

Preparation and Characterization of Organic Montmorillonite and Its Application in Algae Removal

ZHOU Fei^{1,a}, LI Le^{2,b} and ZHENG Jianfang^{3,c}

¹Environmental and Chemical Engineering College, Xi'an Polytechnic University, Xi'an 710048, China

²Environmental and Chemical Engineering College, Xi'an Polytechnic University, Xi'an 710048, China

³Environmental and Chemical Engineering College, Xi'an Polytechnic University, Xi'an 710048, China

^aguozhong4@163.com, ^b792096530@qq.com, ^c1026074776@qq.com

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Abstract. Montmorillonite (MMT) Na-modified by suspensoid was modified using cetyltrimethyl ammonium bromide (CTAB) and dodecyltrimethyl ammonium chloride (DTAC), and CTAB-modified montmorillonite (CTAB-MMT) and DTAC-modified montmorillonite (DTAC-MMT) were obtained at the optimum conditions: the reaction temperature 60 °C, the reaction time 1h, the pH 5 and the reaction temperature 50 °C, the reaction time 1h and the pH 9, respectively. It was confirmed by infrared spectrometer that the quaternary ammonium salts(QAC) had been successfully intercalated into montmorillonite. The activity of removal algae in landscape water for CTAB-MMT and DTAC-MMT were investigated comparatively with MMT, respectively. The results showed that removal rates of CTAB-MMT for *Diatom* and *Cyanobacteria* were 20.75% and 22.89% higher than that of MMT, and similarly these of DTAC-MMT were 25.85% and 24.99%.

Introduction

Montmorillonite, a natural silicate mineral, is piled together by two silicon tetrahedron at top and bottom and an aluminum oxide octahedron in the middle. The Si⁴⁺ in tetrahedral center and Al³⁺ in octahedral center was easily replaced by some low valence ions like the Mg²⁺, Ca²⁺ and Na⁺, so that the crystal structure has negatives^[1]. The excess charge is easy to adsorb Ca²⁺, Na⁺ and other cations in the montmorillonite layer, and the energy for desorption and adsorption of cationic is relatively low. The adsorbed cations are easily exchanged by other cations, inorganic cations and organic cations including alkyl quaternary ammonium salts and alkyl quaternary phosphonium salts, etc, commonly^[2]. After modification by quaternary ammonium salts, organic montmorillonite (O-MMT) has a large layer spacing and large aspect ratio, which reverses the polarity of montmorillonite, reduces surface energy of the silicate sheet and increases the expansibility, dispersibility, emulsifying property and affinity, so the performance of the montmorillonite has been improved^[2-3]. It is one of the research hotspots to remove local algae with organic modified clay flocculation^[3-6]. Yan Xinya et al^[5] studied the removal of *Chattonella marina* with quaternary phosphonium salt of different structures as surfactants. Their results indicated that the clay modified by tetradecyl tributyl phosphorus bromide had the highest algae removal rate, and almost non-toxicity to zebrafish. In this study, sodium-based montmorillonite (Na-MMT) was modified by two kinds of quaternary ammonium salts as modifiers and the optimum modification conditions were investigated. The removal effects of O-MMTs and MMT on algae in landscape water were compared.

Materials and Methods

Materials. Montmorillonite was purchased from Gongyi City Yongshun Purifying Materials Limited, Hexadecyl trimethyl ammonium bromide (CTAB) and dodecyl trimethyl ammonium chloride (DTAC) were from Shanghai Shan Pu Chemical Co., Ltd. and Shanghai Adamas Reagent

Co., Ltd., respectively. *Cyanobacteria* and *Diatom* were separated from the landscape water of Xingqing Park at Xian by our laboratory.

