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Research article

Lanthanum-doped silica xerogels for the removal of fluorides from waters

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ABSTRACT

The objective of this study was to determine the influence of different operational variables on fluoride (F^-) removal from waters using lanthanum (La)-doped silica xerogels and the mechanisms involved in this process. Accordingly, four xerogels were synthesized, one acting as blank (X-B), two doped with $LaCl_3$ and dried at different temperatures (X-LaCl and X-LaCl-M), and a fourth doped with La_2O_3 (X-LaO). The results show that fluorides are only removed when La-doped xerogels are utilized. In addition, X-LaCl yielded the highest adsorption capacity, removing 28.44% of the initial fluoride concentration at a solution pH of 7. Chemical characterization of materials confirmed that fluoride removal from waters is due to the precipitation of LaF_3 on the surface of La-doped xerogels. The presence of dissolved organic matter on the aqueous solution also reduce the removal capacity of La xerogels. Finally, analysis of the influence of solution pH revealed that the adsorption capacity of all xerogels was highest at a solution pH of 7.

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1. Introduction

Fluoride (F^-) contamination of waters that supply some populations is an endemic problem worldwide (Amini et al., 2008) due to the dissolution of minerals such as fluorite [CaF_2], apatite [$Ca_5(PO_4)_3(F, Cl, OH)$], and cryolite [Na_3AlF_6] when they come in contact with groundwaters (Edmunds and Smedley, 2013). Human health can be affected by the insufficient or excessive presence of fluoride. Thus, dental caries can develop at concentrations between 0 and 0.5 mg/L, while dental fluorosis can appear at concentrations between 1.5 and 4 mg/L, and there is an increased risk of skeletal fluorosis, paralysis, disability, or even death at higher fluoride concentrations (Fawell and Bailey, 2006). The most frequent treatments for fluoride removal from waters are membrane separation (Richards et al., 2010), ion exchange resins, electrodialysis (Mohapatra et al., 2009), and adsorption (Landín-Rodríguez, 2006; Leyva-Ramos et al., 2008; Metcalf et al., 2003; Teutli-Sequeira et al.,

2013; Yakun et al., 2011). Adsorption is the most practical and low-cost method for fluoride removal, requiring material that is mechanically resistant and selective with high fluoride removal capacity.

As a member of the halide group, the behavior of fluoride should be the same as that of chloride, iodide, or bromide. Studies have been conducted on its removal from natural waters by adsorption using silver-doped carbon aerogels. Sánchez-Polo et al. (2007a,b) investigated bromide and iodide removal from drinking water silver-doped carbon aerogels, and silver-doped activated aerogels, finding an increased adsorption capacity, especially in the aerogels samples activated by heating at 1173 K in CO_2 flow (100 cm^3/min) for 1 h. It is interesting to note that bromide and iodide adsorption on columns filled with silver-doped aerogels was very efficient. The results obtained show a high column volume breaking point but low height of the mass transfer zone, regardless of the halide used.

Fluoride removal from waters has been studied using activated alumina (Cheng et al., 2014; Craig et al., 2017), bone char (Craig et al., 2017), zeolite modified with Al^{+3} and La^{+3} (Teutli-Sequeira et al., 2013), and spheres of alginate doped with La(III) (Yakun

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et al., 2011). Silica xerogels (SXGs) are currently the most widely studied group of aerogels and are (Teutli-Sequeira et al., 2013) of major interest in the field of wastewater treatment (Han et al., 2016; Mohammadi and Moghaddas, 2015; Perdigoto et al., 2012). SXGs have a large surface area due mainly to the presence of mesopores. They exhibit a greater adsorption capacity in comparison to other frequently used adsorbents, with high mechanical resistance. They proved to be good adsorbent materials when their surface is modified with nanoparticles of iron or other metals that form oxides or hydroxides (Andrade-Espinosa et al., 2010; Andrade Espinosa, 2011; Martinez and Ruiz, 2002). However, no research has been published on SXGs activated with lanthanum (La). With this background, the objectives of this study were to: i) synthesize La(III)-doped SXGs for effective fluoride removal from waters, ii) characterize their physicochemical (X-Ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), Zeta potential and isoelectric point (IEP), and Fourier transform infrared spectroscopy (FTIR)), textural and morphological (N_2 physisorption at 77 K, and high-resolution scanning electron microscopy (HSEM)) properties, and iii) evaluate the influence of operating variables (pH and organic matter) on fluoride adsorption efficiency.

2. Materials and reagents

The following analytical grade reagents were used for the SXG synthesis and evaluation of fluoride removal. Tetraethoxysilane (TEOS, 99.99%), isopropanol (IPrOH, 99.9%), heptahydrate La chloride ($LaCl_3 \cdot 7H_2O$), La oxide (La_2O_3 , 99.95%), hydrochloric acid (HCl, 36.5–38%), ammonium hydroxide (NH_4OH , 28.9%), nitric acid (HNO_3 , 69%), sodium fluoride (NaF), sodium hydroxide (NaOH), sodium nitrate ($NaNO_3$), TISAB. All the solutions were prepared using ultrapure water.

