

Preparation and characterization of CTAB-HACC bentonite and its ability to adsorb phenol from aqueous solution

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ABSTRACT

A novel type of adsorbent was prepared by modifying bentonite with N-2-hydroxypropyl trimethyl ammonium chloride chitosan (HACC) with cetyl trimethylammonium bromide (CTAB). The adsorbent was named CTAB-HACC bentonite. Its characteristics were investigated using thermogravimetric, Fourier-transform infrared spectroscopy (FTIR) and X-ray diffraction. The adsorption of phenol onto CTAB-HACC bentonite was evaluated by changing various parameters, such as contact time, adsorbent dosage, initial pH of the solution, and temperature. The maximum adsorption was observed at pH 12. Adsorption of phenol on CTAB-HACC bentonite favored at lower temperature and established the equilibrium in 30 min. The adsorption efficiency reached 82.1%, and the adsorption capacity was 7.12 mg/g from the phenol solution with a concentration of 500 mg/L at pH 12.0 and 20 °C.

Key words | bentonite, HACC, adsorption, phenol

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INTRODUCTION

Phenol is widely distributed as environmental pollutant due to its common presence in the effluents of many industrial processes, including oil refineries, petrochemical plants, ceramic plants, steel plants, coal conversion processes and phenolic resin industries. Phenol has been considered as priority pollutant because of its potential harm to human health. Various processes have been employed for the removal of phenols from aqueous media including advanced oxidation (Esplugas *et al.* 2002), membrane filtration (Rzeszutek & Chow 1998), biological degradation (Annachhatre & Gheewala 1996), electrochemical oxidation (Rodgers *et al.* 1999), photocatalytic degradation (Guo *et al.* 2006) and adsorption (Senturk *et al.* 2009; Beker *et al.* 2010; Liu *et al.* 2010; Muftah *et al.* 2010). Adsorption technology is currently being used extensively for the removal of organic and inorganic pollutants from aqueous solutions due to several advantages such as high efficiency, simple operation and easy recovery. A wide range of adsorbents have been reported including waste materials from agriculture (activated carbon, agricultural solid wastes and industrial by-products), natural materials (clays, siliceous materials and zeolites), bioadsorbents (chitin, chitosan, peat, starch and biomass) and resins.

Recently, organobentonites have been used as new adsorbents in the treatment of these wastewater from oil (Beall 2003; Carmody *et al.* 2007) and detergents (Rodriguez-Sarmiento & Pinzon-Bello 2001) and the removal of phenols (Huh *et al.* 2000; Shen 2002) and heavy metal ions (Lin & Juang 2002; Asem 2008) from aqueous solutions. Organobentonites are produced by the exchange of organic cations (typically having a quaternary ammonium and aliphatic structure) for inorganic ions (e.g. H⁺, Na⁺, Ca²⁺) on the layer surfaces of bentonite (Zhu & Zhu 2007). The surface properties of modified bentonite may be altered significantly by this exchange reaction. The modified surfaces of organobentonite may become organophilic because that the organic functional groups of quaternary ammonium cations are not strongly hydrated by water. As a result, organobentonites are powerful adsorbents for organic pollutants relative to natural bentonite, and were suggested for use in wastewater treatments (Holsen *et al.* 1991; Park & Jaffe 1993). At present, the modifying reagents applied are often single cationic; there are few reports about the double cationic ones used to modify bentonites.

Chitosan is a kind of polysaccharide prepared by the de-N-acetylation of chitin, which makes up the shells and

shrimps (Chao *et al.* 2004). It has been regarded as a useful material to remove inorganic and organic substances from wastewater (Crini 2006) due to the property of non-toxicity and biodegradability, etc. However, chitosan can only be dissolved when the pH is less than 6.5, which limits its broad application. Quaternized chitosan, which has quaternary amino groups introduced into the chitosan chain, is an effective method to render it soluble in water. Moreover, quaternized chitosan, N-2-hydroxypropyl trimethyl ammonium chloride chitosan (HACC) is itself a good absorbent and flocculent agent due to its unique properties, such as biocompatibility, biodegradation, biological activity, low toxicity and so on. Viviane *et al.* (2004) found that HACC was an effective adsorbent for the removal of Cr (VI) from aqueous solution. Sirlei *et al.* (2008) investigated the adsorption of reactive orange 16 using quaternary chitosan salt (QCS) as an adsorbent. The adsorption rate was dependent on dye concentration at the surface of the adsorbent for each time period and on the amount of dye adsorbed. The maximum adsorption capacity determined was 1,060 mg of reactive dye per gram of adsorbent.

