Research paper

Accelerated sorption of boron from aqueous solution by few-layer hydrotalcite nanosheets

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ABSTRACT

Boron is toxic to humans and animals at high concentrations. Hydrotalcite (HT) is an anion clay mineral capable of removing boron from water. In this work, the strategy of delamination of hydrotalcite was proposed and demonstrated to be effective in accelerating the boron sorption. Few-layer hydrotalcite (FHT) nanosheets were facilely obtained via rinsing the co-precipitated HT with acetone before final isolation, and achieved boron sorption equilibrium about 10 times faster than HT. The 2D nanosheet morphology helped FHT not only to disperse more fully in boron solution but also to expose more active sites on its external surface. As a result, the route for boron transferring from bulk solution to active sorption sites was effectively shortened on FHT, which finally induced a rapid boron removal.

1. Introduction

Element boron is essential for plants (possibly also animals and humans) but only beneficial in extremely small quantities (Theiss et al., 2013). Humans may over-intake boron when consuming boron-enriched water and food, and suffer from health problems such as focal seizure disorders, irritability and gastrointestinal disturbances (Fawell, 2009; WHO, 2011). Thus, the upper limit of boron concentration for drinking water was suggested to be 0.5 mg/L by the World Health Organization (WHO, 2011) and that for irrigation water was advised to be 0.75 mg/L (Rowe and Abdel-Magid, 1995).

The accumulation of boron in water supplies results from both human activities and natural sources. The manufacture industries for electronics, glass, pharmaceuticals, cosmetics, detergents, etc. may produce effluents containing concentrated boron (Fawell, 2009; WHO, 2011). Seawater naturally contains boron (Guler et al., 2015) and more and more groundwater is found to be rich in boron particularly in the regions utilizing geothermal energy (Guo et al., 2013; WHO, 2011). These boron-enriched wastewater and natural water need to be purified before discharging or utilization.

The current methods for boron removal from aqueous solution are mainly adsorption (Morisada et al., 2011; Reinert et al., 2011; Seki et al., 2006), ion exchange (Thakur et al., 2013; Yan et al., 2008), precipitation-coagulation (Isa et al., 2014; Yilmaz et al., 2007), ultra-filtration (Palencia et al., 2014), and solvent extraction after boron complexation (Fortuny et al., 2014) and so on. The ion exchange using

selective resins is feasible and most recommended. However, due to its characterizations of high regeneration cost, high time consumption, low exchange capacity and unstable structure, new sorbents with favorable deboronation performance are being developed to reduce the cost of water treatment (Bodzek, 2016; Theiss et al., 2013; Wang et al., 2014; Zhang et al., 2015).

In recent years, hydrotalcite and hydrotalcite-like compounds are one type of the most attracting sorbents in view of the environment-friendly and cost-effective features. They are classified as layered double hydroxides with the general formula $M_{1-x}^{2+}M_x^{3+}(OH)_2(A^{n-})_{x/n} \cdot mH_2O$, where M^{2+} is a divalent metal ion (Mg^{2+}, Co^{2+}, Ni^{2+}, Zn^{2+}, Mn^{2+}, Cd^{2+}, etc.), M^{3+} is a trivalent metal ion (Al^{3+}, Fe^{3+}, Cr^{3+}, Ga^{3+}, etc.) and A^{n-} is an anion (F^-, Cl^-, Br^-, I^-, NO_3^-, OH^-, $B(OH)_4^-$, CO_3^{2-}, SO_4^{2-}, MoO_4^{2-}, CrO_4^{2-}, AsO_4^{3-}, etc.) (Theiss et al., 2013). The isomorphous substitution of trivalent metal ions for divalent ones generates positive charges on the layers, which are compensated by exchangeable anions intercalated within the interlayer regions. This structure makes hydrotalcite to be the only clay mineral naturally exhibiting anion exchange abilities and allows it to be potential for efficient boron removal in aqueous solution.

