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The sedimentation capabilities of hexadecyltrimethylammonium-modified montmorillonites

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Abstract

Natural montmorillonite was modified with a quaternary ammonium compound, hexadecyltrimethylammonium (HDTMA). The sedimentation capabilities of unmodified and modified montmorillonites were then investigated. The sedimentation velocity of modified montmorillonites increased if the amounts of adsorbed HDTMA were from 0.3 to 1.0 times the cation exchange capacitity (CEC). It also emerged that the sedimentation capability of modified montmorillonites was improved and that the variously CEC-modified montmorillonites had similar sedimentation capabilities after they had sorbed organic matter from oily wastewater. Thus, modified montmorillonites (especially 0.5 CEC treatment) had good sedimentation capabilities for sorbing organic substance and can act as carriers in wastewater biotreatment.

Keywords: Modified montmorillonite; Hexadecyltrimethylammonium; Sedimentation capability; Organic substance

1. Introduction

In recent years there have been reports of the use of surfactant modified clays to sorb neutral organic contaminants (NOCs) from water (e.g. Boyd et al., 1988a,b; Lee et al., 1989; Smith et al., 1990; Staleton and Sparks, 1994; Wagner et al., 1994; Xu and Boyd, 1995a,b; Zhu et al., 1997). These results have demonstrated that modified clays have great sorptive capabilities for NOCs. Clays are ineffective sorbents for NOCs because their surfaces are hydrophilic. However, since there are some exchangeable inorganic cations in clays, their sorptive capabilities for NOCs can be greatly enhanced by substituting them with quaternary ammonium compounds (QACs). Thus modified clays can potentially be used as sorbents to treat wastewater. Modified montmorillonite is one of these organo-clays that has been much researched. It has the capacity to adsorb benzene and oily hydrocarbons in surface water and groundwater (Smith and Jaffe, 1994; Gao et al., 2000). There are many microorganisms with a capacity to degrade oily contaminants in the environment (Cho et al., 1997), and these microorganisms are able to grow very well when a hexadecyltrimethylammonium (HDTMA) loading is less than 0.5 times the cation exchange capacitity (CEC) of modified montmorillonites (Gao et al., 2000). Moreover, contaminants sorbed by HDTMA-modified soil or clays should be largely bioavailable to bacteria since the desorption rates from these materials are high and some degradative bacteria have the ability to directly utilize the sorbed contaminants (Nye et al., 1994; Crocker et al., 1995). Thus, a combination of modified montmorillonite with hydrocarbon-utilizing microorganisms may enhance the efficiency of oil biotreatment.

In order to understand whether modified clays are good carriers in wastewater treatment other characteristics must be considered in addition to their sorptive capabilities. Issues to be considered include: (1) sedimentation rate, (2) stability, and (3) possible desorption

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of the adsorbed organic contaminants from modified clays. If modified clays have good sedimentation capabilities and they are stable, they can be used as sorbents which may be separated immediately from aqueous solution through sedimentation without a need to add flocculants. Moreover, modified clays can become carriers in an aerobic fluidized reactor, because they have small size, high surface area-to-volume ratio and a large capacity for adsorption of organic contaminants. When the adsorbed organic contaminants are bioavailable these sorptive capabilities can buffer the high organic load in the process of wastewater biotreatment.

In the present study, montmorillonite was modified with different amounts of HDTMA. The sedimentation capabilities of these modified montmorillonites were investigated in detail to determine whether or not they sorb organic substances from oily wastewater. The aim of this study was to assess the possibility of using modified clays as carriers in wastewater biotreatment from their sedimentation capabilities. Our findings showed that the modified clays have great potential sedimentation capabilities whether or not they sorb organic substances. Thus, modified montmorillonites may be useful carriers in wastewater biotreatment.

2. Materials and methods

2.1. Clays

Natural montmorillonites were obtained from the Institute of Geology, Nanjing. The properties of these montmorillonites are shown in Table 1. Natural montmorillonites have almost no organic matter content but a high CEC.