Experimental methods. (1)Preparation of Na-MMT. Since sodium-based montmorillonite has stronger cation exchange and adsorption specific surface area than calcareous montmorillonite, so it is necessary to modify montmorillonite with sodium. Accurate weighed montmorillonite 150g and Na_2CO_3 5g in 1000mL of distilled water were shaken for 2h at $200\text{r}\cdot\text{min}^{-1}$. After filtration, washing, drying, grinding 300 mesh sieve, sodium-based montmorillonite was obtained. (2)Determination of cation exchange capacity of MMT. Salt was washed away by full mixing 3.00g MMT or Na-MMT with 25 mL 50% ethanol in 50 mL centrifuge tube, respectively^[12]. The mixtures were centrifuged for 10min at $3000\text{r}\cdot\text{min}^{-1}$ and the supernatants were removed, repetitively 2-3 times. Then 25mL of $0.01\text{mol}\cdot\text{L}^{-1}$ ammonium chloride in 50% ethanol was added and shaken for 0.5h at $200\text{r}\cdot\text{min}^{-1}$. Putted overnight, the supernatant was collected by centrifugal for 10min at $3000\text{r}\cdot\text{min}^{-1}$. The exchange treatment is repeated three times and all of supernatants were mixed to be measured, 25 mL of which was heated to boil, mixed with 8 mL 35% neutral formaldehyde and 5 drops of 0.1% phenolphthalein indicator, then titrated with $0.01\text{mol}\cdot\text{L}^{-1}$ NaOH standard solution. Cation exchange capacity of MMT is calculated according to the following formula:

$$\text{CEC} = \frac{c(\text{NaOH}) \times (V_2 - V_1) \times V_t}{m_s \times V_d} \quad (1)$$

Where, CEC is the exchange capacity ($\text{mmol}\cdot\text{g}^{-1}$); c is NaOH solution concentration ($\text{mol}\cdot\text{L}^{-1}$); m_s is the sample mass (g); V_1 and V_2 are titrating value of supernatant and $0.01\text{mol}\cdot\text{L}^{-1}$ ammonium chloride in 50% ethanol (mL); $V_d = 25\text{mL}$; $V_t = 100\text{mL}$. (3)Preparation of O-MMT. Organic modified montmorillonite and Na-MMT was added to CTAB and DTAC solution, respectively, kept in a constant temperature water bath for a certain time, washed with 50% aqueous ethanol to no Cl^- or Br^- (tested with $0.1\text{mol}\cdot\text{L}^{-1}$ AgNO_3). The modified montmorillonite was dried in a vacuum oven at 80°C and ground through a 300 mesh sieve to obtain CTAB-MMT and DTAC-MMT, respectively. The O-MMT was characterized by NEXUS series of FT-IR infrared spectroscopy. (4)Optimization of orthogonal experimental conditions for O-MMT preparation. According to the orthogonal table of $L_{16}(4^4)$, four factors (amount of quaternary ammonium salt; pH; reaction temperature and reaction time) and four levels orthogonal test was carried out to optimize experimental conditions for O-MMT preparation. (5)Algal cell removal experiment. Fully mix 4 mg O-MMT and 100 mL suspension liquid containing 5×10^6 algae cell per mL, adjusted pH to 7 with 0.1mol/L HCl or NaOH. The mixture was put in light incubator for 24h. The survival algae cell in sample, taken at 3 cm below the liquid level and, with a blood cell count plate. The algal cell removal rate was calculated according to the following formula:

$$\text{R.E.\%} = (1 - \rho_{\text{sample}} / \rho_{\text{reference}}) \times 100\% \quad (2)$$

Where R.E.% is algal cell removal rate, ρ_{sample} and $\rho_{\text{reference}}$ is algae cell count of sample and suspension algae liquid.

Results

Cation exchange capacity. The cation exchange capacity of Na-MMT was $0.3307\text{mmol}\cdot\text{g}^{-1}$, which was $0.12\text{mmol}\cdot\text{g}^{-1}$ higher than that of the original montmorillonite. It was proved that sodium montmorillonite could improve the cation exchange capacity of the original montmorillonite.

Optimization of orthogonal experimental conditions for O-MMT preparation. From table 1 and 2, it can be seen that the dosage of quaternary ammonium salt is the main influencing factors on QAC content in CTAB-MMT. QAC amount 2.0CEC, Temperature 60°C , reaction time 1h and the pH 5 are selected as optimum preparation conditions.

