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Treatment of textile wastewater using organically modified bentonite

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ABSTRACT

The use of anion-cation organobentonite for the treatment of wastewater generated during a textile dyeing and printing process was studied. It was found that the color removal of the organobentonite was higher than that of the natural bentonite. The maximum color removal was obtained by the anion-cation organobentonite with the mass ratio 4:1 of cetyl trimethyl ammonium bromide (cation) to sodium dodecyl sulfate (anion). The concentrations of target constituents, such as chemical oxygen demand (COD) and suspended solids (SS), in the wastewater post-treated by using this organobentonite were determined and summarized. In addition, the pseudo-first-order and pseudo-second-order kinetic equations were rearranged to expediently investigate the adsorption process. The results show that the color removal of the wastewater treated by the organobentonite followed the pseudo-first-order model.

Keywords: Anion-cation organobentonite; Textile wastewater; Color removal; Kinetic model

1. Introduction

Textile manufacturing involves several processes, e.g. scouring, bleaching, dyeing, printing and finishing, which produce large volumes of wastewaters. Most of the textile effluents are highly variable in composition with relatively high levels of COD. The most typical characteristic of textile wastewaters is the strong color due to residual dyes. It is estimated that approximately 15% of the total production of colorants is lost during synthesis and processing, and the main source of this loss is to be found in wastewaters because of incomplete exhaustion [1]. Traditional methods for dealing with this kind of wastewater are the biological, physical and chemical techniques as well as their various combinations. It has been widely reported that many dye chemicals are difficult to degrade using conventional biological treatment processes, such as aerobic digestion. Current research is now focused on the adsorption technique, which does not generate harmful substances [2]. Activated carbon is the most efficient and popular choice of adsorbent but the high cost restricts its use in many countries including China.

In recent years the usage of natural clay adsorbents for wastewater treatment has received considerable attention due to their abundance and low cost. One type of clay is bentonite. It belongs to the 2:1 clay family, which mainly consists of montmorillonite, the basic structural unit of which is composed of two tetrahedrally coordinated sheets of silicon ions surrounding a sandwiched octahedrally coordinated sheet of aluminum ions [3]. The isomorphous substitution of Al^{3+} for Si^{4+} in the tetrahedral layer and Mg^{2+} for Al^{3+} in the octahedral layer results in a net negative surface charge on the bentonite [4]. Thanks to

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its prominent characteristic of adsorbing both organic and inorganic species, bentonite can act as dye-aggregation and dye-mineralization catalysts [5,6]. It can also be intercalated by organic surfactants or hydroxy-metal, and the resulting materials are regarded as organobentonites [7–9] and hydroxy-metal pillared bentonites [10,11], respectively. Because of their unique sorption capabilities, many kinds of organobentonites have been investigated for a wide variety of environmental applications [12,13].

Studies have shown that the mixtures of anionic and cationic surfactants can form mixed micelles which can increase synergistically the aqueous solubility of organic compounds. And it has been reported that the anion-cation modification of bentonite or palygorskite can significantly improve the adsorption capacity for *p*-nitrophenol [14,15]. With this in mind, we prepared the organically modified bentonite by incorporating cationic and anionic surfactants (CTMAB and SDS) to the natural bentonite, and investigated the effectiveness of the synthesized organobentonite in treating textile wastewater. Furthermore, two well-known kinetic equations, i.e. pseudo-first- and second-order equations, were modified to expediently investigate the color removal process.