2.2. Reagents and wastewater

HDTMA bromide (AR grade) used in this study was obtained from Shanghai Reagent Company. Oily wastewater was supplied by the Nanjing Refinery.

2.3. Analytical methods

In order to determine if modified montmorillonites sorbed organic substances in oily wastewater the amounts of organic substances were expressed by total organic carbon (TOC) determined with TOC-500. Sedimentation capabilities of modified montmorillonites in aqueous solution were estimated from the optical density (OD) of the upper suspension measured using a spectrophotometer at 450 nm. Weights of modified montmorillonites were measured in the upper suspension to understand the relationship between their concentrations with OD.

2.4. Modified montmorillonites

HDTMA bromide was dissolved in warm distilled water to produce a 0.03 M solution. To make HDTMA-modified montmorillonites, the natural montmorillonites were mixed with the HDTMA solution according to 0.3–1.0 times their CEC and stirred for about 8 h. The suspensions were then left to stand to separate modified montmorillonites from the liquid phases. The liquid phases were decanted and the modified montmorillonites were washed with distilled water several times until free of Br^+. These modified montmorillonites were dried at 40 °C. Dried samples were then ground in agate mortars, passed through a sieve and stored for future use. The physicochemical characteristics of modified montmorillonites are shown in Table 1.

2.5. Sorption of organic substances in oily wastewater

Weighed batches of the quantitatively modified montmorillonites and measured volumes of oil wastewater were added to appropriate size conical flasks. To obtain the sorption equilibrium a series of suspensions were placed on a thermostatically controlled shaker for 3 h at 30 °C (preliminary experiments indicated that sorption equilibrium was reached in 2.5 h). The sorbed organic substances from the modified montmorillonites were then separated by centrifugation of the suspensions.

2.6. Measurement methods for sedimentation capabilities of modified montmorillonites

Modified montmorillonites were added to distilled water and the suspensions were stirred and then poured into a series of conical flasks. The OD and the weight of

Table 1
The physicochemical characteristics of natural and modified montmorillonites

	Natural	0.3 CEC	0.5 CEC	0.7 CEC	1.0 CEC
CEC (cmol/kg)	94.5				
Organic matter (%)	NM	7.20	11.8	15.8	21.2
The interlayer spacing (nm)	1.54	1.84	2.05	2.31	2.47

NM—organic matter content was below the measure limit.

modified montmorillonite in the upper suspension were measured at hourly intervals until the optical density stabilized. For measurement of sedimentation capabilities of modified montmorillonite sorbed organic substances, centrifuged samples also were added to distilled water in the same way.

3. Results and discussion

3.1. Relationship of OD with concentration of modified montmorillonites

In order to rapidly measure the concentration of modified montmorillonites, the ODs of suspensions were measured while the masses of modified montmorillonites were quantified in suspensions. The results showed that the concentration of modified montmorillonites had a linear relationship with OD of the suspension (Fig. 1). Thus, the concentration of modified montmorillonites could be represented by OD in upper suspension.

3.2. Sedimentation capabilities of differently CEC-modified montmorillonites

The results of the sedimentation capabilities of differently CEC-modified montmorillonites are shown in Fig. 2. The sedimentation capabilities of modified montmorillonites were in the order: 1.0 CEC > 0.7 CEC > 0.5 CEC > 0.3 CEC > natural. When the amounts of HETMA in the modified montmorillonites increased, their sedimentation velocities increased.

The sedimentation capability of clay depends on its composition, size and surface charge in the modified montmorillonite. Natural montmorillonite has permanent negative charges on its surface so it can be modified by a cation surfactant. The amount of negative charges is determined by the quantity of HDTMA in a modified montmorillonite. If an adequate amount of HDTMA (>1.0 CEC) is mixed with montmorillonite, the modified montmorillonite has a positive charges on its surface. The sedimentation capabilities of modified montmorillonites can change, as their surfaces have different kinds and quantities of charges. Thus, if the amounts of HDTMA in modified montmorillonites increased from 0.3 CEC to 1.0 CEC, the hydrophobic tails of adsorbed HDTMA on clay surfaces also increased and total negative charges decreased, then repellency of particles was low and the sedimentation capabilities of modified montmorillonites were improved. This phenomenon was confirmed by testing the electrophoretic mobility of modified clays (Xu and Boyd, 1995a). The decreased turbidity indicated an increase of clay aggregation as cations on natural montmorillonite surfaces were replaced by HDTMA.

