



Characterization and adsorption properties of a lanthanum-loaded magnetic cationic hydrogel composite for fluoride removal



Shuoxun Dong, Yili Wang*

College of Environmental Science and Engineering, Beijing Key Lab for Source Control Technology of Water Pollution, Beijing Forestry University, Beijing 100083, China

ARTICLE INFO

Article history:

Received 30 July 2015

Received in revised form

19 October 2015

Accepted 5 November 2015

Available online 10 November 2015

Keywords:

Adsorption

Fluoride removal

Magnetic cationic hydrogel

Lanthanum-loaded

ABSTRACT

In this study, a novel lanthanum-loaded magnetic cationic hydrogel (MCH-La) was synthesized for fluoride adsorption from drinking water. The adsorption kinetics, isotherms, and effects of pH and co-existing anions on fluoride uptake by MCH-La were evaluated. FTIR, Raman and XPS were used to analyze the fluoride adsorption mechanism of MCH-La. Results showed that MCH-La had positive zeta potential values of 23.6–8.0 mV at pH 3.0–11.0, with the magnitude of saturation magnetization up to 10.3 emu/g. The fluoride adsorption kinetics by MCH-La fitted well with the fractal-like-pseudo-second-order model, and the adsorption capacity reached 93% of the ultimate adsorption capacity within the first 10 min. The maximum fluoride adsorption capacity for MCH-La was 136.78 mg F⁻/g at an equilibrium fluoride concentration of 29.3 mg/L and pH 7.0. Equilibrium adsorption data showed that the Sips model was more suitable than the Langmuir and Freundlich models. MCH-La still had more than 100 mg of F⁻/g adsorption capacity at a strongly alkaline solution (pH > 10). The adsorption process was highly pH-dependent, and the optimal adsorption was attained at pH 2.8–4.0, corresponding to ligand exchange, electrostatic interactions, and Lewis acid–base interactions. With the exception of both anions of HCO₃⁻ and SiO₄⁴⁻, Cl⁻, NO₃⁻, and SO₄²⁻ did not evidently prevent fluoride removal by MCH-La at their real concentrations in natural groundwater. The fluoride adsorption capacity of the regenerated MCH-La approached 70% of the fresh MCH-La from the second to fifth recycles. FTIR and Raman spectra revealed that C–O and C=O functional groups on MCH contributed to the fluoride adsorption, this finding was also confirmed by the XPS F 1s spectra. Deconvolution of C 1s spectra before and after fluoride adsorption indicated that the carboxyl, anhydride, and phenol groups of MCH were involved in the fluoride removal.

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1. Introduction

Fluoride contamination in drinking water has become a global environmental issue that has attracted increasing concerns because of long-term impacts on human health. Excess fluoride ions in drinking water cause human diseases, such as rickets, neurological disorders, ossification of tendons and ligaments, and dental diseases. Hence, a strict rule from World Health Organization (WHO) and Environmental Protection Agency (EPA) is adopted the maximum allowable fluoride concentration level for drinking water at 1.5 mg/L (Chai et al., 2013).

Many treatment methods, including electro-dialysis, ion-

exchange and adsorption processes, and chemical precipitation, have been employed to remove excess fluoride from drinking water to avoid the toxic effects of fluoride on human health (Mohapatra et al., 2009). Among these methods, adsorption has been considered a promising technique for fluoride removal because of its simplicity and selectivity (Bhatnagar et al., 2011). In addition, adsorbent materials for effective fluoride removal have also been developed, such as aluminum-based oxide sorbents (Maliyekkal et al., 2006), iron-based sorbents (Eskandarpour et al., 2008), and carbon-based sorbents (Ma et al., 2009). Besides these adsorbents with large surface area and high mass transfer efficiency, rare-earth metal composites also provide major active sites for complexation or ligand exchange with fluoride, including La–Al (Zhang et al., 2014), lanthanum-modified chitosan (Kamble et al., 2007), and Fe–Al–Ce trimetallic hydrous oxide (Wu et al., 2013). Lanthanum is a widely used rare-earth metal that has a high fluoride adsorption

* Corresponding author.

