



# Efficient defluoridation of water using reusable nanocrystalline layered double hydroxides impregnated polystyrene anion exchanger



Jianguo Cai, Yanyang Zhang, Bingcai Pan<sup>\*</sup>, Weiming Zhang, Lu Lv, Quanxing Zhang

State Key Laboratory of Pollution Control and Resource Reuse, School of the Environment, Nanjing University, Nanjing 210023, China

## ARTICLE INFO

### Article history:

Received 15 March 2016

Received in revised form

2 June 2016

Accepted 13 June 2016

Available online 15 June 2016

### Keywords:

Water defluoridation

Adsorption

Al/Li LDH

Polymer nanocomposite

Chemical stability

Efficient regeneration

## ABSTRACT

Water decontamination from fluoride is still a challenging task of global concern. Recently, Al-based layered double hydroxides (LDHs) have been extensively studied for specific fluoride adsorption from water. Unfortunately, they cannot be readily applied in scaled-up application due to their ultrafine particles as well as the regeneration issues caused by their poor stability at alkaline pHs. Here, we developed a novel (LDH)-based hybrid adsorbent, i.e., LALDH-201, by impregnating nanocrystalline Li/Al LDHs (LADLH) inside a commercial polystyrene anion exchanger D201. TEM image and XRD spectra of the resultant nanocomposite confirmed that the LDHs particles were nanosized inside the pores of D201 of highly crystalline nature and well-ordered layer structure. After impregnation, the chemical and mechanical stability of LALDH were significantly improved against pH variation, facilitating its application at a wide pH range (3.5–12). Fluoride adsorption onto LALDH-201 was compared to D201 and activated alumina, evidencing the preferable removal fluoride of LALDH-201. Fluoride adsorption onto LALDH-201 followed pseudo-second-order model, with the maximum capacity (62.5 mg/g from the Sips model) much higher than the other two adsorbents. Fixed-bed adsorption run indicated the qualified treatable volume of the fluoride contaminated groundwater (4.1 mg/L initially) with LALDH-201 was about 11 times as much as with the anion exchanger D201 when the breakthrough point was set as 1.5 mg/L. The capacity of LALDH-201 could be effectively refreshed for continuous column operation without observable loss by using the mixed solution of 0.01 M NaOH + 1 M NaCl. The above results suggested that the hybrid adsorbent LALDH-201 is very promising for water defluoridation in scaled-up application.

© 2016 Elsevier Ltd. All rights reserved.

## 1. Introduction

Fluorine is one of the essential trace elements in human body. On the other side, excessive uptake of fluoride can cause fluorosis, which is currently recognized as one of the most serious endemic disease in at least 28 countries from Africa, America, and Europe (Ayoob and Gupta, 2006; Fawell et al., 2006). The World Health Organization (WHO) has recommended a guideline of 1.5 mg/L as the maximum fluoride concentration level in drinking water (WHO, 1996). It was estimated that 200 million people globally are drinking groundwater of excessive fluoride levels and suffering from fluorosis. Efficient defluoridation of water has become a major concern in water treatment for decades (Ayoob and Gupta, 2006). So far, several methods have been developed to remove excessive

fluoride from water, such as coagulation-precipitation, membrane-based process, ion exchange, and adsorption (Bhatnagar et al., 2011; Jagtap et al., 2012; Sternitzke et al., 2012; Pan et al., 2013; Zhao et al., 2015). Among these, adsorption is an attractive option and widely used in real application. Various adsorbents such as activated alumina, calcium-based sorbents, iron-based sorbents, ion exchange resins and fibers, metal oxides and hydroxides have been used in water defluoridation (Ku et al., 2002; Turner et al., 2005; Meenakshi and Viswanathan, 2007; Kumar et al., 2009; Biswas et al., 2010; Kameda et al., 2015). Of the available adsorbents, activated alumina is the most commonly used one because it exhibits specific affinity and selectivity for fluoride. One of the disadvantages of activated alumina is that the optimum pH value for fluoride removal is below 6.0, which heavily limits its practical applications (Jagtap et al., 2012). In addition, the alumina leaching into water possibly results in secondary contamination.

Layered double hydroxides (LDHs) belong to lamellar compounds containing exchangeable anions in the interlayer space. In

<sup>\*</sup> Corresponding author.

