Adsorption of Direct Green B on mixed hydroxy-Fe-Al pillared montmorillonite with large basal spacing

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Abstract: Through cation-exchanging of montmorillonite, mixed hydroxy Fe-Al-pillared montmorillonites with large basal spacing were synthesized. The application of these mixed hydroxy Fe-Al-pillared montmorillonites as adsorbents in the areas of environmental protection and pollution control was investigated. Adsorption of Direct Green B, an organic dye, on OH—Fe—, OH—Al—, OH—Fe—Al— pillared montmorillonites was studied. Results showed that these pillared montmorillonites had much better adsorption properties than traditional Na-organo-montmorillonite. It was also found that pH of the solutions had great effect on the performance of these hydroxy-metal pillared montmorillonites in treating the wastewater containing Direct Green B.

Keywords: hydroxy-Al-Fe; montmorillonite; preparation; characterization; Direct Green B; adsorption

Introduction

Montmorillonite, the primary constituent of bentonite, is a clay mineral with expandable layer structure. Isomorphous substitution of montmorillonite results in a net permanent positive charge, therefore it has the reversible cation exchange capability and plastic properties. Pillared montmorillonite can be prepared by introducing gallery templates, such as simple metal cations, quaternary ammonium cations, long chain amines cations, and hydroxyed inorganic metal ions. These mesoporous pillared-montmorillonites have been widely applied as wastewater sorbents and as catalysts (Pusino, 1995; Steven, 1998; Christophe, 2000; James, 1994; Wibulswas, 1999; Zhang, 1993; Dentel, 1998; Hermosin, 1992). Nevertheless, previous research activities paid much attention to organo- and simple metal pillared-montmorillonite.

In a previous paper, we reported a new method for the synthesis of mixed hydroxy-Al-Fe montmorillonite with large basal spacing. With this method, we successfully obtained OH-Fe-(m = OH^-/Fe = 1.0)-montmorillonite with d(001) value of 77.5×10^{-10} m, OH-Fe-Al(m = 1.0, Fe/(Fe + Al) = 0.5)-montmorillonite with d(001) value of 81.8×10^{-10} m (Zeng, 2004).

Since OH-Fe-, OH-Fe-Al-montmorillonites prepared in our lab have the largest basal spacing so far reported in the literatures (Rightor, 1991; Doff, 1988; Mandalia, 1998), we anticipated that these pillared montmorillonites would have superior adsorption properties than other pillared montmorillonites. To verify this, we carried out experimental studies on the adsorption of Direct Green B, an organic dye, on OH—Fe—, OH—Fe—Al-montmorillonites. The work is reported and discussed in this paper.

1 Materials and methods

1.1 Materials

The raw bentonite used in this work was a naturally occurred mineral located in Lin'an, Zhejiang Province, China. It contains about 60% montmorillonite with cation exchange capacity (CEC) of 62 meq/100g. The composition of this clay by XRF spectroscopy analysis showed that it contains 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, 0.3% TiO_2, and 0.03% P_2O_5.

Before being used, the raw bentonite was first purified with 0.3 wt% ($NaPO_3$)$_6$ solution for three times. The content of montmorillonite in the purified clay increased to more than 98% (determined by XRD analysis). This purified montmorillonite was then fully converted into Na-form by further washing with 1.0 mol/L NaCl solution for five times, and then again washed with deionized water to remove residual Cl^- completely (determined by $AgNO_3$ test). Thus obtained sample was centrifuged, and dried at room temperature, then ground and sieved into powder with particle size < 2 μm. The final sample was calcinated at 105℃ for 1 h. XRF spectroscopy analysis showed that the montmorillonite contains 1.1% CaO, 2.8% Na_2O after the above processing.

NaCl, $AlCl_3$, Fe(NO_3)$_3$, NaOH, H_2SO_4, $AgNO_3$ and hexadecyltrimethylammonium bromine, were of analytical grade and used as received. The Direct Green B was obtained from Hangzhou Xidebao Silk Ltd, Zhejiang Province, China. Solutions were prepared with deionized water. The pH of Direct Green B solution was adjusted to the range of 2—12 by adding either concentrated H_2SO_4 or NaOH solution.