E-mail address: wangyilimail@126.com (Y. Wang).

capacity. [Huo et al. \(2011\)](#) prepared a lanthanum alginate bead that showed a maximum adsorption capacity of 197.2 mg/g for fluoride removal. The Mg–Fe–La composite synthesized by [Wang et al. \(2015\)](#) presented a fluoride adsorption capacity as high as 112.17 mg/g at near natural pH. Even the lanthanum hydroxide-anchored granular activated carbon also showed an increased maximum adsorption capacity of 9.98 mg/g ([Vences-Alvarez et al., 2015](#)).

In general, the aforementioned de-fluoridation adsorbents show one-dimensional states and are limited by a complex separation process ([Chai et al., 2013](#)). Traditional separation methods, such as filtration and sedimentation, are unsuitable for separating adsorbents from water or wastewater. Thus, magnetic adsorbents have received considerable attention in the recent years ([Reddy and Lee, 2013](#)). Magnetic separation method has several advantages, including high separation efficiency, low energy consumption, short time, and high selectivity, over other separation methods ([Dong et al., 2015](#)). Magnetic nanoparticles are usually prepared as an adsorbent with magnetite (Fe_3O_4) or ($\gamma\text{-Fe}_2\text{O}_3$) ([Tang and Lo, 2013](#)). [Lo et al. \(2011\)](#) and [Rao et al. \(2011\)](#) reported a magnetic cationic hydrogel (MCH) for chromate and humic acid removal. This MCH material had a high zeta potential of about 48–30 mV at pH 3–12 and shows a good performance toward removal of anionic pollutants ([Rao et al., 2011](#); [Lo et al., 2011](#)). Fluoride ion is classified as a hard base with high electronegativity and small ionic size. Given this electronegative characteristic, MCH can be used in removing fluoride from water through electrostatic adsorption, which can also be strengthened by loading lanthanum in MCH.

However, to the best of our knowledge, a MCH loaded with lanthanum (MCH-La) for de-fluoridation of water has not been reported. In the present study, a MCH-La was prepared and used as an adsorbent for fluoride removal. The de-fluoridation performance of MCH-La was evaluated through the kinetic and isothermic analyses. The effects of solution conditions and number of recycles on de-fluoridation performance were also investigated. Furthermore, the fluoride adsorption mechanism on MCH-La was elucidated using FTIR, Raman, and XPS techniques.

2. Materials and methods

2.1. Materials

All chemicals are of analytical grade. Analytical (3-Acrylamidopropyl) trimethylammonium chloride (APTMAcI) (75wt.% solution in water), N,N'-methylenebisacrylamide (MBA), N,N,N',N'-tetramethylethylene-diamine (TEMED), potassium persulfate (KPS), and lanthanum nitrate were purchased from Sino-pharm Chemical Reagent Co., Ltd. (China). NaF was dissolved in distilled water to prepare a stock solution containing 200 mg/L F^- . Co-existing ion solutions were prepared by dissolving their salts in deionized water.

2.2. Preparation of MCH-La

2.2.1. Magnetic iron oxide ($\gamma\text{-Fe}_2\text{O}_3$) synthesis

$\gamma\text{-Fe}_2\text{O}_3$ was synthesized by the chemical co-precipitation of ferric and ferrous ions in an alkali solution. $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (24.4 g) and $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (16.6 g) were dissolved in 400 mL of deionized water. NaOH (6.5 M) was then added to adjust the pH and mixed for hours after the addition of NaOH was completed. The obtained black precipitates, i.e., Fe_3O_4 , were washed with deionized water three times, and then collected and heated in air for 3 h at 150 °C. The brown powder was collected after filtering, drying, and milling ([Rao et al., 2011](#)).

