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Efficient and rapid adsorption of iodide ion from aqueous solution by porous silica spheres loaded with calcined Mg-Al layered double hydroxide

Chunmin Li[a], Yuezhou Wei[a,c], Xinpeng Wang[a,*], Xiangbiao Yin[b,*]

[a] Guangxi Key Laboratory of Processing for Non-ferrous Metal and Featured Materials, Guangxi University, Nanning 530004, China
[b] Laboratory for Advanced Nuclear Energy, Tokyo Institute of Technology, 2-12-1, Ookayama, Meguro -ku Tokyo 152-8550, Japan
[c] School of Nuclear Science and Engineering, Shanghai Jiao Tong University, Shanghai 200240, China

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ABSTRACT

In this study, magnesium and aluminum ion was firstly inhaled into the silica sphere by low-vacuum impregnation technique, and subsequently hydrotalcite (Mg-Al-LDH) was synthesized inside the silica-based mesoporous material using in-hole precipitation method. Metal composite oxide (Mg-Al-LDO) was the calcined product by calcining Mg-Al-LDH at 450 °C and the composite material Mg-Al-LDO/SiO_2 was the main absorbent for absorbing iodine ion (I^-) in this study. The characteristics of SEM inner-morphology, FT-IR spectroscopy and X-ray diffraction strongly demonstrated hydrotalcite admirably grew in the channel of silica matrix. The influence of composite material dosage, pH values of aqueous solution, and initial concentration of I^- on adsorption capacity was investigated in detail. The batch experiment results showed that Mg-Al-LDO/SiO_2 had an excellent adsorption performance on I^- and the removal efficiency reached 99.81% from a 30 mg/L I^- solution in 5 min, with a dosage of 0.05 g/100 ml. The adsorption kinetics was fitted well by pseudo -second-order model. The column experiment data demonstrated that the application of Mg-Al-LDO/SiO_2 in a column model for the continuous treatment of iodine ion effluents exhibited optimum breakthrough curves by adjusting the bed heights. The experimental breakthrough curves were correlated with Thomas, Adams–Bohart and Yoon–Nelson models.

1. Introduction

Iodine ion (I^-), as a typical toxic anion contaminant which tends to accumulate in thyroid gland of animal body via the food-chain leading to the increase of thyroid cancer, leukemia and metabolic disorders, has drawn much concern since its great threat to human health after iodine pollution [1]. To remove I^- from aqueous solution, various trials have been timely conducted using different methods such as surface adsorption, ion exchange, chemical precipitation, solvent extraction, and membrane separation, among others [2–5]. Notably, adsorption is an efficient and clean approach in light of its facile handling, high treatment efficiency, and suitability for treating large volumes of water especially under the continuous operations [6–8]. Thus, the synthesis of reliable adsorbents is beneficial in the field. As such, much attention has been paid to the development of various functional adsorbents, such as metal-modified activated carbon, and inorganic silver-/bismuth-/cuprous-based adsorbents for I^- removal from water [9–12]. These kinds of inorganic materials possess quite a few advantages over the organic resin as adsorbents to dispose wastewater, such as tolerance to higher temperature etc. Nevertheless, small mechanical size, slow sorption rate, low loading capacity, high cost, and inherent metal toxicity of some of these adsorbents are still the troubles, which lead to their great limit in column packing and on large scale applications, especially for the treatment of radioactive wastewater calling for continuous processing. Therefore, an effective adsorbent is urgently needed to achieve efficient I^- removal within a short reaction time.

Layered double hydroxides (LDHs) and its modified form, recognized as the anionic clay minerals consisting of the lamellar structure similar to that of the mineral brucite, are promising adsorbents for the removal of numerous ionic contaminants from aqueous solution, such as UO_2^{2+} [13,14], $^{241}Am^{3+}$ [15], Cu^{2+}, Pb^{2+}, and Cr^{6+} [16] and so on. Typically, partial divalent cations (M^{2+}) in the lamellar structure of LDHs are substituted by isomorphous trivalent cations (M^{3+}) resulting in the net permanent positive charge in trioctahedral position of the hydroxide layers, which is balanced by exchangeable anions intercalated into the interlayers.

* Corresponding authors.
E-mail addresses: wangxinpeng@gxu.edu.cn (X. Wang), yin.x.aa@m.titech.ac.jp (X. Yin).

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Depending on the type of metal cations in the layered structure and exchangeable anions present in the interlayers, the LDHs can exhibit various adsorption, magnetic, optical, catalytic, and electrochemical properties [17]. Another important property of LDHs is the restoration (or memory) effect of their layered structure. In detail, on calcination at 300–500 °C, thermally activated LDHs decompose to form layered double oxides (LDOs) by eliminating the interlayer water and original anions [18–20]. Once the LDOs is exposed in aqueous solutions with additional anions, restoration of the lamellar structure will occur ensuing the spontaneous intercalation of charged balancing anions into the interlayer. These reconstituted LDHs may distinguish with their original structure since the interlayer incorporation of different anions. The above-mentioned structure memory effect has been successfully applied to increase the adsorption capacity of LHDs for anions.

In the present study, porous silica sphere was selected as the substrate to support the loaded LDHs nanoparticles, which could not only significantly inhibit the nanoparticles aggregating, but also greatly enhance the abrasion resistance, mechanical endurance, and the hydraulic performance of LDHs. Furthermore, the porous silica sphere could also maintain its good porous microstructure and morphology during the transformation of LDHs to LDOs by calcining at high temperature. Subsequently, the properties of these as-prepared porous Mg-Al-LDO/SiO_2 composites for I^-adsorption were measured in various experimental conditions.

