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Enhanced fluoride removal by La-doped Li/Al layered double hydroxides

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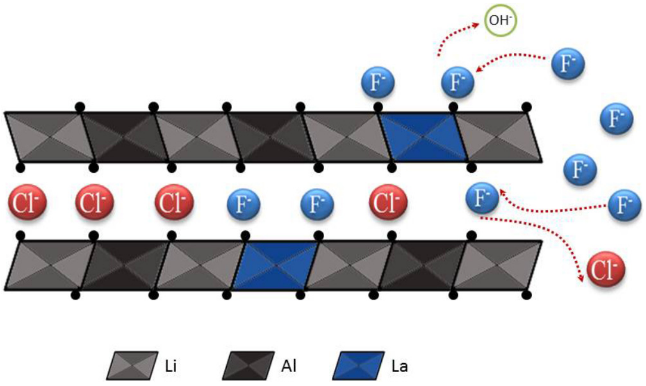
GRAPHICAL ABSTRACT



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ABSTRACT

In this study La intercalated Li/Al layered double hydroxide (LDH) was developed for efficient water defluoridation. The La-modified material, i.e., La doped Li/Al-LDH, exhibits more preferable fluoride adsorption than Li/Al-LDH in a broad pH range of 5–9, with the working capacity twice of the latter and seven times of magnitude higher than activated alumina. The fluoride removal kinetics is well fitted by pseudo-second order model, and the adsorption isotherm is well described by Freundlich model. Effect of pH and competing ions was examined during fluoride sequestration. The underlying mechanism for such enhanced adsorption of fluoride by La doped Li/Al-LDH was further revealed based on XPS and FTIR analysis. The presence of La and Al was found to be responsible for the satisfactory defluoridation of La doped Li/Al-LDH, and chloride replacement with fluoride occurred from both LDHs during fluoride adsorption. Also, the capacity of La doped Li/Al-LDH could be refreshed by alkaline solution (pH = 12) for cyclic runs. All the results implied that La doped Li/Al-LDH could serve as a potential adsorbent for efficient fluoride removal from water.

1. Introduction

Fluoride is one of the essential trace elements for its beneficial effects on skeleton and teeth in adequate amounts. On the other hand, excessive intake of fluoride is thought to cause health issues due to its effect on assimilation of calcium and phosphorus over a long period of time [1–5]. Nowadays, endemic fluorosis has become a worldwide disease that endangers human health [1]. Among various methods for water defluoridation, adsorption has been considered as an attractive option due to its low cost and simplicity of design and operation [6–7]. Different materials have been developed for fluoride removal including aluminum-based oxide

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sorbents [8], iron-based sorbents [9], and carbon-based sorbents [10].

In the recent decade, layered double hydroxides (LDHs) have attracted considerable attentions for their excellent anion exchange performance and outstanding thermal stability. The general formula of LDHs could be described as $[M_x^{2+}M_{1-x}^{3+}(OH)_2]^{x+}(A^{n-})_{x/n}\cdot mH_2O$, indicating that they are composed of replaceable metal hosts and exchangeable anions. Due to the specific structural characteristics, LDHs have been explored in removing organic anions, oxyanions and monatomic anions from aqueous solutions [11–12]. As one of the unique compounds in the LDH group, Li/Al-LDH has been proved to be an efficient adsorbent for fluoride removal [13–15]. Li/Al-LDH presented higher capacity and preference for fluoride sequestration than the widely used adsorbent activated alumina, and both of them exhibited favorable performance at weakly acidic pHs (5–6). However, the real pH of fluoride contaminated groundwater falls into the weakly alkaline range (~8) [16], and further improvement of the performance of LDH on fluoride removal particularly at weakly alkaline pHs is urgently desired.

Rare-earth metal elements like Ce, Zr, and La could provide active sites for complexation or ligand exchange with fluoride, so that they have been reported as modifiers for improving defluoridation performance of adsorbents, such as Mg-Fe-La composite [17], Fe-Al-Ce composite [18]. A few other novel materials such as La incorporated carboxylated chitosan composite, La modified activated alumina, La impregnated silica gel were also reported [19–23] to exhibit promising results for fluoride removal. Compared to other metals like Zr, La modification is generally believed to enhance fluoride removal more significantly.

In this work, a new composite La doped Li/Al-LDH was designed by doping lanthanum into Li/Al-LDH to further improve its defluoridation performance in water. Li/Al-LDH and active alumina were adopted for comparison. The kinetic and isotherm analysis was performed to study the adsorption behavior of the LDHs. Effects of pH and co-existing anions on their defluoridation performance were also investigated. Furthermore, XRD, BET, FTIR and XPS techniques were employed for characterization of the materials and elucidation of their defluoridation mechanism.