2.2.2. MCH-La synthesis

MCH was synthesized by the radical polymerization of APTMAcI. Briefly, 0.05 g of MBA was dissolved in 2.5 g of APTMAcI with the addition of 0.8 mL of deionized water. After the MBA was dissolved, 20 mL of TEMED and 0.3 g of $\gamma\text{-Fe}_2\text{O}_3$ were then added into the matrix. When the matrix was homogeneously mixed, 0.6 mL of saturated potassium persulfate (KPS) solution was added. The reaction continued at 50 °C in a water bath for 10 min. Afterward, the generated MCH was transferred into a glass bottle and immersed in deionized water for 5 d. Water was replaced every 8 h to remove the unreacted species. The MCH was dried and milled with a blender, and then the powder was collected and impregnated in the saturated lanthanum nitrate solution under vigorous stirring for 24 h. The suspensions were centrifuged at 5000 rpm for 15 min and washed three times with deionized water. The centrifuged solid was freeze-dried in vacuum for 24 h. The product was collected for further use ([Lo et al., 2011](#)).

2.3. Adsorbents characterization

Zeta potentials were determined using a Zetasizer Nano Z analyzer (Malvern, UK). Transmission electron microscopy (TEM, Hitachi H800, Japan) and field-emission scanning electron microscopy (FESEM, FEI, the Netherlands) with energy-dispersive spectroscopy (EDS) were utilized to analyze the surface morphology and detect the surface elements of the materials. Thermogravimetric analysis (TA Corporation, United States) was carried out in nitrogen atmosphere from 25 °C to 500 °C at a heating rate of 10 °C/min. The magnetism degree of MCH or MCH-La was tested using a vibrating sample magnetometer (VSM, 7037/9509-P, LakeShore, Lake Shore Cryotronics, Inc., USA). The exchanges of the surface groups before and adsorption were recorded by FTIR spectroscopy (Vector 22 spectrophotometer (Bruker, Germany) at a 2 cm^{-1} resolution) and Raman spectroscopy (950 FT-Raman spectrometer, Thermo Nicolet, USA) at a 2 cm^{-1} resolution. The valances of specific elements before and after adsorption were analyzed by XPS spectra (PHI Quantera spectrometer, USA). An Al-K α anode radiation source was employed as the excitation source. The curve fittings of the C 1s and F 1s spectra were performed using a Gaussian–Lorentzian peak shape after Shirley background correction in XPS Peak software 4.1 by Raymond W. M. Kwok (The Chinese University of Hong Kong, China).

2.4. Batch adsorption experiment

An F^- stock solution and deionized water were added into several 2000 mL glass conical flasks to yield a total volume of 1000 mL in each. Then, 0.3 g/L MCH-La was dosed. The pH of each suspension was adjusted and maintained at 7.0 ± 0.2 throughout the experiments. The suspensions were stirred at 150 rpm and kept the temperature at 25 ± 1 °C. Approximately 4 mL aliquots were taken from the suspension at predetermined intervals. These aliquots were immediately filtered through a 0.45 μm membrane, and then the residual F^- in each solution was analyzed by using a thermo combination fluoride electrode. The leaching concentrations of La^{3+} and Fe^{3+} from MCH-La were measured by arsenazo ([Aneesh et al., 2009](#)) and 1,10-phenanthroline ([Jan Jezek et al., 2007](#)) procedure using UV–Visible spectrophotometer, respectively.

F^- adsorption isotherms on MCH-La were obtained at initial F^- concentrations from 0 to 80 mg/L, using the same experimental conditions above. The effect of the solution pH on fluoride removal was analyzed at pH values from 3 to 11.

The effect of common anions (Cl^- , NO_3^- , SO_4^{2-} , HCO_3^- , and SiO_4^{4-}) on fluoride removal was evaluated in batch tests that employed an

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