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Continuous treatment of boron and fluoride in aqueous solutions using a column loaded with granulated Mg–Al layered double hydroxides intercalated with nitrates

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ABSTRACT

Mg–Al layered double hydroxides intercalated with NO_3^- (NO_3·Mg–Al LDHs) were mixed with various amounts of epoxy resin to obtain granulated NO_3·Mg–Al LDH samples. The granulated NO_3·Mg–Al LDH samples were shown to be capable of adsorbing B from aqueous solutions and the experimental adsorption isotherm data fit well to the Langmuir model. In order to evaluate the continuous treatment of B and F^- in aqueous solutions, a chromatographic column was loaded with granulated NO_3·Mg–Al LDH with an LDH/epoxy resin ratio of 1:0.5 and H_3BO_3 and NaF solutions were passed through the columns under various conditions. The concentrations of B and F^- in the elutions were found to increase with time. In addition, the concentrations of B and F^- in the elutions also increased with increase in the flow rates and initial concentrations of H_3BO_3 and NaF, respectively, which were attributed to the flow of large amounts of B and F^- into the column in a short duration. The experimental data from the column experiments were fit to the Thomas model. The relatively high R^2 values under all the conditions suggest that the Thomas model adequately represents the results of the adsorption experiments. For the adsorption of both B and F^-, the calculated q_T from the Thomas model showed good agreement with the experimental q_E values, confirming the validity of the Thomas model for the column experiments.

1. Introduction

Layered double hydroxides (LDHs) are capable of anion-exchange and have therefore, gained attention as promising materials for a number of applications including water purification [1]. LDHs are typically represented by the general formula $[M^{2+}{}_{1-x}M^{3+}{}_x(OH)_2](A^{n-})_{x/n}\cdot mH_2O$, where M^{2+} and M^{3+} are divalent and trivalent metal ions, respectively, x is the $M^{3+}/(M^{2+}+M^{3+})$ molar ratio ($0.20 \leq x \leq 0.33$), and A^{n-} is an anion such as CO_3^{2-} or Cl^- [2,3]. An LDH consists of a stack of brucite-like octahedral layers, where some of the M^{2+} is replaced with M^{3+}. The positive charge in the layer arising from this substitution is neutralized by the interlayer anions [4], and the interlayer space is occupied by the water molecules present in the hydration shell of the anions. Recently, LDHs have been investigated as adsorbents for removing hazardous materials from wastewater. For example, Mg–Al LDH has been found to remove B from aqueous solutions [5–8]. In addition, Mg–Al LDH has also been shown to remove F^- from aqueous solutions [9–11]. In particular, we have previously clarified that the removal of B and F^- by Mg–Al LDH intercalated with NO_3^- and Cl^- (NO_3·Mg–Al LDH and Cl·Mg–Al LDH) is described by pseudo-second-order reaction kinetics with Langmuir-type adsorption characteristics [8,11].

Adsorption-based wastewater treatment processes are mainly classified into two types, namely batch and column operations. In the case of batch operations, large quantities of wastewater can be easily treated. However, batch treatment is ineffective for treating wastewater with low concentrations of the ion of interest. On the other hand, wastewater containing low concentrations of the target material can be treated in column operations with high efficiency. However, column operations are not appropriate for the treatment of large quantities of wastewater. Therefore, in practical applications, selecting a suitable treatment method based on the nature of wastewater is important. Since Mg–Al LDH consists of fine particles, it is difficult to use it in column operations owing to the low flow of wastewater. Therefore, it is usually studied in the batch operation mode for the treatment of wastewater. In order to render it suitable for use in column operations, it is necessary to increase the particle size of Mg–Al LDH by granulating it using a binder. In this study, the granulation of NO_3·Mg–Al LDH using epoxy resin has been investi-

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gated. Further, the removal of B and F^- from aqueous solutions by treating with granulated NO_3·Mg–Al LDH has been evaluated using column operations.

2. Experimental

All of the reagents used were of chemical reagent grade and were used without further purification.

2.1. Evaluation of granulated Mg–Al LDH intercalated with NO_3^-

NO_3·Mg–Al LDH with a Mg/Al molar ratio of 2 was prepared by co-precipitation and mixed with epoxy resin at LDH/epoxy resin mass ratios (*L*/*e*) of 1:0, 1:0.3, 1:0.5, 1:0.7, and 1:1. The mixed materials were dried under reduced pressure (133 Pa) at 40 °C for 24 h and sieved to obtain granulated NO_3·Mg–Al LDH with particle size in the range of 500 μm–1 mm. The reason for selecting this particle size range of 500 μm–1 mm is as follows. At a particle size below 250 μm, the solution could not be passed through a column packed with granulated NO_3·Mg–Al LDHs in preliminary experiments, owing to the tight packing caused by the low particle size. When the particle size was in the range of 250–500 μm, while the solution could be passed through the column packed with granulated NO_3·Mg–Al LDHs, the velocity of the solution was very low. On the other hand, when the particle size was in the range of 500 μm–1 mm, the solution could be passed through the column packed with granulated NO_3·Mg–Al LDHs. In addition, the velocity of the solution was sufficient for achieving acceptable B and F^- removal. Therefore, this particle size range was chosen.

To determine the adsorption isotherm for the adsorption of B on granulated NO_3·Mg–Al LDH adsorbents, 20 mL of H_3BO_3 solution (0.005–0.4 mol L^{-1} with an initial pH of 10) and 0.1 g of granulated NO_3·Mg–Al LDH were placed in 50 mL screw-top tubes and shaken at 30 °C for 24 h. The suspension was then filtered through a 0.45 μm membrane filter and the filtrate was analyzed for residual B.