2. Experimental

2.1. Materials

Sodium bentonite used was supplied by Zhejiang Sanding Technology Co., Ltd. The cation exchange capacity (CEC) of the clay bentonite is about 60 meq./100 g. The cationic surfactants of cetyl trimethyl ammonium bromide (CTMAB) and the anionic surfactant of sodium dodecyl sulfate (SDS) were purchased from Shanghai Jingwei Chemical Co., Ltd, and were used without further purification. The industrial textile wastewater was kindly supplied by the Wensli Silk Science and Technology Co., Ltd, Hangzhou, China. Silk and silk-like polyester are the main products in this company. This wastewater may contain acid dyes, reactive dyes and disperse dyes used for dyeing and printing of silk or polyester. Most of adsorption studies were carried out using lab simulated dye solution, which contains only dyes. Various kinds of dyes can be used as adsorbate, and Basic blue 9, Acid blue 25, Direct red 28 and Reactive blue 114 were the commonly-used dyes [16]. However, in this real industrial textile wastewater, besides the dyes, there may also be some surfactants, carbamide, sodium bicarbonate, NaOH, sodium 3-nitrobenzene sulfonate, alginate, and polyvinyl alcohol (printing sizing). The pH value of the wastewaters was found to be 8.5 due to the presence of NaOH and rongalite in the printing process to remove the unstable dyes. The main water quality parameters are listed in Table 2.

2.2. Preparation of organically modified bentonite

The natural bentonite and water were stirred into a splitter machine for 30 min (model MBP, DingSheng Paint Chemical Machinery Co., Ltd, China) so that bentonite could expand and separate into layers. The clay was then filtrated, dried and ground for further use. The organobentonite was prepared by addition of 40 mL of aqueous solution containing 1 g of surfactants to 4 g of previously dried bentonite. The complex was stirred in a water bath at 60°C for 3 h. It was centrifuged and washed several times with distill water. The organobentonite was dried in hot air oven, activated at 105°C for 1 h, and ground with a laboratory mortar.

2.3. Characterization methods

The SEM micrographs were obtained using model SIRION-100 microscope (Fei Company, Holland). FTIR spectra were recorded at room temperature using a Nicolet 560ESP spectrometer. The particle-size distribution of the solid sample was determined using the model BT-1500 particle size analyzer (Dandong Bettersize Instruments Co., Ltd, China).

2.4. Adsorption studies

The adsorption experiment was carried out by agitating 0.2 g of adsorbent with 100 mL of textile wastewater in a set of 250 mL PE flasks. The flasks were shaken at 130 rpm in an isothermal shaker for 4 h to reach the equilibrium at constant temperatures (20°C). After being centrifuged, the visible spectra of the solution were recorded using a Cary 50 UV-Vis Spectrophotometer (Varian Incorporation, USA). The color remains ratio was calculated as follows [17]:

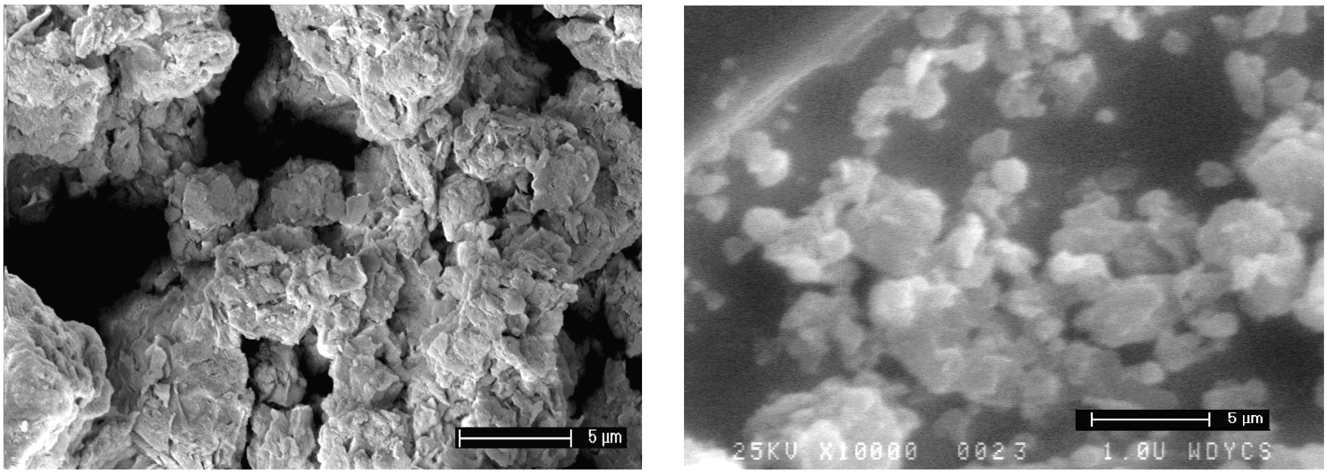
$$\text{Color remains \%} = \text{ABS}/\text{ABS}_0 \times 100\% \tag{1}$$

