

Organobentonites as adsorbents for some organic pollutants and its application in wastewater treatment

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Abstract— Two organobentonites were synthesized by placing quaternary ammonium cations cetyltrimethylammonium bromide (CTMAB) and cetylpyridinium chloride (CPC) on bentonite by cation exchange. Their ability to adsorb phenol, aniline, nitrobenzene and p-nitrophenol were examined. The optimal conditions for organobentonites to remove the organic pollutants from water were studied. The removal rates for organobentonites to treat the organic compounds in water were found to be over 8 times for the original mineral (untreated bentonite). The removal rates of organic pollutants and COD of wastewater were further improved by organobentonites in the presence of aluminum sulfate. The structure of organobentonites and the mechanism for their adsorption were investigated by X-ray diffraction (XRD) analysis, infrared spectra and BET surface area.

Keywords: organobentonites; adsorbents; organic pollutants; wastewater treatment.

1 Introduction

Adsorption is the most common method for treating organic pollutants in wastewater. Activated carbon has been used almost exclusively to adsorb the 129 priority pollutants from wastewater.

The most common component of bentonite is montmorillonite. Bentonite has been used in the water and wastewater treatment (Olin, 1937; 1942), but few studies has been undertaken on specific pollutant of using clay. El-Dib *et al.* (El-Dib, 1978) studied untreated kaolinite and bentonite as adsorbents for removal of soluble aromatic hydrocarbons from drinking water. Zhu *et al.* (Zhu, 1993) reported the removal of heavy metals from wastewater by acidic bentonite. Zhang *et al.* (Zhang, 1994) treated dyeing wastewater by modified bentonite Scpb as a coagulant. McBride *et al.* (McBride, 1977) showed that different kinds of clay-organic complexes have widely different adsorption properties for benzene, phenol and chlorobenzenes. Organobentonites were also used to treat the dyeing wastewater (Zhu, 1994) and organic pollutants (Srinivasan, 1990).

Two organobentonites were synthesized to improve their capacities for adsorbing organic pollutants from water and wastewater by placing cetyltrimethylammonium bromide (CTMAB) or cetylpyridinium chloride (CPC) on bentonite by cation exchange. Quaternary ammonium cations were exchanged for charge-compensating sodium ions in the montmoril-

lonite structure to separate further the montmorillonite unit layers and expose the large interlamellae clay surfaces. The interlamellar surface thus became available for adsorbing organic pollutants from the aqueous phase. The quaternary ammonium ions can also alter the nature of their exposed interlamellar surfaces by making them more hydrophobic and causing certain types of organic to be more strongly attracted. Organobentonites were examined for their ability to adsorb phenol, aniline, nitrobenzene and *p*-nitrophenol. The optimal conditions for organobentonites to adsorb the organic pollutants were studied. The structure of organobentonites and the mechanism for their adsorption were discussed by X-ray diffraction (XRD) analysis, infrared spectra and BET surface area.

2 Experimental

2.1 Materials

The clay used was bentonite from Linan County, Zhejiang Province. Bentonite was prepared from original mineral by drying, grinding into powder (100-mesh). All reagents used were of analytical grade.

2.2 Analytical methods

Phenol, nitrobenzene, aniline and *p*-nitrophenol were determined by ultraviolet spectrophotometry (Ouyang, 1986).

2.3 Preparation of organobentonites

40g previously dried bentonite was mixed with 0.1%–10% cetyltrimethylammonium bromide (CTMAB) or cetylpyridinium chloride (CPC) solutions. The mixtures were subjected to mechanical stirring for 2 hours in 50–60°C water-bath. The treated bentonites were separated by vacuum filtration, washed twice by distilled water. The bentonites were dried at 80–90°C, activated for 1 hour at 105°C and mechanically grinded to less than 100-mesh. Thus, a series of organobentonites were made by placing quaternary ammonium cations on bentonite by cation exchange.

2.4 Procedures for water treatment

0.500g organobentonite was added into 125-ml Erlenmeyer flask containing 50 ml appropriate concentration of organic compound. The flasks were shaken for 1 hour at 25°C on the gyratory shaker at 120 r/min. After centrifuging, the organic compound in the aqueous phase was determined by UV spectrophotometry. The removal rates for organobentonites to treat the organic compounds in water were calculated. The experiments were duplicated.

