Research paper

Evaluation of reusable organic-inorganic nafion/layered double hydroxide nanohybrids for highly efficient uptake of mercury ions from aqueous solution

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ABSTRACT

In this study, we introduced a new strategy for efficient uptake of toxic mercury ions (Hg^{2+}) from aqueous solutions using hybrid organic-inorganic nafion intercalated layered double hydroxide (Naf-LDH) with the molecular formula $[Zn_{0.77}Cr_{0.23}(OH)_2] (NO_3)_{0.02} (nafion)_{0.21}(nH_2O)$. The resulting Naf-LDH exhibited both high uptake affinity ($K_d = 6.0 \times 10^7 \, mL \, g^{-1}$) and remarkable uptake capacity ($302.14 \, mg \, g^{-1}$) for Hg^{2+} uptake from water, clearly demonstrating that Naf-LDH could act as a useful and effective adsorbent for removing Hg^{2+} from contaminated water. The uptake kinetic curves for Hg^{2+} fitted well with the pseudo-second order model, suggesting a chemical uptake mechanism via $SO_3^-…Hg^{2+}$ and $C-F…Hg^{2+}$ bonding. For the highly toxic Hg^{2+} (at $\sim 30 \, ppm$ concentration), the uptake was exceptionally rapid, showing a 77.6% uptake within 25 min, 92.7% uptake within 40 min, and 98.5% uptake within 1 h. The sorption isotherm for Hg^{2+} agrees with the Langmuir model, suggesting a monolayer uptake. Finally, application of Naf-LDH for the extraction and pre-concentration of trace amounts of Hg^{2+} provided satisfactory results in terms of sensitivity, linearity, and reproducibility, representing its high capability for use in the analysis of trace amounts of Hg^{2+}.

1. Introduction

Nowadays, mercury is widely considered to be one of the most dangerous pollutants and highly toxic elements for the environment, biological organisms, and human life (Clarkson and Magos, 2006). The Word Health Organization (WHO) has announced a maximum Hg^{2+} uptake of 0.3 mg per week and a maximum acceptable Hg^{2+} concentration of $1 \, \mu g \, L^{-1}$ in drinking water (Ji et al., 2010; Donia et al., 2012; Zhang et al., 2012; Cai et al., 2015). Hence, rapid detection and uptake of Hg^{2+} from industrial waste water have been a significant concern in most industrial branches (Li et al., 2010; Wang et al., 2013; Li et al., 2016; Manos et al., 2008). Conventional methods for the uptake of Hg^{2+} including chemical precipitation, flocculation, membrane separation, ion exchange, and evaporation are suboptimal because of low capacities and low uptake rates for metals other than Hg^{2+} (Ke et al., 2011). Unlike them, uptake technology has attracted considerable attention due to its simplicity, high uptake efficiency, easy operation, green structure and low costs.

In recent years, layered double hydroxides (LDH) have attracted increasing interest in the field of heavy metal ions uptake because of their high surface area, layer structure, simple synthesis, low cost,

environmental friendliness, hydrophilic character, and high uptake sites (Wang and Hare, 2012). LDH are a large class of inorganic layered materials consisting of positively charged layers and charge balancing anions between the layers (Wang and Hare, 2012; Sels et al., 1999). LDH can be represented by the general formula $[M^{2+}_{1-x}M^{3+}_x (OH)_2]^{x+}(A^{n-})_{x/n} \cdot mH_2O$, where M^{2+} and M^{3+} represent divalent and trivalent metal cations, respectively. A^{n-} denotes the inter-layer anions that balance the positive charges on the layers. However, these materials suffer from low uptake kinetic and weak uptake capacity for metal ions (Ling et al., 2016). The uptake capacity of LDH for specific metal ions can be improved by intercalating the suitable inter-layer anion (Asiabi et al., 2017; Ma et al., 2016; Ma et al., 2014; Gu et al., 2008). Generally, various inorganic and organic anions intercalated into the interlayer space of the LDH make these materials highly applicable for efficient and selective uptake of heavy metal ions. The structure of the inter-layer anions has a key role in the adsorption of metal ions. Obtained results from previous works showed that the use of interlayer anions with suitable functional groups can effectively improve the uptake capacity of intercalated-LDH (Asiabi et al., 2017; Kameda et al., 2016; Liang et al., 2010).