where ABS_0 is the absorbance value before adsorption, and the ABS is the value after adsorption. The absorbance values were determined using the UV-Vis spectrophotometer at 612 nm. This is the wavelength maximum absorbance for the real textile wastewater employed. The COD values of the solution were determined using Lovibond ET99731 water analyzer (Tintometer GmbH, Germany).

3. Results and discussion

3.1. Characterization of adsorbents

The surface morphology of the natural bentonite and the modified product are shown in Fig. 1. The clay comprises layered sheets and the distance between the layers can be adjusted by swelling [18]. Just because of this special layered structure, the pillared interlayer bentonites and organobentonites have attracted extensive attention



(a) (b)

Fig. 1. Scanning electron micrograph of (a) bentonite and (b) SDS/CTMAB-bentonite.

in past decades. As shown in Fig. 1a, the bentonite contains much coarse particle/sheet. After the mechanically grinding by splitter and the modification, it can be seen from Fig. 1b that the whole size of the organically modified bentonite is far finer than the original bentonite. The particle-size distribution analysis (Fig. 2) of the modified bentonite shows that about 50% of the particle is less than 0.41 µm and about 90% less than 0.99 µm.

The FTIR spectra over the range of 400–4000 cm^{-1} for original bentonite and modified bentonite are shown in Fig. 3. The characteristic bands of montmorillonite at 1038.7 cm^{-1} and 918.4 cm^{-1} correspond to stretching vibration of –Si–O–Si– group and Al_2–OH bending vibration, respectively. The band at 520.3 cm^{-1} was from the Si–O–Al (where Al is an octahedral cation) in the bentonite. The band at 1635.9 cm^{-1} reflects the OH deformation of water, while the bands at 3000–4000 cm^{-1} are attributed to stretching vibrations of OH groups of the octahedral layer [19]. The appearance of characteristic bands of surfactant confirms the change of bentonite surface properties. The bands at 2921.7 cm^{-1} and 2851.2 cm^{-1} can be assigned to the stretching vibrations of CH_2 and CH_3 groups. Moreover, the appearance of characteristic bands at 1465.9 cm^{-1} for the RNH_3^+ groups and 1382.9 cm^{-1} for the sulfate groups [20] may indicate the intercalation of CTMAB and SDS molecules between the silica layers of the bentonite. The XRD patterns (Fig. 4) show that the silica layers space of the bentonite increased from 1.65 nm to 1.85 nm after the CTMAB–SDS modification.

3.2. *Adsorption studies*

A series of organobentonites were prepared by incorporating bentonite with a mixture of cationic and anionic surfactants with different ratio of CTMAB to SDS, i.e., 1:4, 2:3, 1:1, 3:2 and 4:1. Fig. 5 shows the visible spectra of the original textile wastewater and the wastewater treated by these different organobentonites. It indicates that the

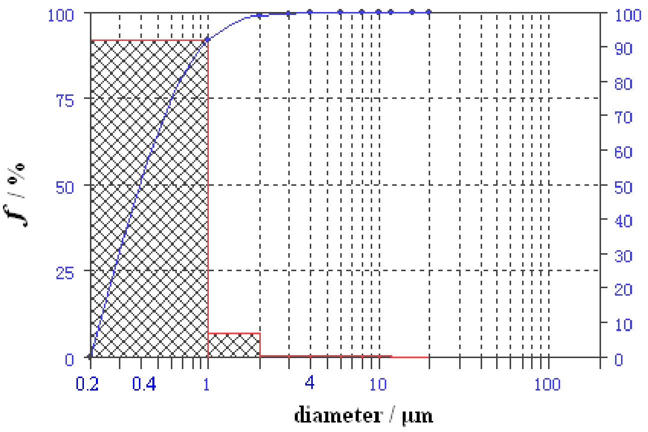


Fig. 2. Particle-size distribution of SDS/CTMAB-bentonite.