In this research, a novel type of adsorbent was prepared by modifying bentonite with HACC together with cetyl trimethylammonium bromide (CTAB). On one hand, it would improve the adsorption capacity of organic pollutants on bentonite; on the other hand, it could keep the flocculation capacity of HACC. The adsorbent was named as CTAB-HACC bentonite. It was characterized by thermogravimetric (TG), Fourier-transform infrared spectroscopy (FTIR) and X-ray diffraction (XRD), and its ability to adsorb phenol from aqueous solution was evaluated.

EXPERIMENTAL

Materials

HACC, with a substitution degree of 86.9%, was prepared in our laboratory. The surfactant was CTAB which was purchased from Sigma-Aldrich Singapore (purity 99%). Bentonite powder with a particle size of 200-mesh was acquired from the chemical factory of Shentai, Xinyang, Henan, China. All other chemicals were of analytical grade and were used as received.

Instruments/apparatus

FTIR of the samples was taken by using an Avatar-360 IR spectrometer from Nicolet in the wave number range of

400–4,000 cm^{-1} . These samples in dry state were mixed with KBr in an agate mortar and finely powdered to prepare the KBr pellets. TG analysis was done by using a Simultaneous DTA-TG apparatus (DTG-60AH, SHIMADZU) with a heating rate of 10 °C/min. The flow rate of N₂ was adjusted at 20 cm^3/min . XRD patterns of the samples were done using an XRD with Cu anode, running at 40 kV and 40 mA. Diffraction measurements were conducted within the 2θ angle of 0–50°, at the scanning rate of 4°/min. The pH of the solution was measured with a laboratory scale pH meter (LiDa instrument, Shanghai, China). A temperature controlled water bath flask shaker (Kanghua, Jiangsu, China) was used for shaking the solutions. The determination of phenol concentration in solution was done on a UV-visible spectrophotometer (model 754N) made in Shanghai, China.

Adsorbent preparation

The procedure for the adsorbent preparation was as follows. Bentonite (5 g) was soaked in 30 mL water. The resulting mixture was placed in a three-neck round bottom flask, and 1.5 g of CTAB in 20 mL of distilled water was added to it. The contents were stirred thoroughly using a magnetic stirrer for 30 min, and then 1.5 g of HACC in 30 mL distilled water was added. The suspension was kept for 2 h at 70 °C in a temperature-controlled water bath. The composite obtained was then washed with distilled water until it was free from unreacted HACC and CTAB. The product was then dried in an oven at 105 °C for 2 h and then ground to obtain a particle size of 200 mesh.

Adsorption experiments

Adsorption experiments were conducted to study the adsorption of phenol on CTAB-HACC bentonite. These experiments were carried out by shaking clay with 50 mL aqueous solutions of phenol at different pH values (3.0–13.0), contacting temperatures, and adsorbent dosages in 100 mL stoppered bottles in a water bath shaker at 200 rpm. The initial pH values were adjusted with HCl and NaOH solutions. At the end of the predetermined time intervals, the solutions were centrifuged and the supernatant solutions were analyzed for residual phenol at $\lambda_{\text{max}} = 510 \text{ nm}$, using a UV-visible spectrophotometer. The amount of phenol adsorbed was calculated by the difference between the initial and final solution concentrations. The results were reported as the average value of three measurements.