E-mail address: [bcpan@nju.edu.cn](mailto:bcpan@nju.edu.cn) (B. Pan).

the recent decade, they have been extensively studied in removing numerous oxyanions from aqueous solutions (Goh et al., 2008). Besides, LDHs have also been reported to be effectively used in water defluoridation (Lv et al., 2007; Mandal and Mayadevi, 2009; Zhang et al., 2012; Ghosal et al., 2015; Oladoja et al., 2016). Compared to activated alumina, LDHs can be used in a broader pH range (Mandal and Mayadevi, 2009). However, several inherent defects of LDHs are very unfavorable for their large-scale applications. First of all, the nanocrystalline particles of LDHs tend to agglomerate into larger size, resulting in a significant drop of active sites and capacity. Secondly, the powder form of LDHs may generate unavoidable problems in solid/liquid separation process, such as blockage in the facilities and/or excessive pressure drop. Thirdly, the potential leakage risk of the precursor metals of LDHs is also unamiable to drinking water treatment. Last but not least, the operation of LDHs in water treatment is still cost ineffective, since regeneration of the spent LDHs is still challenging and costly now (Goh et al., 2008; Wang, 2010; Mandel, 2013).

To face the above-mentioned problems, hybridizing LDHs with other potential mechanically and chemically stable materials may be a potential option. To the best of our knowledge, there are few open literatures regarding LDHs based hybrid adsorbents. The very few cases included LDHs loaded cellulose, carbon nanosphere and super paramagnetic microparticle (Mandal and Mayadevi, 2008; Gong et al., 2011; Mandel, 2013). Compared to the bare LDHs, the LDHs composite show better applicability in terms of feasible operation as well as enhanced stability.

Recently, macroporous ion-exchange resins (MIER) have been widely employed to support nanosized active inorganic particles for water purification. Polymeric hosts are superior to other traditional supports (activated carbon, silica, etc.) because of their satisfactory hydrodynamic performance and loading efficiency, relying on its flexibility in size, porosity, and surface chemistry of the MIER beads (Blaney et al., 2007; Pan et al., 2010; Jiang et al., 2011; Du et al., 2013; Zhang et al., 2013, 2016). The immobilized charged groups of MIER are favorable for the dispersion of active nanoparticles inside the nanopores of the hosts, resulting in an increasing accessible surface. In addition, the crosslinking and wrapping of the polymer chains can effectively restrain the loss of the nanoparticles, thus ensuring the stability of hybrid adsorbents (Xie et al., 2011). Therefore, a hybrid adsorbent made by impregnating nanosized LDHs into MIER can be expected to enhance defluoridation efficiency and improve practical applicability.

The objectives of the present work were: (1) to fabricate a reusable nanocrystalline Li/Al LDHs hybrid adsorbent LALDH-201 for fluoride removal from water; (2) to evaluate the chemical and mechanical stability of the hybrid adsorbent and investigate the effect of solution chemistry; (3) to preliminarily probe the defluoridation mechanism; and (4) to examine the performance of fixed-bed column tests for practical application.

## 2. Materials and methods

### 2.1. Materials

All chemicals used in this study were of analytical grade or higher.  $\text{Na}_3\text{AlO}_3$ ,  $\text{LiCl} \cdot \text{H}_2\text{O}$ ,  $\text{NaF}$ ,  $\text{HCl}$ ,  $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ ,  $\text{Na}_3\text{PO}_4 \cdot 10\text{H}_2\text{O}$ ,  $\text{NaHCO}_3$ ,  $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ ,  $\text{Na}_2\text{HPO}_4$ ,  $\text{NaNO}_3$ ,  $\text{Na}_2\text{SiO}_3$ ,  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ , and  $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$  were purchased from Shanghai Chemical Reagent Plant (Shanghai, China) and used without further purification. Aqueous stock containing 1000 mg/L of fluoride ion was prepared by dissolving desired amount of  $\text{NaF}$  into the deionized water. The commercial macroporous strongly basic anion exchanger D201 was provided by Jiangsu NJU Environmental Technology Co., Ltd. (Nanjing, China). Activated alumina was provided by Suzhou

HongPeng Adsorbent Factory (Suzhou, China). Prior to use, D201 was subjected to flushing with  $\text{HCl}$  solution (5% in mass) followed by rinsing with deionized water until neutral pH, and then vacuum desiccated until constant weight.

