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Surface structure of CTMA$^+$ modified bentonite and their sorptive characteristics towards organic compounds

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Abstract

This work was to examine the correlation between surface structure and sorptive characteristics of cetyltrimethylammonium cations (CTMA$^+$) modified bentonite, which will provide novel information for exploring the sorptive mechanisms of organoclays. Various amounts of CTMA$^+$ (0.21–1.98 mmol/g) were intercalated into bentonite to prepare a series of organobentonites with different structures. N_2 adsorption–desorption isotherms were plotted for the organobentonites to obtain the surface structure information, and sorption capacities of these organobentonites toward phenol, aniline, nitrobenzene and naphthalene were examined. It was shown that surface areas, pore volumes and surface fractal dimension of the organobentonites decreased with increasing CTMA$^+$ loading amount. Sorption capacities of the organobentonites towards the four organic compounds have no evident correlation with their surface structures, and K_{oc} values of the organic compounds were shown to first increase until the maximum and then decrease as CTMA$^+$ loading amount further increased. Combining with the surface structure and sorption capacities of the organobentonites, we proposed that the solute molecules were penetrated into the CTMA$^+$ aggregates, and partition rather than adsorption mechanism dominated the sorption processes. The CTMA$^+$ aggregates formed optimal partition phases in the intermediate surfactant loading range.

Keywords: Organobentonites; Organic pollutants; Sorption; Surface structure

1. Introduction

Organoclays, prepared by intercalating clays with surfactant cations, have been considered as potential sorbents for removing organic pollutants from water [1–7]. Compared with activated carbons, organoclays have their special sorptive characteristics. The organoclays can keep relative constant removal efficiency in a wide range of solute concentration [8], which means the organoclays are suitable for the treatment of water with high pollutant concentration. Moreover, the organic compounds have no evident competitive sorption on the organoclays, which means the organoclays can be used for the treatment of waters containing different organic pollutants [9,10].

Understanding the sorptive mechanism is critical for further improving the sorption capacities of the organoclays. Partition of organic compounds to the organic phase created by the adsorbed surfactants was considered as the predominant mechanism controlling the sorption process [9,11]. However, an increasing number of studies have observed that the organic-carbon content (f_{oc}) normalized sorption coefficient (K_{oc}) of an organic compound is not a constant, which strongly depends on the microstructures of the organoclays [6,10,12]. Different explanations were presented for this phenomenon. Sheng et al. [10,13] proposed that sorption of organic compounds to organoclays included the salvation of solutes by the surfactant alky chains, adsorption by the siloxane surfaces. Chen et al. [12,14] believed that in the low surfactant loading range, the organic compounds would be primarily adsorbed on the alkyl chain covered siloxane surface; while in the high loading range, the organic compounds would be primarily partitioned into the alkyl chain formed organic phases. However, some researchers also

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hypothesized that the surfactant alkyl chains could form different organic phases as the microstructures of the organoclays changed, and the sorption capacities of the organoclays will change accordingly [6,15]. Until now, the sorptive mechanism of organoclays is still ambiguous, and there is no clear idea for how to improve their sorption capacities.

As we know, for the adsorption mechanism controlled sorption process (e.g., sorption of organic compounds to activated carbon), the sorption capacity of the sorbent will directly relate to its surface structure [4,16,17]. However, few investigations have concerned the correlation between their sorption capacities and surface structures until now. This work is to investigate the surface structures of the organoclays and examine the correlation between sorption capacities and surface structures, which will provide additional information for understanding the sorptive mechanisms of the organoclays. Cetyltrimethylammonium cations ($CTMA^+$) modified bentonite was selected as a representative of organoclays. Phenol, aniline, nitrobenzene and naphthalene were selected as representative of ionizable and nonionizable organic compounds. These aromatic compounds are usual pollutants that can be found in different types of polluted water, and they are often used for examining the sorption capacities of organoclays [12,15,18].

