Adsorption of benzoic acid by CTAB exchanged montmorillonite

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Received 6 June 2006; received in revised form 25 December 2006; accepted 30 December 2006

Available online 17 January 2007

Abstract

This paper reports the adsorption of benzoic acid from water on cetyl trimethylammonium exchanged montmorillonite (CTAB-montmorillonite). Important factors are the adsorbent concentration, ionic strength, equilibrium time and pH. The largest adsorption is at pH 9. The adsorption kinetics data fitted the pseudo-second-order equation. The adsorption isotherms at different pH were linear indicating a partition mechanism. Up to about 61% of the dissolved benzoic acid was adsorbed by CTAB-montmorillonite. These results indicate that CTAB-montmorillonite is a potential adsorbent for benzoic acid.

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Keywords: Organo-montmorillonite; Adsorption; Benzoic acid; Adsorption kinetics

1. Introduction

The current rapid growth of industry in China is accompanied by an increase in the amount of wastewater discharged, as is the case in many regions with rapid industrial growth. These wastewaters contain many toxic organic and inorganic materials, such as aromatic compounds, heavy metals and dyes. Many of them have been classified as hazardous pollutants because of their potential toxicity to human health. Benzoic acid and its sodium benzoate are widely used as preservatives in beverages, fruit products, chemically leavened baked goods, and condiments. Also, chemical intermediates are of great relevance in the chemical industry (World

Health Organization, 2000). The wastewater discharged from processes of manufacture and application can pollute water, soil and atmosphere. The concentration of benzoic acid was found to range from 10 to 27500 µg/L in the groundwater of Florida (Goerlitz et al., 1985).

In order to meet the increasing stringent environmental regulations, many technologies such as chemical oxidation, biological degradation, solvent extraction, and adsorption were developed to remove the toxic organic compounds from industrial wastewaters. Adsorption on carbon is most popular. Because of the relative high costs of activated carbon, attempts have been made to use clays and clay minerals and some oxides as adsorbents, such as kaolins, bentonites and iron oxides (Krishna et al., 2001; Rosen and Li, 2001; Angove et al., 2002; Espantaleon et al., 2003; Ferreiro and Bussetti, 2003; Hizal and Apak, 2006). The application of clays, especially bentonites has

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attracted more and more interest because of their high cation exchange capacity, surface area and wide availability. The adsorption of neutral organic contaminants can be greatly improved by replacing the inorganic interlayer cations by organic cations such as quaternary ammonium cations (Boyd et al., 1988). At present, organo-montmorillonite can act as adsorbent for a great variety of organic pollutants, such as phenols (Lawrence et al., 1998; Jiang et al., 2002; Juang et al., 2002; Barhoumi et al., 2003), trichlorobenzene and aniline (Dentel et al., 1998).

Benzoic acid is a weakly acid. Several studies have been reported in the literature on the adsorption by various materials, such as activated carbon (Chern and Chien, 2003; Ayranci et al., 2005), metal(hydr)oxides (Horányi, 2002), modified loess soil (Zhou et al., 2003) and mesoporous materials (Huang et al., 2004; Tozuka et al., 2005). However, very little information is available regarding the adsorption of benzoic acid by organo-montmorillonite (Yıldız et al., 2005). We found that adsorptive capacity of CTAB-montmorillonite for benzoic acid is much better than that of natural montmorillonite.

2. Materials and methods

2.1. Materials

The bentonite used for this study was natural montmorillonite, purchased from Beijing Youlichuangjia Science and Technology Developing Company and mined in Yixian, Hebei province, China. According to the supplier, the sample contained 98% montmorillonite, 0.5% kaolinite and 1.0% quartz. The chemical composition was SiO₂, 50.90%, Al₂O₃, 18.36%, Fe₂O₃, 1.03%, CaO, 3.97%, MgO, 4.14%, TiO₂, 0.02%, K₂O, 0.72%, Na₂O, 1.18%, P₂O₅, 2.15%.

Benzoic acid, CTAB and sodium, potassium and calcium chloride were of analytical grade.