1.2 Preparation of mixed hydroxy Fe-Al-pillared montmorillonite with large basal spacing

The mixed hydroxy Fe-Al-pillared montmorillonite samples were prepared with the following procedures: (1) mix Na-montmorillonite powder with certain amount of deionized water to make a 1.0 wt.% Na-montmorillonite aqueous suspension; (2) add hydroxy Al, hydroxy Fe, or mixed hydroxy Fe-Al pillaring oligocations solution slowly into the Na-montmorillonite suspension while stirring vigorously until the final ratio of metal cation to Na-montmorillonite was reached (10 mmol/g for hydroxy Al-montmorillonite, 70 mmol/g for other hydroxy metal pillared montmorillonite); (3) age above-obtained mixture for 2 d at 60 ± 0.5℃ for hydroxy Al-montmorillonite, or at room temperature for

hydroxy Fe and mixed hydroxy Fe-Al-montmorillonite; (4) the solid materials were collected from the above-aged mixture by filtration; (5) remove the excess salt from the above-collected solid by washing with deionized water until it was free of Cl^- ions(determined by $AgNO_3$ test); (6) the solid samples were dried at room temperature and then ground and sieved them to < 2 μm powder.

Hexadecyltrimethyl$^+$ was used as the organic cation in this study. Organo-montmorillonite sample was synthesized by mixing 1.0 wt% Na-montmorillonite aqueous suspension with hexadecyltrimethylammonium bromine. The procedure was the same as for making mixed hydroxy Fe-Al-pillared montmorillonite samples, except that there was no aging time for making organo-montmorillonite sample.

1.3 Characterizations

The above-made Na-organo-, OH-Al-, OH-Fe- and mixed OH-Al-Fe-pillared montmorillonites were characterized with XRD, BET and XRF analysis. Samples for XRD analysis were prepared in thin films, and recorded by a Philips X' Pert MPD instrument. Porosity and surface areas of the samples were measured with the three-point BET method on a Coalter Omnisorp 100 surface analyzer. Prior to BET analysis, samples were outgassed at 300℃ under a flow of argon for 3 h. XRF data of samples were heated at 105℃ for 24 h, and obtained on a Siemens SRS-3000 Sequential X-ray Fluorescence(XRF) Spectroscopy.

1.4　Adsorption of Direct Green B on pillared montmorillonites

The Direct Green B contaminated wastewater was simulated by dissolving Direct Green B into deionized water. The concentration of Direct Green B in this wastewater was 0.0250 g/L. Pillared montmorillonites were weighed and added into 25 ml of the above Direct Green B solution in a pluged glass jar. The mixture was then mixed for 1.0 h in a shaker to allow the adsorption to be fully completed. The solid-liquid separation of above mixture was conducted using a high-speed centrifuge for 10 min. The liquid layer was collected and analyzed with UV-spectrophotometer at the wavelength of 618.8 nm to determine the concentration of Direct Green B in the liquid phase. The amount of Direct Green B adsorbed by montmorillonite was calculated by different concentrations of Direct Green B in the liquid before and after adding pillared montmorillonites.

2　Results and discussion

Direct Green B is one of the commonly used organic dyes in textile mills. Its molecular structure is shown in Fig. 1. Due to several double-single-double chemical bindings in the molecules of Direct Green B, it exhibits a dark green color in aqueous solution. There are two absorbance peaks in its UV-spectrum, one in visible light range with maximal absorbance wavelength at 618.8 nm, and the other one in invisible light range with maximal absorbance wavelength at 368.8 nm.
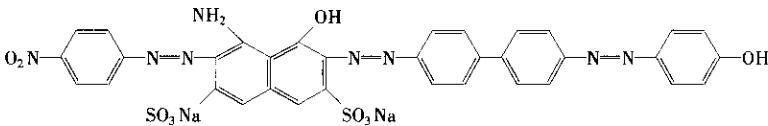

Fig.1　The structure of Direct Green B

Table 1 shows the percentage of Direct Green B removed from the wastewater as a function of the amount of pillared montmorillonites used. It includes the data for Na-organo-, OH-Al-, OH-Fe-, and OH-Fe-Al-montmorillonites. Since the adsorption of Direct Green B on Na-montmorillonite was too low(close to 0%), its results is not listed in the table. The experiments were conducted at temperature of 25℃ with a mixing time of 1.0 h. As shown in the table, all four pillared montmorillonites exhibit up to 84%—99.8%. OH-Fe-Al-montmorillonite showed the highest adsorption capacity among all the montmorillonite with the removing rate of Direct Green B close to 100%.

