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Adsorption of benzoic acid from aqueous solution by three kinds of modified bentonites

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ABSTRACT

Benzoic acid removal is important for the water treatment, and adsorption is an efficient treatment process. Three kinds of modified bentonites, hydroxy-aluminum pillared bentonite (Al(OH)-Bent), octadecyl trimethyl ammonium chloride modified bentonite (OTMAC-Bent), and both octadecyl trimethyl ammonium chloride and hydroxy-aluminum modified bentonite (Al(OH)-OTMAC-Bent) were prepared and characterized by XRD, FTIR, and BET analysis. Experiments were conducted on the adsorption of benzoic acid by the prepared modified bentonites at different temperatures in batch experiments. The results show benzoic acid adsorption capabilities of Na-Bent and Al(OH)-Bent are even low, but high for OTMAC-Bent and Al(OH)-OTMAC-Bent. Optimal conditions for the adsorption of benzoic acid on OTMAC-Bent and Al(OH)-OTMAC-Bent were as follows: pH of 3.5, 0.04 g/mL adsorbent, and contact time of 90 min. Increased adsorption with temperature indicates that the adsorptions of benzoic acid onto Al(OH)-OTMAC-Bent and OTMAC-Bent are spontaneous and endothermic. The adsorption data could be well interpreted by the Langmuir model and Temkin Equation. The adsorption efficiency was higher than 85%, suggesting that OTMAC-Bent and Al(OH)-OTMAC-Bent are excellent adsorbents for effective benzoic acid removal from water.

1. Introduction

Industrial wastewater contains many organic and inorganic matters, such as aromatic compounds, heavy metals, and dyes. Many organic compounds have been classified as hazardous pollutants due to their potential toxicity to human health. Nowadays, the excessive and uncontrolled use of chemical preservatives which are mainly composed of organic compounds become a major problem. Benzoic acid, as a major kind of chemical preservatives, is one of the most important additives in the food industry. Because of the toxicity, its usage has been prohibited as food additive in many countries, such as in China, Japan, and the European Union. But now, benzoic acid could still be detectable in industrial sewage, which could affect the human health. Therefore, the removal of benzoic acid in water brings much public attention [1,2], and there is currently an urgent demand for improved chemical preservatives emoval methods.

There are many methods for the removal of organic pollutants from aqueous solutions, such as adsorption, chemical precipitation, ion exchange, membrane processes, biological degradation, chemical oxidation, and solvent extraction. Adsorption is the most popular method. There are many studies for the adsorption of benzoic acid from aqueous solutions [3–6].

Activated carbons have the advantages of high adsorption capacity for benzoic acid [5,6]. However, because of its relatively high cost, there have been attempts to utilize low cost, naturally occurring adsorbents, to remove contaminants from wastewater [4,7,8]. Recently, the usage of natural mineral adsorbents for wastewater treatment is increasing due to their abundance and low price. One type of clay minerals is bentonite, the main component of which is montmorillonite. Simple ion-exchange reactions can significantly modify the surface properties of natural bentonite. The cations of bentonite (Na^+, Ca^{2+}) can be replaced by inorganic hydroxyl-metal polycations acting as pillars, which increase the interlayer spacing of bentonite. Moreover, when organic cations (such as cationic surfactants) occupy the exchange sites of bentonite clay, the surface properties transform from hydrophilic to hydrophobic. There has been much interest in the use of modified bentonites as adsorbents to prevent and remediate environmental contamination. Previous studies show that inorganic pillared bentonite and organic modified bentonite have been widely used to adsorb heavy metals [9], dyes [10–12], gases [13], organic pollutants such as benzoic acids [3,4], catechol [14], chlorobenzene [15], phenol [16,17] and other environmental pollutants [18–21].

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The objective of this study is to examine the feasibility of using differernt kinds of bentonites as adsorbents for benzoic acid removal. In the present study, three different bentonites, hydroxy-aluminum pillared bentonite (Al(OH)-Bent), octadecyl trimethyl ammonium chloride modified bentonite (OTMAC-Bent), and both octadecyl trimethyl ammonium chloride and hydroxy-aluminum modified bentonite (Al(OH)-OTMAC-Bent) were synthesized. The synthesized bentonites were characterized by FTIR, XRD, and BET analysis. The benzoic acid adsorption properties (effect of operating variables, adsorption isotherms, and adsorption thermodynamics) were also evaluated utilizing batch experimental methods.

2. Materials and methods

2.1. Materials

The bentonite used in this study was purchased from the Fangzi bentonite plant (Weifang, Shandong Province, China). Octadecyl trimethyl ammonium chloride (OTMAC), NaCl, Na_2CO_3, $AlCl_3$, NaOH, KH_2PO_4 were all of analytical grade, obtained from Sinopharm Chemical Reagent Beijing Co., Ltd., China. All of the reagents were used as received.

2.2. Preparation of modified bentonites

2.2.1. Preparation of sodium bentonite

The natural bentonite was converted to sodium bentonite (Na-Bent) before the synthesis of modified bentonites. Firstly, 100 g of the natural bentonite was dispersed in 2.0 L of deionized water by intense shaking for about 6 h. The <2 μm fraction of the bentonite was collected. Then, the bentonite was dispersed in 500 mL 0.5 mol/L NaCl solution and stirred for 24 h. The supernatant was removed after settling. This procedure was repeated 2 times. After complete exchange, Na-Bent was washed with deionized water repeatedly until free of chloride ions as indicated by $AgNO_3$ solution. The product was dried at 80 °C, gently ground in an agate mortar to 200 mesh, and kept in a sealed bottle. The cation exchange capacity (CEC) of this Na-Bent is 0.835 mmol/g.