Nafion is an organic polymer that consists of perfluorosulfonic acid

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resin with terminal sulfonic acid groups (Leroux and Besse, 2001; Asiabi et al., 2016; Sun et al., 1997; Lien and Zhang, 2007). Nafion has high mechanical stability, excellent protonic conductivity, high ion exchange capacity, and good affinity towards polar analytes (Schrenk et al., 2002). The terminal $-SO_3^-$ group of Nafion, with good cation-exchange capacity, can be suitable for the uptake of cationic heavy metals. Also, Takemura et al. showed that the C−F unit forms stable complexes with soft cations (Takemura et al., 2001).

In the present study, we report the intercalation of the Nafion into a NO_3^- type ZnCr-LDH. The physical and chemical properties of the synthesized material were studied. Then, uptake capacity, distribution coefficient, uptake kinetics and isotherms of the sorbent for the uptake of Hg^{2+} were investigated.

2. Experimental section

2.1. Reagents and materials

All chemicals were of analytical reagent grade. $Hg(NO_3)_2 \cdot H_2O$, $Zn(NO_3)_2 \cdot 6H_2O$, $Cr(NO_3)_3 \cdot 9H_2O$ and Nafion® 117 solution were purchased from Sigma-Aldrich (Milwaukee, WI, USA). The Hg^{2+} aqueous solution $(10,000 \, mg \, L^{-1})$ was prepared with $Hg(NO_3)_2 \cdot H_2O$. The water consumed was purified with a Youngling ultrapure water purification system model Aqua MaxTM-ultra (Seoul, South Korea). Other chemicals applied were of analytical reagent grade or of the highest purity available.

2.2. Instrumental analysis

The concentrations of Hg^{2+} in the solutions were determined by a Varian Vista-Pro simultaneous inductively coupled plasma atomic emission spectrometry (ICP-AES) and a Perkin-Elmer 503 atomic absorption spectrometer with a deuterium lamp background correction, equipped with a HGA-2100 electro thermal controller.

2.3. Synthesis of Nafion intercalated LDH

Naf-LDH was directly synthesized using separate nucleation and aging steps (Reichle, 1986; Reichle, 1985). In the present work, different molar ratios of $Zn^{2+}: (Cr^{3+})$ (1:1, 2:1, 3:1, 4:1) were used and 3:1 was selected as the best molar ratio for the synthesis. Briefly, aqueous solution A $(0.03 \, mol \, Zn(NO_3)_2 \cdot 6H_2O$ and $0.01 \, mol \, Cr(NO_3)_3 \cdot 9H_2O$ in 300 mL of CO_2-free deionized water) and solution B $(0.015 \, moL$ Nafion in 150 mL of CO_2-free deionized water) were first prepared. The pH of solution B was adjusted to 10.0 by the addition of 2 M of NaOH solution and solution A was added dropwise to solution B while stirring. The pH of the solution was kept in the range of 9.5–10.5. The resulting gelatinous precipitate was aged at 80 °C for 48 h and the final product was collected by centrifugation (4000 rpm for 5 min), washed with water and ethanol five times, and dried at 70 °C for 6 h.

