

# Elimination of Fluoride from Water using Limestone and Common Laboratory Acids

SURESH KUMAR NATH

*Department of Chemistry, Kokrajhar Government College, Kokrajhar, 783370, BTR, Assam, India*

E-mail: [nathsuresh2009@gmail.com](mailto:nathsuresh2009@gmail.com)

## ABSTRACT

An efficient and simple defluoridation method has been evaluated using locally available limestone and some acidic chemicals. For efficient fluoride removal, it requires more time, about 20 hr, because limestone dissolves in small amounts at neutral pH. In this work, two common laboratory acids were added to the fluoride water before filtration through the limestone column and it was found that in the presence of acid, the removal capacity of limestone not only increased but also became quicker. It was possible to bring down the fluoride level from 10-15 mg/L to below 1 mg/L. High dissolution of limestone in the presence of acids generates a high amount of calcium ion in the water, which precipitates the fluoride as calcium fluoride. The dissolution process by the acids creates new surfaces of the limestone which also helps in adsorption of fluoride onto the surface of the limestone. These two phenomena, precipitation and adsorption of fluoride, were proved as the mechanism of fluoride removal in this process. The limestone has been analyzed before and after the treatment process and it was found that it retains its quality for reuse in the defluoridation process.

**Key words:** Defluoridation; Hydrochloric acid; Sulfuric acid; Calcium carbonate

## INTRODUCTION

Fluoride exists in trace amounts in almost all groundwater throughout the world. A small amount of fluoride is required to strengthen our teeth and bones. However, long term ingestion of fluoride in high doses can lead to severe dental and skeletal fluorosis (Ayooob and Gupta 2006). More than 30 countries of the world are highly endemic of fluorosis as per the latest status (Chen et al. 1996, Reardon and Wang 2000, Kahama et al. 1997, Dissanayake and Rohana 1999, Hillier et al. 2000). In Africa, China, the Middle East and southern Asia (India and Sri Lanka), the groundwater has been found with high fluoride. High fluoride belts on land comprise the East African Rift from Eritrea to Malawi, followed by another belt from Turkey through Iraq, Iran, Afghanistan, India, northern Thailand and China. The Americas and Japan have similar belts (Fawell et al. 2006).

The extent of fluoride contamination in groundwater in India varies from 1.0 to 48 mg/L. The fluoride affected states are: Andhra Pradesh, Assam, Bihar, Chattishgarh, Delhi, Gujarat, Haryana, Jammu and Kashmir, Jharkhand, Karnataka, Kerala, Madhya Pradesh, Maharashtra, Orissa, Punjab, Rajasthan, Tamil Nadu, Uttar Pradesh, Uttaranchal and West Bengal (Anonymous 2002). There were

reports about people in several districts of Rajasthan and Assam consuming water with fluoride concentration up to 44 mg/L and 23 mg/L, respectively. The capital of India, Delhi, is endemic for fluorosis with maximum natural fluoride concentration of 32 mg/L (Susheela and Bhatnagar 1999).

The prevention of fluoride contamination of water is critical; however, fluoride removal from water has been in practice for several decades to prevent fluorosis. Although a lot of methods for excess fluoride removal from water are there, still a low-cost solution with minimized disadvantages to this problem is rare. The principles that have been used for fluoride removal are based on adsorption (Raichur and Basu 2001), precipitation-coagulation (Reardon and Wang 2000, Saha 1993), ion-exchange (Durmaz et al. 2005), membrane separation process (Cohen and Conrad 1998), and electro dialysis (Hichour et al. 1999) etc. However, it may be due to high cost, low efficiency or production of huge amounts of sludge containing fluoride that have no proper practical field utility.

Calcium metal containing compounds have constantly been used many times in many fluoride affected areas to remove fluoride from water due to the potentiality of this metal for this process (Reardon and Wang 2000). Calcium hydroxide [Ca(OH)<sub>2</sub>],

calcium chloride [CaCl<sub>2</sub>] and calcium sulphate [CaSO<sub>4</sub>] have already been used for fluoride removal (Nath and Dutta 2013). Treatment of fluoride water by limestone has been proven to be a good method for fluoride removal. It takes about 20 hrs of residential time to remove fluoride without adding any acid to the water (Reardon and Wang 2000). After addition of the acid, the time was reduced to 3-6 hrs, and the removal also increased. Such effects were reported earlier with acetic, citric, oxalic and phosphoric acid (Nath and Dutta 2010, 2012, 2009, 2017, Nath et al. 2011, Gogoi et al. 2015). Therefore, in this work, fluoride removal from water has been tried by using limestone and two common laboratory acids, H<sub>2</sub>SO<sub>4</sub> and HCl. The limestone easily dissociates in the presence of acid, liberating free calcium ions which can precipitate the fluoride present in water. Simultaneously, with degradation, new surfaces of the limestone will be created which can also absorb fluoride. Applying these two principles, the work has been carried out and the findings are presented below.