RESULTS AND DISCUSSION

Characterization of CTAB-HACC bentonites

TG analysis

The thermograms of raw, HACC, and CTAB-HACC bentonites are shown in Figure 1. For raw bentonite, the thermogram exhibits the mass loss of 7.5% below 100 °C, which could be attributed to the desorption of physically adsorbed water of the surface layer. A 2.5% loss at 100–800 °C could be attributed to the dehydroxylation of the aluminosilicate layer. The mass loss of HACC bentonite sample is 2.5% below 250 °C, due to the partial replacement of HACC on the physically adsorbed water, and 16.0% at 250–800 °C from the decomposition of HACC loaded in bentonite and the dehydroxylation of the clay layers. However, the mass loss of CTAB-HACC bentonite shows a trend similar to the one of HACC bentonite. It differed from the latter in having a markedly higher value with an increase by 11.5% at 250–800 °C. Therefore, the bentonite was successively modified by HACC and CTAB.

FTIR spectroscopy analysis

The FTIR spectra reveal the specific surface functional groups on the bentonite and organobentonite surface based on the characteristic absorbed energy by the bonds in certain groups (Putra *et al.* 2009). The FTIR spectra of bentonite and organobentonite are shown in Figure 2, which reveals the presence of symmetric and asymmetric

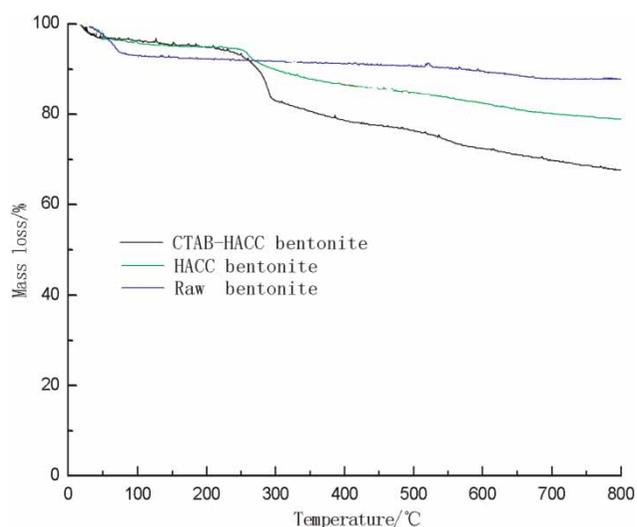


Figure 1 | TG plots of raw, HACC and CTAB-HACC bentonites.

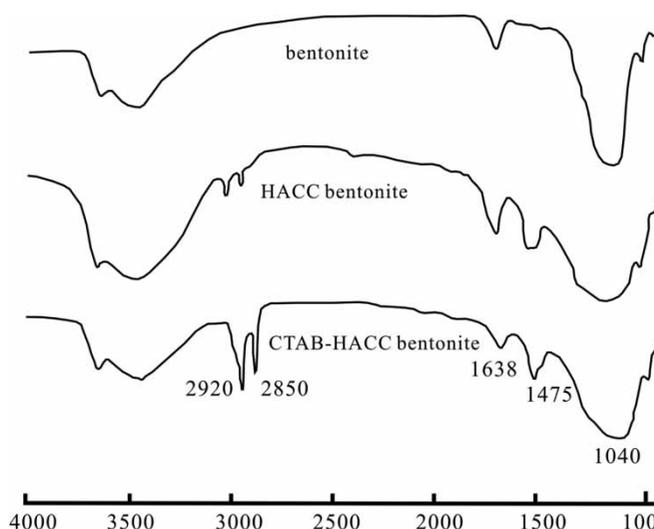


Figure 2 | The FTIR spectra of raw, HACC and CTAB-HACC bentonites.

stretching vibration at 2,850 and 2,920 cm^{-1} , respectively. These bands correspond to the vibrations of the methylene (CH_2) and methyl (CH_3) groups of the aliphatic chain of CTAB or HACC. In addition, a bending vibration of the methylene groups can be seen at 1,475 cm^{-1} , verifying the introduction of $(\text{CH}_3)_3\text{N}^+\text{R}$. All these bands (at 1,475, 2,850 and 2,920 cm^{-1}) are only detected for both HACC and CTAB-HACC bentonite samples. However, these bands in CTAB-HACC bentonite are stronger than the ones in HACC bentonite due to the introduction of more methylene and methyl groups. Besides, the characteristic peaks of glucopyranoside at 1,060 cm^{-1} overlaps with the stretching bands of Si-O-Si at 1,039 cm^{-1} in HACC and CTAB-HACC bentonite samples; thus, the bands at 1,040 cm^{-1} in HACC and CTAB-HACC bentonite samples are wider than the ones in raw bentonite. These observations also show that the CTAB-HACC bentonite had been modified by HACC together with CTAB.

