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Sorption of wastewater containing reactive red X-3B on inorgano-organo pillared bentonite*

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Abstract: Bentonite is a kind of natural clay with good exchanging ability. By exchanging its interlamellar cations with various soluble cations, such as quaternary ammonium cations and inorganic metal ions, the properties of natural bentonite can be greatly improved. In this study, hexadecyltrimethylammonium bromide (HDTMA), $CaCl_2$, $MgCl_2$, $FeCl_3$, $AlCl_3$ were used as organic and inorganic pillared materials respectively to produce several kinds of Ca-, Mg-, Fe-, Al-organo pillared bentonites. Sorption of reactive red X-3B on them was studied to determine their potential application as sorbents in wastewater treatment. The results showed that these pillared bentonites had much improved sorption properties, and that the dye solutions' pH value had some effect on the performance of these inorgano-organo pillared bentonites. Isotherms of reactive X-3B on these pillared bentonites suggested a Langmuir-type sorption mechanism.

Key words: Reactive red X-3B, Sorption, Pillared, Bentonite
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INTRODUCTION

Dye wastewaters containing various kinds of soluble organic dyes are big sources of present industrial pollutants. In the past, granulated activated carbon (GAC) was widely used for treating dye wastewater as a useful sorbent. As GAC is a comparably expensive material; it is worthwhile to find much cheaper substitutes. Researchers pay more and more attention to bentonite, a widely found natural clay. Bentonite belongs to 2:1 layered silicates with very good exchanging properties, and has a large percentage of ditrigonal cavities formed by six corner sharing silica tetrahedrals on the siloxane planar surface. The outer cations from solutions can enter the inner layer of bentonite and form pillared bentonites by replacing its own cations. Over the past 50 years, pillared bentonites have been used as catalysts in a wide variety of organic reactions (Breen and Moronta, 2000; Jang *et al*., 2005; Wang and Ferris, 2005) and as sorbents in wastewater treatments (Egirani *et al*., 2005; Akcay, 2005; Rodriguez *et al*., 1993).

In our previous work, we got fully organic pillared bentonite by intercalating hexadecyltrimethylammonium cations ($HDTMA^+$) into bentonite suspension (Zeng and Liu, 2004; 2005). Its d(001) value increased from 12.3 Å to 18.9 Å, compared to that of the raw material. In this study, soluble inorganic metal ions were introduced to thus-produced organo pillared bentonite to reduce the total amount of HDTMA, and form inorgano-organo pillared bentonites.

Reactive X-3B is an organic substance with double-single-double band in its molecule structure (Fig.1), and widely used in the textile industry as an organic dye. Reactive X-3B's sorption on inorgano-organo pillared bentonites was studied to test the potential application of these pillared bentonites as pollutant sorbents.

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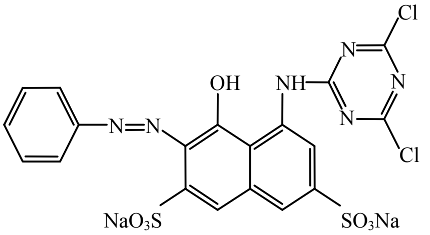

Fig.1 The structure of reactive red X-3B

MATERIALS AND METHODS

Materials

The natural bentonite, used in this study, was obtained from clay found in Linan, Zhejiang Province, China. The composition of this natural clay, as analyzed by XRF spectroscopy method, was 59.8% SiO_2, 14.3% Al_2O_3, 4.0% CaO, 2.1% Na_2O, 1.7% Fe_2O_3, 1.7% MgO, 1.4% K_2O, 0.4% MnO_2, 0.3% TiO_2, 0.03% P_2O_5. Its cation exchange capacity (CEC) is about 62 meq/100 g.

NaCl, $CaCl_2$, $MgCl_2$, $AlCl_3$, $FeCl_3$, NaOH, H_2SO_4, $AgNO_3$ and hexadecyltrimethylammonium bromide ($HDTMA^+$), were of analytical grade and used as received. Reactive red X-3B was obtained from Hangzhou Xidebao Silk Ltd., Zhejiang Province, China. The pH of reactive red X-3B solution was adjusted to 2~12 by H_2SO_4 or NaOH.