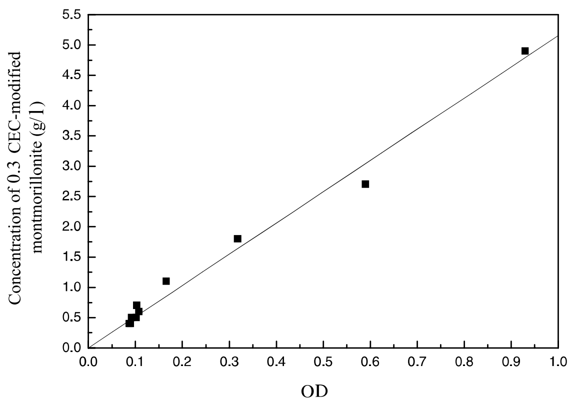

Fig. 1. The relationship of OD with concentration of 0.3 CEC-modified montmorillonite in suspension.

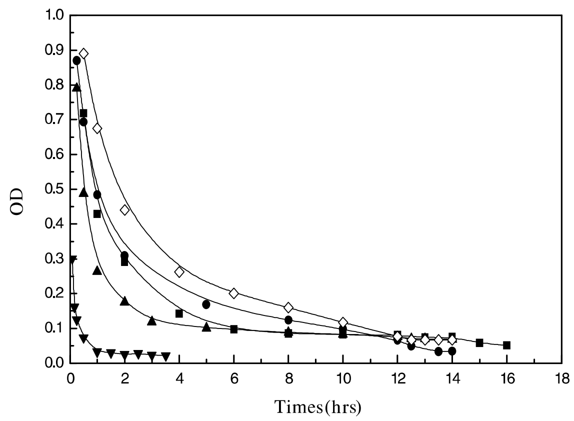

Fig. 2. The sedimentation capabilities of modified montmorillonites: 0.3 CEC (■), 0.5 CEC (●), 0.7 CEC (▲), 1.0 CEC (▼) and natural (◇).

3.3. Sedimentation capabilities of modified montmorillonite sorbed organic substances

The organic substances here were NOCs which were aromatic compounds and long-chain hydrocarbons in oily wastewater. After the various CEC-modified montmorillonites sorbed the organic substances from 500 ml oily wastewater, their sedimentation capabilities showed a predictable trend (Fig. 3), and their sedimentation velocities were improved after they sorbed organic substances (Fig. 4). The sedimentation velocities of 1.0 CEC-modified montmorillonite did not change. These results indicated that the turbidity of suspension of modified montmorillonites had nothing to do with their interlayer structures but their surface structures. There were many long-chain hydrocarbons on their surfaces no matter how much HDTMA they adsorbed, so the differences of their surface characteristics disappeared.

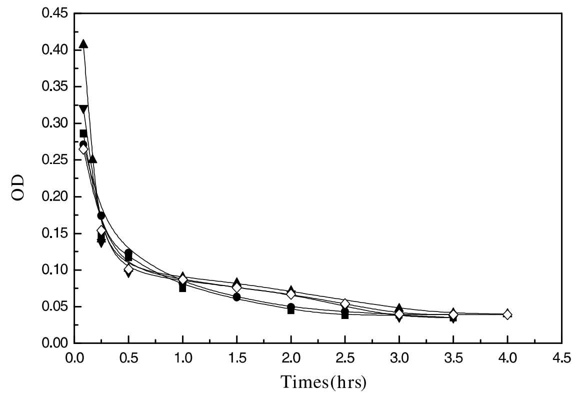

Fig. 3. The sedimentation capabilities of modified montmorillonites sorbed organic substances: 0.3 CEC (■), 0.5 CEC (●), 0.7CEC (▲), 1.0 CEC (▼) and natural (◇).