XRD analysis

XRD is an effective method for the investigation of the intercalation in bentonite. Figure 3 shows the XRD patterns of raw, HACC and CTAB-HACC bentonite samples. Compared to raw bentonite, HACC bentonite shows a similar diffraction peak (d_{001}) at 6.06°, revealing that HACC was only adsorbed on the surface of bentonite. The peak (d_{001}) of CTAB-HACC bentonite clearly shift to a smaller angle (at 4.60°) relative to raw or HACC bentonites, that is, the CTAB-HACC bentonite has a larger interlayer distance. This is because when CTAB was added first in the

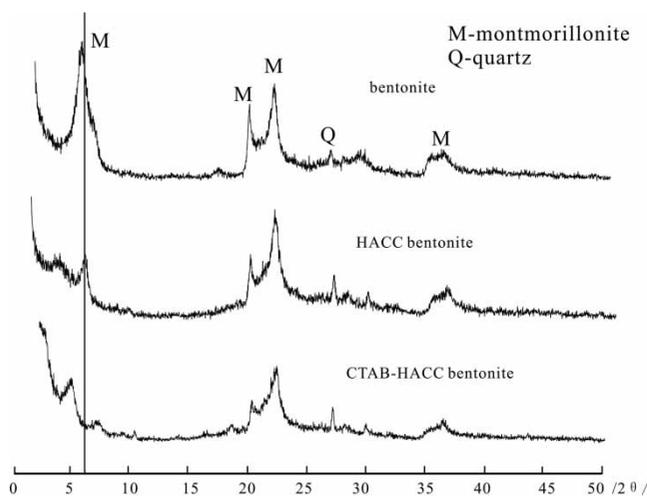


Figure 3 | XRD patterns of raw, HACC and CTAB-HACC bentonites.

preparation process of CTAB-HACC bentonites, a bigger interlayer distance is produced in bentonite. This facilitates the following intercalation of HACC in bentonite: the CTAB-HACC bentonite has a larger interlayer distance. The phenomena verify the results mentioned in the sections on TG analysis and FTIR spectroscopy analysis.

Effect of adsorption conditions on removal

Effect of pH value on removal

Figure 4 illustrates the dependence of adsorption of phenol on the pH of the aqueous dispersion (50 mL of 50 mg/L phenol solution) onto CTAB-HACC bentonite with a

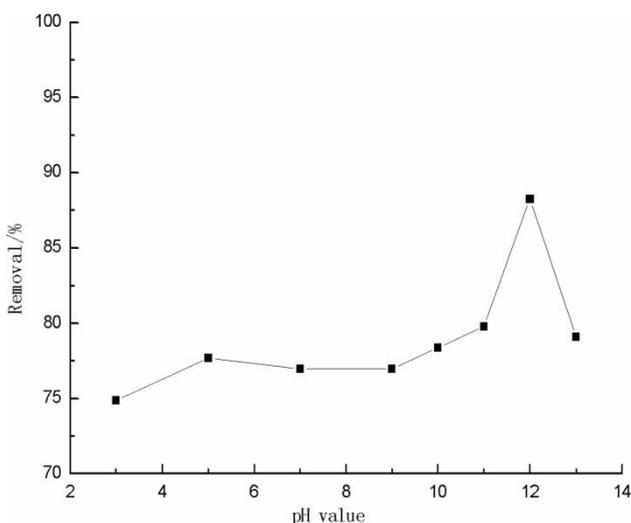


Figure 4 | Effect of pH value on removal.

