A STUDY ON REMOVAL OF FLUORIDE FROM CONTAMINATED WATER

ABSTRACT

This thesis describes a systematic study of fluoride removal from contaminated water using limestone and phosphoric acid (PA). This includes the fluoride removal from water using PA-limestone combination in different ways, *viz*., (i) fluoride removal by limestone powder in presence of phosphoric acid (PA), (ii) fluoride removal by hydrothermally modified limestone powder in presence of PA, (iii) the performance of fluoride removal by PA-crushed limestone treatment (PACLT) in continuous-flow mode, (iv) a laboratory-scale pilot test of the PACLT for optimizing the PA dose and other process parameters and a field trial of the chosen PACLT method in domestic and small community level at some fluoride affected rural areas. The thesis has been organized in four chapters dealing with different aspects of the study as follows:

1. Introduction: Narrates the background, motivation and the scope, objectives and plan of the present work.
2. Experimental: Describes the materials and the general experimental methods.
3. Results and discussion: Presents the results, observations, their interpretations and explanations.
4. Conclusions: Summarizes the important findings of the present investigation and future scopes of work in the study area.

Chapter 1

1. Introduction

Chapter 1 contains the introduction part of the thesis with detailed analysis of contamination of fluoride, its toxicity and health impacts. Mitigation of fluoride menace including various existing fluoride removal technologies, their merits and demerits are also discussed in this chapter with reference to the literature. The lacuna remaining in the area and the scope of the present topic of research has been discussed. The aims and objectives along with the strategy of the present work have been narrated in the last part of this chapter.

Chapter 2

2. Experimental

This chapter consists of the description of the materials and the methods applied in this study. The crude limestone sample and powdered limestone of ≤170 μm size were obtained from Bokajan Cement Factory, Bokajan, Assam, India. The limestone was crushed into particle size of 1.0-1.5 cm. All the other required chemicals were Analytical Reagents, obtained from Merck, Mumbai, and were used without purification. The procedures for batch study of PA-powdered limestone, hydrothermal modification of limestone powder, PA-crushed limestone treatment in continuous-flow mode and laboratory-scale pilot test including field trial of fluoride removal method have been described here. The field trial was conducted at all together six spots water sources which included five households with 15 L and one small community system with 220 L water holding capacity units at different fluoride affected villages in Karbi Anglong District of Assam.

Concentration of fluoride was measured on an ion-meter using an ion selective electrode for fluoride. The pH of the samples was measured using an Orion multiparameter kit. The metal ions, other than sodium and potassium, in water before and after treatment were determined by using an atomic absorption spectrophotometer. The sodium and potassium ion were determined by using a flame photometer. Other ions were determined by UV-Visible spectroscopic measurements. The characterization of limestone and other solids were done by using FTIR, XRD, SEM and EDX. Statistical analysis has been done using SPSS 16. The detailed description of the instruments along with methods has been included in this chapter.

Chapter 3

3. Results and discussion

This chapter describes the results of the experiments, their interpretation, explanation and study of the mechanism involved in the removal process. For systematic organization, this chapter has been sub-divided into five major sections as follows.

3.1 Fluoride removal by limestone powder in presence of PA

The results of batch experiments on fluoride removal by limestone powder in presence of PA and their interpretations have been presented in this section. The batch experiment is

carried out in 250 mL Erlenmeyer flasks in presence of different initial PA concentrations, $[PA]_0$. Other parameters varied in this study were the effect of adsorbent dose, contact time and initial F^- concentrations ($[F^-]_0$). Results of the batch experiment have been analysed to assess performance for fluoride removal. The kinetics of fluoride removal and the thermodynamic parameters of adsorption of fluoride have been studied. The limestone powder was analysed by FTIR and XRD before and after fluoride-loading. The fluoride adsorption capacity of limestone has been found to be 4.38 mg/g which is better than the capacity of 0.39 mg/g reported for limestone alone. Physical adsorption of fluoride on newly formed HAP through reaction between limestone and PA and exchange between OH^- and F^- ions inside HAP are the dominant fluoride removal mechanisms.

3.2 Fluoride removal by hydrothermally modified limestone powder using PA

The section describes the modification of limestone powder by hydrothermal treatment in presence of PA. The characterization of the modified limestone was done by using FTIR, XRD and SEM-EDX analysis. Fluoride removal by the modified limestone powder was studied with respect to experimental parameters such as adsorbent dose, contact time and initial fluoride concentrations. The kinetics and thermodynamics of its fluoride adsorption were studied using various models. The modified limestone powder modified using 0.90 M PA showed an adsorption capacity of 6.45 mg/g. The fluoride adsorption capacity is found to be better than that of capacity of limestone powder in presence of PA. The isotherm models indicated physisorption of fluoride along with ion-exchange of OH^- ions of HAP by F^- ions.