2. Materials and methods

2.1. Materials

All chemicals used in this study are of analytical grade (purity ≥ 99.7%). Aluminum chloride, lithium chloride, lanthanum chloride, sodium hydroxide, hydrochloric acid, sodium fluoride, sodium nitrate, and sodium citrate were obtained from Shanghai Chemical Reagent Plant (Shanghai, China). Activated alumina (AA) was provided by Suzhou HongPeng adsorbent factory (Suzhou, China). It was present as spherical beads of 2–3 mm in diameter.

2.2. Synthesis of LDHs

La doped Li/Al-LDH was synthesized based on traditional co-precipitation method. The detailed procedures are described as follows: 100 mL solution with constant Li/(La + Al) molar ratio of 3 and varying La/Al molar ratio of 0.1, 0.2, 0.3, 0.5 or 0.8 respectively was prepared by dissolving $LiCl\cdot H_2O$, $AlCl_3\cdot 6H_2O$ and $LaCl_3\cdot 6H_2O$ of preset concentration in deionized water. NaOH (0.02 M) was added dropwise into the solution simultaneously under rapid stirring to keep the uniform precipitates, and the dropping speed was auto-controlled to maintain pH 9–10. The quantity of NaOH and salts required for the reaction were predetermined through stoichiometric calculation. When all the NaOH solution was dripped off, the slurry was kept stirring for additional 1 h to ensure homogeneity, then aged at 338 K for 15 h. The final precipitate was filtered, washed, dried. For simplicity, samples with $Li_{3.3}Al_1La_{0.1}$, $Li_{3.75}Al_1La_{0.25}$, $Li_{4.5}Al_1La_{0.5}$, $Li_6Al_1La_1$ and $Li_{15}Al_1La_4$ are denoted as LAL01, LAL02, LAL03, LAL05 and LAL08, respectively.

Li/Al-LDH was prepared by a similar procedure as above for comparison. Samples with Li/Al molar ratio of 2, 3, or 4 were synthesized and noted as LA2, LA3 and LA4, respectively.

2.3. Characterization of the LDHs

The molar ratio of Li, Al and La in the synthesized materials was verified by Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES, PerkinElmer USA). To determine the metal contents in the solids, the LDH powder was first digested in nitric-perchloric acid solution prior to analysis by ICP-OES. The specific surface area and total pore volume of adsorbents were determined by N_2 adsorption experiments at 77 K on a Micro Meritics ASAP-2010C Instrument (Norcross, GA). The crystalline of LDHs was analyzed by X-ray diffraction analysis Instrument (XRD, XTRA, Switzerland) with Cu/Ka radiation (40 kV, 25 mA). The morphology of LDHs was observed with transmission electron microscopy (JEM-200CX, JEOL, Japan) operating at 200 kV with a field emission gun. The adsorbents were also characterized by Fourier transform infrared spectroscopy (FTIR, Nexus, Nicolet) using KBr pellets at room temperature. The interactions between LDHs and fluoride was reflected by X-ray Photoelectron Spectrum (XPS, PHI 5000 VersaProbe, Japan). The binding energies were referenced to the C1s peak at 284.8 eV.

2.4. Batch adsorption/desorption experiments

All batch studies were carried out in a thermostatic shaker at 298 K and 180 rpm. The dosage of LDHs was kept 0.50 g/L, and the contact time was 24 h. NaF solution was used as simulated fluorine water and the fluoride concentration was measured by a fluoride ion selective electrode (PF-1) with sodium citrate ($C_6H_5Na_3O_7$, 0.2 mol/L) and $NaNO_3$ (1 mol/L) as total ion strength adjustment buffer. The pH value of the solution was adjusted by 0.10 mol/L HCl or NaOH. The initial fluoride concentration in the experiments was 20 mg/L except for specific note. The effect of pH on adsorption was investigated by adjusting the initial pH value from 4 to 12. Effect of coexisting anions on fluoride retention was investigated in the presence of NO_3^-, SO_4^{2-}, HCO_3^-, PO_4^{3-} or Cl^- at 5, 10 or 20 mg/L.

Batch desorption study was carried out under similar experimental conditions as above to test the reusability of the LDHs. The F-loaded LDHs was dispersed in a 1.0 M NaCl-0.01 M NaOH solution with the same S/L ratio as in the adsorption, and shaken for 24 h. Then, the particles were vacuum filtered and dried, collected for the next cycle.

3. Results and discussion

3.1. Characterization of LDHs

3.1.1. Crystal structure

XRD analysis was performed to identify the phase structure of the synthesized materials. As shown in Fig. 1a, La doped Li/Al-LDH samples exhibited sharp and symmetric peaks at 11.68° (0 0 3), 23.59° (0 0 6) and 20.56° (1 0 0), which is consistent with that for $LiAl_2(OH)_6\cdot xH_2O$ (JCPDS card No. 31-0704), and the diffraction peaks at 27° and 29° could be assigned to $La(OH)_3$ (JPCDS card No. 06-0585). The intensity of the specific diffraction peaks (0 0 3)