The adsorption characteristics of an adsorbent are strongly correlated to its micro- or meso-pore structure and surface properties. One major parameter for characterizing the pores in the montmorillonites is the basal spacing. We determined the basal spacing of all the montmorrillonites used in this study by XRD analysis. The results are listed in Table 2.

Table 1　Effect of the amount of pillared montmorillonites (g) used on the percentage of Direct Green B (%) removed from the wastewater

	0.0100	0.0150	0.0200	0.0250	0.0300	0.0350
Na-organo-Mt	45.3	54.4	67.1	73.9	79.8	84.1
OH-Al-Mt	26.5	45.4	69.4	72.7	85.7	96.0
OH-Fe-Mt	32.9	55.3	75.4	82.8	86.9	88.9
OH-Fe-Al-Mt	42.4	73.7	82.1	93.0	99.3	99.8

Notes: Mt = montmorillonite

As shown in Table 2, the basal spacings of the unpillared montmorillonites, i. e., raw bentonite (Ca-montmorillonite) and Na-montmorillonite, are as low as 15.2 × 10^{-10} m and 12.6 × 10^{-10} m. The raw bentonite has a basal spacing slightly larger than the Na-montmorillonite. This is because the hydration radius of Ca^{2+} is larger than that of Na^+. Hydroxy Al pillaring solution contains large inorganic Keggin ions, $[AlO_4Al_{12}(OH)_{24}(OH_2)_{12}]^{7+}$ (Al_{13}^{7+} ions). The basal spacing value of OH-Al-montmorillonite in Table 2 is close to that reported by other researchers.

Table 2　XRD data of raw and pillared montmorillonites: d(001) × 10^{-10} m

	Raw clay	Na-Mt	Na-organo-Mt	OH-Al-Mt	OH-Fe-Mt	OH-Fe-Al-Mt
d(001) × 10^{-10} m	15.2	12.6	22.8	18.6	81.8	77.5

Note: Mt = montmorillonite

More notably, the basal spacings of the montmorillonites increase as much as five folds after being pillared with OH-

Fe- and OH-Al-Fe- cations, the d(001) value of the pure

OH-Fe-montmorillonite was 81.8×10^{-10} m, while that of mixed OH-Al-Fe-montmorillonite was 77.5×10^{-10} m. The hydrolysis of ferric ion with bicarbonate led to the formation of a large polymer of $[Fe(OH)_x(NO_3)_{3-x}]_n$ (Spiro, 1966). Most of polymer particles were isolated spheres with about 70 $\times 10^{-10}$ m in diameter. Therefore, the intercalation of these polycations into montmorillonite can dramatically increase basal spacing of pillared montmorillonite.

Besides the basal spacing, other two parameters that are used to characterize the pore structures of adsorbents are surface area and pore volume. In this study, the surface area and pore volume of the montmorillonites are measured by BET method in which N_2 was used as the probe gas and the measurement was conducted at 77 K(liquid N_2). The results are given in Table 3. As shown in the table, the montmorillonites pillared with OH-Al-, OH-Fe- and OH-Fe-Al- ions have surface areas 7—9 times that of Na-montmorillonite. This is consistent with the results that the former have much larger basal spacing than the latter. It also explains why OH-Al-, OH-Fe- and OH-Fe-Al-montmorillonites have much higher adsorption capacity than Na-montmorillonite. On the other hand, OH-Al-, OH-Fe- and OH-Fe-Al- montmorillonites also showed little improvement on their pore volumes over the Na-montmorillonite.