3 Results and discussion

3.1 Properties of organobentonites

The properties of organobentonites were investigated by X-ray powder diffraction analysis, infrared spectra and N_2 -BET surface areas. The properties of CTMAB-bentonite are listed in Table 1.

Table 1 The properties of CTMAB-bentonite

Surfactant concentration, %	Interlayer spacing, Å	Surface area, m ² /g
2.0	18.181	—
3.0	19.209	13.684
5.0	19.719	9.644
10.0	19.643	—

By placing quaternary ammonium cations on the cation-exchange sites of bentonite, the properties may be significantly altered. The XRD analyses showed that the interlayer spacing of original bentonite is 17.194 Å the interlayer spacing of organobentonites were gradually increased with CTMAB or CPC concentrations used in synthesizing organobentonites. The interlayer spacing of CTMAB-bentonite and CPC-bentonite synthesised in 10% CTMAB or CPC solution were found to be 19.643 Å and 19.533 Å respectively. It was showed CTMAB or CPC surfactant was entered into the interlamellar of bentonite by cation exchange.

Table 1 lists N₂-BET surface areas of several organobentonites. Organobentonite surface areas were decreased with increasing quaternary ammonium surfactant concentrations used in synthesizing because CTMAB or CPC was exchanged into the bentonite interlamellar. For example, the surface area of original bentonite was 43.376 m²/g; the surface areas of 5% CPC-bentonite and 5% CTMAB-bentonite were found to be 10.015 m²/g and 9.644 m²/g, respectively. In addition, it was confirmed by infrared spectra analysis that CTMAB or CPC surfactant entered into bentonite interlamellae by cation exchange.

3.2 Optimal conditions for adsorbing organic compounds

At 25°C, optimal conditions for CTMAB-bentonite or CPC-bentonite to adsorb organic compounds were investigated in detail. The results were listed in Table 2 and Table 3. Concentrations of organic compounds were as follows: aniline, 5 µg/ml; phenol, 10µg/ml; nitrobenzene, 50 µg/ml; p-nitrophenol, 100 µg/ml.

Table 2 Optimal conditions and removal rates for CTMAB-bentonite to treat organic compounds

Condition	Aniline	Phenol	Nitrobenzene	p-nitrophenol
pH	6-12	11-12	3-11	7-9
Shaking time, min	60	10	60	60
CTMAB concentration used in synthesis, %	5.0	12.5	2-3	2.5-7.5
CTMAB-bentonite, g/50ml	2.5	1.0	3.0	1.0
Removal rates, %	63.0	98.0	75.2	91.7

Table 3 Optimal conditions and removal rates for CPC-bentonite to treat organic compounds

Condition	Aniline	Phenol	Nitrobenzene	<i>p</i> -nitrophenol
pH	7-10	11-12	3-11	7-12
Shaking time, min	90	10	60	120
CPC concentration used in synthesis, %	5.0	15.0	2.0-2.5	3.0-5.0
CPC-bentonite, g/50ml	2.0	1.0	2.5	1.0
Removal rates, %	52.0	100	75.8	94.3

3.3 Adsorption characteristics of organobentonites

By placing quaternary ammonium cations with strongly bound organic ligands on the cation-exchange site of bentonite, the surface properties may be significantly altered. Adsorption characteristics of bentonite may be improved. Organobentonites were examined for their ability to adsorb organic pollutants in water. It was showed that the adsorption equilibrium for organobentonites to adsorb organic compounds in water was more quickly reached than the original bentonite. The saturation adsorbing capacities for CTMAB-bentonite and CPC-bentonite to adsorb organic compounds in water were 1-8 times higher than that for the original bentonite (untreated bentonite). The removal rates for organobentonites to treat organic pollutants in water were 4-10 times higher than that for the untreated bentonite. For example, the removal rates for CPC-bentonite and CTMAB-bentonite to treat phenol in wastewater were 8 and 8.6 times higher than that for the untreated bentonite.

The saturation adsorbing capacities of organobentonites and the untreated bentonite were described in Table 4.