## MATERIAL AND METHODS

Crude limestone was obtained from Bokajan Cement Factory, Cement Corporation of India at Bokajan, Assam, India. The X-ray diffraction (XRD) and infrared (IR) absorption analysis indicate the crude limestone to be high purity calcite. It mostly comprised of CaCO<sub>3</sub>, CaO and Silica. The limestone was crushed and segregated into different particle sizes, viz. 2-3 and 3-4 mm. Among these two sizes, 3-4 size has been selected for the experiments as it gives a better solid-liquid ratio, since larger gaps between the particles provide space for more water. AR grade H<sub>2</sub>SO<sub>4</sub> and HCl acids and NaF (S.D. Fine Chemicals, Mumbai) were used. The fluoride solutions of 5, 10, and 15 mg/L concentrations were prepared using NaF and groundwater after amending the F<sup>-</sup> concentration.

Batch tests were performed with crushed limestone using synthetic fluoride solutions pre-acidified with varying amounts of HCl and H<sub>2</sub>SO<sub>4</sub>. A set of half litre-sized bottles were filled with 3-4 mm sized limestone particles (500 g in each bottle) and 5 mg/L F<sup>-</sup> solutions having HCl concentrations of 0.01, 0.05 and 0.1 M of were added to fill up to the top level of limestone. The volume of fluoride

solution filled in between the limestone particles is 240 mL. They were allowed to stand without shaking. Just after 1 minute, 20mL of fluoride solution was taken out and filtered using Whatman 40 filter paper and collected in a plastic sample bottle for analysis of F<sup>-</sup> and pH. In a similar way, samples were collected after 5, 10, 15, 20, 30, 45, 60, 120, 180 min and after 24 hrs to observe the fluoride removal capacity of the limestone and the pH of the effluent water with variation of time and to determine the other parameters. The remaining solutions of the bottles were drained. Fresh F<sup>-</sup> solutions were put into the respective bottles for the next day containing the limestone packs. This experiment was repeated using H<sub>2</sub>SO<sub>4</sub> under similar concentrations.

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-pH meter. Ca was determined by using an atomic absorption spectrophotometer Perkin Elmer AA200. The XRD spectra were recorded on a Rigaku X-ray diffractometer, Miniflex UK, respectively. 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.

## RESULTS AND DISCUSSION

### Fluoride removal performance in presence of 0.1, 0.05 and 0.01 M acid

The limestone used in this process contains a good amount of CaCO<sub>3</sub>. CaCO<sub>3</sub> dissolves in water only in the presence of acid, thus, when the fluoride water containing 0.1, 0.05 and 0.01 M acid concentration, it can easily dissociate the CaCO<sub>3</sub> and liberate a free Ca<sup>2+</sup> ion. These free Ca<sup>2+</sup> ions can precipitate the fluoride present in the water. The possible reactions were:

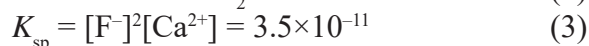
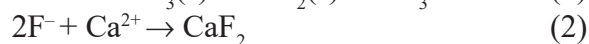
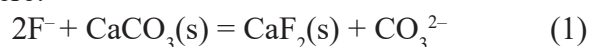


Figure 1 shows the results of batch experiments of limestone for removal of fluoride from water when it contains sulfuric acid in different concentrations