Researches about the boron removal by hydrotalcite and hydrotalcite-like compounds in wastewaters and natural water sources have been widely carried out. Attention was mainly paid to the deboronation performance and mechanism of hydrotalcite and hydrotalcite-like compounds with different compositions, for example, by regulating the type of cations/anions (Ay et al., 2007; Ferreira et al., 2006; Kameda

et al., 2015; Lee et al., 2016; Ulibarri et al., 2001; Yan and Yi, 2010) and the ratio of trivalent cations to bivalent ones (Galindo et al., 2014; Liu et al., 2014), or controlled-calcining them into bimetal oxides with the ability of structural recovery (Delazare et al., 2014; Guo et al., 2013; Kameda et al., 2016; Sanchez-Cantu et al., 2016; Wang et al., 2007).

In this study, we were interested in the effect of the structure dimension of hydrotalcite on its deboronation behavior. We proposed and demonstrated that delaminating 3D hydrotalcite into 2D nanosheets could efficiently accelerate the boron removal process in water. A traditional 3D hydrotalcite and its 2D counterpart were synthesized. Boron sorption kinetics and isothermal experiments were carried out and the sorption behavior and mechanism were discussed.

2. Experimental

The following reagent grade chemicals were provided by Sinopharm Chemical Reagent Co. Ltd. and used as received: magnesium chloride ($MgCl_2 \cdot 6H_2O$), aluminum chloride ($AlCl_3 \cdot 6H_2O$), sodium hydroxide (NaOH), acetone (CH_3COCH_3) and boron acid (H_3BO_3). All solutions were prepared with deionized water.

2.1. Synthesis of hydrotalcite (HT) and few-layer hydrotalcite (FHT)

HT and FHT samples were synthesized by a co-precipitation method. A NaOH solution (1 mol/L, 200 mL) was added dropwise into an aqueous solution (100 mL) containing 0.075 mol of $MgCl_2 \cdot 6H_2O$ and 0.025 mol of $AlCl_3 \cdot 6H_2O$ at 65 °C under vigorous magnetic stirring. The obtained slurry was then kept stirring for 2 h at 65 °C. The precipitate was separated by centrifugation and washed repeatedly with deionized water until pH 7–8. Parts of the washed precipitate was dried at 65 °C in an electric oven for 24 h, crushed to powders and named as HT. The rest of the water-washed precipitate, in a humid status without drying, was re-dispersed in acetone and stirred at room temperature for 1 h. Then, the solid was centrifuged and again dispersed in acetone under stirring. After 5 cycles of the acetone wash, the solid was centrifuged and dried at 65 °C in the oven for 24 h and named as FHT.

2.2. Characterizations of the HT and FHT samples

X-ray powder diffraction (XRD) patterns of the samples were recorded by a *Rigaku D/Max-3B diffractometer* using Cu Kα radiation at 35 kV and 40 mA. Field emission transmission electron microscopy (TEM) analysis was conducted on a *JEOL 200CX electron microscope* operated at 200 KV. Atomic force microscopy (AFM) images were obtained on a *Bruker Dimension Icon* platform. Nitrogen adsorption/desorption isotherms at 77 K were measured on a *Micromeritics TriStar 3020 porosimeter*. Samples were outgassed at 150 °C for > 8 h under a nitrogen flow before the nitrogen adsorption/desorption measurement. The total specific surface area (S_{BET}) was calculated by the Brunauer-Emmet-Teller (BET) method, the micropore surface area (S_{micro}) was determined by the t-plot method and the mesopore surface area ($S_{external}$) was obtained by subtracting S_{micro} from S_{BET}. The pore size distributions were analyzed by the Barrett-Joyner-Halenda (BJH) method. X-ray photoelectron spectroscopy (XPS) measurements were performed on a *VG Multilab 2000*.