Table 4 The saturation adsorbing capacities of organobentonite and untreated bentonite

Unit: mg/g

Organics	Original bentonite	CTMAB-bentonite	CPC-bentonite
Aniline	37.5	130.0	87.5
Phenol	—	75.0	103.5
Nitrobenzene	58.1	117.0	87.6
<i>p</i> -nitrophenol	125.0	475.0	400.0

The adsorption characteristics were improved after placing quaternary ammonium cations on bentonite by cation exchange. The optimal concentration ranges of surfactant in synthesizing organobentonites was studied. The higher removal rate of organic compounds from water were acquired. It was indicated that the order of removal rates for organobentonites to treat organic compounds in water was as follows: phenol > *p*-nitrophenol > nitrobenzene > aniline. The removal rate for CPC-bentonite to treat phenol in water was 100% and the removal rates of phenol related with pH of media.

The mechanism for organobentonites to adsorb organic compounds in water including:

(1) ion-association, i. e. ions of organic compounds were associated with quaternary ammonium cations or metal ions existed in interlamellae of organobentonites; (2) "extraction", i. e. organic compounds in water were extracted into organobentonites by micellar solubilization of surfactant. The "extraction" efficiency depended on the amounts of surfactants exchanged into organobentonites. Thus, the removal rates for organobentonites to treat organic pollutants in water were higher than that for the original bentonite. Under experimental conditions, phenol and *p*-nitrophenol were existed in anionic forms, may be associated with quaternary ammonium cations or metal ions of the organobentonites. They may also be extracted into the organobentonites. Phenol and *p*-nitrophenol were readily removed from water. Moreover, when treating aniline and nitrobenzene, the interaction between organic compounds and organobentonites was only "extraction". The removal rates of aniline and nitrobenzene from water by organobentonites were lower than that of phenol and *p*-nitrophenol. It was showed that the removal rates for organobentonite to treat organic pollutants were negatively interlinked with the hydrophobic of organic compounds.

To sum up, the quaternary ammonium ions were exchanged for charge-compensating sodium, potassium and calcium ions in the bentonite structure to separate the bentonite unit layers. The properties of bentonite, such as the capacities for adsorbing organic pollutants, the removal rates of organic compounds from water, were improved by placing quaternary ammonium cations on bentonite.

3.4 Application of organobentonites in wastewater treatment

Organobentonites were applied to wastewater treatment, organic pollutants were removed in different degrees. The removal rates related to the properties and concentrations of organic compound as well as the water quality. Moreover, COD (chemical oxygen demand) of wastewater was not apparently decreased because of release of some surfactant (CTMAB or CPC) from organobentonites. Thus, mixed flocculants were studied for wastewater treatment. It was indicated that the removal rates of organic pollutants and COD were improved by using the mixture of the organobentonites and aluminum sulfate (Table 5). The speed for separating the solid from liquid was accumulated because of addition of aluminum sulfate.

Table 5 The removal rates of COD_{Cr} by mixed flocculants

Unit: %

Flocculant	Phenol	Aniline	Nitrobenzene	<i>p</i> -nitrophenol
Al ₂ (SO ₄) ₃	11.3	47.2	5.1	11.5
CTMAB-bentonite	—	42.9	—	—
CPC-bentonite	—	45.3	—	4.0
Al ₂ (SO ₄) ₃ + CTMAB-bentonite	37.4	70.0	48.1	27.2
Al ₂ (SO ₄) ₃ + CPC-bentonite	47.4	62.4	45.6	32.1

Note: 1.0g organobentonite/500 ml wastewater, COD_{Cr}200—500 mg/L

The optimal component ratio between organobentonite and aluminum sulfate was investigated.

In order to avoid the secondary contamination of organic pollutants removal from wastewater, the organobentonites adsorbed organics were treated and recycled in wastewater treatment. The procedure was as follows; the organobentonites adsorbed organic pollutants were separated from wastewater and dried at the room temperature, then roasted in the presence of nitrogen gas at 200–500°C. Modified bentonites containing activated carbon were made from organobentonite and preliminarily studied to remove organic pollutants from wastewater. It was indicated that the removal rates of aniline from wastewater by modified bentonite were higher than 80%. Therefore, it is possible that organobentonites were resourced or recycled in wastewater treatment. The secondary contamination of organic pollutants was decreased or eliminated.

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