Table 1 The content of QAC in CTAB - MMT under different conditions

No.	Temp. (°C)	QAC dosage (CEC)	Time (h)	pH	QAC content in CTAB-MMT (mg/g)
1	40	0.5	0.5	5.0	24.08
2	40	1.0	1.0	7.0	47.46
3	40	1.5	2.0	9.0	95.61
4	40	2.0	4.0	11.0	158.21
5	50	0.5	1.0	9.0	35.08
6	50	1.0	0.5	11.0	66.72
7	50	1.5	4.0	5.0	113.50
8	50	2.0	2.0	7.0	138.95
9	60	0.5	2.0	11.0	38.52
10	60	1.0	4.0	9.0	93.55
11	60	1.5	0.5	7.0	123.82
12	60	2.0	1.0	5.0	182.29
13	70	0.5	4.0	7.0	30.95
14	70	1.0	2.0	5.0	77.73
15	70	1.5	1.0	11.0	120.38
16	70	2.0	0.5	9	149.96
Mean1	81.340	32.157	91.145	99.400	
Mean2	88.563	71.365	96.302	85.295	
Mean3	109.545	113.328	87.703	93.550	
Mean4	94.755	157.352	99.053	95.957	
Range	28.205	125.195	11.350	14.105	

Table 2 Analysis of variance

Factor	Sum of variances	Degrees of freedom	F ratio	F critical value	Significance
Temp.	1725.005	3	0.185	3.49	*
QAC amount	34892.487	3	3.736	3.49	
Time	311.324	3	0.033	3.49	
pH	432.654	3	0.046	3.49	

Table 3 The content of QAC in DTAC-MMT under different conditions

No.	Temp. (°C)	Time (h)	QAC dosage (CEC)	pH	QAC content in DTAC-MMT (mg/g)
1	30	0.5	0.5	5	22.01
2	30	1	1.0	7	47.83
3	30	2	1.5	9	63.28
4	30	4	2.0	11	106.62
5	40	0.5	1.0	9	54.34
6	40	1	0.5	11	28.20
7	40	2	2.0	5	105.93
8	40	4	1.5	7	86.67
9	50	0.5	1.5	11	85.30
10	50	1	2.0	9	121.75
11	50	2	0.5	7	24.76
12	50	4	1.0	5	44.02
13	60	0.5	2.0	7	103.18
14	60	1	1.5	5	81.86
15	60	2	1.0	11	55.03
16	60	4	0.5	9	28.89
Mean1	59.935	66.208	25.965	63.455	
Mean2	68.785	69.910	50.305	65.610	
Mean3	68.957	62.250	79.278	67.065	
Mean4	67.240	66.550	109.370	68.787	
Range	9.022	7.660	83.405	5.332	

Table 4 Analysis of variance

Factor	Sum of variances	Degrees of freedom	F ratio	F critical value	Significance
Temp.	218.458	3	0.055	3.49	
QAC amount	117.943	3	0.029	3.49	
Time	15624.691	3	3.901	3.49	*
pH	61.292	3	0.015	3.49	

Similarly, from table 3 and 4, it can be seen that the amount of quaternary ammonium salt is the main influencing factors on QAC content in DTAC-MMT. QAC amount 2.0CEC, Temperature 50 °C, reaction time 1h and the pH 9 are selected as optimum preparation conditions.

O-MMT characterization. The infrared spectra of CTAB-MMT and DTAC-MMT are in figure 1, by which it can be seen that there are two strong absorption peaks at 2925cm^{-1} and 2855cm^{-1} , meaning C-H antisymmetric stretching vibration peak and symmetrical stretching vibration peak of CH_2 , which indicate that CTAB and DTAC have been adsorbed into the montmorillonite. The -OH peak at 3620cm^{-1} , 3400cm^{-1} and 1640cm^{-1} is reduced because the quaternary ammonium salt is exchanged into the clay layers replacing H_2O .