2.2. Continuous treatment of B and F^- in aqueous solutions using a column loaded with granulated NO_3·Mg–Al LDH

A chromatographic tube (inner diameter of 15 mm) with a filter and cock was loaded with 5 g of granulated NO_3·Mg–Al LDH with an *L*/*e* mass ratio of 1:0.5. The length and bed depth of the column packed with granulated NO_3·Mg–Al LDH were 35 and 8 cm, respectively. The temperatures of H_3BO_3 (50 or 100 mg L^{-1}; initial pH of 10) and NaF (initial pH was not controlled) solutions were maintained at 30 °C using a water bath. The solutions were passed through the top of the chromatographic column using a pump at a flow rate of 5 or 10 mL min^{-1} and the eluent from the bottom of the column was sampled every 20 min and analyzed for residual B and F^-.

2.3. Characterization methods

The materials were analyzed using X-ray diffraction (XRD) measurements with Cu Kα radiation. Further, the adsorbents were observed by scanning electron microscopy (SEM) and by acquiring digital photographs. For the adsorption and column experiments, the residual concentrations of B in the filtrates and eluents were determined using inductively coupled plasma-atomic emission spectrometry (ICP-AES). Furthermore, the residual concentrations of F^- in the filtrates and eluents were determined using a Dionex DX-120 ion chromatograph and Dionex model AS-12A column (eluent: 2.7 mM Na_2CO_3 and 0.3 mM $NaHCO_3$; flow rate: 1.3 mL min^{-1}).

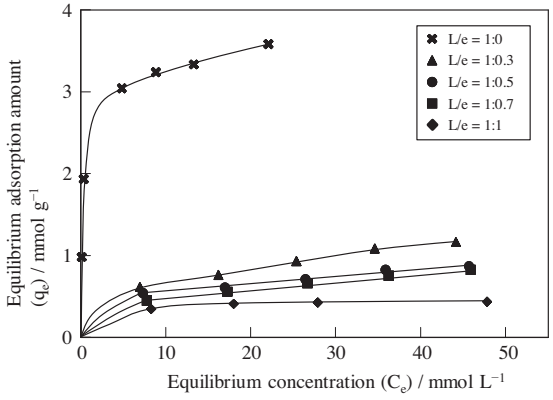

Fig. 1. Adsorption isotherms for the adsorption of B on granulated NO_3·Mg–Al LDH with various *L*/*e* mass ratios. Amount of granulated NO_3·Mg–Al LDH: 0.1 g; initial B concentration: 0.005–0.4 M; initial pH: 10; temperature: 30 °C; time: 24 h.

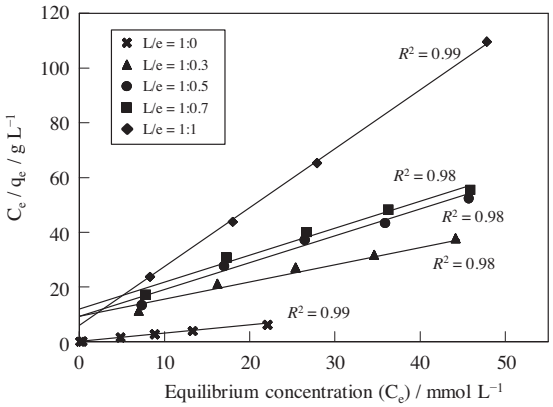

Fig. 2. C_e/q_e versus C_e plots derived from the B adsorption isotherms on granulated NO_3·Mg–Al LDH with various *L*/*e* mass ratios. Amount of granulated NO_3·Mg–Al LDH: 0.1 g; initial B concentration: 0.005–0.4 M; initial pH: 10; temperature: 30 °C; time: 24 h.

3. Results and discussion

3.1. Evaluation of granulated Mg–Al LDH samples intercalated with NO_3^-

The adsorption isotherms measured for the adsorption of B on granulated LDH materials with various *L*/*e* mass ratios are shown in Fig. 1. In all the cases, the equilibrium adsorption amount increased with increase in the equilibrium concentration of B in the solution, indicating that the granulated NO_3·Mg–Al LDH materials are capable of adsorbing B from aqueous solutions. However, it may be noted that the equilibrium adsorption amounts of B for the granulated NO_3·Mg–Al LDH materials were much lower than those for the unmodified NO_3·Mg–Al LDH (*L*/*e* = 1:0) materials. The hydrolysis of H_3BO_3 may be represented by Eq. (1).

$$H_3BO_3 + H_2O \rightleftarrows H^+ + B(OH)_4^- \quad (1)$$

The acid dissociation constant (pK_a) of H_3BO_3 is 9.2 [12]. Since the initial pH of the solution is 10, the concentration of $B(OH)_4^-$ is likely to be higher than that of H_3BO_3 in the solution. Therefore, during adsorption, $B(OH)_4^-$ is thought to be the predominant B species removed and the removal of $B(OH)_4^-$ by the granulated NO_3·Mg–Al LDHs may be represented by Eq. (2).

$$Mg_{0.67}Al_{0.33}(OH)_2(NO_3)_{0.33} + 0.33B(OH)_4^- \rightarrow$$
$$Mg_{0.67}Al_{0.33}(OH)_2(B(OH)_4)_{0.33} + 0.33NO_3^- \quad (2)$$