3. Experimental

3.1. Xerogel synthesis by two-step sol-gel process

The precursor used was tetraethoxysilane, which was dissolved in deionized water in the presence of isopropanol and hydrochloric acid as acid catalyst to favor hydrolysis, maintaining the solution at a constant temperature of 60 °C for 1 h. The molar ratio used in the synthesis was TEOS: IPrOH: $H_2O = 1:4:10$ (Andrade Espinosa, 2011), given that high molar ratios of H_2O with TEOS favor complete hydrolysis, facilitating polymer chain cross-linking and producing a tridimensional interconnected siloxane network (Martinez and Ruiz, 2002). Hydrochloric acid (1 M) was gradually added until pH = 2 was reached during synthesis in the sol step, followed by a condensation reaction through the addition of ammonium hydroxide (0.6 M) as basic catalyst, reaching pH = 6. The structure consolidated and xerogel ageing began after gelation for 4–6 h at 60 °C. After obtaining the SXG matrix, it was impregnated with La(III) for 3 days, using a solution of 0.1 M $LaCl_3 \cdot 7H_2O$, and it was then washed with IPrOH for 2 days and maintained at a constant temperature of 60 °C for 3 days. Another SXG was also synthesized and impregnated with pure La_2O_3 before its condensation. Four xerogels were prepared following the next procedure. Two doped with La^{+3} , based on $LaCl_3 \cdot 7H_2O$ (one dried at 60 °C [X-LaCl] and the other heated at 450 °C after drying at 60 °C [X-LaCl-M]), a third doped with La_2O_3 (X-LaO), and a reference blank (X-B). They were characterized by N_2 adsorption at 77 K, HSEM, Zeta potential measurement, FTIR, XRD, and XPS (see details below).

3.2. Xerogel characterization

Xerogel surface area and pore size and volume were determined

using N_2 -physisorption equipment at 77 K (Micromeritics ASAP 2010 V4.02). Zeta potential was determined by adding a specific mass of SXG to different volumetric ratios of HNO_3 , $NaNO_3$, and NaOH at a concentration of 0.01 M for 7 days at constant temperature under agitation. Potential values were determined in a nano-ZS ZETASIZER. Morphological characteristics were evaluated by HSEM using a scanning electron microscope (Hitachi S-510). Samples were covered with a thin layer of gold to provide conductive properties for elemental surface microanalysis. The SXGs were analyzed in the mid-infrared region, from 670 to 4000 cm^{-1} , using the attenuated total reflectance (ATR) technique. The SXGs were analyzed by XRD using a BRUKER D8 VENTURE diffractometer and BRUKER LYNXEYE detector with Cu $K\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$, voltage of 40 KV, current of 40 mA, in the range of $2\theta = 5^\circ - 80^\circ$, step size $\approx 0.02^\circ$, and 96 s/step. SXG surface chemistry was analyzed using a Kratos Axis Ultra-DLD X-ray photoelectron spectrometer.

3.3. Fluoride ion adsorption

Adsorption isotherms were obtained to study the adsorption process and evaluate the capacity of the SXGs to remove fluoride ions from the medium. Adsorption was analyzed by evaluating the effects of: i) pH (range 5–9), ii) presence of organic matter (5, 50, and 250 mg/L) and v) use of groundwater intended for human consumption. Fluoride concentration was measured by using a selective electrode (Crison).

4. Results and discussion

4.1. Silica xerogel characterization

Fig. 1 depicts the nitrogen adsorption isotherms for the SXGs under study. According to the classification of Sing, the X-B xerogel can be classified as type I, characteristic of microporous solids, in which a plateau is reached after micropore filling, whereas the three La-doped xerogels are type IV, characteristic of mesoporous materials. The initial part of a type IV isotherm corresponds to monolayer filling, while the inflection point of the curve, after which multilayer adsorption begins, is associated with the relative nitrogen pressure produced by monolayer filling. Fig. 1 B, C, and D depict the isotherms of the three La-doped xerogels, showing a hysteresis cycle corresponding to capillary condensation in mesopores.

Table 1 exhibits the results of applying the BET equation to the N_2 isotherms, showing that the surface area was smaller in the non-La-doped (X-B) versus La-doped samples. The surface area of sample X-B was 506.94 m^2/g , the pore volume 0.25 cm^3/g , and the mean pore diameter 19.66 cm^3/g , identifying it as a microporous material according to the IUPAC classification. In comparison to this sample, the surface area, pore volume, and mean pore diameter were higher in samples X-LaCl and X-LaCl-M, which may result from their doping with lanthanum chloride, which increases the surface area through the adherence of its nanoparticles. Sample X-LaO had the largest surface area (732.81 m^2/g), pore volume (0.81 cm^3), and mean pore diameter (44.38 \AA), which may be attributable to spaces created by the entry of La oxide particles into the xerogel structure, given the simultaneous gelation and impregnation of this material. The mechanism of La^{+3} integration into the xerogel starts with the adsorption of La^{3+} ions and silanol (SiOH) groups, which continue to be present in the xerogel. Two unpaired electrons of the oxygen atom in the silanol group are shared with La(III), and a water molecule rapidly interacts with the hydroxyl by the nucleophilic attack of two unpaired electrons that promote H^+ as a good salient group that pass to the solution; the water molecules present in the solution interact with La, forming

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