2.2. Preparation of CTAB-montmorillonite

The bentonite was dispersed in 500 mL 0.5 mol/L NaCl solution, shaken for 24 h before the clear supernatant was discarded. The bentonite was again dispersed in 500 mL 0.5 mol/L NaCl solution. The remaining solid was washed with deionized water several times until absence of chloride ions (tested with AgNO₃ solution). The product was dried at 80 °C and gently ground in an agate mortar. The cation exchange capacity (CEC) of this Na⁺-exchanged montmorillonite (1.0 mmol/g) was determined by reacting with BaCl₂–H₂SO₄ (Leij and Dane, 1989). 25 g of Na⁺-exchanged montmorillonite were reacted with CTAB solution equivalent to the CEC, and then shaken for 24 h, the clear supernatant was discarded. The organo-modified montmorillonite was washed several times with deionized water, until bromide ions were absent in the supernatant. The organo-montmorillonite was

dried at 80 °C, then crushed and sieved to a size range of 0.3 ~ 0.5 mm.

2.3. Characterization

The X-ray diffraction (XRD) patterns were measured on a Rigaku D/MAX 2200 (Tokyo, Japan) instrument with CuK α radiation ($\lambda=1.5405$ Å). Surface area measurement was performed on NOVA 2000e surface area and pore size analyzer (Quantachrome, American). The samples were out-gassed overnight (20 h) under nitrogen prior to the adsorption measurement. The specific surface area was calculated on the basis of the BET equation.

2.4. Adsorption experiments

The adsorption experiments were performed by a batch technique at room temperature. Briefly, 0.2 g of CTAB-montmorillonite were placed in a series of glass centrifuge tubes, and supplemented with 10 mL different concentrations of benzoic acid solution and 0.1 mL of 0.4 mol/L CaCl₂. The pH of the suspensions was adjusted to 3.0, 7.0 and 9.0 with 1:1 HCl or NaOH. The flasks were shaken for 24 h. After equilibrium, the suspensions were centrifuged at 4000 *r*/min for 30 min and the supernatants were analyzed by a UV spectrophotometer. The adsorbed amounts of benzoic acid were calculated by the difference between the initial and final concentration in the equilibrium solution.

2.5. Determination of benzoic acid

The concentration of benzoic acid was determined in the UV-2450 spectrometer (Shimadzu, Japan) at 223 nm between 0 and 0.1 mmol/L. The linear regression was $A=7.82c-0.0283$ with a regression coefficient of 0.998.

3. Results and discussion

3.1. Characterization of montmorillonite

Data of natural montmorillonite, Na⁺-montmorillonite and CTAB-montmorillonite were listed in Table 1. It is interesting to note that the specific BET surface area of the organo-montmorillonite was only 4 m²/g because the organic ions had been intercalated into the interlayer spaces.

3.2. Preliminary determinations

As shown in Fig. 1, the proportion of benzoic acid adsorbed increased slightly with the mass of the organo-montmorillonite and 0.02 g/mL CTAB-montmorillonite was used in the following experiments. We observed an influence of the added salts on the adsorption (Fig. 2)

Table 1

Summary of XRD analysis results and BET surface area of natural montmorillonite, Na⁺-montmorillonite and CTAB-montmorillonite

Sorbent	BET surface area (m ² /g)	2θ (°)	d ₀₀₁ (Å)
Natural montmorillonite	10.15	5.722	15.43
Na ⁺ -montmorillonite	10.52	7.024	12.57
CTAB-montmorillonite	4.050	4.661	18.94

which increased in the order: NaCl < KCl < CaCl₂. Therefore, CaCl₂ was chosen as the background electrolyte and at an ionic strength of 0.004 mol/L.

3.3. Adsorption kinetics

The relationship between contact time and benzoic acid uptake by CTAB-montmorillonite is presented in Fig. 3. The equilibrium time required for the adsorption of benzoic acid is almost 12 h. To ensure equilibrium, all the experiments were left for 24 h.

The adsorption of benzoic acid onto CTAB-montmorillonite fits the pseudo-second-order equation

$$\frac{dq_t}{dt} = k(q_e - q_t)^2 \quad (1)$$

Integrating the equation for the boundary conditions $t=0$ to $t=t$ and $q_t=0$ to $q_t=q_t$, and rearrangement into the linear form gives:

$$\frac{t}{q_t} = \frac{1}{kq_e^2} + \frac{1}{q_e}t \quad (2)$$

where q_e (mmol/g) and q_t (mmol/g) are the amount of solute adsorbed by adsorbent at equilibrium and at time t (h), k (g/mmol/h) is the rate constant. The plot of t/q_t against t should give a linear relationship with a slope of

Fig. 1. Effect of CTAB-montmorillonite concentration on the adsorption of benzoic acid at an initial concentration of 10 mmol/L in deionized water.

