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Acid-enhanced limestone defluoridation in column reactor using oxalic acid

*Suresh K. Nath, Robin K. Dutta**

Department of Chemical Sciences, Tezpur University, Napaam, Tezpur 784028, India

ABSTRACT

Acid enhanced limestone defluoridation of water has been studied in a crushed limestone column reactor using oxalic acid (OA). The defluoridation has been studied with varying initial fluoride concentrations of 5, 10, 15 and 20 mg/L and acid concentrations of 0.01, 0.05 and 0.1 M. The fluoride removal was found to increase with increase in the concentration of the acid, removing fluoride up to 95% with 0.1 M OA. The observed good fluoride removal has been attributed to a combination of two mechanisms of fluoride removal, *viz.*, precipitation of calcium fluoride and adsorption of fluoride ions on limestone surfaces. While the removal by precipitation remains same on repeated use of the same limestone column, the adsorption is more with the fresh limestone and decreases gradually on repeated use of the same limestone column. The precipitate has been characterized using various analytical tools, *viz.*, X-ray diffraction, IR spectroscopy, thermogravimetric analysis, scanning electron microscopy combined with energy dispersive X-ray spectroscopy and X-ray photoelectron spectroscopy. The Ca^{2+} ions, formed due to dissolution of limestone by the acid, precipitate calcium fluoride along with precipitation of calcium oxalate. A good fluoride removal ability, low residual oxalate, acceptable final pH, low-cost and simplicity of the process make the present acid-enhanced limestone defluoridation process with OA a potential method for defluoridation of groundwater.

Keywords: Limestone; Defluoridation; Oxalic acid; Calcium fluoride; Calcium oxalate

1. Introduction

Occurrence of high level of fluoride in groundwater is a matter of worldwide concern (Mohapatra et al., 2009; Meenakshi and Maheswari, 2006; Global fluoride and arsenic contamination of water map). The situation in some parts of India and Bangladesh is grave with prevalence of severe fluorosis problems among the people (Meenakshi and Maheswari, 2006; Global fluoride and arsenic contamination of water map; Fluoride and Fluorosis). Although a small quantity of fluoride is required for healthy teeth and bone in human as well as in animals, a long term consumption of water containing high level of fluoride can cause severe skeletal and dental fluorosis. In India the maximum permissible limit of fluoride in drinking water is 1.5 mg/L (BIS, 1991) which is the same as the WHO guideline value (WHO, 2008).

The development of an efficient and low-cost fluoride removal method with minimized disadvantages is still a challenge for environmental chemists and engineers. The available technologies for defluoridation of groundwater and industrial effluent are based on the principles of precipitation, ion-exchange, electrolysis, electrodialysis (Mohapatra et al., 2009; Meenakshi and Maheswari, 2006; Menkouchi Sahli et al., 2007), membrane-separation and adsorption (Nath and Dutta, 2010a,b; Thakre et al., 2010; Karthikeyan et al., 2009; Davila-Rodriguez et al., 2009). Conventionally, F^- removal from wastewater involves addition of Ca^{2+} to precipitate CaF_2 (Dahi et al., 1996; IISc method of defluoridation). Adsorption of fluoride on various adsorbents, *viz.*, laterite (Sarkar et al., 2007), waste residue from alum manufacturing plant (Nigussie et al., 2007), activated carbon prepared from *Morringa indica* bark (Karthikeyan and Ilango, 2007), carboxymethylated starch-based hydrogels loaded with Fe^{2+} (Chauhan et al., 2007), alum-impregnated activated alumina (Tripathy et al., 2006), and natural chitosan (Menkouchi Sahli et al., 2007), have been reported. Fan et al. reported the adsorption capacities of some fluoride adsorbents in the order: Hydroxyapatite > Fluorspar > Quartz activated using fer-

* *Corresponding author*. Tel.: +91 3712 267007/8/9x5055; fax: +91 3712 267005/6; mobile: +91 94350 06674.
E-mail addresses: suresh@tezu.ernet.in (S.K. Nath), robind@tezu.ernet.in (R.K. Dutta).
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ric ions > Calcite > Quartz (Fan et al., 2003). Calcite has been used for precipitation and adsorption of fluoride from industrial wastewater and groundwater (Yang et al., 1999; Reardon and Wang, 2000). The reaction between fluoride solution and calcite was reported to replace calcite with fluorite (Augustyn et al., 1978; Glover and Sippel, 1962).

The concentration of fluoride in the effluent of a fluoride removal process using calcite was related to the concentration of Ca^{2+} through Eqs. (1) and (2) (Yang et al., 1999):

$$2F^- + Ca^{2+} \rightarrow CaF_2 \quad (1)$$

$$K_{sp} = [F^-]^2[Ca^{2+}] = 3.5 \times 10^{-11} \quad (2)$$

Supersaturation of F^- and Ca^{2+} is the necessary condition for precipitation of CaF_2. The supersaturation can be easily achieved at a high initial F^- concentration. So, the performance of a F^- removal process not only depends on the Ca^{2+} doses but also is largely affected by the initial F^- concentration making it difficult to remove fluoride from low initial concentrations (Majima and Takatsuki, 1987).

