Preparation, characterization and adsorption performance of cetyltrimethylammonium modified birnessite

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ABSTRACT

Cetyltrimethylammonium modified birnessite (CTMA-birnessite) is prepared by a simple hydrothermal method. The synthetic birnessite materials are characterized by a number of characterization techniques, including powder X-ray diffraction (XRD), scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FTIR), and X-ray photoelectron spectroscopy (XPS). The results indicate that the prepared CTMA-birnessite has a basal spacing up to 3.28 nm and that both the CTMA-birnessite and the birnessite have layer structures and plate-like forms with a thickness of less than 0.1 μm. The relative contents of Mn^{2+}, Mn^{3+} and Mn^{4+} on the sample surfaces are about 22.1%, 56.4% and 21.5% for birnessite, and 9.5%, 62.4% and 28.1% for CTMA-birnessite. The CTMA-birnessites show excellent adsorption/desorption properties for benzoic acid. At least 20% of the benzoic acid is adsorbed to the CTMA-birnessite in the adsorption experiment.

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1. Introduction

Birnessite is a layered manganese oxide mineral, which can be found in nature (in soils and ore deposits [1,2]) or produced synthetically. It is known to have a two-dimensional layer structure, consisting of edge-shared MnO_6 octahedra in the sheets and metal cations and water molecules in the interlayer space [1–4]. This hydrated layer structure promises large surface areas of birnessite and allows the metal cations to easily transport into and out of the interlayer region [3,5,6]. Possessing excellent molecular transport properties, birnessite has been widely applied for intercalation, ion-exchange, and secondary battery applications [4,7]. In addition, birnessite also shows high oxidizing capacity [8] and can also serve as a scavenger of trace metals in soils and aqueous environments [9,10]. However, relatively few studies have focused on the adsorption of organic contaminants by birnessite [11].

To address the issue of adsorbing the organic contaminants, the birnessite need to be first surface modified by organic moieties. The preparation organo-birnessite has been developed by ion-exchange or intercalation reactions in the earlier studies [12–15]. Organic cations, such as tetramethylammonium (TMA) and tetraethylammonium (TEA) ions [12,13] are often introduced into layered birnessite-type manganese oxides. Amine salts have been applied generally as cost-effective reagents of organoclays to enhance the adsorption capacity. Inserting hydrocarbon chain into layers can increase the interlayer distance and hydrophobic property, resulting in higher affinity toward organic substances [16–19]. In fact, the adsorption of organic contaminants has been found to be enhanced by the intercalation of quaternary ammonium ions in natural, lamellar clays, such as montmorillonite and bentonite [20–26]. Thus, the synthesis and characterization of cetyltrimethylammonium (CTMA+) modified birnessite (CTMA-birnessite) should be studied in hopes of enhancing the adsorption capacity.

The main novelty of this work is the synthesis, comprehensive characterization, and adsorption applications of layered CTMA-birnessite. The organo-containing birnessite was prepared by exchanging the hydrated inorganic cations of birnessite using cetyltrimethylammonium. Cetyltrimethylammonium is likely to convert the interlayer surface properties from hydrophilic to hydrophobic. The present study extends upon our recent investigations on CTMA-birnessite as an adsorbent for benzoic acid [10] with a presentation of the detailed characterization of synthesized birnessite and CTMA-birnessite. Detailed discussion on the findings from X-ray diffraction (XRD), scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FTIR), and X-ray photoelectron spectroscopy (XPS) are provided. The adsorption performance of benzoic acid onto CTMA-birnessite is also evaluated. Initial ion exchange and desorption studies were also conducted on selected CTMA-birnessite samples.

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2. Experimental

2.1. Materials

The various reagents used were as follows: Manganese(II) nitrate tetrahydrate (analytical grade, >98.5%, Merck), cetyltrimethylammonium bromide (CTAB, analytical grade, >96%, Merck), sodium hydroxide (>98.0%, Merck), calcium chloride dehydrate (analytical grade, >99.0%, Merck), potassium chloride (analytical grade, >99.5%, Merck), and benzoic acid (analytical grade, >99.5%, Merck). All chemicals were used without further purification. Water used in this study was distilled and doubly deionized.

2.2. Preparation of CTMA-birnessite and birnessite

CTMA-birnessite was prepared using a hydrothermal method. 7.3 g (0.5 wt%) CTAB was mixed with 750 mL of water to get a homogenous solution before 500 mL diluted NaOH (1.07 g) was added into it with stirring. After a short time for the mixing of CTAB and NaOH, 200 mL $Mn(NO_3)_2$ (1.67 g) solution was introduced, producing a brown slurry. The whole mixing process was conducted at about 343 K and the stirring speed was set at 450 rpm. CTAB, NaOH and $Mn(NO_3)_2$ solutions were all purged separately before mixing, with nitrogen gas of high (>99.9%) purity, at a rate of >0.5 L/min for 5 min in order to remove oxygen before they mixed [27,28]. After being stirred for 2.5 h, the whole mixture was aged at 393 K in an autoclave for 48 h. The resulting product was centrifuged (11,510g for 5 min), filtered, and rinsed 3 times with water. Finally, the sample was freeze-dried overnight.