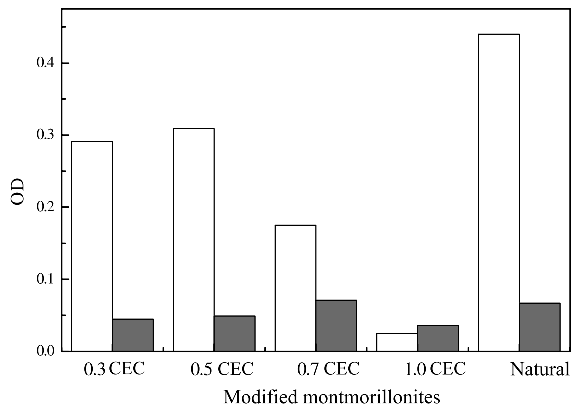

Fig. 4. The comparison between sedimentation capabilities of modified montmorillonites sorbed organic substances and that not sorbed organic substances after 2 h: without sorbed organic substance (□) and with sorbed organic substance (■).

The sedimentation capability of unmodified montmorillonite with organic substance was better than that without organic substance. The reason for its good sedimentation capability was that the covered organic substances enhanced its hydrophobic characteristics.

Modified montmorillonites had many hydrophobic tails of HDTMA on their surfaces; the long-chain hydrocarbons contacted them easily from wastewater and the amounts of hydrocarbons were high on their surfaces. Thus, the modified montmorillonites had similar surface characteristics if their surfaces were covered with enough organic compounds, because the surface charges on montmorillonites covered with organic compounds could not contact water directly. The increased hydrophobic characteristics of their surfaces facilitated their sedimentation.

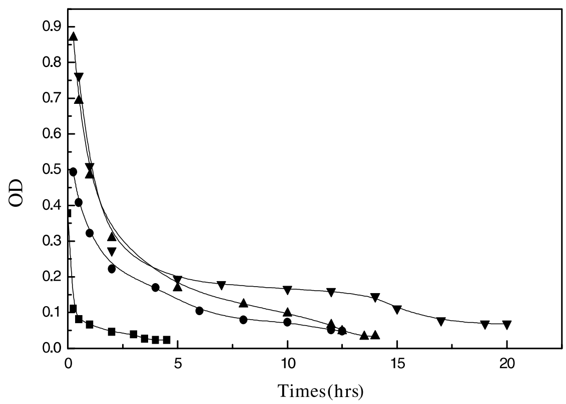

Fig. 5. The sedimentation capabilities of different concentrations of 0.5 CEC-modified montmorillonite in the aqueous solution: 1 g/l (■), 3 g/l (●), 5 g/l (▲) and 7 g/l (▼).

3.4. Sedimentaton capabilities of different concentrations of 0.5 CEC-modified montmorillonite in suspension

When the amount of added modified montmorillonites was enlarged in suspension, turbidity increased and the time of sedimentation was long in the upper suspension (Fig. 5). If its concentration was above 5 g/l, the aggregation of organo-clay particles was improved, so the measured ODs at 5 and 7 g/l were similar from 0 to 5 h.

The sizes of particles were variable for 0.5 CEC-modified montmorillonite in the aqueous solution, and the sedimentation velocity of small particles was slow. Thus, the greater the amount of 0.5 CEC-modified montmorillonite in the aqueous solution, the greater was concentration of small particles. This was the reason that the OD of upper suspension increased as the concentration of modified montmorillonite increased in the aqueous solution. If the concentration of modified montmorillonite was higher enough, the interaction of particles increased, and it was easy for small organo-clay particles to aggregate to form larger particles. Thus, it is very important that appropriate contents of modified montmorillonite are chosen, when modified montmorillonite are used as carriers to treat wastewater.

