Adsorption of Crystal Violet onto BTEA- and CTMA-bentonite from Aqueous Solutions

Ren Jian-min, Wu Si-wei, Jin Wei

Abstract—CTMA-bentonite and BTEA-Bentonite prepared by Na-bentonite cation exchanged with cetyltrimethylammonium(CTMA) and benzyltriethylammonium (BTEA). Products were characterized by XRD and IR techniques.The d_{001} spacing value of CTMA-bentonite and BTEA-bentonite are 7.54Å and 3.50Å larger than that of Na-bentonite at 100% cation exchange capacity, respectively. The IR spectrum showed that the intensities of OH stretching and bending vibrations of the two organoclays decreased greatly comparing to untreated Na-bentonite. Batch experiments were carried out at 303 K, 318 K and 333 K to obtain the sorption isotherms of Crystal violet onto the two organoclays. The results show that the sorption isothermal data could be well described by Freundlich model. The dynamical data for the two organoclays fit well with pseudo-second-order kinetic model. The adsorption capacity of CTMA-bentonite was found higher than that of BTEA-Bentonite. Thermodynamic parameters such as changes in the free energy ($\Delta G°$), the enthalpy ($\Delta H°$) and the entropy ($\Delta S°$) were also evaluated. The overall adsorption process of Crystal violet onto the two organoclays were spontaneous, endothermic physisorption. The CTMA-bentonite and BTEA-Bentonite could be employed as low-cost alternatives to activated carbon in wastewater treatment for the removal of color which comes from textile dyes.

Keywords—Characterization, Adsorption, Crystal violet, Bentonite, BTEA,CTMA.

I. INTRODUCTION

QUEOUS effluents are well known as massive industrial wastewater. The presence of very low concentrations of these effluents are highly visible and undesirable and potentially inhibiting photosynthesis. The main pollution source of colored effluents comes from textiles, leather, printing, laundry, tannery, rubber, painting, etc., processes[1]. Untreated disposal of this colored water into receiving water body causes damage to aquatic life and also severe damage to the human health[2-4]. Removal of color from wastewater effluents is an important issue faced by the texile dyeing industring.

Various physical, chemical and biological treatment techniques can be employed to remove dyes from wastewater.

Many synthetic dyes do not easily decompose in biological treatments due to their toxic effects on microorganisms, adsorption is suitable under field condition due to the flexibility, easy operation and no/lesser sludge disposal problems, high efficiency and for treating a large volume of

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effluent especially in removing dyes from dilute solutions[5-11]. It is considered to be a potential technique for the treatment of wastewater and reclamation of water containing dyes.

Activated carbons with large surface area have shown high adsorption capacities for many adsorbates containing dyes, but they are mainly composed of less than 2nm and thus are not effective for large sized synthetic dyes. Forthermore, the commercial activated carbon has also disadvantages such as high price, and high cost of regeneration. Activated carbon adsorption has been limited greatly[12-13]. Hence, alternative low-cost, novel, locally available adsorbents are currently used for the removal of textile dye effluents from aqueous solutions, instead of activated carbon. For instance, natural clays such as sepiolite[2-4], zeolite[14-17], montmorillonite[18-20] and bentonite[21-25] can be used in these aspects.

Bentonite is one of the clay minerals, which is composed of units made up of two silica tetrahedral sheets with a central Al octahedral sheet. It has a negative surface charge created by the isomorphous substitution of Al^{3+} for Si^{4+} in tetrahedral layer and Mg^{2+} for Al^{3+} in octahedral layer. The charge imbalance is offset by exchangeable cations as H^+,Na^+,K^+ or Ca^{2+}. If a clay mineral has metal cations in the cations exchange sites, its surface and interlayer space is hydrophilic and it is not a good sorbent for organic species. Meanwhile, hydration and solvation of the interlayer cations create high swelling properties to make separation difficult in industrial wastewater treatment.