To use as-made birnessite as a control material, the preparation of as-made birnessites were kept essentially the same as preparing CTMA-birnessite, except that CTAB was not added in the synthesis solution.

2.3. Characterization of CTMA-birnessite and birnessite

X-ray diffraction (XRD) patterns of all the synthesized materials were recorded using a Bruker D8 Advance X-ray diffractometer with monochromatized Cu $K\alpha$ radiation (λ = 1.5418 Å). The morphology of all of the materials was visually investigated using a JEOL JEM-6500F field emission scanning electron microscope.

Fourier-transform infrared spectra (FTIR) were obtained on a Perkin Elmer spectrum 100 FTIR spectrometer. Samples were analyzed using the KBr pellet method. A small mass of 3 mg of a selected sample was mixed with a spectroscopic grade potassium bromide (KBr) powder to obtain 300 mg of a mixture. The mixture was then ground in a mortar and compressed into a pellet in a die. Spectra were obtained by adding 16 scans at 1 cm^{-1} resolution in the range from 450 to 4000 cm^{-1}. The background spectrum was obtained from a pure KBr pellet of the same weight and size.

XPS measurements were performed with a Thermo VG Scientific Theta Probe system. The instrument uses a focused, monochromated X-ray beam. Al $K\alpha$ radiation was used throughout the work (photo energy 1486.6 eV) with an X-ray spot size of 400 μm. XPS spectra were charge referenced to adventitious carbon at 284.6 eV. Spectra were analyzed with Thermo Avantage software. Peak fitting of photolines was performed with a Shirley background correction and Voigt (Gaussian–Lorentzian = 70:30) curve-fitting function.

The organic carbon contents of the samples were analyzed with an organic carbon analyzer (O.I. Analytical model SOLIDS). The amounts of Br in selected samples were determined by X-ray fluorescence (XRF) using a PANalytical Axios XRF spectrometer.

2.4. Ion exchange

A volume of 50 mL of 1 M $CaCl_2$ solution was mixed with 0.015 g of synthesized materials and left at room temperature for 24 h. Exchange products were filtered, rinsed 3 times with water, and freeze-dried overnight. The exchange properties were investigated using calcium chloride dehydrate and potassium chloride.

2.5. Adsorption and desorption of benzoic acid

For the adsorption of benzoic acid (BA), a stock solution of 4 mmol/L of benzoic acid was prepared by dissolving 0.49 g of benzoic acid in water and diluting to 1 L. The adsorption capacity of CTMA-birnessite was preliminarily evaluated in our previous studies [10], and the adsorbent concentration of 4 g/L was used in our subsequent experiments. For the adsorption experiments, 0.04 g of the synthesized materials (birnessite and CTMA-birnessite), 0.1 mL of 58.8 g/L $CaCl_2$, and 10 mL of benzoic acid solution were mixed in a 50-mL polypropylene (PP) centrifuge tube. The procedure mentioned above was repeated for at least two times with different BA concentrations, ranging from 0.8 to 4 mmol/L. The initial pH values of BA working solution were adjusted by adding 1 mol/L HNO_3 or NaOH solution. The centrifuge tubes were capped and placed on an orbital shaker for 24 h. After equilibrium, the solutions were centrifuged at 11,500g for 10 min. After filtration with Millipore (0.22 μm pore diameter) syringe filters, the supernatants were analyzed by the UV–vis spectrophotometer. The concentration of benzoic acid was determined by a UV–vis spectrophotometer (GBC UV–visible Cintra 20 spectrometer) at a wavelength of 229 nm [29] between 0 and 0.4 mmol/L using matrix-matched calibration curves. Blank samples (samples containing only deionized water and corresponding synthesized materials) and samples containing only benzoic acid and $CaCl_2$ were prepared and monitored for the duration of the experiment as a control. The supernatants (before and after filtration) of samples used in the adsorption experiments were also used for evaluating the losses during filtration. The pH value of the standard solutions used for spectrophotometric quantification of benzoic acid was the same as in the adsorption batch experiments. All experiments were repeated at least two times.

The amounts of benzoic acid per unit mass of synthesized materials, q_e, were obtained by

$$q_e = (C_0 - C_e)\frac{V}{W} \tag{1}$$

where C_0 and C_e are the initial and equilibrium liquid-phase concentrations of benzoic acid, respectively, V is the volume of the solution, and W is the amount of dry adsorbent used.

In order to confirm that BA was indeed adsorbed on CTMA-birnessite, the initial desorption studies were conducted. In the desorption experiments, CTMA-birnessite samples with BA adsorbed were centrifuged (11,510g for 5 min), filtered and rinsed 3 times with water. After being freeze-dried overnight, BA-adsorbed CTMA-birnessite samples were obtained. 0.02 g of samples were placed in PP centrifuge tubes and supplemented with 5 mL aliquots of water. The total volume was 5 mL for the desorption measurements, but the ratio of solid to liquid was the same as the ratio described in the adsorption experiments. The pH of the suspensions was adjusted by HNO_3 or NaOH. The centrifuge tubes were then capped and shaken using an orbital shaker for 24 h. Subsequently, the samples were centrifuged and filtered. The supernatants were analyzed with the UV–vis spectrophotometer. Two replications were used for desorption.