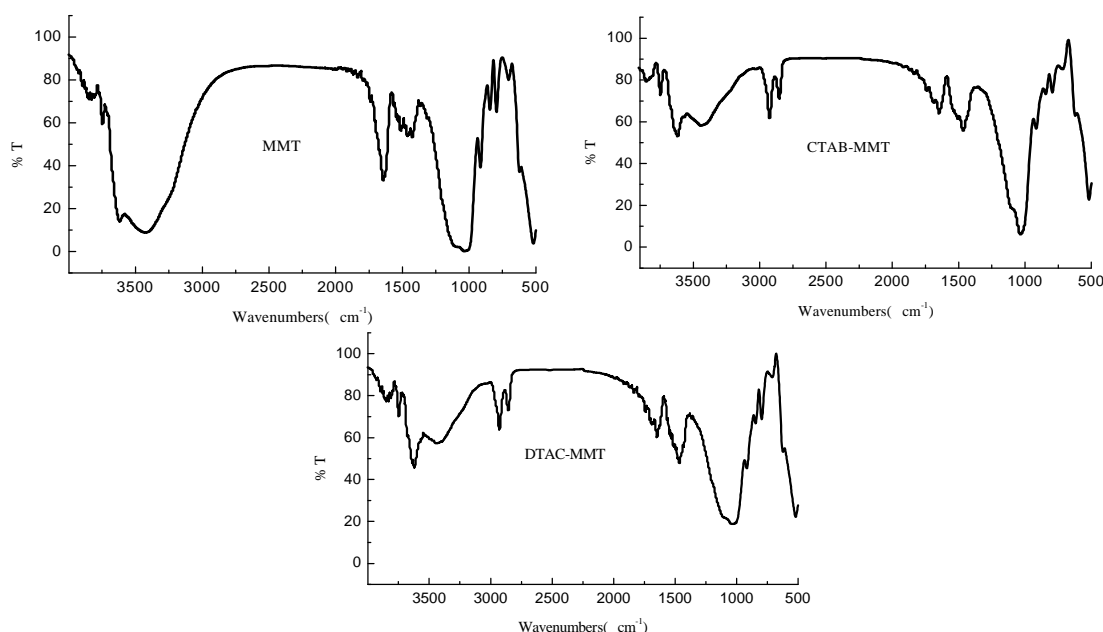


Fig.1 Infrared Spectar of MMT and O-MMTs

Removal affects algae of O-MMT and MMT. O-MMT adsorbs algae cells by charge adsorption and net catching. The CTAB and DTAC in the modified Montmorillonite turned its surface charge positively to adsorb and flocculate algal cells with negatively charge inhibiting flocculation phenomenon. Results showed that the removal rates against *Diatom* and *Cyanobacteria* by CTAB-MMT 20.75% and 22.89% were higher than those of MMT, respectively, and were 25.85% and 24.99% higher for these of DTAC-MMT.

Conclusion

The preparation of DTAC-MMT and CTAB-MMT has been successful under the optimization experimental conditions: QAC amount 2.0CEC, reaction temperature 60°C, reaction time 1h and pH5 for CTAB, and QAC amount 2.0CEC, reaction temperature 50°C, reaction time 1h and pH9 for DTAC. DTAC-MMT and CTAB-MMT were characterized by infrared spectroscopy analysis. The removal rate of *Diatom* and *Cyanobacteria* by CTAB-MMT was 20.75% and 22.89% higher MMT, and the set of DTAC-MMT was 25.85% and 24.99% higher.

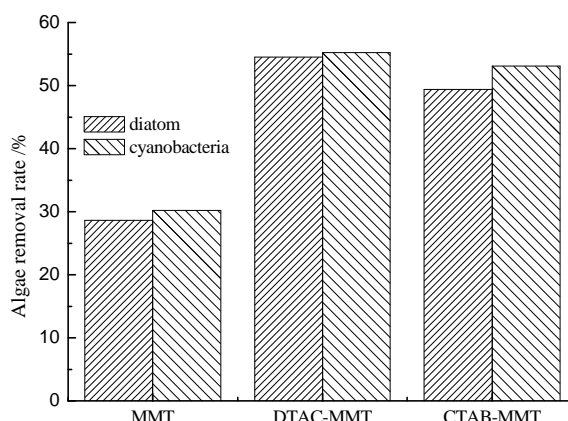


Fig.2 Algae Removal Effect of O-MMT and MMT

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