dosage of 3.0 g for a contact time of 30 min at 30 °C. The removal increases slightly with the increasing pH. The maximum takes place at pH 12.0. With further increase in pH up to 13, it shows the trend to decrease. The pH dependence of adsorption suggests that the adsorption of phenol from aqueous solution onto CTAB-HACC bentonite is primarily influenced by the form of the adsorbent. According to previous reports (Zhu *et al.* 2000; Rawajfih & Nsour 2006), the pKa value of phenol at 30 °C is 9.89. When the pH of the solution exceeds the pKa of phenol, the phenol molecules are ionized to the negative phenolate ions. Therefore, the high adsorption of phenol at very high pH (pH > 9.89) is due to the electrostatic interaction between sufficient positively-charged groups and the anionic phenol. At low pH, the adsorption of phenol is mostly achieved by partition effects. However, the adsorption reduces due to the competitive adsorption of excessive OH⁻ at a relatively high pH. The optimal pH, 12.0, was applied.

Effect of the dosage of CTAB-HACC bentonite on removal

Figure 5 shows the effect of the dosage (1.0–5.0 g) on 50 mL of 50 mg/L phenol solution for a contact time of 30 min at 30 °C and pH 12. The removal increases with an increase in the dosage. The maximum removal efficiency is 88.2% when the dosage is 3.0 g. The adsorption sites increase in number due to the increasing dosage, so the removal improves accordingly. However, no change in adsorption is basically due to the sites remaining saturated during the adsorption process when the dosage exceeded 3.0 g. Hence, 3.0 g was considered as the optimal dosage.

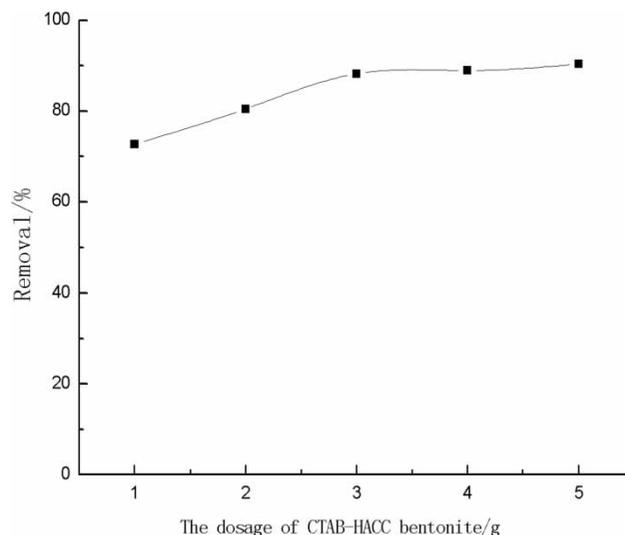


Figure 5 | Effect of the dosage of CTAB-HACC bentonite on removal.

Effect of contact temperature on removal

The adsorption studies were carried out with a dosage of 3.0 g and 50 mL of 50 mg/L phenol solution for a contact time of 30 min at pH 12 at four different temperatures: 20, 30, 40 and 50 °C. Table 1 shows that the removal decreases with the increasing temperature, which indicates that the adsorption of phenol onto the adsorbent surface is favored at lower temperature and it is controlled by an exothermic process. The low removal is partly due to a weakening of the attractive forces between phenol and the CTAB-HACC bentonite at higher temperature. Therefore, 20 °C was adopted.

Effect of contact time on removal

For this test, the adsorption experiments were conducted with a dosage of 3.0 g and 50 mL of 50 mg/L phenol solution at pH 12 and 20 °C. The removal of phenol onto CTAB-HACC bentonite for versus contact time is illustrated in Figure 6. The removal of phenol increases with contact time up to 30 min, and slightly decreases afterward. The