### 2.2. Fabrication and characterization of LALDH-201

The nanocrystalline Li/Al LDHs hybrid adsorbent LALDH-201 was fabricated through the direct reaction between lithium salt and nanosized aluminium hydroxide inside the nanopores of D201 followed by hydrothermal treatment. In detail, 200 g  $\text{NaAlO}_2$  was dissolved in 2000 mL deionized water, and the solution passed through a column packed with 1000 mL (wet volume) of D201 at the volumetric flow rate of 20 mL/min. Then, the D201 beads were transferred into 1000 mL deionized water, and the mixture was stirred continuously.  $\text{HCl}$  solution (20% in mass) was used to titrate the solid/water mixture to a constant pH of 7.0, where  $\text{Al}(\text{OH})_3$  gradually precipitated inside the pore of D201. The resultant D201 beads containing  $\text{Al}(\text{OH})_3$  were added into  $\text{LiCl}$  solution (10% in mass), and the mixture was heated at 373 K for 12 h to ensure the formation of Li/Al LDHs ( $\text{LiCl} \cdot 2\text{Al}(\text{OH})_3 \cdot m\text{H}_2\text{O}$ ), and the hybrid adsorbent LALDH-201 was obtained. In addition, a Li/Al LDHs named LALDH with Al: Li molar ratio of 2:1 was prepared by the conventional coprecipitation method modified from the literature (Mandal and Mayadevi, 2008). Briefly, the initial mixture with molar ratio of Al: Li = 2:1 was stirred for 30 min, and then  $\text{NaOH}$  solution (5% in mass) was used as the precipitant to prepare the LDHs at 363 K. The precipitate was aged for 24 h at the same temperature. Afterward, the slurry was filtered and washed three times with distilled water. The wet solid was dried at 333 K for 24 h, and then milled and sieved to get granular LALDH sample with the size of 0.5–1.0 mm.

The morphology of Li/Al LDHs particles dispersed in the inner pore of D201 was observed with transmission electron microscopy (Tecnai F20, FEI, USA) operating at 200 kV with a field emission gun, and its mineralogy was analyzed by X-ray diffraction analysis Instrument (XRD, XTRA, Switzerland) with  $\text{Cu}/\text{K}\alpha$  radiation (40 kV, 25 mA). The pore size distribution and specific surface area of LALDH-201 was determined by  $\text{N}_2$  adsorption-desorption test at 77 K on a Micro Meritics ASAP-2010C Instrument (Norcross, GA). The elemental contents of lithium and aluminum of LALDH-201 were determined by inductively coupled plasma atomic emission spectrometry (ICP-AES, PerkinElmer, USA) after nitric-perchloric acid digestion. The fluoride-sorbent interaction was preliminarily probed by X-ray photoelectron spectroscopy (XPS, ESCALAB-2, UK). An Al  $\text{K}\alpha$  anode radiation was employed as the excitation source. The binding energies were referred to C1s peak at 284.8 eV.

### 2.3. Stability of LALDH-201

The mechanical stability of the solid adsorbent was examined as referred to the mechanical strength test for ion exchange resins with a slight modification (GB/T12598-90, 1992). In detail, 15 mL of solid sample (LALDH-201 or LALDH) and 45 mL pure water were transferred into the ball mill (QM-3SP04 Ball Mill, Nanjing University Instrument Factory, China). Subsequently, 30 steel balls ( $\Phi$  5 mm) were then added into the mill. The mixture was subjected to rolling at 140 r/min for 30 min  $\pm$  2 S. Finally, the sample was dried at 333 K for 3 h, and the percentage of the broken sample was determined. D201 was also tested as reference.

Effect of pH on the chemical stability of LALDH-201 was evaluated by adding 0.10 g of LALDH-201 into 200 mL  $\text{HCl}$  or  $\text{NaOH}$  solution at different pHs and vibrating for 7 days. Then, the dissolved lithium and aluminum in solution was determined by using ICP-AES. The stability of LALDH was also examined as above.

Download English Version:

<https://daneshyari.com/en/article/4480844>

Download Persian Version:

<https://daneshyari.com/article/4480844>

[Daneshyari.com](https://daneshyari.com)