Purification and transformation to Na-bentonite

Because of its low useful contain, this natural bentonite should first be purified with $(NaPO_3)_6$ as dispersant: 50 g of clay powder (size<2 μm) were added slowly into 1000 ml of 0.3 wt% $(NaPO_3)_6$ solution in 1 L Pyrex distilling flasks. Thus obtained suspensions were shaken for 2 h, and kept at room temperature overnight for further aggradations. Then the suspensions were filtered, and the solid phrase was dispersed again to 0.3 wt% $(NaPO_3)_6$ solution. The bentonite contain could be increased to 98% (determined by XRD measurement) after three times treatments. Then this purified bentonite was fully converted into Na-form by further washing with 1.0 mol/L NaCl solution for five times, and then again rinsed with deioned water until the suspensions was free of chloride (by $AgNO_3$ test). Then Na-bentonite sample was centrifuged, and dried, ground and fractioned to get the particle size<2 μm. XRF spectroscopy analysis showed that this Na-montmorillonite sample contains 1.1% CaO, 2.8% Na_2O after the above processing. Compared to original Ca-montmorillonite, CaO contain in thus produced Na-bentonite decreased from 4.0% to 1.1%.

Preparation of inorgano-organo pillared bentonites

Ten grams the above-purified Na-bentonite was weighed out and put into a 250 ml conical flask. Some volumes of $CaCl_2$, $MgCl_2$, $AlCl_3$, $FeCl_3$ solutions were added and stirred for 2 h at 60 °C to complete ion-exchange with bentonite, after which the Na-bentonites were changed into Ca-, Ma-, Al-, Fe-bentonites. Taking Fe-bentonite for example, the composition was found to be 59.86% SiO_2, 11.47% Al_2O_3, 0.52% CaO, 0.59% Na_2O, 9.53% Fe_2O_3, 1.77% MgO, 0.84% K_2O, 0.38% MnO_2, 0.31% TiO_2, 0.025% P_2O_5 by XRF spectroscopy analysis in which Fe content was about 5 times higher than that of Na-bentonite.

Then after an appropriate amount of hexadecyltrimethylammonium bromine was added, the mixture was stirred for another 2 h at the same temperature. The detailed description of these pillared chemicals is given in Table 1. The mixtures were separated with a filter. The solid phrase was collected and washed with

Table 1 The prescription of pillared bentonite and removal (%) of dye

Number	$1^{\#}$	$2^{\#}$	$3^{\#}$	$4^{\#}$	$5^{\#}$	$6^{\#}$	$7^{\#}$	$8^{\#}$	$9^{\#}$	$10^{\#}$
Bentonite (g)	10.0	10.0	10.0	10.0	10.0	10.0	10.0	10.0	10.0	10.0
$CaCl_2$ (mmol)	0	2.0	0	0	0	0	5.0	0	0	0
$MgCl_2$ (mmol)	0	0	2.0	0	0	0	0	5.0	0	0
$AlCl_3$ (mmol)	0	0	0	2.0	0	0	0	0	5.0	0
$FeCl_3$ (mmol)	0	0	0	0	2.0	0	0	0	0	5.0
HDTMA (mmol)	0	0.4	0.4	0.4	0.4	1.6	0	0	0	0
Removal (%)	10.1	94.8	91.4	95.8	96.2	93.0	28.8	23.0	75.3	72.4

Note: All data were the average of 3 times measurements deionized water for several times until it was Cl^- free (by $AgNO_3$ test). Then pillared bentonites were then dried at room temperature, ground to powder, and pass through less than 2 μm sieve.

Characterizations of inorgano-organo pillared bentonites

The above-made pillared bentonites were characterized by XRD, BET and XRF analysis. Samples prepared in thin films for XRD analysis, whose results were recorded by a Philips X'Pert MPD instrument. XRF data of samples heated at 105 °C for 24 h, were obtained on a Siemens SRS-3000 Sequential X-ray Fluorescence Spectroscope (XRF).