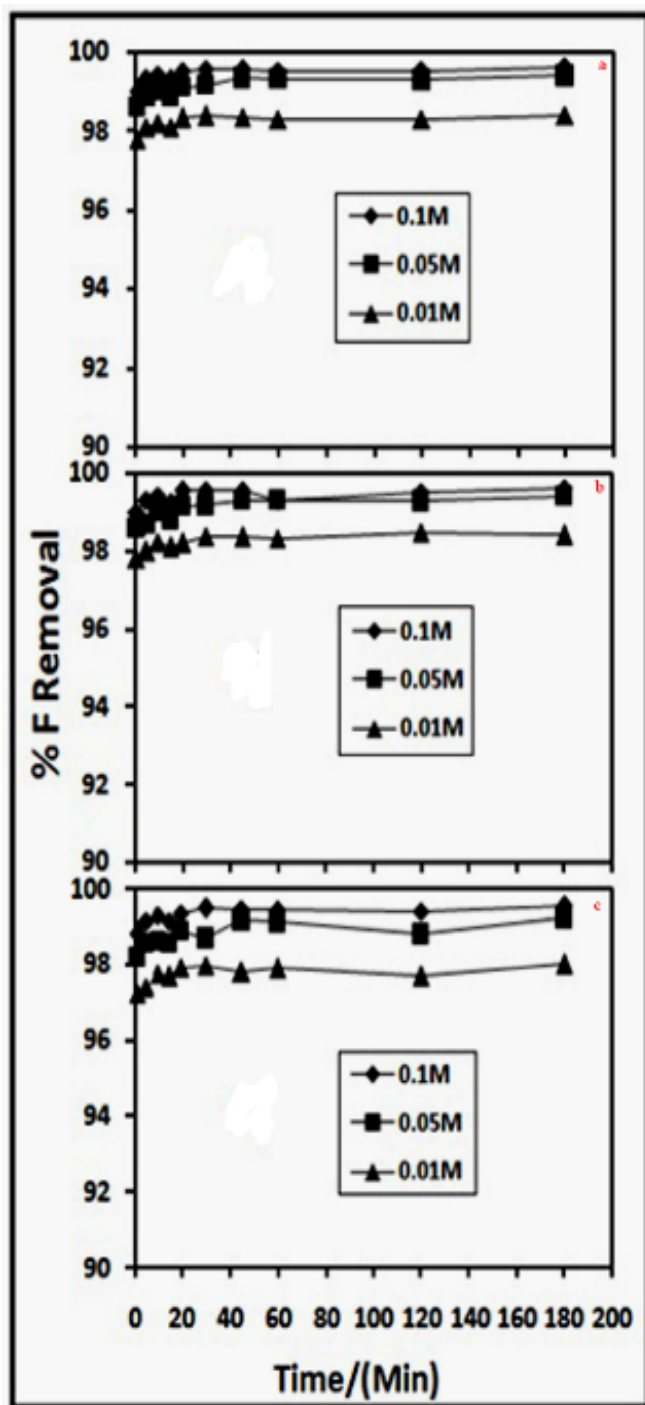


Figure 1. A plot of % fluoride removal vs. time using  $\text{H}_2\text{SO}_4$  from initial fluoride conc. of fluoride (a) 5mg/L, (b) 10 mg/L and (c) 15 mg/L

*viz.*, 0.1, 0.05 and 0.01M. The percentage of fluoride removed from the water containing an initial fluoride conc. of 5, 10 and 15 mg/L is plotted against the time required for the process. It is clear from the result that within 1-15 min of contact time 90% fluoride was removed. The percentage removal is a factor of contact time and sulfuric acid concentration.

The presence of acid in the fluoride containing water dissolutes the limestone and liberates free calcium ions, which precipitates fluoride. The surface of the limestone is also capable of adsorbing fluoride ions. Since the surface of limestone is degrading continuously and regenerating new surfaces, so the fluoride ions can easily adsorb on the new surface created by the process. Therefore, within a very short time the fluoride is removed from 15mg/L to below 1.5mg/L which is the permissible limit of fluoride in water (Anonymous 2011).

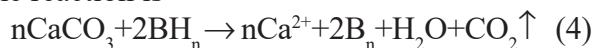
While fluoride is removed within a very short time initially but after around 30 mins of contact time the removal becomes almost constant. This means after 30 minutes the vacant spaces on the surface of the limestone may become saturated with fluoride, so less adsorption of fluoride is happening. One conclusion may be drawn here that the process needs a maximum of half to one hour of treatment time and 0.01M concentration of acid may be sufficient for the process. Similar results were also found in the case of hydrochloric acid treatment (Fig 2). The percentage removal of fluoride with the acid under three concentrations vs. time clearly shows the high rate of removal ability of the limestone in the presence of the acids. The high rate of removal of the fluoride thus can be still achieved with reduced acid concentration of less than 0.01 M which is similar to sulfuric acid treatment.

Since the acids  $\text{HCl}$ , and  $\text{H}_2\text{SO}_4$  leave  $\text{Cl}^-$  and  $\text{SO}_4^{2-}$  ions, respectively, in the treated water, an optimized minimum amount of acid should be added to the water before filtration to avoid an increase of these ions in the treated water. The time required for treatment of the fluoride water may also be reduced to less than 1 hr.