Bentonite in which the inorganic exchangeable cation is replaced with an organic cation, such as tetrametylammonium, tetramethylphosphonium, benzyltriethylammonium, cetyltrimethylammonium and dodecyltrimehylammonium, modified the clay's surface properties from organophobic to strongly organophilic and therefore the adsorption capacity of organic substances increases. More importantly, the substituted organic are weakly hydrated. The complex obtained is referred to as organoclay.

In this study, Na-bentonite is used to prepare CTMA-bentonite and BTEA-Bentonite by Na-bentonite exchanged with cetyltrimethylammonium(CTMA) and benzyltriethylammonium (BTEA). The organoclay was characterized by XRD and FT-IR techniques. Crystal violet was used a model compound of water soluble aromatic dyes to investigate the sorption equilibria onto the two organoclays. The Freundlich equations was used to fit the equilibrium isotherm. The adsorption rates of Crystal violet onto the two organoclays were determined quantitatively and compared by

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the first and second-order kinetic model. Thermodynamic parameters such as the thermodynamic functions changes ($\Delta H°$, $\Delta S°$ and $\Delta G°$) are evaluated and discussed. This information will be useful for further applications of system design in the treatment of practical waste effluents contain aromatic dyeing materials.

II. Experiments

A. Materials

A commercial dye Crystal violet, as monovalent cationic dye (analytical reagent-grade),cetyltrimethylammonium bromide (CTMAB) and Benzyltriethylammionium chloride(BTMAC) were provided by Chongqing chemical Co. The chemical structure of Crystal violet is illustrated in Fig. 1. The natural Na-bentonite was obtained from Xinyang Henan, China. Na-bentonite was sieved through a 300 mesh sieve (average particle diameter 40 μm), and then dried at 110 in a laboratory oven for 2 h prior to use. All the reagents used were of analytical-reagent grade. Doubly distilled water used to prepare all the solutions.
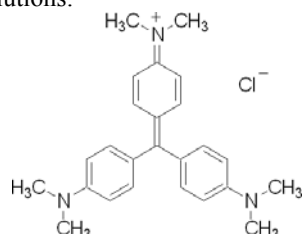
Fig. 1 Chemical structure of Crystal violet

B. Preparation of CTMA- and BTEA-bentonite[13,27]

CTMA- bentonite and BTEA-bentonite were prepared by a conventional ion-exchange method using aqueous solutions of CTMAB and BTEAC. The amount of added CTMAB and BTEAC were sufficient to give fully saturated CTMA-bentonite and BTEA-bentonite, (i.e., more than 100% of the cation exchange capacity,CEC). The mixtures of Na-bentonite and each of the organic cation solutions were placed in a water bath at 50℃ and constantly shaken for 4 hours. After the ion exchange, the treated bentonite was then recovered by centrifugation.The products were washed with deionized water repeatedly until a negative chloride or bromide test was obtained. The final products were dried at 60℃ for 12 hours, then ground into powder to 300 mesh size.

C. X-ray diffraction measurements (XRD)

The X-ray powder diffraction (XRD) patterns of Na-bentonite and the organoclays were recorded on a D/MAX- C automatic powder diffractometer employing Cu radiation $K\alpha=1.5406$ Å at 40.0KV and 30.0mA with a 2θ angle scanning angle ranging from 2° to 20° at 1.0s step^{-1}. The basal distance d_{001} for each sample was calculated using Bragg's equation.

D. FT-IR analysis

Infrared analysis was used to differentiate between the structures of Na-bentonite and the organoclays. This analysis was carried out between 4000 and 400cm^{-1} by a IRPrestige spectrophotometer. Powdered samples were pressed into pellets with optically pure KBr.

E. Batch Adsorption Experiments

Absorption experiments on each of the two organoclays was performed in order to determine the time needed to reach equilibrium and the pattern of the kinetics. For this purpose, a stock solution of 1000 mg·L^{-1} was prepared by dissolving the 0.2500 g weight of Crystal violet in 250 mL distilled water. Sample of 0.05 g of organoclay was transferred into 50 mL of Crystal violet solution at known concentration and the medium pH (6.8-7) in a 100 mL flask. Several 100 mL flasks with stopper are placed in a thermostatic bath (SHA-C, Jiangsu, China) and individually agitated. Samples from the solution were taken at predetermined time intervals. The sorbents were separated from the samples by centrifugation (TDZ4-WS, Hunan, China) and the supernatant was analysed spectrophotometricaly at a wavelength of 590 nm for the residual concentration of Crystal violet.