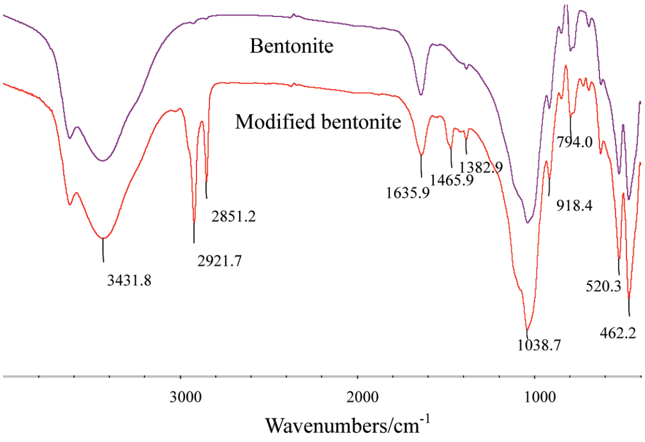


Fig. 3. FTIR spectra of bentonite and SDS/CTMAB-bentonite.

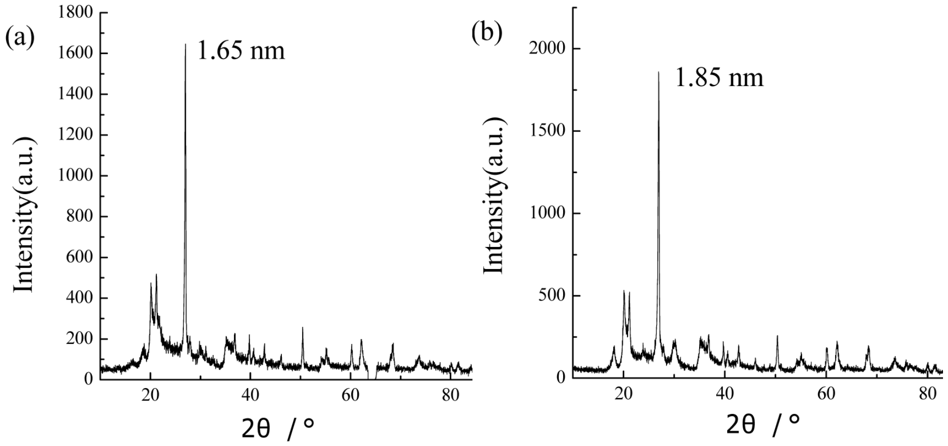


Fig. 4. XRD patterns of (a) bentonite and (b) organobentonite.

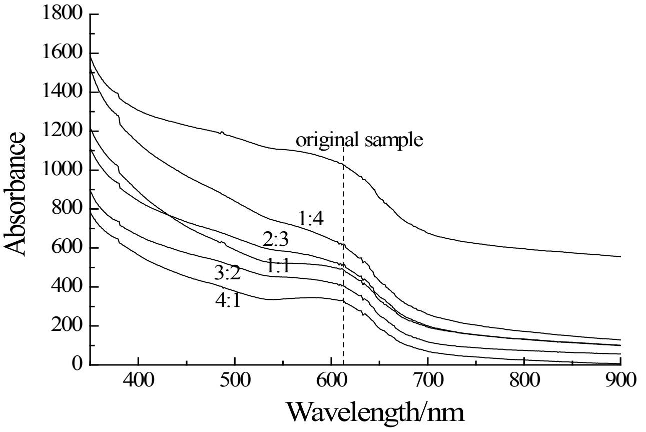


Fig. 5. Visible spectra of original wastewater and the wastewater treated by organobentonites with different ratio of CTMAB to SDS.