#### pH of the water after treatment

The variation in pH of the treated water with time has been shown in Figure 3 for the three acids. The pH of the treated water was found to be in the range 6.0-7.5 with all three concentrations of the acids, indicating complete neutralization of the acids by limestone.

The reaction is



where  $\text{BH}_n$  and  $2\text{B}_n$  are the acid and its conjugate base. Further work on this method needs optimization of the time and the reduction of the amount of acids.

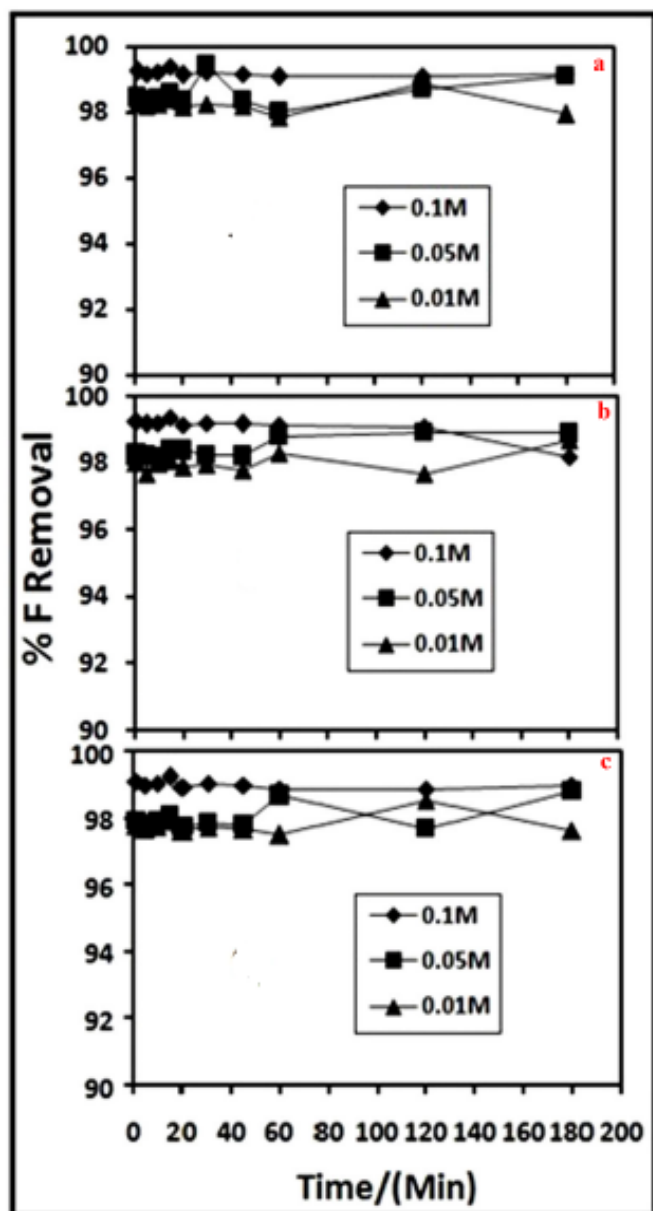


Figure 2. Fluoride removal (%) vs. time (a) 5mg/L, (b) 10 mg/L and (c) 15 mg/L using HCl.

#### Evaluation of mechanism of the process

The removal of fluoride by this method may have two mechanisms - precipitation and adsorption of fluoride (Nath and Dutta 2010, 2012, 2009, Nath et al. 2011, Gogoi et al. 2015). Calculation of the Saturation Index (SI) of fluorite ( $\text{CaF}_2$ ) can be used to determine if precipitation is the major mechanism of fluoride removal by the AELD process. The SI values were calculated for different types of experiments using the remaining  $\text{F}^-$  and  $\text{Ca}^{2+}$  concentration in the treated water and solubility product of  $\text{CaF}_2$ . When the limestone was used for the first time, the SI value was negative, which