The parameters varied in the experiments are the agitation time, the initial concentration of Crystal violet ranging from 100 to 500 mg·L-1) and the temperature (303 K, 318 K and 333 K). All the experiments are duplicated. Only the mean values are reported in this paper. The maximum deviation observed is less than 5%.

The adsorption capacity of an adsorbent, q_t, is calculated by means of the following equation:

$$q_t = \frac{(c_0 - c_t)V}{W} \qquad (1)$$

where q_t is the adsorbent capacity, mg·g^{-1}; c_t is the adsorbate concentration, mg·L^{-1}; c_0 is the initial concentration of adsorbate, mg·L^{-1}, W, is the adsorbent mass, g, and V is the solution volume, L. If the adsorption arrives equilibrium, c_t equals to c_e, (the adsorbate equilibrium concentration), while q_t equals to q_e (the equilibrium adsorption capacity).

III. Results and Discussion

A. X-ray and FT-IR spectroscopy

Figure 2 shows the X-ray diffractograms obtained for Na-bentonite and the two organoclays, the interlaminar distances were calculated using Bragg's equation based on the position of the first-order reflection d_{001}. The d_{001} spacing value of CTMA-bentonite and BTEA-bentonite were 19.98Å and 15.94Å at 4.42 and 5.74(2θ) and the inter-lamellar spacing for each of the organoclays increased 7.54Å and 3.50Å comparing with that of Na-bentonite, respectively. This indicated that the long-chain CTMA cation form a bilayer in the interlayer of CTMA-bentonite, while short chain BTEA cation lied parallel to siloxane interlayer of BTEA-bentonite and form a flat-monolayer [26,28,29].

The FTIR spectrum of Na-bentonite and the two organoclays was shown in Figure 3. The band at 3400-3618cm^{-1} correspond to stretching vibrations of OH groups attached to octahedral layer. The H-O-H bending vibrations in the 1643 cm^{-1}, and the

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Si-O stretching bands in the 1100cm-1, the Si-O-Si asymmetric stretching bands in the 1038cm^{-1}, the Si-O-Al bending bands in the 520 cm^{-1} are clearly seen. The spectrum of BTEA-bentonite and CTMA-bentonite exhibits the characteristic absorption bands of BTEA cation CTMA cation corresponding to[30]: (1) the symmetric and asymmetric stretching vibrations of the methylene and methyl group CH2, CH$_3$ at 2920 cm^{-1}and 2850 cm^{-1}; C-H bending bands of methylene and methyl group CH$_2$, CH3 at 1454cm^{-1}; (3) aromatic C=C skeleton stretching at 1500 cm^{-1}. It was concluded from the vibrations of aromatic ring and alkyl groupa that organic compound could penetrate into the interlayer space of Na-bentonite as organic cation, displacing inganic cations. Surfactant cations can interact with Na-bentonite through electrostatic interactions,π interactions and van der Waals forces. The surface properties of Na-bentonite would change considerably from highly hydrophilic to increasingly hydrophobic as a result of the replacement of inorganic cations with organic cations. The decrease in the intensities of OH stretching and bending vibrations of the two organoclays comparing to untreated Na-bentonite confirm this phenomenon. In this case, after sorption of the organic cation, the spectrum in the region of the Si-O bending vibrations, corresponding to the intercystalline structure of the clays, remained almost unchanged.
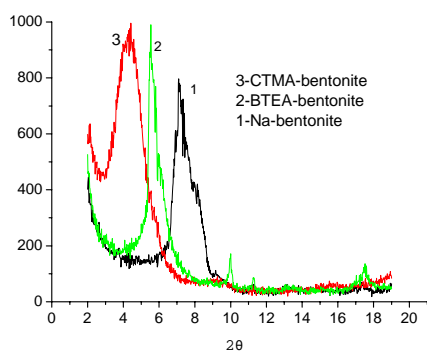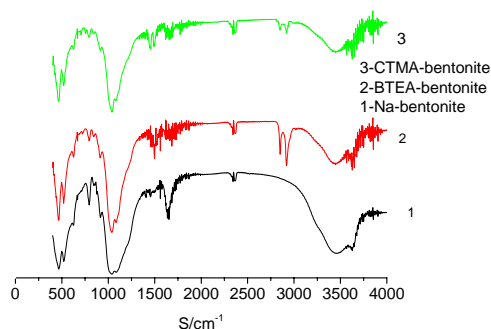

