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Defluoridation from aqueous solution by lanthanum hydroxide

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ABSTRACT

This research was undertaken to evaluate the feasibility of lanthanum hydroxide for fluoride removal from aqueous solutions. A batch sorption experiments were conducted to study the influence of various factors such as pH, presence of competing anions, contact time, initial fluoride concentration and temperature on the sorption of fluoride on lanthanum hydroxide. The optimum fluoride removal was observed in the $pH_{eq} \leq 7.5$. The presence of competing anions showed no adverse effect on fluoride removal. The equilibrium data reasonably fitted the Langmuir isotherm model, and the maximum monolayer sorption capacity was found to be 242.2 mg/g at $pH_{eq} \leq 7.5$ and 24.8 mg/g at $pH_{eq} > 10.0$. The pseudo-second-order kinetic model described well the kinetic data, and resulted in the activation energy of 53.4–68.8 kJ/mol. It was suggested that the overall rate of fluoride sorption is likely to be controlled by the chemical process. Thermodynamic parameters such as ΔG°, ΔH° and ΔS° indicated that the nature of fluoride sorption is spontaneous and endothermic. The used lanthanum hydroxide could be regenerated by washing with NaOH solution. Results from this study demonstrate the potential usability of lanthanum hydroxide as a good fluoride selective sorbent.

1. Introduction

Fluoride in the environment occurs through natural presence in the earth's crust and industrial activities, especially, semiconductor, electroplating, coal fired power stations, aluminum, glass, ceramic and fertilizers industries [1,2]. The effluents of these industries have higher fluoride concentrations than natural waters, ranging from ten to thousands of mg/L [3]. The discharge of such wastewater leads to the fluoride contamination of surface and ground water. Fluoride is known as both beneficial and detrimental effect on human health. It is well known that fluoride can effectively prevent dental caries when a relative low level is constantly maintained in the oral cavity. On the contrary, an excessive fluoride intake leads to various diseases such as dental and skeletal fluorosis and non-skeletal fluorosis [4,5]. The optimum level of fluoride in drinking water for general good health is considered to be between 1.0 and 1.5 mg/L [6]. US EPA established a discharge standard of 4 mg/L for fluoride from wastewater treatment plant [7].

Various treatment technologies based on adsorption and biosorption [9–11], ion-exchange [12], chemical precipitation including electro-coagulation/flotation [13,14], and membrane processes, such as reverse osmosis [15], Donnan dialysis [16], nano-filtration [17], and electrodialysis [18] have been suggested for fluoride removal. Most of these methods suffer from various problems such as high operational and maintenance costs, low selectivity and capacity, secondary pollution and complicated procedure involved in the treatment. Comparatively, adsorption seems to be a more attractive method for the fluoride removal in terms of cost, simplicity of operation and selectivity. Numerous adsorbents like activated alumina [19], clay [8,20], hydroxyapatite [21], activated carbon [22], ion-exchange resin [23], quick lime [24], waste residue [25,26], and geomaterials [27–30] have been tested for fluoride removal. In recent years, rare earth element impregnation of porous adsorbents or carrier materials was found to be significantly effective for improving the selectivity and sorption of fluoride. For example, lanthanum-impregnated silica gel [31], lanthanum- and yttrium-impregnated alumina [32], lanthanum-impregnated chelating resins [33], lanthanum-loaded fiber [34], neodymium- and lanthanum-modified chitosan [35,36] have shown very promising results for fluoride removal from aqueous solutions.

The aim of this study is to understand the role of lanthanum for fluoride removal. In the present study, the sorption properties of lanthanum hydroxide, $La(OH)_3$ for fluoride removal from aqueous solution have been investigated in a batch mode. Sorption studies were conducted under various experimental conditions, such as contact time, initial fluoride concentrations, temperature, pH and the presence of competing anions. The experimental data were described with various isotherms and kinetic models generally adapted in the literatures to identify the adsorption mechanism. The possibility of lanthanum hydroxide for repeating use was also examined by a desorption study.

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2. Experimental

2.1. Materials and reagents

Lanthanum hydroxide ($La(OH)_3$, 99.9%) used as the sorbent for defluoridation experiments was purchased from Daejung Chemical Co., Korea. The lanthanum hydroxide used has a grain size range of 0.36–76.32 μm (mean diameter 10.20 μm) and the specific surface area of 715.4 m^2/g. The pH of point of zero charge (pH_{pzc}) determined by the potentiometric titration method was between 8.7 and 8.8. A stock solution of fluoride (0.1 mol/L) was prepared by dissolving NaF (Sigma–Aldrich Co., USA) in deionized water and diluted to 0.002–0.008 mol/L as needed. The chemicals, NaCl, $NaHCO_3$, $NaNO_3$, NaH_2PO_4, and Na_2SO_4 were used as the anion sources competing with fluoride ion in the working solution for sorption experiment. All reagents were of the highest grade available and were used as received. Polystyrene-based PA308 resin ($-N^+(CH_3)_3Cl^-$, Samyang Co., Korea) which is a strong base anion-exchange resin was used as a comparative sorbent.