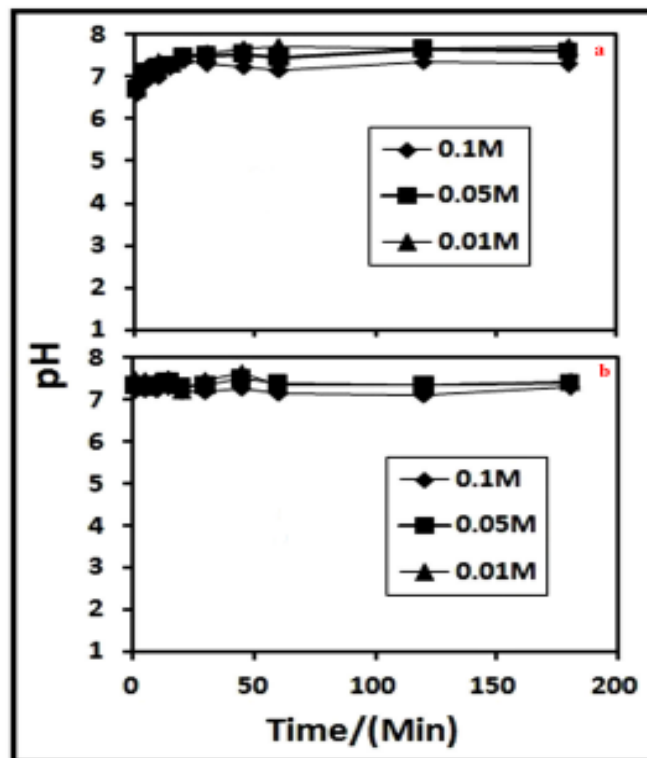


Figure 3. Variation of pH with time in defluoridation process using (a)  $\text{H}_2\text{SO}_4$  and (b) HCl.

gradually increased with the increase in  $n$ . The values became positive after 3-5 times use of the same limestone bed (Table 1). The observed negative SI with lower  $n$  indicates adsorption to govern the removal of fluoride on calcite (Turner et al. 2005).

Table 1. Saturation Index (SI) values for the defluoridation processes using all acids with number of times ( $n$ ) use of the same limestone bed.

$n$	$\text{H}_2\text{SO}_4$	HCl
1	-2.187	-2.008
2	-1.09	-1.943
3	-0.636	-0.886
4	-0.204	0.1574
5	-0.1649	0.3521
6	0.0759	0.468
7	0.1574	0.78
8	0.3213	0.82
9	0.493	0.932
10	0.585	0.783

The positive SI values increased with increase in  $n$ , indicating precipitation of fluorite to be the major

mechanism of fluoride removal above. As acids are neutralized for the first time in addition to limestone, precipitation occurs from the beginning. That is why the negative values are increasing to become positive.

The adsorption sites of the limestone surface are gradually saturated and a gradual decrease in the adsorption of fluoride on continuous use of the same limestone chips. On the other hand, the dissolution of calcite by the acids may create new adsorption sites on the calcite surface which further allow the adsorption process.

### XRD analysis

During the process of defluoridation, it is possible that the free calcium ion can form calcium chloride and calcium sulphate by combining with the free ions of the acids. However,  $\text{CaCl}_2$  is highly soluble in water and  $\text{CaSO}_4$  is sparingly soluble. The latter one may improve the fluoride removal percentage by absorbing the fluoride present in the water. The presence of these compounds with the used limestone was found when the surface part of the limestone was studied under X-ray. Figure 4 shows the X-ray diffraction spectra of the limestone before and after use and the calcium fluoride found in the used limestone. The XRD study reveals that the limestone is highly pure and the quality remains intact even after use of 18 times. Figure 5 shows the X-ray diffraction spectra of the different compounds produced on the surface of the limestone. The limestone precipitates as the respective salts of the acid and fluoride removal occurs via precipitation of  $\text{CaF}_2$ . There is only a slight morphological effect of the acids on the limestone and only the surface part of the limestone was degraded and the inner part remains intact, which indicates that those can be reused after the experiment.

### SEM-EDX study

The SEM-EDX study was done to predict the surface adsorption of fluoride on the surface of the limestone. Figure 6 shows the SEM micrographs of limestone before and after use in the experiment. The SEM pictures show the rough surfaces of the limestone and EDX shows the different types of elements are present on the surface of the limestone. The presence of a good amount of Calcium is found in all three samples. The EDX of crude limestone shows no