Fig. 2 The XRD of Na-bentonite and the two organoclays

Fig. 3 The FTIR of of Na-bentonite and the two organoclays

B. The adsorption of Crystal violet by the two organoclays

A series of contact time experiments for Crystal violet on each of the two organoclays was carried out at initial Crystal violet concentrations 200 mg·L^{-1} at the medium pH and the different temperatures (303 K, 318 K and 333 K). Fig.4 shows the contact time necessary for Crystal violet onto the two organoclays to reach equilibrium is about 70 min. At this point, the amount of the aromatic dye desorbing from the two organoclays is in a state of dynamic equilibrium with the amount of the dye being adsorbed onto the two organoclays. Hence, 70 min was fixed as the equilibrium time which reflected the maximum adsorption capacity of the two organoclays and was used in all subsequent experiments.
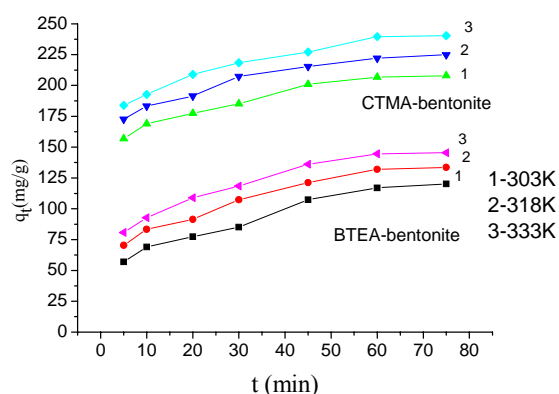

Fig. 4 The influence of reaction time for the adsorption

To verify the possible dynamic mechanism during this sorption process by the two organoclays, the following kinetic models were used[28]:

(1) Lagergren pseudo-first-order model:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303}t \tag{2}$$

where k_1 (min^{-1}) is the adsorption rate constant. The model can be checked by the linearized plots of log(qe-qt) versus t (Fig5,a).

(2) The pseudo-second-order kinetic model:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{3}$$

where k_2 is the pseudo-second-order rate constant (g·mg^{-1}·min^{-1}).

An adequate pseudo-second-order kinetics model should show a linear plot of t/q_t versus t (Fig 5,b). The value of q_e is easily deduced from the slope of the plot of t/qt versus t. Once q_e was identified, the value of k_2 can be obtained from the intercept.