Table 1 | Effect of contact temperature on removal

Temperature/ °C	Removal/%
20	92.0
30	88.2
40	85.4
50	81.9

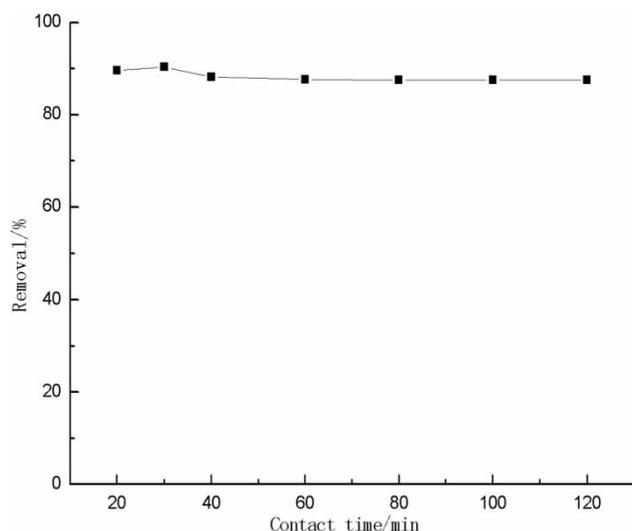


Figure 6 | Effect of contact time on removal.

nature of adsorbent and the available adsorption sites affect the rate of adsorption of phenol. During the process of adsorption, the adsorbate needs to transfer from the solute to the solid including the diffusion through the fluid film around the adsorbent particle and the diffusion through the pores to the internal adsorption sites. In the initial stages of adsorption of phenol, the concentration gradient between the film and the available pore sites is large, and hence the rate of adsorption is faster. The equilibrium time obtained is 30 min for the adsorption of phenol on CTAB-HACC bentonite. For this reason, the optimum contact time was selected as 30 min.

Effect of the initial concentration of phenol on removal

The effect of the initial concentrations of phenol between 50 and 500 mg/L on the adsorption onto CTAB-HACC bentonite was investigated with a dosage of 3.0 g at pH 12 and 20 °C for 30 min. When the initial concentration increases from 50 to 400 mg/L, the removal decreases from 92.0 to 82.7% (Figure 7). With further increase of initial concentration, it decreases slightly. However, the amount of adsorbed phenol increases from 0.764 to 7.12 mg/g. This is attributed to the increase in the driving force of the concentration gradient with the increasing initial concentration. This adsorption capacity for phenol is higher compared to the value of 6.6 and 1.7 mg g⁻¹ obtained with sodium dodecylsulphate (SDS)-alumina (Adak *et al.* 2006) and bentonite (Banat *et al.* 2000), respectively. The equilibrium, kinetics and thermodynamics of adsorption of phenol onto this adsorbent will be studied further.

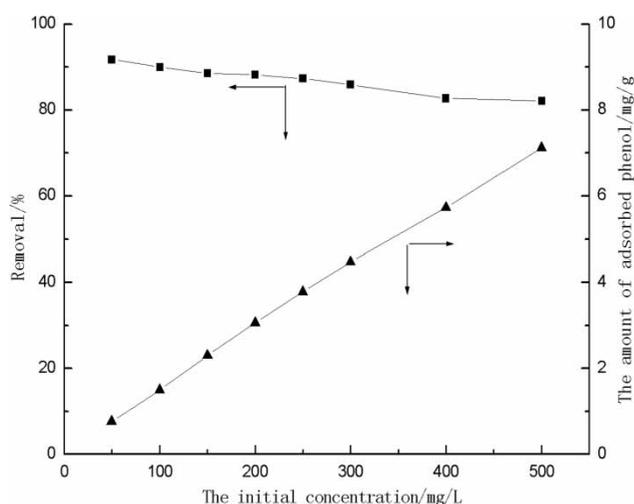


Figure 7 | Effect of the initial concentration of phenol on removal.

CONCLUSION

CTAB-HACC bentonite was prepared by modifying bentonite with HACC together with CTAB. The results from FTIR, TG, and XRD suggest that the HACC intercalated in CTAB bentonite successively. The adsorption of phenol onto CTAB-HACC bentonite was favored at low temperature. The maximum adsorption was attained in a short time (30 min). The CTAB-HACC bentonite had a removal of 82.1% and an adsorption capacity of 7.12 mg/g in a 500 mg/L phenol solution at pH 12.0 and 20 °C.

ACKNOWLEDGEMENT

Financial support Project supported by the National Natural Science Foundation of China (Grant No. 51003086) is gratefully acknowledged and National Higher-education Institution General Research and Development Project is gratefully acknowledged.

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First received 18 January 2011; accepted in revised form 3 March 2011