2.2.2. Preparation of OTMAC-Bent

Twenty grams of Na-Bent was reacted with OTMAC solution equivalent to the CEC, shaken for 24 h, and the clear supernatant was discarded. The final organic modified bentonite mixture was washed several times with deionized water until free of chloride ions in the supernatant. The samples were dried at 80 °C, activated for 1 h at 105 °C, ground in an agate mortar to pass through a 200 mesh sieve, and kept in a sealed bottle. The organic modified bentonites were designated as OTMAC-Bent.

2.2.3. Preparation of Al(OH)-Bent

According to the method described by Yan et al. [22], the pillaring solution of hydroxy-aluminum oligomeric cations was prepared by slowly adding 0.48 mol/L NaOH solution to 0.2 mol/L $AlCl_3$ solution under vigorous stirring at 60 °C, until the OH^-/Al^{3+} molar ratio reached 2.4. The solution was stored at 60 °C for 24 h.

The resulting pillaring solutions were added drop-wise to a 1% (by weight) Na-Bent suspension by stirring for 12 h at the ratio of 10 mmol oligomeric cations per gram of Na-Bent. The slurry was stirred for 24 h at room temperature and washed repeatedly with deionized water until there was no chloride. The solid was dried at 80 °C, ground in an agate mortar to pass through a 200 mesh sieve, and kept in a sealed bottle. The inorganic pillared bentonites were designated as Al(OH)-Bent.

2.2.4. Preparation of Al(OH)-OTMAC-Bent

The pillaring solution of hydroxy-aluminum oligomeric cations and the OTMAC solution were drop-wise added into stirred bentonite suspension. The Na-Bent was reacted with OTMAC solution equivalent to the CEC. And the pillaring solution of hydroxy-aluminum oligomeric cations was the same as that of Al(OH)-Bent. The products were washed with deionized water until chloride free (as judged by the silver nitrate test) and collected by centrifugation. Finally, the product dried at 80 °C, ground in an agate mortar to pass through a 200 mesh sieve, and kept in a sealed bottle. The inorganic–organic modified bentonites were designated as Al(OH)-OTMAC-Bent.

2.3. Characterization methods

XRD patterns of the prepared samples were acquired with a Rigaku D/MAX 2200 X-ray diffractometer (Tokyo, Japan). BET analysis was performed on Micromeritics ASAP 2020 surface area and porosity analyzer (Quantachrome, United States). Pore distributions and pore volume were calculated using the adsorption branch of the N_2 isotherms based on the BJH model. Specific surface area was calculated on the basis of the BET equation. FTIR spectra were recorded in the spectral range of $4000 \sim 400\,cm^{-1}$ on a Perkin–Elmer Spectrum One FTIR spectrometer (Perkin–Elmer, United States).

2.4. General batch adsorption procedure

Benzoic acid stock solution of 15 mmol/L was prepared by dissolving benzoic acid in deionized water, and dilutions of the stock solution were used in subsequent experiments. In the isotherm experiments, 0.4 g of modified bentonite (OTMAC-Bent, Al(OH)-OTMAC-Bent) and 10 mL 2–12 mmol/L benzoic acid solution were mixed in a series of Teflon centrifuge tubes. The pH was adjusted to the optimum pH by adding a few drops of 1 mol/L HCl or 1 mol/L NaOH. The tubes were capped and placed on an orbital shaker at 170 rpm for 90 min to ensure equilibrium. The suspension was separated by filter. The residual concentration of benzoic acid was determined by Lambda 35 UV–vis spectrophotometer (Perkin–Elmer, United States) at a wavelength of 227 nm. Each experiment was duplicated under identical conditions.

Blank samples (containing only deionized water and corresponding modified bentonites) were prepared and monitored for the duration of the experiment as a control. These blank samples indicated insignificant benzoic acid volatilization or adsorption losses on the glassware for the duration of the experiment.

3. Results and discussion

3.1. Characterization of bentonites

X-ray diffraction (XRD) was performed on dried natural bentonite, Na-Bent, OTMAC-Bent, Al(OH)-Bent, and Al(OH)-OTMAC-Bent, as shown in Table 1. For natural bentonite, the main compensating cations were calcium and magnesium, which was in agreement with the observed d_{001} distance of 14.73 Å. The d_{001} value decreased to 12.17 Å when Ca^{2+} and Mg^{2+} ions were fully exchanged by Na^+ ions for their lower radii in the layer of bentonite. After hydroxy-aluminum polycations exchange, the d_{001} value increased to 18.97 Å. After OTMAC cation exchange, the d_{001} value increased to 20.22 Å. For the Al(OH)-OTMAC-Bent, the d_{001} value is 20.73 Å, which is larger than that of OTMAC-Bent and Al(OH)-Bent, and is also larger than that of Zhu and Zhu [23], who reported the 19.11 Å basal spacing for the CTMAB-Al-Bent. The result may be due to OTMAC molecule is larger than CTMAB molecule.