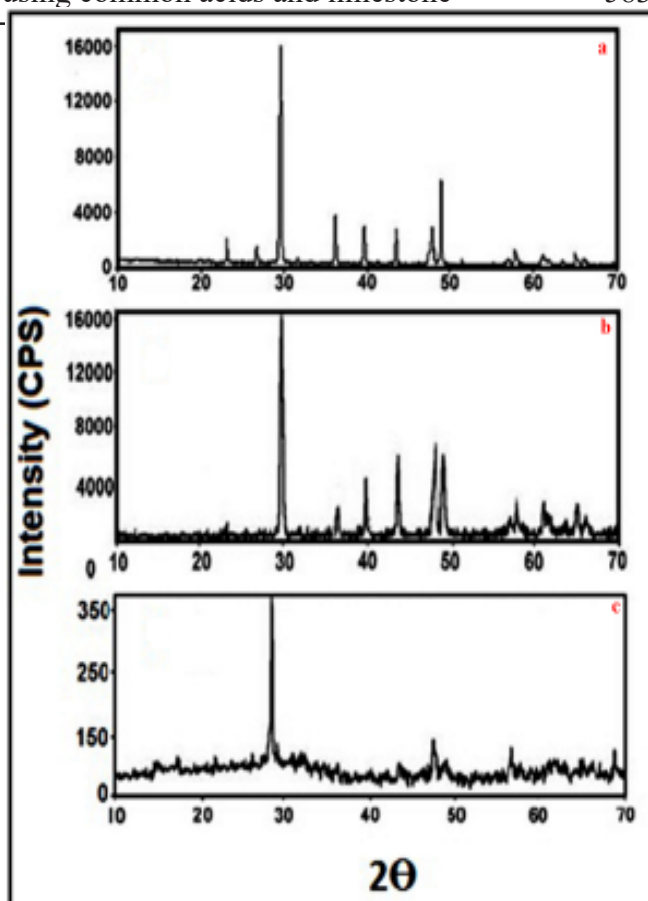


Figure 4. The XRD spectra of (a) crude limestone; (b) limestone after use and (c)  $\text{CaF}_2$  produced on the surface of the limestone

presence of fluoride whereas the EDX of both used limestone shows the presence of fluoride. This predicts that the fluoride is absorbed onto the surface of the limestone after being used in the experiment (Nath et al. 2011).

### CONCLUSION

The acid enhanced limestone defluoridation method has been found to be effective. The significance of this work is that within 1 min of the treatment time the amount of fluoride has been decreased to below 0.5 mg/L from the initial concentration of 5 mg/L. The acid concentration and the treatment time can be reduced to remove the fluoride to the required amount. The pH of the water after treatment remains within the range of drinking water, which indicates the neutralization of the acids has been occurring during the treatment process. The limestone is degraded into free  $\text{Ca}^{2+}$  which removes fluoride. The

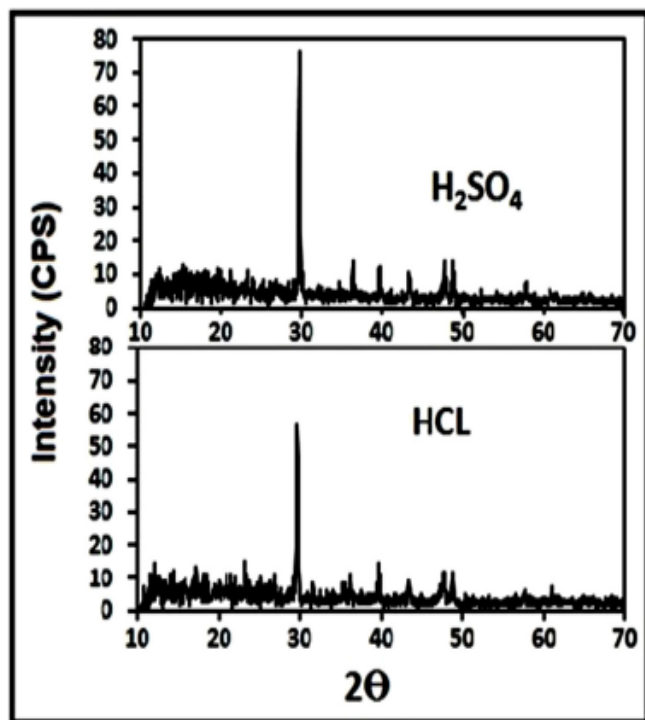


Figure 5. The XRD spectra of the salts produced after use of the limestone with  $H_2SO_4$  and HCl

saturation index calculation reveals that precipitation of fluoride as  $CaF_2$  and adsorption of fluoride on the surface of the limestone may be the main mechanism of fluoride removal. The X-ray diffraction study gives information about the quality of the limestone before and after use and the different types of the products produced during the course of the reaction. The SEM-EDX analysis shows the surface adsorption of fluoride on the limestone after use. Saturation index calculation, XRD analysis and SEM-EDX study reveal the mechanism of the process. This method of defluoridation using limestone and three acids may be a potential method for use in large scale. The experiment can be done using the same limestone bed for repeated use and the scope of reusability of the limestone can also be studied.