2. Experimental section

2.1. Materials

Silicon-F50 is self-made, for which the particle size distribution is 75–150 um. Analytical -grade reagents of salts, including $AlCl_3 \bullet 6H_2O$, $MgCl_2 \bullet 6H_2O$, KI, $NaCO_3$ and NaOH were purchased from Guanghua Sci-Tech Industries (Guangdong, China) and were used as received, unless otherwise noted.

2.2. Preparation of Mg-Al-LDO/SiO_2

Mg-Al-LDO/SiO_2 was synthesized by dissolving $AlCl_3 \bullet 6H_2O$ and $MgCl_2 \bullet 6H_2O$ (molecular proportion of Mg and Al was 3:1) into deionized water, forming a homogeneous metal ion solution. Then, SiO_2 powders were added to the above mixed solution and the suspension solution with SiO_2 powders was moved into vacuum rotary evaporator vacuumizing for 6 h to ensure the mixed metal ion sufficiently filling into the channel of SiO_2 powders. Subsequently, the suspension solution was added dropwise into a caustic solution which prepared by dissolving $NaCO_3$ and NaOH (mass ratio was 2:1) into deionized water and the caustic solution value of pH was kept above 10 by adding NaOH during the course of the reaction process. SiO_2 powers loaded with Mg-Al-LDH were obtained after vacuum filtration of the reacted solution. Finally, Mg-Al-LDH/SiO_2 powers were washed by 0.1 M $NaCO_3$ solution to remove heteroions and then dried at 80 °C for 4 h. Mg-Al-LOD/SiO_2 composite was obtained by calcining Mg-Al-LDH/SiO_2 powers at 450 °C for 5 h.

2.3. Batch-wise adsorption

The adsorption property of Mg-Al-LDO/SiO_2 sphere for I^- was conducted by mixing the as-prepared adsorbent with I^- aqueous solution to which dosage of adsorbent, initial concentration of I^-, pH value, and contact time were changed. The pH value of solution was adjusted by HCl and NaOH (0.1 mol/L). The solution was separated by drainage pin type filter (0.45 μm in diameter) after adsorption. The adsorption efficiency (R%) and adsorption amount Q_e(mg/g) were calculated according to the equation as follows [21]:

$$R\% = (C_0 - C_e)/C_0 \quad (1)$$

$$Q_e = V(C_0 - C_e)/m \quad (2)$$

where C_0 and C_e are the initial and equilibrium concentration of I^- solution, respectively. V (ml) is volume of the solution and m (g) is quality of the adsorbent.

2.4. Atmosphere pressure column experiment

Column experiment was carried out to evaluate the continuous treatment capability and industrial adsorption processing for capturing I^- by Mg-Al-LDO /SiO_2 powder. The composite powder was packed in a glass tube with diameter of 0.5 cm to various height of 2 cm, 3 cm and 4 cm, in which the corresponding weight of powder was 3.67 g, 6.42 g and 7.34 g, respectively; The flow rate (F) of the fluid sample was 1 ml/min; The pH value of aqueous solution was 6.5. The breakthrough curve which was denoted by C_t/C_0, as a function of time could thus be obtained.

To simulate and predict the dynamic column adsorption behavior, three mathematical models were proposed. The Thomas model [22] has been usually used to describe the dynamic adsorption curve of adsorption column and calculate the adsorption capacity and adsorption rate constant. The Adams–Bohart model [23] assumes that the adsorption rate is proportional to both the residual capacity of the adsorbent and the concentration of the adsorbing species. The Yoon–Nelson model [24] is a semi-empirical model and it does not need to consider the adsorption velocity and the amount of adsorbent at model fitting. The equations are given as follows:

$$\text{Thomas model}: \quad \ln(C_0/C_t - 1) = K_{Th}q_0 m/F - K_{Th}C_0 t \quad (3)$$

$$\text{Adams} - \text{Bohart model}: \quad \ln(C_t/C_0) = K_{AB}C_0 t - K_{AB}N_0 H/V \quad (4)$$

$$\text{Yoon} - \text{Nelson modle}: \quad \ln(C_t/(C_0 - C_t) = K_{YN}t - K_{YN}t_{50} \quad (5)$$

where C_0 is the influent concentration (mg/L), C_t is the effluent concentration at time t, K_{Th} is the rate constant of Thomas (/Ld/mg), q_0 (mg/g) is the maximum concentration of I^- in the solid phase; K_{AB} [mL/(min mg)] is the Adams–Bohartkinetics constant, N_0 (/mg/L) is the maximum volumetric sorption capacity and V (cm/min) is the linear flow rate; K_{YN} (/min) is the Yoon–Nelson proportionality constant, and t_{50} (min) is the time required for retaining 50% of the initial adsorbate.

3. Results and discussion

3.1. Synthesis and characterization of Mg-Al-LDO

Firstly, the mixed metal ion solution (molecular proportion of Mg and Al was 3:1) was inhaled into the channel of SiO_2 spheres. As shown in the EDS analysis of the cross section in Fig. 1, the content of aluminum and magnesium was 0.1wt% and 0.3wt%, respectively. The molecular ratio of aluminum and magnesium was about 3:1 conforming to the molecular ratio in typical LDHs. Secondly, growth units $[Mg(OH)_6]^{4-}$ and $[Al(OH)_6]^{3-}$ gradually increased with the addition of alkaline solution and then begun to superimpose. During the superimposition process, the unites dehydrated with each other and the metal layer structure ($[Mg_3{}^{2+}Al^{3+}(OH)_2]^{7+}$) was formed with edge-shared octahedral. At last, one metal layer could absorb free $CO_3{}^{2-}$ through electrostatic interaction and one metal layer with $CO_3{}^{2-}$ will attract another metal

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