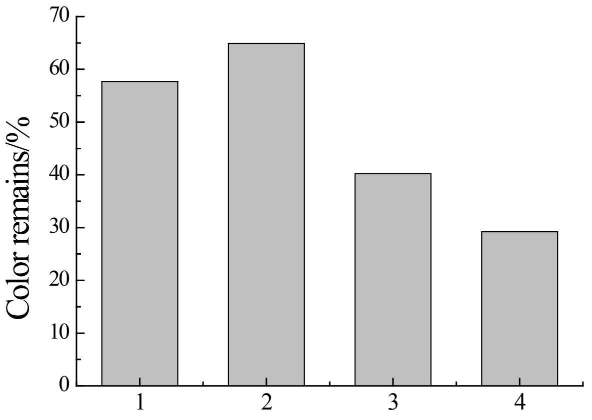


Fig. 6. Color remains of (1) original bentonite, (2) SDS-bentonite, (3) CTMAB-bentonite and (4) SDS/CTMAB-bentonite.

best ratio of CTMAB (cationic) to SDS (anionic) is 4:1. This result is in agreement with the literature [14]. It may be because that such mixed surfactants on anion–cation organobentonite excellently created a partition medium for organic pollutants in the wastewater. Moreover, the dyes used in the dyeing process are expected to be negative in all cases. So, the higher ratio of cationic surfactant to anionic surfactant in bentonite should improve the sorption capacity of the organobentonite.

Fig. 6 displays the color remains of original bentonite, SDS modified bentonite (SDS-bentonite), CTMAB modified bentonite (CTMAB-bentonite) and 20%SDS/80%CTMAB modified bentonite (SDS/CTMAB-bentonite). It shows that the value of color remains of the anion–cation organobentonite is the lowest among the organobentonites, indicating that it has the greatest affinity for the dyes in the wastewater. As stated above, the natural bentonite has an excess of negative charge on its surface, thus the CTMAB can interact by electrostatic sorption, while the SDS can interact by ion-exchange and hydrophobic interaction with bentonite. The introduction of CTMAB and SDS changes the bentonite from hydrophilic to hydrophobic, which has a great affinity for organic compounds.

The influence of contact time on color remains of wastewater post-treated by bentonite and the anion–cation organobentonite is shown in Fig. 7. It took about 50 min to reach the equilibrium for both the samples, while the color removal of organobentonite was higher than that of bentonite. Furthermore, the kinetics of the color removal process was studied by applying two well-known kinetic equations, i.e. pseudo-first- and second-order models. The pseudo-first-order kinetic model, proposed by Lagergren [21] for adsorption analysis, is in the form

Table 1
Parameters of pseudo-first-order and pseudo-second-order kinetic model of color removal by SDS/CTMAB-bentonite

	Pseudo-first-order			Pseudo-second-order		
	a	k_{r1} (min^{-1})	R^2	a	k_{r2} (min^{-1})	R^2
Original bentonite	0.4761	0.0694	0.9746	0.4539	0.0715	0.9452
Modified bentonite	0.7369	0.0478	0.9941	0.8120	0.0586	0.9801

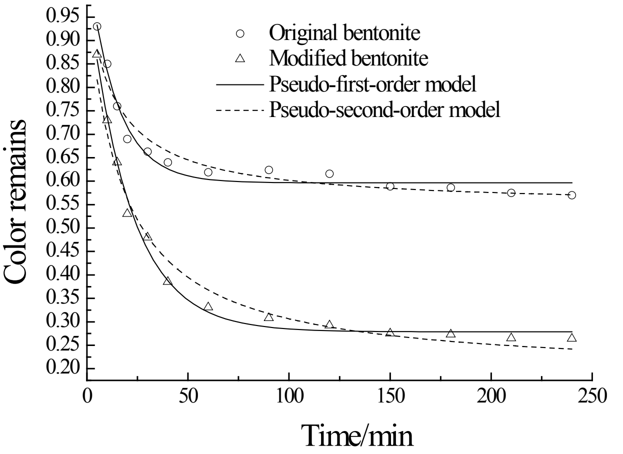


Fig. 7. Effect of contact time on color remains of the wastewater and the fit of experimental data to pseudo-first-order and pseudo-second-order models.