#### ACKNOWLEDGMENT

The author gratefully acknowledge financial assistance from the University Grant Commission, under the project UGC-NERO MRP No. F.5-88/2012-13/MRP/NERO/719, and the Principal, Kokrajhar Government College, Kokrajhar, Assam for encouragement during the course of the research work.

**Conflict of interest:** Author declares no conflict of interest

#### REFERENCES

- Anonymous. 2002. Water supply and sanitation—A WHO-UNICEF sponsored study report. Planning Commission, Government of India, New Delhi, <https://admin.indiawaterportal.org/sites/default/files/iwp2/wtrsani.pdf>
- Anonymous. 2011. Guidelines for Drinking-water Quality, Recommendations, Fourth ed. World Health Organization, Geneva, Switzerland. [https://apps.who.int/iris/bitstream/handle/10665/44584/9789241548151\\_eng.pdf](https://apps.who.int/iris/bitstream/handle/10665/44584/9789241548151_eng.pdf)
- Ayoob, S. and Gupta, A.K. 2006. Fluoride in drinking water: A review on the status and stress effects. *Critical Reviews in Environmental Science and Technology*, 36, 433-487.
- Chen, Y.X., Lin, M.Q., He, Z.L., Xiao, Y.D., Chen, C., Min, D., Liu, Y.Q., Yu, M.H. 1996. Relationship between total fluoride intake and dental fluorosis in areas polluted by airborne fluoride. *Fluoride*, 29, 7-12.
- Cohen, D. and Conrad, M.H. 1998. 65,000 GPD fluoride removal membrane system in Lakeland, California, USA. *Desalination*, 117, 19-35.
- Dissanayake, C.B. and Rohana, C. 1999. Medical geochemistry of tropical environments. *Earth-Science Reviews*, 47, 219-258.
- Durmaz, F., Kara, H., Cengeloglu, Y. and Ersoz, M. 2005. Fluoride removal by Donnan dialysis with anion exchange membranes. *Desalination*, 177, 51-57.
- Dutta, R.K. and Nath, S.K. 2012. A highly efficient defluoridation method by in-situ generation of an efficient precipitant and strong adsorbents of fluoride in crushed limestone fixed-bed column and plug flow reactors. *Indian Patent No. 289204*.
- Fawell, J., Bailey, K., Chilton, J., Dahi, E., Fewtrell, L. and Magara, Y. 2006. *Fluoride in Drinking-water*, Published on behalf of the World Health Organization by IWA Publishing, Alliance House, 12 Caxton Street, London SW1H 0QS, UK.
- Gogoi S., Nath S.K., Bordoloi S. and Dutta R.K. 2015. Fluoride removal from groundwater by limestone treatment in presence of phosphoric acid. *Journal of Environmental Management*, 152, 132-139.
- Hichour, M., Persin F., Molénat J., Sandeaux, J. and Gavach C. 1999. Fluoride removal from diluted solutions by Donnan dialysis with anion-exchange membranes. *Desalination*, 122, 53-62.
- Hillier, S., Cooper, C., Kellingray, S., Russell, G., Hughes, H. and Coggon, D. 2000. Fluoride in drinking water and risk of hip fracture in the UK: A case-control study. *The Lancet*, 335, 265-269.
- Kahama, R.W., Karuiki, D.N. and Njenga, L.W. 1997. Fluorosis in children and sources of fluoride around lake Elmentaita region of Kenya. *Fluoride*, 30, 19-25.
- Nath, S.K. and Dutta, R.K. 2009. Fluoride removal from water