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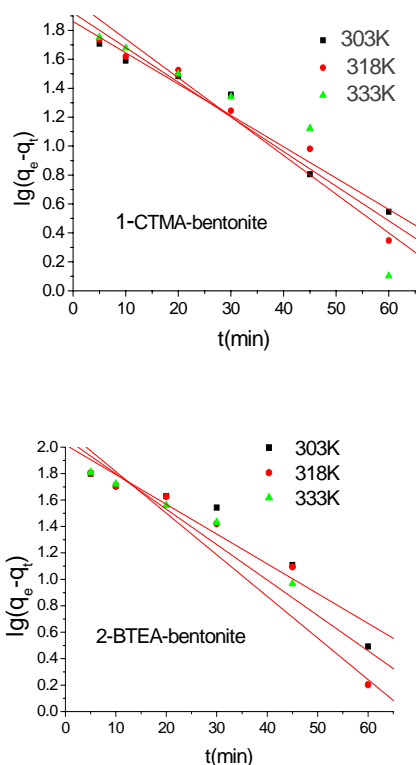International Journal of Chemical and Molecular Engineering
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Fig. 5(a) pseudo -first-order of Crystal violet onto the two organoclays
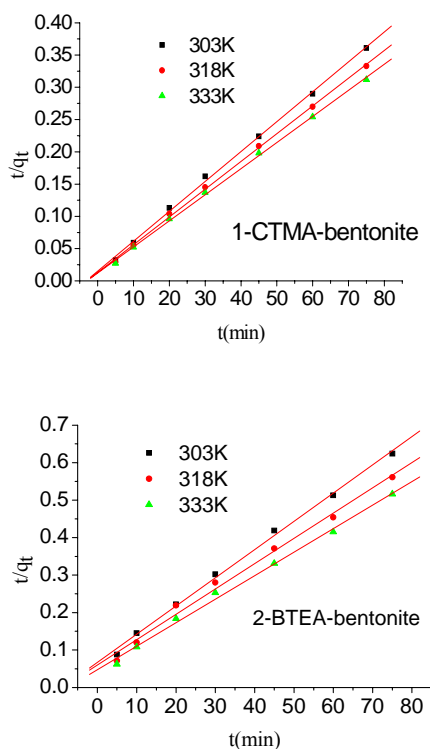

Fig. 5 (b) pseudo-second-order of Crystal violet onto the two organoclays

Based on the correlation coefficients, the adsorption of Crystal violet on the two organoclays is best described by the second-order equation. The application of a pseudo-second-order model leads to much better regression coefficients, all greater than 0.99. Furthermore, the experimental and calculated values of q_e are very close (on shown), thus, the pseudo-second-order kinetic model is well suitable to model the sorption process of Crystal violet on the two organoclays. Simlar trends were observed for the adsorption of an industrial dye Supranol Yellow 4GL onto Cetyltrimethylammonium bentonite and Erionyl Red RS on polyaluminium hydroxide exchanged bentonite[31]. In Fig.5, it can be observed an increase in Crystal violet uptake onto the organoclays when the temperature was risen. This indicate that adsorption of Crystal violet onto each of the two organoclays is an endothermic process. The experimental adsorption amount for Crystal violet on CTMA-bentonite and BTEA-bentonite was 204.36 mg·g^{-1}, 222.69 mg·g^{-1}, 239.10 mg·g^{-1} and 117.01 mg·g^{-1}, 132.05 mg·g^{-1}, 144.55 mg·g^{-1} at 303 K, 318 K and 333 K, respectively.

C. Adsorption Isotherms

The isotherms of Crystal violet on each of the two organoclays generated in batch experiments using different initial concentrations ranging from 100-500 mg·L^{-1} at the medium pH and the different temperatures (303 K, 318 K and 333 K) are presented in Fig. 6.
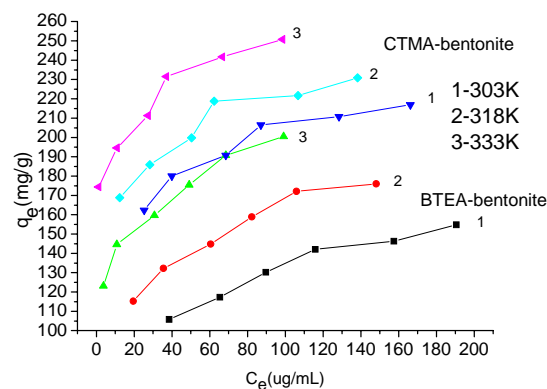

Fig. 6 Adsorption isotherm for Crystal violet on the two organoclays

The isotherms for Crystal violet on the two organoclays are nonlinear. This indicated that partitioning was also not the dominant mechanism of sorption for Crystal violet on CTMA-bentonite with long chain, with not consistent with the sorption of small molecule sorbates, such as benzene[32], 2,4,6,-Trinitrotoluene, 2-amino-4,6-dinitrotoluene and 2-amino-2,6-dinitrotoluene, on CTMA-bentonite[33]. The small sized sorbates may be sorbed by solute partitioning between water and the amorphous organic phase of CTMA-bentonite created by the exchanged organic cations.