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \tag{2}$$

where k_1 (1/min) is the rate constant of pseudo-first-order model, q_t (mg/g) is the amount of adsorbate adsorbed on the adsorbent at time t (min) and q_e (mg/g) is its value at equilibrium. When rearranging q_t as the concentration form, and integrating over the concentration with time, the following equation can be obtained [22,23]

$$\frac{C_t}{C_o} = \left(1 - \frac{m_s q_e}{C_o}\right) + \frac{m_s q_e}{C_o} e^{-k_1 t} \tag{3}$$

where C_o and C_t (mg/L) are the concentrations of adsorbate at initial time 0 and any time t, respectively, and m_s (g/L) is the dosage of adsorbent in the solution. Therefore, the color remains ratio at time t, C_r, can be written as

$$C_r = 1 - a + ae^{-k_{r1} t} \tag{4}$$

where the constant a is related to the adsorption capacity, and k_{r1} (1/min) is the rate constant. The pseudo-second-order equation proposed by Blanchard [24], developed by Ho [25] is written as

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \tag{5}$$

Table 2
Water quality parameters before and after treatment by SDS/CTMAB-bentonite at the dosing rate of 2 g/l

	Water sample	Sample treated by SDS/CTMAB-bentonite
COD$_{cr}$, mg·L^{-1}	525	168
BOD$_5$, mg·L^{-1}	123	37
SS, mg·L^{-1}	126	67
NH$_4$-N, mg·L^{-1}	86	49
Color remains, %	100	29.2

where k_2 (g/mg min) is the rate constant of pseudo-second-order model. When rearranging q_t as the concentration form, the concentration of solute can vary with time according to

$$\frac{C_t}{C_o} = 1 - \frac{m_s q_e}{C_o} \frac{q_e k_2 t}{1 + q_e k_2 t} \tag{6}$$

Thus, the color remains ratio at time t, C_r, can be written as

$$C_r = 1 - a\frac{k_{r2} t}{1 + k_{r2} t} \tag{7}$$

where k_{r2} (1/min) is the rate constant of the model.

As color remains are the most intelligible information in the dye sorption, the new forms of pseudo-first-order and pseudo-second-order equations obtained by us, Eqs. (4) and (7), were employed for nonlinear fitting of the experimental results, as shown in Fig. 6, and their model parameters obtained from nonlinear regression are listed in Table 1. As can be seen from the correlation coefficients, the pseudo-first order is better than the pseudo-second order, suggesting that the adsorption process of dyes onto bentonite follows the pseudo-first-order model. In addition, the higher a value of the organobentonite confirms its higher adsorption capacity for organic compounds.

The concentrations of target constituents in the post-treated water are summarized in Table 2. For simplicity, presented in the table are only results from the treatment at the dosing rate of 2 g/l of SDS/CTMAB-bentonite. It shows that the COD, BOD and color removal of the organobentonite is more effective than the SS and NH$_4$-N removal.

4. Conclusions

The treatment of the textile wastewater generated from the dyeing and printing process has been successfully carried out by using the anion–cation organobentonite (SDS/CTMAB-bentonite). The FTIR analysis of the organobentonite confirmed the intercalation of CTMAB and SDS molecules between the silica layers of the bentonite. It was found that the maximum color removal was obtained with the mass ratio 4:1 of CTMAB to SDS. The color removal of the organically modified bentonite was more effective than that of the natural bentonite. The adsorption process could be equilibrated within about 50 min, and it followed the pseudo-first-order kinetic model.

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