2.2. Sorption experiments

Sorption experiments were carried out in batch conditions where 0.01–0.1 g of sorbent was added to 250 mL HDPE bottles containing 100 mL of working solution of known ion species and concentrations. The effect of different pH values on fluoride sorption was studied by adjusting the pH of solution using either 0.1 M HCl or 0.1 M NaOH solutions to the required pH range of 2.5–10.5. The bottles were settled in an incubator shaker and then continuously shaken at 120 rpm for a predetermined time period. The reaction temperature was set in the range of 25–45 °C. After the predetermined sorption time, solid and liquid phases were separated using 0.2 μm membrane filter, fluoride concentrations in the liquid phase were measured. The sorption capacity, q (mg/g) was calculated using the following mass balance equation:

$$q = \frac{V(C_0 - C)}{W} \quad (1)$$

where C_0 and C are the initial and final liquid-phase concentrations of fluoride (mg/L), respectively. V is the volume of solution (L) and W is the dry weight of sorbent used (g).

For desorption study, fluoride-loaded lanthanum hydroxide that was separated from solution by filtration after the sorption experiment was washed with deionized water and dried at 80 °C. 0.1 g of dried fluoride-loaded lanthanum hydroxide was placed in a HDPE bottle containing 20 mL of 0.1–2.0 M NaOH, and then shaken at 120 rpm for 1 h at 25 °C. The final concentration of fluoride in the desorption medium separated by filtration was determined using ion chromatography. The percentage of desorption was calculated from the amount of fluoride-loaded on lanthanum hydroxide and the final concentration of fluoride in the desorption medium.

2.3. Analysis

The concentration of fluoride and other anions in the solution were determined by single-column ion chromatography (Waters LC, USA) assembled with a 50 μL injection loop, analytical column (Waters IC-pak A, 4.6 mm × 50 mm), suppressor module (Alltech model 335 SPCS), conductivity detector (Waters 432), and data module (Autochro-Win, Young-in Instrument Co., Korea). The pH of the solutions was measured using an Orion 3-Star bench-top pH meter (Thermo Fisher Scientific Inc., USA). The point of zero surface charge (pH_{pzc}) value of the lanthanum hydroxide was estimated by the potentiometric titration method as described [37]. The surface area and particle size of the lanthanum hydroxide used were analyzed by a TriStar II 3020 surface area and porosity measuring system (Micromeritics Instrument Co., USA) and a laser particle size analyzer (Mastersizer S, Malvern Instruments Ltd., UK), respectively. The mineral composition of the lanthanum hydroxide was characterized by X-ray diffractometer (X'pert-pro MPD, PANalytical, The Netherlands).

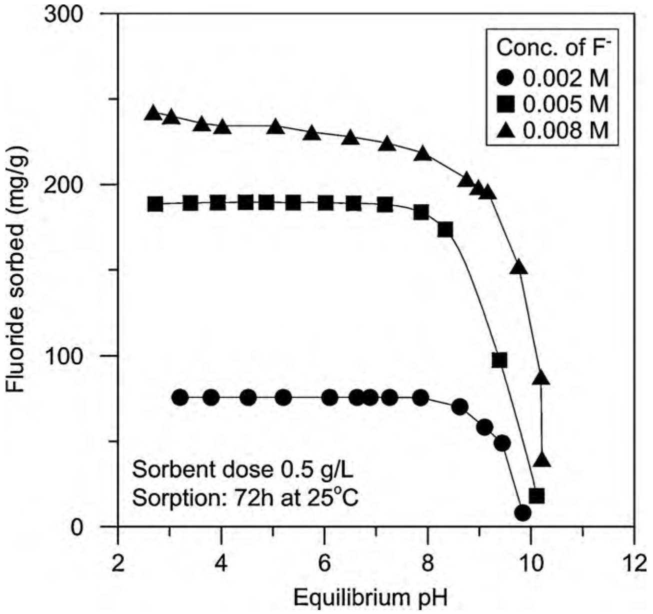

Fig. 1. Effect of pH on the defluoridation capacity of lanthanum hydroxide.

3. Results and discussion

3.1. Effect of pH on defluoridation

The effect of pH on the sorption of fluoride on the lanthanum hydroxide was examined at different initial fluoride concentrations ranging from 0.002 to 0.008 M and a constant dosage of sorbent of 0.5 g/L. The pH of solution was controlled to be 2.5–10.5 after the sorption equilibrium by adding HCl and NaOH solution. Fig. 1 shows the results of the equilibrium uptake of fluoride ion onto the lanthanum hydroxide as a function of the equilibrium pH of solution. As shown in Fig. 1, the equilibrium uptake of fluoride ion onto the lanthanum hydroxide slightly decreased at high initial fluoride concentration but remained nearly constant at low initial fluoride concentration with increasing the pH of solution up to 7.5–8.0. The maximum sorption pH range was broader at lower fluoride concentrations. This implies that some surface sites were saturated for higher surface loadings. When pH approached pH_{pzc} (8.7–8.8), fluoride sorption sharply decreased with the increase of pH regardless of the initial fluoride concentrations because the positively charged surface sites, which served as fluoride binding sites, significantly decreased with the increase in pH. At high pH, furthermore, it is also inferable that the competition between hydroxide ion (OH^-) and fluoride ion (F^-) limits the uptake efficiency. The results are in good agreement with the similar work done by other workers for granular ferric hydroxide [38]. They have reported that the mechanism of fluoride sorption on metal oxide surfaces can be described as an exchange reaction against OH^- of surface groups [39,40]. It is expected that similar process will occur on the lanthanum hydroxide. Thus, it is believed that ion-exchange reaction is a major mechanism for removal of fluoride ion by lanthanum hydroxide:

$$La(OH)_3 + 3F^- \rightarrow LaF_3 + 3OH^- \quad (2)$$