Sorption of reactive red X-3B by inorgano-organo pillared bentonites

A portion (0.100 g) of the above-obtained inorgano-organo pillared bentonites was put into a 250 ml conical flask, and mixed with 25 ml of reactive red X-3B solution. The mixture was then stirred for 1.0 h in a shaker to allow the sorption to be fully completed. After that, the mixture was separated by a high-speed centrifuge. The supernatant was used to determine the residual reactive red X-3B concentration with UV-spectrophotometer. The amount of reactive red X-3B adsorbed by bentonite was calculated according to the following equation $(1-A/A_0)\times 100\%$. A_0, A: the absorbance of reactive red X-3B in the liquid before and after adding pillared bentonite.

Determination of sorption isotherms

Pillared bentonite and 250 ml of reactive red X-3B were blended and shaken in 250 ml conical flask, for 2 h at room temperature. After shaking, the mixture was kept overnight at room temperature to allow full sorption. Then the concentration that remained in the dye solution was determined as above. Six different concentrations of reactive red X-3B were measured in each isotherm line.

RESULTS AND DISCUSSION

Effect of pillaring chemicals on the sorption ability of bentonite

In this work, various inorganic, organic pillared bentonites have been produced according to the prescription listed in Table 1. The sorption of reactive red X-3B on these pillared bentonites was also measured.

It was shown that natural bentonite has poor sorptionability; the removal of reactive red X-3B on it was only 10.1%. Bentonite belongs to 2:1 type mineral. Si^{4+} ions in Si-O tetrahedrals and Al^{3+} ions in Al-O octahedrons could be exchanged by other cations with lower valence charges such as Mg^{2+}, Na^+, K^+, Li^+, Ca^{2+} etc. Therefore bentonite has a permanent net negative charge and good exchanging ability. The outer cations from the solutions could enter the inner layer of bentonite. $7^\#$, $8^\#$ were the bentonites made from pure inorganic pillared materials. They are poor at sorption of organic dye molecules due to their hydrophile properties. So the removal of reactive red X-3B on $7^\#$, $8^\#$ were only 28.8% and 23% respectively.

$HDTMA^+$ has a hydrophile group at one end, a hydrophobe group at the other end. By following cation-exchanging with Na-bentonite, organo pillared bentonite can be produced ($2^\#$, $3^\#$, $4^\#$, $5^\#$, $6^\#$ in Table 1):

$$\text{Na-bentonite}+[\text{HDTMA}]^+ \rightarrow [\text{HDTMA}]\text{-bentonite}+\text{Na}^+$$

$6^\#$ was the purely organo pillared bentonite, and also had very good sorption ability. It could remove above 90% of reactive red X-3B from the dye solution. As shown in Table 1, only 1/4 the amount of $HDTMA^+$ and half the amount of inorganic chemicals used in $6^\#$ were needed to produce $2^\#$, $3^\#$, $4^\#$, $5^\#$. These four inorgano-organo pillared bentonites also showed the same or even better sorption abilities: the removal of reactive red X-3B on $2^\#$, $3^\#$, $4^\#$, $5^\#$ could reach about 95%. By this way, the amount of $HDTMA^+$ used could be reduced, and the price to produce these pillared could also be decreased. XRD data on some pillared bentonites are given in Table 2. In general, the higher the basal spacing [d(001)], the better the sorption abilities of bentonites.

$9^\#$, $10^\#$ have notably much better sorption abilities than $7^\#$, $8^\#$, although all of them belong to 100% purely inorgano pillared bentonites because of 2 reasons: (1) Hydration number of Ca^{2+}, Mg^{2+} in $7^\#$, $8^\#$ were less than that of Al^{3+}, Fe^{3+}, so the d(001) values of $7^\#$, $8^\#$ were smaller. That means these two pillared bentonites could supply less free space to hold reactive red X-3B molecules as sorption sites; (2) Al^{3+}, Fe^{3+} cations have good flocculation properties (Doff *et al*., 1988). Al^{3+} and Fe^{3+} could occur as hydration proceeds when dispersing into water, and form $[Al(H_2O)_6]^{3+}$ and $[Fe(H_2O)_6]^{3+}$ hydration cations. Organic dye solutions normally show negative charges with ζ value being −7 mV to −20 mV. $[Al(H_2O)_6]^{3+}$ and $[Fe(H_2O)_6]^{3+}$ hydration cations could neutralize these surface negative charges, and form large flocculate.