Table 3 Surface areas, pore volumes of Na- and pillared montmorillonite

	Na-Mt	OH-Al-Mt	OH-Fe-Mt	OH-Fe-Al- Mt
$S.A.$, m^2/g	26.9	229.6	201.0	213.4
$V_p.$, cm^3/g	0.13	0.21	0.19	0.20

Notes: Mt = montmorillonite; $S.A.$: surface areas; V_p: pore volumes

In addition to the pore structure, the surface properties of the montmorillonites can also greatly affect their adsorption capability. For removing or adsorbing organic materials, it is expected that the surface of the adsorbent to be hydrophobic. The low adsorption capacity of raw bentonite and Na-montmorillonite is consistent with the fact that their surfaces are hydrophilic and therefore prevent organic substance to be adsorbed onto their surface. When Na-montmorillonite was ion-exchanged with long chain alkyl group (hexadecyl-trimethylammonium bromine), the large organic cations have been inserted into its layer structure. These organic cations not only increase the basal spacing of the montmorillonites as shown in Table 2, but also turn their surfaces from hydrophilic to strongly hydrophobic. Therefore, Na-organo-montmorillonites also showed much improved capability for removal of Direct Green B.

Although the OH-Al-montmorillonite has a much smaller basal spacing than OH-Fe-montmorillonite as shown in Table 2, the former has the same adsorption capability for Direct Green B as the latter, as indicated in Table 1. This could be explained by the fact that OH-Al-montmorillonite has slightly larger surface area and pore volume than OH-Fe-montmorillonite, as shown in Table 3. This illustrated that the adsorption capability of montmorillonites is also ultimately affected by their pore structures, not only by the values of basal spacing.

As we know, a good adsorbent has not only high equilibrium capacity but also fast adsorption rate, i. e.,

kinetics. To study the adsorption kinetics of the montmorillonites, we investigated effect of mixing time on the adsorption of Direct Green B on montmorillonites (shown as removal percentage). The amount of montmorillonite used was 25 mg and the amount of Direct Green B was 0.625 mg in 25 ml aqueous solution. The experiments were conducted at 25 ℃. The results are given in Fig.2.
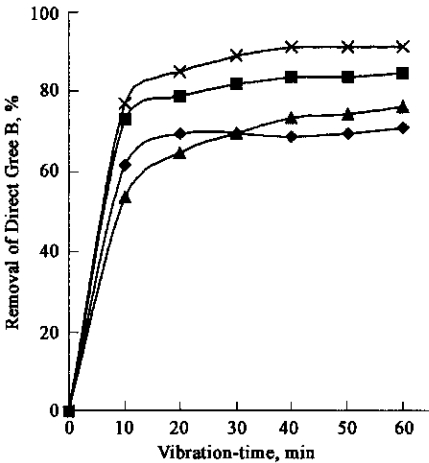

Fig.2   Effect of mixing time on the removal of Direct Green B
× : OH-Fe-Al-Mt; ■ : OH-Fe-Mt; ◆ : Na-organo-Mt; ▲ : OH-Al-Mt; Mt: montmorillonite

As shown above, the adsorption of Direct Green B on the montmorillonites, except OH-Al-montmorillonite, reached their equilibrium capacity in less than 30 min. The slower adsorption kinetics of OH-Al-montmorillonite reveals that its pore size is much smaller than those of other montmorillonites. This is consistent with the fact that it has higher surface area and similar pore volume as compared with other montmorillonites. It must be pointed out that all montmorillnites reached their equilibrium adsorption capacity in less than one hour. Therefore, the mixing time for other experiments in this study was selected as 1.0 h to ensure that the adsorption of Direct Green B by montmorillonite was completed.

Since the montmorillonites contain cations in their basal space, the pH of the wastewater solution would affect their adsorption capability. In this study, experiments were also designed and carried out to investigate the effect of pH on the adsorption of Direct Green B on the montmorillonites. The experiment conditions were the same as those conducted. The results are illustrated in Fig.3. As shown in the figure, the change of pH value from the range of 2.0 to 12.0 had little effect on the adsorption capability of Na-organo-montmorillonite. Because the polar side of hexadecyl-trimethylammonium ion is strongly bound to the montmorillonite, organo-pillared montmorillonite has a hydrophobic property. The adsorption of Direct Green B on it is essentially a non-polar molecule interaction process. Since the organic side of Na-organo-montmorillonite could not be affected by the change of solution pH, it maintained the performance of removing 90% of Direct Green B throughout the pH range used in this study.

