonite. In the experiment, we compare with the difference of the settling rate of decolorization. Weigh

TABLE-1
RESULT OF ORTHOGONAL TEST

| Serial number | Experimental condition | | | | Experimental result | | | |
|---|---|---|---|---|---|---|---|---|
| | (A) | (B) | (C) | (D) | Decolorization rate (%) | To rate of turbidity (%) | COD removal rate (%) | $Cr^{6+}$ removal rate (%) |
| 1 | 1 | 1 | 1 | 1 | 98 | 92.02 | 86.32 | 83.07 |
| 2 | 1 | 2 | 2 | 2 | 96.68 | 81.85 | 86.53 | 82.09 |
| 3 | 1 | 3 | 3 | 3 | 98.1 | 86.55 | 79.55 | 82.56 |
| 4 | 2 | 1 | 2 | 3 | 96.28 | 86.21 | 86.22 | 82.09 |
| 5 | 2 | 2 | 3 | 1 | 94.55 | 90.51 | 78.89 | 82.31 |
| 6 | 2 | 3 | 1 | 2 | 94.69 | 91.75 | 77.67 | 77.76 |
| 7 | 3 | 1 | 3 | 2 | 96.15 | 91.61 | 80.66 | 77.67 |
| 8 | 3 | 2 | 1 | 3 | 94.29 | 91.07 | 79.89 | 77.02 |
| 9 | 3 | 3 | 2 | 1 | 96.02 | 91.52 | 80.08 | 76.89 |

Note: Three levels A: 3 %, 5 %, 7 %; B: 1.0:1, 1.2:1, 1.5:1; C: 55 ºC, 65 ºC, 75 ºC; D: 4 h, 6 h, 8 h.

TABLE-2
RANGE ANALYSIS TABLE

| | | | | | |
|---|---|---|---|---|---|
| Decolorization rate | $K_1$ | 292.78 | 290.43 | 286.98 | 288.57 |
| | $K_2$ | 285.52 | 285.52 | 288.98 | 287.52 |
| | $K_3$ | 286.46 | 288.81 | 288.80 | 288.67 |
| | $R_i$ | 7.26 | 4.91 | 2.00 | 1.15 |
| | Majorization | $A_1$ | $B_1$ | $C_2$ | $D_3$ |
| To rate of turbidity | $K_1$ | 260.42 | 269.84 | 274.84 | 274.05 |
| | $K_2$ | 268.47 | 263.43 | 259.58 | 265.21 |
| | $K_3$ | 274.20 | 269.82 | 268.67 | 263.83 |
| | $R_i$ | 13.78 | 6.41 | 15.26 | 10.22 |
| | Majorization | $A_3$ | $B_1$ | $C_1$ | $D_1$ |
| COD removal rate | $K_1$ | 252.40 | 253.20 | 243.88 | 245.29 |
| | $K_2$ | 242.78 | 245.31 | 252.83 | 244.86 |
| | $K_3$ | 240.63 | 237.30 | 239.10 | 245.66 |
| | $R_i$ | 11.80 | 15.90 | 13.73 | 0.80 |
| | Majorization | $A_1$ | $B_1$ | $C_2$ | $D_3$ |
| $Cr^{6+}$ removal rate | $K_1$ | 247.72 | 242.83 | 237.85 | 242.27 |
| | $K_2$ | 242.16 | 241.42 | 241.07 | 237.52 |
| | $K_3$ | 231.58 | 237.21 | 242.54 | 241.67 |
| | $R_i$ | 16.14 | 5.62 | 4.69 | 4.75 |
| | Majorization | $A_1$ | $B_1$ | $C_3$ | $D_1$ |

TABLE-3
COMPARISON OF SEVERAL KINDS OF MODIFIED BENTONITE FLOCCULATION

| Flocculant | Dosage (g/L) | Decolorization rate (%) | To rate of turbidity (%) | COD removal rate (%) | $Cr^{6+}$ removal rate (%) |
|---|---|---|---|---|---|
| Sodium bentonite | 6 | 79.54 | 51.97 | 30.02 | 48.73 |
| CTMAB bentonite | 6 | 92.02 | 86.32 | 86.32 | 63.07 |
| CPAM-CTMAB bentonite | 6 | 95.22 | 88.92 | 92.02 | 93.21 |
| Ni/Si- CTMAB bentonite | 6 | 97.01 | 81.02 | 92.93 | 96.10 |

TABLE-4
INTERPLANAR SPACING OF SEVERAL KINDS OF MODIFIED BENTONITE

| Flocculant | Sodium bentonite | CTMAB bentonite | CPAM-CTMAB bentonite | Ni/Si- CTMAB bentonite |
|---|---|---|---|---|
| Interplanar spacing $d_{100}$/nm | 1.27 | 2.98 | 4.32 | 4.61 |

two kinds of modified bentonite 100 mg, respectively. Adding 200 mL organic dye simulated wastewater with concentration of 30 mg/L. Stirring for 20 min, measure its absorbancy, recording the indication every 1 min (Fig. 1).

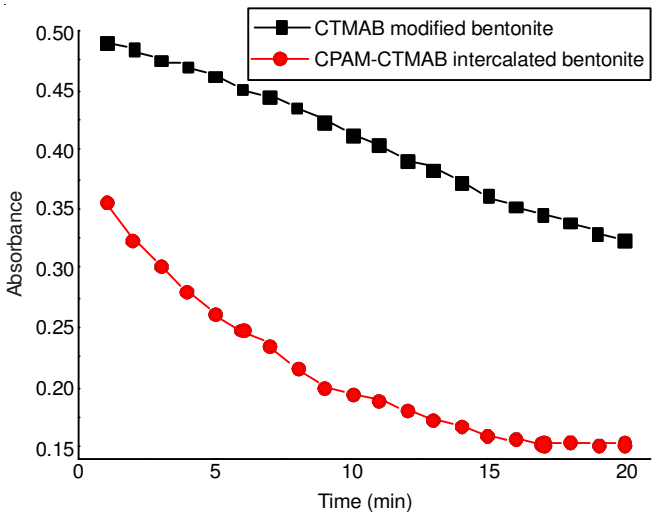


Fig. 1. Comparison of setting rate

From Fig. 1 we can get CPAM second intercalated modified bentonite has higher significant setting rate than CTMAB modified bentonite, after 15 min it can achieve basically stable. This shows the CPAM after second modification, significantly accelerate the sedimentation rate of bentonite, improve the ability of decolorization adsorption.

**Comparison of $d_{100}$ interplanar spacing of modified bentonite:** There is a certain distance between the bentonite cell, interplanar spacing, more value more strong ability of lipophilicity. Examine different kinds of modified bentonite through XRD and calculate the interplanar spacing (Table-4).

From Table-4, we can get through a series modification to bentonite interplanar spacing $d_{100}$ incresing from 1.27 to 4.61 nm. This shows all kinds of modifier molecules have been significantly into the layered structure of bentonite. Make its hydrophilic layer hydrophobic. So It has higher adsorption ability and cation exchange ability.

## Conclusion

Using crosslinking of CPAM-CTMAB and the removal colour rate of Ni/Si intercalated bentonite, removal rate of COD and removal of $Cr^{6+}$ has reached more than 90 %. Removal rate of turbidity close to 90 %. It has the most ideal effect on the Ni/Si intercalated bentonite flocculation. Using quaternary ammonium salt CTMAB, removal colour rate of organic modification, removal rate of turbidity, removal rate of COD are close to the above two kinds of modification methods. The $Cr^{6+}$ processing ability is relatively weak, but the flocculation ability is stronger than sodium bentonite.

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