The equilibrium isotherm data can be described by linearized Freundlich isotherm model [29]:

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$$\lg q_e = \lg K + \frac{1}{n} \lg c_e \qquad (5)$$

The value of the Freundlich constants are summarized in table 1.

TABLE I ISOTHERM OF ADSORPTION OF CRYSTAL VIOLET ON THE TWO ORGANOCLAYS

	T(K)	Freundlich型		
		K	1/n	R_F^2
CTMA-bentonite	303	100.56	0.1535	0.9824
	318	120.54	0.1331	0.9813
	333	166.95	0.0840	0.9671
BTEA-bentonite	303	43.26	0.2437	0.9985
	318	60.17	0.2187	0.9982
	333	100.56	0.1466	0.9961

As seen from the table 1, The Freundlich isotherm fits very well the experimental data for Crystal violet on the two organoclays. the R values were all higher than 0.96, indicating a very good mathematical fit.

The value of the constant 1/n in Freundlich model being smaller than 1, implies that the adsorption process of the dye on the two organoclays is favourable. The results coincided with the report of A.Khenifi et al[28].

The thermodynamic properties: enthalpy change (ΔH°), free energy change (ΔG°) and entropy change (ΔS°) for the adsorption of Crystal violet on the two organoclays are calculated by the methods [13] .

The related thermodynamic parameters are are summarized in table 2:

TABLE II THE RELATED THERMODYAMIC PARAMETERS

	T(K)	ΔG° (kJ/mol)	ΔH° (kJ/mol)	ΔS° (J/mol.k)
CTMA-bentonite	303	-3.92		
	318	-5.15	27.02	0.10
	333	-6.99		
BTEA-bentonite	303	-4.11		
	318	-6.15	54.28	0.19
	333	-9.92		

The negative values of ΔG° for the adsorption reflect the feasibility of the process. With increase in temperature, the values of ΔG° become more negative, implies that the adsorption on each of the two organoclays is a spontaneous, endothermic process.The value of ΔH° for the adsorption is lower than 80 kJ·mol^{-1}, suggesting the physical nature of the sorption [34], i.e., physisorption condcted with van der Waals forces.

In fact, organoclays can sorb organic contaminants through adsorption or partitioning. The Organoclays with greater than 12 carbons long chain tend to sorb small sized organic contaminants through partitioning, organoclays with short chain or benzyl groups tend to sorb organic contaminants through adsorption[32,33]. Although porosity and total pore volume of the organoclays increase with the increase of the temperature, it is hard for the nonplanar large sized Crystal

violet to penetrate into the two organoclays, In the present work, ΔH° for CTMA-bentonite is lower than ΔH° for BTEA-bentonite, the adsorption capacity for the former higher than that for the latter. This may be large sized Crystal violet on the external surfaces of the BTEA-bentonite through adsorption by strong π - π interactions between aromatic sorbates and aromatic sorbents. While on CTMA-bentonite with long chain more Crystal violet molecule can be sorbed by a more partition-like process, in which Crystal violet "dissolves" in the fluid-like phase created by the concentrated tails of the CTMA cation.

IV. CONCLUSIONS

X-ray and FT-IR spectroscopy analyses confirmed the intercalation of CTMA and BTEA in Na-bentonite. The intensities of OH stretching and bending vibrations of the two organoclays are much weaker than that of untreated Na-bentonite. The expansion thickness of the basal spacing CTMA-bentonite and BTEA-bentonite were 7.54Å and 3.50Å comparing with that of Na-bentonite, respectively, corresponding to a bilayer and monolayer of organic cations between the silicate layers. The adsorption process of Crystal violet on CTMA- and BTEA-bentonite could be best described by the second-order equation. Furthermore, the equilibrium data of adsorption are in good agreement with the Freundlich. The results revealed that the two organoclays can be employed as adsorbent for treatment of aqueous waste streams.

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