3.5. Sedimentation capabilities of 0.5 CEC-modified montmorillonite sorbed different amounts of organic substances

Fig. 6 shows the results of the experiment to show sorption of organic substances by modified montmorillonite. As the volume of wastewater treated by modified montmorillonites increased, the sorption capacity of 0.5 CEC-modified montmorillonite tended to saturation. The maximum amount of organic substances was

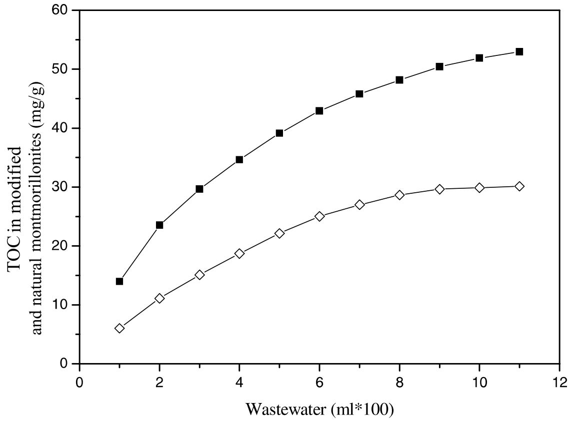

Fig. 6. The relationship of content of organic substances sorbed by modified and natural montmorillonites with the volume of oily wastewater: 0.5 CEC (■) and natural (◇).

less than 60 mg (TOC)/g in 0.5 CEC-modified montmorillonite.

After 0.5 CEC-modified montmorillonite sorbed more amounts of organic contaminants, its sedimentation capability improved (Fig. 7). If the surface of modified montmorillonite was covered with organic compounds it became hydrophobic. Thus, the sedimentation capability increased.

The organic substances sorbed by modified montmorillonites could be made up two parts. One entered into organo-clay interlayers, the other covered the organo-clay surfaces. The amounts of oily hydrocarbons covered on surfaces of modified montmorillonite determined its hydrophobic characteristics. When the amounts of hydrophobes were higher, the aggregation capabilities of particles were improved. Thus, the organic substances sorbed on modified clays could enhance sedimentation capability.

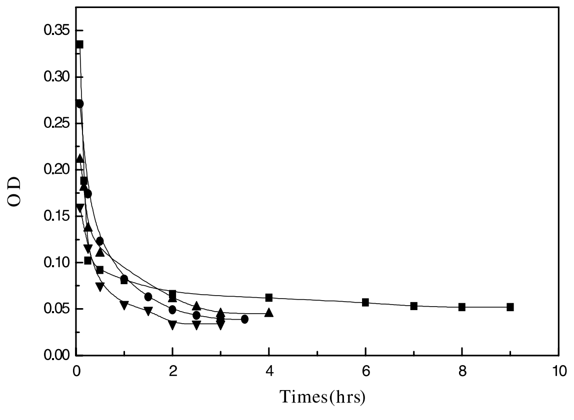

Fig. 7. The sedimentation capabilities of 0.5 CEC-modified montmorillonites sorbed different contents of organic substances: 23.53 mg/g (■), 39.15 mg/g (●), 48.18 mg/g (▲) and 52.95 mg/g (▼).

4. Conclusion

Montmorillonite was modified with QACs HDTMA, before its sedimentation characteristic was investigated. The experimental results showed that the modified montmorillonite had a good sedimentation capability whether or not it had sorbed organic matter. Sedimentation velocity of modified montmorillonite was higher in aqueous solution if the amounts of HDTMA and organic substances from water sorbed on it were larger. Thus modified montmorillonites can be separated from water quickly when they sorb organic contaminants. In order to understand whether they could act as carriers in wastewater biotreatment, the next step is to research the numbers of microorganisms adhering to the modified montmorillonite. If there are abundant microorganisms on modified montmorillonites, and a combination of modified montmorillonite with microorganisms has improved sedimentation characteristics, they may provide new materials for wastewater biotreatment.

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