Effect of vibration-time

Two of the following properties are very important for a good adsorbent: one is high sorption quantity and another is fast sorption equilibrium. To study the sorption kinetics of reactive red X-3B with pillared bentonites, we investigated the effect of vibration-time on the sorption (shown as removal percentage in Fig.2). The experiments were conducted at room temperature (about 25 °C). The results are given in Fig.2.

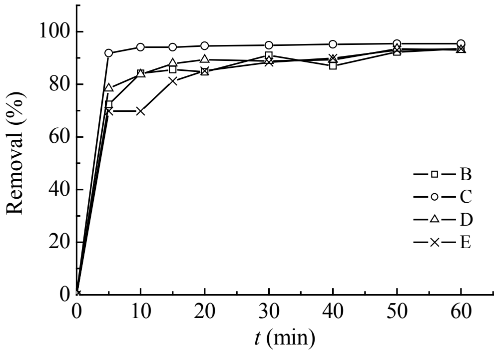

Fig.2 The effect of vibration-time on the sorption of reactive red X-3B
B: Al-HDTMA pillared bentonite; C: Fe-HDTMA pillared bentonite; D: Mg-HDTMA pillared bentonite; E: Ca-HDTMA pillared bentonite

Fig.2 shows that the sorption of reactive red X-3B on all these 4 pillared bentonites reached their equilibrium within a very short time. This fast sorption-rate kinetics means (1) the surface of bentonite has turned from hydrophile to hydrophobe. Molecules of reactive red X-3B can be easily and rapidly adsorbed on the bentonites; (2) d(001) value of bentonite has been increased. It must be pointed out that all montmorillnites reach their equilibrium sorption in less than 10 min. Therefore, the vibration-time for other experiments except those mentioned in this study was selected as 30 min to ensure complete sorption of reactive red X-3B.

Effect of pH value

Because dye wastewater from textile industry sometimes varied in acidity, it is very important for researchers to investigate the effect of pH value on the sorption of reactive red X-3B. The results are shown in Table 3.

Under strong acid system, all the 4 pillared bentonites gained the highest sorption of reactive red X-3B with removal rate of about 95%. H^+ ions in the acid solution can enter the interlayer of bentonite, permute with the exchangeable cations, and occupy the effective sorption-sites. Compared to the original Na^+ ions, it is easier for H^+ to combine with the molecules of reactive red X-3B. Because of these two reasons, pillared bentonites have better sorption abilities in acid system.

On the other hand, the removal of reactive red X-3B still remained above 70%, when the pH value changed from 3.0 to 11.0. As we mentioned above, natural bentonite could adsorb only 10.1% reactive red X-3B from solution. There is one hydrophile group

Table 2 XRD data on some pillared bentonites

No.	$1^{\#}$	$4^{\#}$	$5^{\#}$	$6^{\#}$	$7^{\#}$	$9^{\#}$
d(001) (Å)	12.7	14.2	15.6	22.8	17.3	17.4

Table 3 Effect of pH value of solution on the removal (%) of reactive red X-3B

	pH					
	3.0	4.0	6.0	8.0	10.0	11.0
Ca-HDTMA pillared bentonite	96.2	94.2	95.1	92.9	94.9	93.4
Mg-HDTMA pillared bentonite	99.5	63.1	71.8	72.9	76.0	95.2
Al-HDTMA pillared bentonite	93.7	91.0	76.4	71.9	77.1	83.9
Fe-HDTMA pillared bentonite	93.1	87.0	84.7	88.3	90.6	89.1

in the HDTMA$^+$, which forms the fixed force with the ions from the bentonite surface. The other end with hydrophobe long carbon chain group of HDTMA$^+$ is freely exposed to the solution, and strongly adsorbs the organic dye molecule or ions from the solution. This hydrophobe group can maintain the same properties when the pH value of the solution changes.