2. Materials and methods

2.1. Materials

The natural bentonite (Bent) was primarily calcium form obtained from Inner-Mongolia, China, with montmorillonite purity more than 95%. The structural formula is $Na_{0.02}K_{0.02}Ca_{0.39}$ $[Fe_{0.45}Mg_{1.10}Al_{2.51}]$ $[Si_{7.91}Al_{0.09}]O_{20}(OH)_4{\cdot}nH_2O$. The total cation exchange capacity (CEC) was 108 cmol kg^{-1}. Cetyltrimethylammonium bromide (CTMAB), phenol, aniline, nitrobenzene and naphthalene were of analytical grade, and they were obtained from Shanghai Chemical Co., China. The critical micelle concentration (CMC) value of CTMAB was 0.9 mmol L^{-1} [19].

2.2. Preparation of organobentonites

Organobentonites were synthesized according to the following procedure: 5.0 g original bentonite was dispersed in 200 mL of distilled water, and then a desired amount of CTMAB varying from 79 to 790 mg g^{-1} bentonite was added to saturate 20–200% of the natural bentonite's CEC. The suspensions were stirred at 60 °C for 10 h. The products were washed with distilled water six times, and dried at 70 °C for 12 h. The final products were grounded to pass 100 mesh sieves. The obtained products were denoted as *x*C-Bt, e.g., 198C-Bt represented the production with the $CTMA^+$ loading amount equal to 1.98 mmol g^{-1}.

2.3. Characterization

Organic-carbon content (f_{oc}) was analyzed with a SHIMADZU TOC-V CPH organic-carbon analyzer, and $CTMA^+$ loading amounts of the samples were calculated according to the obtained f_{oc} values. If the surfactant loading amounts were below the bentonite's CEC, they were expected to be adsorbed as cations; if the surfactant loading amounts were above the clay's CEC, they were expected to be adsorbed as both cations and molecules. The natural bentonite had organic-carbon content less than 0.04%.

Nitrogen adsorption–desorption isotherms were plotted at 77 K with an NOVA 2000e Surface Area & Pore Size Analyzer from Quantachrome. Prior to adsorption, the samples were degassed in a vacuum at 100 °C for 12 h. The relative pressure (P/P_0) between 0.05 and 0.35 was applied for the calculation of BET-N_2 surface areas. The total pore volumes of the samples were calculated at $P/P_0 = 0.98$. The micropore surface areas and volumes were obtained from the *t* method [20]. The surface fractal dimensions (*D*) of the samples were calculated using the FHHs method [21].

The X-ray diffraction (XRD) patterns were recorded using a Rigaku D/max-2550PC diffractometer with Cu Kα radiation. The samples were pressed in glass sample holders, and the range between 1° and 20° (2θ) was recorded with a scanning speed of 2°/min.

2.4. Procedures of sorption

Sorption experiments were carried out with batch equilibration technique. 0.05–0.4 g of the organobentonites (to obtain the removal rates within 30–90%) was combined with 20 mL solution containing 5–200 mg L^{-1} solutes (phenol, aniline and nitrobenzene) or 0.5–10 mg L^{-1} naphthalene in 25 mL centrifuge tubes, and sealed with Teflon-lined caps. The tubes were shaken at 25 °C for 6 h (preliminary experiments showed that 2 h were enough to obtain sorption equilibrium). After centrifugation at 4000 rpm for 15 min, the solute concentration in solution was detected with UV spectrophotometer (with the absorbance wavelength 270, 230, 268 and 219 nm for phenol, aniline, nitrobenzene and naphthalene, respectively). The sorbed amounts of the solutes were calculated by the concentration difference between the initial and equilibrium concentration.

Control experiments (without addition of organobentonites) showed that during the period of experiments the losses of solutes were less than 2% for phenol and aniline, less than 3% for nitrobenzene and less than 5% for naphthalene, which would not evidently influence the experimental results. Organic-carbon analysis of another series control samples (without addition of solutes) showed that the released surfactant amounts were far below its CMC. Thus, solubilization of the solutes by the released surfactants was negligible.

3. Results and discussion

3.1. Surface structures of the organobentonites

Fig. 1 presented the XRD patterns of the original bentonite and organobentonites. Basal spacing values of the samples were calculated from 2θ values of the peaks in the patterns. As shown, d_{001} values of the organobentonites increased with $CTMA^+$