3.3 Fluoride removal by phosphoric acid-crushed limestone treatment in continuous-flow mode

The results of the fluoride removal performance by phosphoric acid-crushed limestone treatment (PACLT) in continuous-flow mode experiment have been described in this section. The results have been analysed to assess and optimize the process with respect to the operational parameters. The different operational parameters considered for this experiment were the effect of influent PA and F^- concentrations, effect of flow rate, pH of effluent water, effect of co-existing ions. Regeneration and performance of regenerated column have also been studied. The precipitate found in the column has also been tested for leaching of F^-. The mechanism of fluoride removal has also been discussed using FTIR, XRD, SEM-EDX and Saturation Index (SI). Fluoride can be removed from

contaminated water from 5-10 mg/L to 0.1-1.5 mg/L in the continuous flow mode through a fixed-bed crushed limestone reactor in presence of PA.

3.4 Fluoride removal by phosphoric acid-crushed limestone treatment: *A laboratory pilot test*

The results of fluoride removal from synthetically prepared fluoride contaminated water in the laboratory-scale pilot tests of the PACLT method have been presented in this section. The effects of variation in $[F^-]_0$, initial PA concentration ($[PA]_0$), co-existing ions and regeneration of limestone have been addressed. The regeneration of exhausted limestone has been done under three different conditions. The mechanisms of fluoride removal have been investigated through analysis of the solids and the treated water. One way analysis of variance (one-way ANOVA) was performed using SPSS 16 to examine the real variations amongst the results of treatments under different conditions by calculating the least significant difference (LSD) amongst the data of fluoride removal with $[F^-]_0$, $[PA]_0$ and final pH. The results show that this method can efficiently remove fluoride from 10 mg/L to 0.01-1.0 mg/L. The fluoride removal is significantly increased with $[PA]_0$ as evident from LSD value 0.25 and $p < 0.05$. The PACLT in plug-flow fixed bed method has been found to be suitable in terms of safety, acceptability, cost and non requirement of electricity.

3.5. Field study of fluoride removal by phosphoric acid-crushed limestone treatment: *Fluoride Nilogon*

The results of the field trial of the fluoride removal by phosphoric acid-crushed limestone treatment method, named Fluoride Nilogon ('Nilogon' for removal) carried out in different fluoride affected areas in Assam have been presented here. The dose of $[PA]_0$ for field application had been optimized as 0.68 mM through another experiment carried out in the laboratory using a replica of the field units. The $[F^-]_0$ in the groundwater of the different sources used for treatment was in the range of 2.8-20.0 mg/L. After the PACLT by Fluoride treatment the final concentration of fluoride dropped to the ranges of 0.5-0.8 mg/L with pH in the range of 7.4-7.8. The results of the field trial clearly demonstrate the PACLT as a suitable fluoride removal method for rural applications.

Chapter 4

4. Conclusions and future scope

This is the concluding chapter of the thesis which delineates the conclusions and future scope of the present work. The main conclusions, in brief, are:

- Presence of phosphoric acid in water increases the fluoride adsorption capacity of limestone powder from 0.39 mg/g to 4.38 mg/g.
- Hydrothermal modification of limestone powder in presence of PA leads to formation of HAP. The modified limestone powder, with a fluoride adsorption capacity of 6.45 mg/g, has a potential for application in fluoride removal.
- Fluoride removal by crushed limestone bed with added phosphoric acid in the influent water in a continuous-flow mode removes fluoride from 5-10 mg/L to 0.1-1.5 mg/L indicating the method as having a potential for on-line application.
- The laboratory-scale pilot tests of the phosphoric acid-crushed limestone (PACLT) method showed fluoride removal from 10 mg/L to 0.01-1.0 mg/L in three hours treatment time using 0.01M PA. The simplicity of operation, high efficiency, a high capacity of limestone, low cost, non-requirement of energy, safety and environment-friendliness together make the PALCT method in plug-flow mode suitable for field application.
- The user trial in fluoride-affected villages, with groundwater contaminated with 2.8-20 mg/L fluoride, showing a very good fluoride removal at a $[PA]_0$ dose as low as 0.68 mM, has proven the PACLT method in plug-flow mode as one of the most competent low-cost method for fluoride removal in affected rural areas.

Finally, the finding of the present work open up scopes for future research and development works, *viz*., field trial of the phosphoric acid-crushed limestone method for large community piped drinking water supply schemes and agricultural use. Pilot and field test of the phosphoric acid-crushed limestone in continuous-flow mode has also been explored.