2.4. Metal uptake experiments

The uptake of Hg^{2+} using LDH was studied by batch experiments. To investigate the Hg^{2+} ions uptake at high concentrations, 20 mg of Naf-LDH was added to 20 mL of the metal ion solution (the concentration of Hg^{2+} ions varied from 30 to 1000 $mg \, L^{-1}$) at a constant temperature of 25 °C. After mixing the solid sorbents with the solutions, centrifugation was performed and the metal concentrations in the supernatant solutions were determined using ICP-AES. The uptake efficiency %, distribution coefficient (K_d) and the amount of metal ions adsorbed q_t ($mg \, g^{-1}$) were calculated according to:

$$\%\text{Uptake} = \frac{(C_o - C_t)}{C_o} \times 100 \tag{1}$$

$$K_d = \frac{(C_o - C_t)V}{C_t \times m} \tag{2}$$

$$q_t = \frac{(C_o - C_t)V}{m} \times 10^3 \tag{3}$$

where C_o ($mg \, L^{-1}$) is the initial concentration of metal ions, C_t ($mg \, L^{-1}$) is the metal ions concentration at time t (min), m (g) is the mass of adsorbent, V (mL) is the volume of adsorbate solution and q_t ($mg \, g^{-1}$) is the adsorbed amount at time t (min).

2.5. Uptake model fitting

The uptake isotherms for the metal ions were established as follows: 10 mg of Naf-LDH was added to 20 mL of the aqueous solution of Hg^{2+} (pH = 6.0), with the concentration varying from 30 to 1000 $mg \, L^{-1}$, and stirred for 9 h at a constant temperature of 25 °C. Then, centrifugation was performed and the metal concentrations in the supernatant solutions were determined. The uptake isotherms for metal ions were established as follows: 10 mg of Naf-LDH was added to 20 mL of the aqueous solution of metal ions (pH = 6.0) with the concentrations varying from 30 to 1000 $mg \, L^{-1}$, and stirred for 9 h at a constant temperature of 25 °C. Then, centrifugation was performed and the metal concentrations in the supernatant solutions were determined. The uptake isotherm data were fitted to the Langmuir and Freundlich equations (Shan et al., 2015; Shen et al., 2016). In order to evaluate the uptake kinetics of the metal ions onto Naf-LDH adsorbent, pseudo-first order and pseudo-second order kinetics models were applied to fit the experimental data. Uptake isotherms and kinetic models equations are completely explained in supporting information section.

2.6. Metal detection experiments

The online packed solid phase extraction system combined with HG-AAS (see supporting information) was used to determine trace amounts of Hg^{2+} in the aqueous solution (Shamsayei et al., 2016). The injected volume of the extracted analytes into HG-AAS was kept constant at 150 μL during the experiments. The best results were obtained under the following experimental conditions: (a) a sample pH value of 6.0; (b) an extraction time of 20 min (c) a desorption time of 7 min (d) an extraction flow rate of 3.5 $mL \, min^{-1}$, and (e) a desorption flow rate of 3.0 $mL \, min^{-1}$. Under optimal conditions, the calibration curve was plotted and figures of merit were calculated for Hg^{2+}.

2.7. Characterization techniques

The crystalline structure of the obtained samples was characterized by X-ray diffraction model XRD, X'Pert Pro Super from Philips Co. (the Netherlands) with Cu Kα radiation (1.5478 Å). The morphologies observations were carried out on SEM (KYKY EM-3200). Energy-dispersive X-ray (EDX) maps were taken on the SEM with an EDX spectrometer. FT-IR spectra of the samples were recorded on a Thermo Nicolet NEXUS FI-IR spectrophotometer (Madison, WI, USA) using the KBr pellet method in the wave number range of 400 ~ 4000 cm^{-1} at a resolution of 4 cm^{-1}. The Brunauer–Emmet–Teller (BET) surface area analysis was performed on an ASAP 2020 apparatus (Micromeritics, USA) using nitrogen uptake with the degassing conditions of 150 °C for 3 h.

3. Results and discussion

3.1. Characterization of NO₃-LDH and Naf-LDH

The FTIR spectrum of NO₃-LDH (Fig. 1A) was roughly attributed to what follows: 3440 cm^{-1} to the O−H stretching vibration (νO–H) of the metal hydroxide layer and the inter-layer water molecules; 1627 cm^{-1} to the OH stretching band of H_2O; 1357 cm^{-1} to the stretching