2.3. Boron sorption experiment

The water deboronation experiments were carried out by reacting 0.1 g of sorbent (HT or FHT) with 25 mL of boric acid solution in sealed 50 mL polyethylene bottles. The sample bottles were placed in a water-bath shaker with a speed of 150 rpm for a predetermined period at 25 or 65 °C. Then, the solution was filtered through 0.45 μm cellulose acetate filters. The boron concentration in the filtrate was analyzed by inductively coupled plasma mass spectrometry (ICP-MS) on an *Agilent 7700×*. The boron concentration in the solid at equilibrium, q_e (mg/g),

was calculated using the Eq. (1):

$$q_e = \frac{(C_0 - C_e)v}{m} \tag{1}$$

where C_0 and C_e (mg/L) are the initial and equilibrium concentrations of boron in solution; v (L) is the volume of solution and m (g) is the mass of sorbent.

The sorption kinetics experiments were investigated with 6.25 and 25 mg/L boron solutions. The experimental data was fitted to the Lagergren first-order and pseudo second-order models. The Lagergren first-order model assumes irreversible sorption in solid/liquid systems, while the pseudo second-order model adopts an assumption that chemical sorption is one factor controlling the sorption kinetics. The nonlinear forms of Lagergren first-order and pseudo second-order models are given successively in Eqs. (2) and (3):

$$q_t = q_e(1 - e^{-k_1 t}) \tag{2}$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \tag{3}$$

where q_t (mg/g) is the amount of boron in the solid at time t, q_e (mg/g) is the amount of boron in the solid at equilibrium, k_1 (h^{-1}) is the Lagergren first-order rate constant, and k_2 (h^{-1}) is the pseudo second-order rate constant.

In the sorption isotherm experiments, a series of initial boron concentrations of 1.25, 2.5, 6.25, 8.75, 12.5, 15.0, 18.75, 22.5 and 25.0 mg/L were used. The experimental data was fitted to the Langmuir and Freundlich isotherm models, which are expressed in Eqs. (4) and (5), respectively.

$$q_e = \frac{q_m b C_e}{1 + b C_e} \tag{4}$$

$$q_e = K C_e^n \tag{5}$$

where q_m (mg/g) and b (L/mg) are the Langmuir constants reflecting the maximum sorption capacity and the affinity of sorbent towards sorbate, respectively. K [(mg/g) (L/mg)^n] and n are the Freundlich equilibrium parameters indicating the sorption capacity and sorption intensity, respectively.

3. Results and discussion

3.1. Characterization of HT and FHT

The synthesized HT has the typical XRD pattern (Fig. 1) of hydrotalcite crystal (PDF 22-0700). The symmetric peaks for the 003 and 006 planes and asymmetric peaks for others indicate the layered structure of anion clay minerals. FHT has a XRD pattern (Fig. 1) with the same peak locations as those of HT, meaning that FHT is also hydrotalcite. Nevertheless, in contrast with HT, FHT has a relatively lower and boarder peak for the 003 plane, which suggests that the crystal size of FHT is smaller than HT along the platelet stacking axis (the direction perpendicular to the layers). The TEM observations show visually that HT is thick granules (Fig. 2a) while FHT is composed of thin slices (Fig. 2b). The dark lines presented in Fig. 2b correspond to the folds of the nanosheets. 2D materials fold easily since they are small in thickness and large in wideness. The representative AFM image (Fig. 2c) of FHT shows the edges of several stacked nanosheets, and the thickness fluctuation (Fig. 2d) determined along the line between point 1 (P1) and point 2 (P2) across the edges indicates that the FHT nanosheets are about 4 nm in thickness.

The porosity features of the two samples measured by N_2 adsorption-desorption lead to a conclusion accordant to above. As plotted in Fig. 3, HT has a flat curve for N_2 adsorption-desorption isotherm, reflecting its non-porous feature. The N_2 adsorption-desorption isotherm of FHT is a typical IV type curve with a H3 type hysteresis loop. It