H^+ ions from the acid solution can be exchanged with other exchangeable cations in the interlayer of
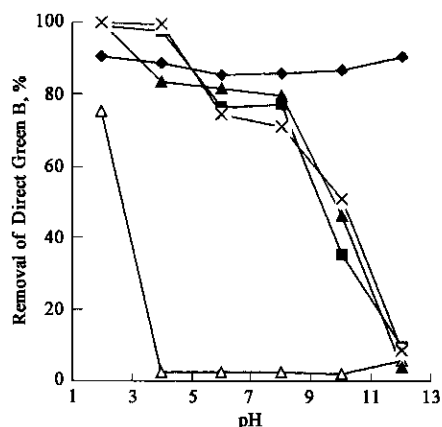
Fig.3   Removal of Direct Green B as a function of pH
× : OH-Fe-Al-Mt; ■ : OH-Fe-Mt; ◆ : Na-organo-
Mt;   ▲ :   OH-Al-Mt;   △ :   Na-Mt;   Mt:
montmorillonite

montmorillonite, such as Na^+ . Therefore, they can enter the porous basal space, and occupy the active sites for the adsorption. On the other hand, the aquatic particles of Direct Green B have negative charges, thus they can be readily attracted and adsorbed by H^+ -montmorillonite, and removed from the aqueous phase. This is why all of five montmorillonites exhibited good adsorption capability under strong acid conditions. The pH effect becomes more prominent for the montmorillonites with very small adsorption capacity at higher pH, such as Na-montmorillonite, it can remove almost 80% of Direct Green B when pH is 2.0, while it adsorbs little Direct Green B when pH is higher than 2.

At pH lower than 5, the adsorption capacities of Direct Green B on OH-Fe-, and OH-Fe-Al-pillared montmorillonites are very high. They removed almost 100% of Direct Green B from the wastewater solution. Besides their big spacing basal which enable them to take great amount of Direct Green B onto their porous structures, another important reason is that the metal atoms of these polymerized cations may form coordination binds with organic dye molecules. To verify this, we measured UV-spectrums of Direct Green B in aqueous and adsorption phases. The results are summarized in Table 4. As shown in the table, the wavelength values of two absorbance peaks (λ_{max1} = 618.4 nm; λ_{max2} = 368.8 nm) in UV-spectrum of Direct Green B before and after adsorption showed little changes when it is adsorbed onto Na- and Na-organo montmorillonites. This means that the adsorption is truly physical one.

Table 4 λ_{max} data of Direct Green B after treated by pillared-montmorillonites

	Na-Mt	Na-organo-Mt	OH-Al-Mt	OH-Fe-Mt	OH-Fe-Al-Mt
λ_{max1} , nm	619.0	614.0	668.0, 614.2	674.2, 623.2	671.6, 620.4
λ_{max2} , nm	376.4	369.0	385.0, 338.4	376.6, 328.4	384.6, 339.0

Notes: Mt = montmorillonite

As shown in Table 4, after being adsorbed with OH-Fe-, OH-Fe-Al, OH-Al-pillared montmorillonites, first

absorbance peak (λ_{max} at 618.4 nm) of Direct Green B is split into two absorbance peaks with λ_{max} relative to about 660—670 nm and 610—623 nm respectively. The difference between these two maximal absorbance wavelengths is about 50 nm. The second absorbance peak (λ_{max} at 376.4 nm) is also separated into two, one at 376—387 nm, another at 328—339 nm. All these changes strongly suggested that some coordination binds have been formed between the active groups of Direct Green B and the Fe or Al atoms of hydroxy metal pillared montmorillonite.

When pH is adjusted into basic range, the adsorption capacities of Direct Green B on hydroxy Fe, Al pillared montmorillonites sharply decrease. Less than 10% of Direct Green B is removed at pH value of 12.0. This is due to the instability of hydroxy metal ions in basic solution. With the increase of basicity, most of hydroxy metal ions are decomposed and the interlayer structure of these pillared montmorillonite is also collapsed.

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