Fig. 2. Effect of NaCl, KCl and CaCl₂ concentrations on the adsorption of benzoic acid on CTAB-montmorillonite. Initial concentration of benzoic acid was 10 mmol/L and the amounts of adsorbent were 0.02 g/mL.

$1/q_e$ and an intercept of $1/kq_e^2$. The measured kinetic data fitted this model (Fig. 4) with a correlation coefficient of 0.991. The rate constants k and adsorption capacity at saturation q_e were calculated from the values of the slopes and the intercepts. They were 0.4497 g/mmol/h and 0.3904 mmol/g. Similar second order kinetics has been reported for phenol adsorption by organo-clays by other authors (Juang et al., 2002; Yilmaz and Yapar, 2004).

3.4. Adsorption isotherms

The adsorption isotherms of benzoic acid onto CTAB-montmorillonite are linear (Fig. 5):

$$q_e = K_p C_e \quad (3)$$

where q_e (mmol/g) is the amount of adsorption and C_e (mmol/L) is the equilibrium concentration of the

Fig. 3. Adsorption kinetics of benzoic acid adsorption on CTAB-montmorillonite at an initial concentration of 10 mmol/L. The amounts of adsorbent were 0.02 g/mL and the background electrolyte was 0.004 mol/L CaCl₂.

Fig. 4. Pseudo-second-order kinetics for the adsorption of benzoic acid on CTAB-montmorillonite.

adsorbate. The K_p (g/L) represents the ratio of the amount of a material adsorbed to the amount in solution. Linear regressions were thus performed for each isotherm and the results were given in Table 2.

The isotherms are linear over a wide range of equilibrium concentrations, up to about 61% of the solubility of benzoic acid in water. The linearity of the isotherms indicates a partition mechanism in the adsorption of benzoic acid by CTAB-montmorillonite, as reported (Boyd et al., 1988; Lee et al., 1989; Smith et al., 1990) for the adsorption of other hydrophobic organic compounds by organo-clays.

3.5. Effect of pH

According to Fig. 5 and Table 2, the adsorption of benzoic acid onto CTAB-montmorillonite increases as the pH value increases from 3.0 to 9.0. Generally, benzoic acid

Fig. 5. Adsorption isotherms of benzoic acid at different pH values. The amounts of adsorbent were 0.02 g/mL and the background electrolyte was 0.004 mol/L CaCl_2 .

Table 2

Linear regression parameters of benzoic acid adsorption on CTAB-montmorillonite

pH	K_p	Intercept	R^2
3	0.0548	−0.0349	0.9548
7	0.0867	−0.0574	0.8850
9	0.2051	−0.1567	0.9140

is present in neutral form when pH is less than 2 units of its pK_a 4.21. At pK_a , 50% of the benzoic acid is present as anion, and at $\text{pH} > 4.21$, anions are predominated. Benzoic acid and the conjugated base are of different hydrophobicity. Hence the amount of benzoic acid partitioned to CTAB-montmorillonite should be pH dependent.

4. Conclusion

Optimal conditions for the adsorption of benzoic acid on CTAB-montmorillonite were 0.02 g/mL adsorbent, CaCl_2 as electrolyte at an ionic strength of 0.004 mol/L and pH of 9.0. The observed adsorption kinetics fitted the pseudo-second-order kinetics equation. The adsorption isotherms were linear which indicated a partition mechanism. Amounts up to about 61% of the maximum solubility of benzoic acid in water were adsorbed on CTAB-montmorillonite. Thus, CTAB-montmorillonite might be used as potential adsorbent for removing benzoic acid from water.

Acknowledgements

This study was supported by Natural Science Foundation of China (Grant No.20577016), the Natural Science Foundation (Y2004B11), the Science and Technology Program of Shandong Province (03C05) and the Jinan University Doctoral Foundation (B0405), and all the authors express their deep thanks.

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