Several researchers have used limestone to reduce F^- concentration in contaminated water to a level acceptable for drinking (Yang et al., 1999; Reardon and Wang, 2000; Nordstorm and Jenne, 1977; Turner et al., 2005, 2008). Nordstorm and Jenne (1977) could achieve only a level of 4 mg/L of F^- by limestone treatment (Nordstorm and Jenne, 1977). Reardon and Wang achieved F^- removal to below 2 mg/L by passing CO_2 through crushed limestone columns during filtration (Reardon and Wang, 2000). Yang et al. (1999) reported adjustment of H^+ concentration to be an important factor for fluoride removal by calcite since it controls dissolution of $CaCO_3$. Addition of HCl or H_2SO_4 to calcite determines the extent of dissolution of calcite, in which the concentration of H^+ ion is an important factor for the dissolution (Yang et al., 1999). However, the method leaves the concentration of chloride and sulfate in the treated water too high to be used for drinking water. Use of HNO_3 leaves NO_3^- ion in the treated water, which is harmful even in trace amount. On the other hand use of strong acids in liquid form is unsuitable for water purification by a layman. We have recently reported that the removal of fluoride by crushed limestone column was enhanced significantly in presence of edible acids, *viz.*, acetic acid (AA) and citric acid (CA). The fluoride removal from initial 10 mg/L was achieved up to 1 mg/L (Nath and Dutta, 2010a,b). The removal of fluoride in such acid-enhanced limestone defluoridation (AELD) takes place through precipitation as well as adsorption (Nath and Dutta, 2010a,b; Nath et al., 2011).

In a search for a more suitable acid for the AELD method we have carried out a systematic study with oxalic acid (OA) keeping in mind that being a stronger acid it should increase the concentration of the Ca^{2+} in the limestone column more than that by AA or CA. Moreover, very little of oxalate should remain in the treated water due to low solubility of calcium oxalate and high concentration of calcium ion produced in the column. The solid acid, OA has also a practical advantage over liquid AA.

Attempts have been made to optimize different operational variables like, quantity of the acid added, contact time and the final pH of the treated water. The effect of the initial concentration of fluoride and the effect of competing anions present in the water have also been considered. Groundwater and wastewater contain several types of anions which may interfere in the adsorption or precipitation of fluoride during limestone defluoridation. The interference by some competing anions, *viz.*, Br^-, Cl^-, PO_4^{3-}, SO_4^{2-} and NO_3^- has been investigated by adding the sodium salts of the anions in the concentration range of 100–500 mg/L to fluoride solution in groundwater along with OA before the limestone treatment. The limestone samples before and after use, and the precipitate formed in the column have been analyzed using X-ray diffraction (XRD), FT-IR spectroscopy (FTIR), thermogravimetric analysis (TGA), scanning electron microscopy combined with energy dispersive X-ray spectroscopy (SEM–EDX) and X-ray photoelectron spectroscopy (XPS) in order to evaluate reusability of the used limestone and to examine the precipitation and adsorption of fluoride during the process.

2. Materials and methods

2.1. Materials

A crude limestone sample was obtained from Bokajan Cement Factory, a Govt. of India enterprise at Bokajan, Assam, India. X-ray diffraction and infra-red absorption analyses indicated the crude limestone to be high purity calcite. The limestone was crushed and segregated into different particle sizes and the 2–3 mm diameter segment has been used for the experiments. AR grade oxalic acid (OA) was obtained from Merck, Mumbai and used as such. Synthetic fluoride containing groundwater was prepared using AR grade NaF (Merck, Mumbai) for amending the fluoride concentration. All the inorganic salts used for the study of the effects of competing ions were of AR grade and used as such. The composition of the groundwater was as follows: Na^+, K^+, Ca^{2+}, Mg^{2+}, Hg^{2+}, F^-, SO_4^{2-}, hardness and alkalinity equal to 5.62, 8.75, 0.72, 2.61, 0.028, 0.206, 200, 12.6 and 69.5 mg/L, respectively and pH 6.80 (Das et al., 2007).

2.2. Equipment

Concentrations of fluoride were measured on an Orion Multiparameter Kit using an Orion ion selective electrode for fluoride. TISAB-III was used to control ionic strength and de-complex fluoride. The calibration of the ion meter was done at 10, 1.0 and 0.1 mg/L of fluoride. The pH was measured on a Systronics μ-pH meter. Ca was determined by using an atomic absorption spectrophotometer Perkin Elmer AA200. The IR and XRD spectra were recorded on a Nicolet FTIR spectrophotometer and a Rigaku X-ray diffractometer, Miniflex UK, respectively. The thermal properties of the precipitate produced in the column are measured using TGA/DSC analyzer models Shimadzu TGA50 and DSC 60. A scanning electron microscope combined with energy dispersive X-ray spectroscopy (SEM–EDX), make JEOL model JSM-6390LV, was used to record the SEM micrographs and EDX spectra. Limestone surface analysis before and after the treatment was performed on KRATOS ESCA model AXIS 165 with accuracy <0.3 eV. An inductively coupled plasma optical emission spectrophotometer (ICP-OES), model Perkin Elmer Optima 2100DV, was used to determine the heavy metals in the water after treatment.

2.3. The AELD process

The fluoride removal experiments were carried out in plexiglass columns of length 44 cm and diameter 4 cm. The synthetic groundwater having 10 mg/L of F^- and 0.1 M OA was