Sorption isotherms

To gain further understanding of the behavior and mechanism of pillared bentonites with reactive red X-3B, the isotherms of these 4 pillared bentonites were studied (results shown in Fig.3, where C_e represents the equilibrium concentration of reactive red X-3B in the solution). All isotherm curves of reactive red X-3B on these pillared bentonites showed the classical characteristics of the Langmuir-type sorption equation with R^2 of 0.99 (Table 4). This sorption has been also analyzed using a double reciprocal plot based on the following Langmuir-type sorption equation (Fig.4, data in the plots were obtained from Fig.3):

$$1/q=1/q_0+1/kq_0C,$$

where q is the surface-bound reactive red X-3B (mg/g), q_0 is the monolayer capacity for reactive red X-3B sorption (mg/g), C is the solution-phrase reactive red X-3B concentration (mg/L), and k is the binding constant (ml/g). The straight lines drawn through the data points represent the best least square fits of the data for a value of 0.99 for the 4 pillared bentonites. The plots for these 4 pillared bentonites are statistically indistinguishable, and fit very well with Langmuir-type sorption equation.

Table 4 Regression data for sorption isothermal curves

No.	Regression equation	Regression coefficient
2#	$y=-0.0006x^2+0.2992x-0.7444$	$R^2=0.9947$
3#	$y=-0.0002x^2+0.3099x-0.07226$	$R^2=0.9967$
4#	$y=-0.0003x^2+0.2592x-0.4101$	$R^2=0.9994$
5#	$y=-0.0008x^2+0.3069x-0.4830$	$R^2=0.9967$

Note: Data was got from Fig.3

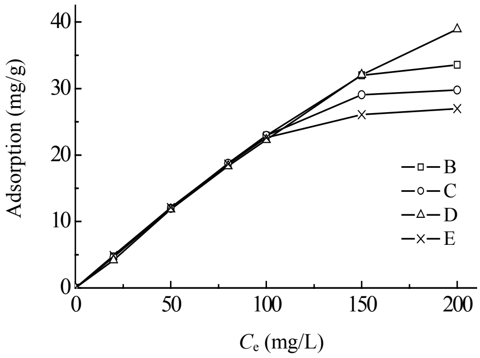

Fig.3 Isotherms of reactive red X-3B on pillared bentonites

B: Fe-HDTMA pillared bentonite; C: Ca-HDTMA pillared bentonite; D: Al-HDTMA pillared bentonite; E: Mg-HDTMA pillared bentonite

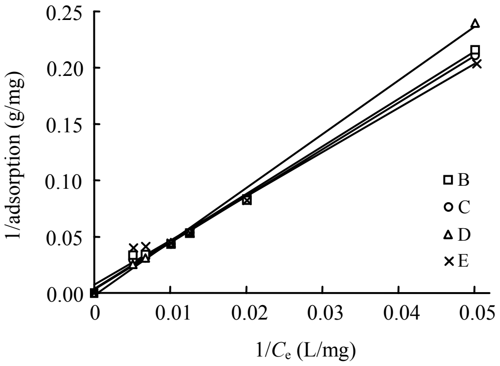

Fig.4 Double reciprocal plot of sorption of reactive X-3B

B: Fe-HDTMA pillared bentonite; C: Ca-HDTMA pillared bentonite; D: Al-HDTMA pillared bentonite; E: Mg-HDTMA pillared bentonite

CONCLUSION

When normal inorganic and organic cations were intercalated into natural bentonite, pillared inorgano-organo bentonites could be prepared with much better improved physical properties. These pillared bentonites can remove reactive red X-3B from the simulated dye wastewater with 90% removal, suggesting that they would be better and cheaper sorbents in the treatment of industrial organic pollutants. The sorption isotherms fit very well with Langmuir-type sorption equation, showing Langmuir-type sorption mechanism.

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