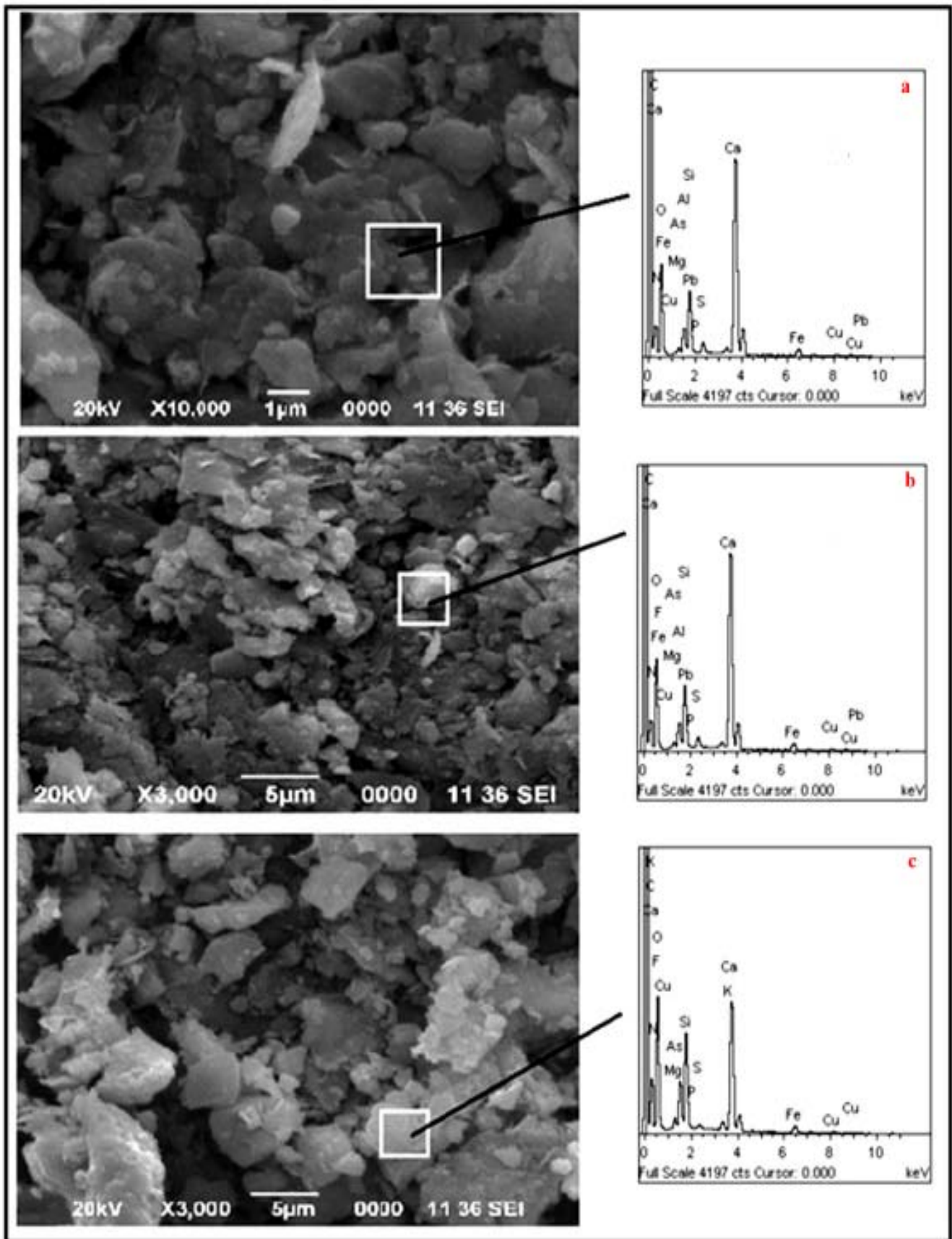


Figure 6. SEM-EDX evidence of adsorption of fluoride on the surface of the limestone; (a) Crude limestone, (b) limestone after use with H<sub>2</sub>SO<sub>4</sub> and (c) limestone after use with HCl

- using crushed limestone. *Indian Journal of Chemical Technology*, 17, 120-125.
- Nath, S.K. and Dutta, R.K. 2010. Enhancement of limestone defluoridation of water by acetic and citric acids in fixed bed reactor. *Clean Soil Air Water*, 38, 614-622.
- Nath, S.K. and Dutta, R.K. 2012. Acid-enhanced limestone defluoridation in column reactor using oxalic acid. *Process Safty and Environmental Protection*, 90, 65-75.
- Nath, S.K. and Dutta, R.K. 2013. Significance of calcium containing materials for defluoridation of water: a review. *Desalination and Water Treatment*, 53(8), 2070-2085.
- Nath, S.K., Bordoloi, S. and Dutta, R.K. 2011. Effect of acid on morphology of calcite during acid enhanced defluoridation. *Journal of Fluorine Chemistry*, 132, 19-26.
- Raichur, A.M. and Basu, J.M. 2001. Adsorption of fluoride onto mixed rare earth oxides. *Separation and Purification Technology*, 24, 121-127.
- Reardon, E.J. and Wang, Y. 2000. A Limestone Reactor for Fluoride Removal from Wastewaters. *Environmental Science and Technology*, 34, 3247-3253.
- Saha, S. 1993. Treatment of aqueous effluent for fluoride removal. *Water Research*, 27, 1347-1350.
- Susheela, A.K. and Bhatnagar, M. 1999. Structural aberrations in fluorosed human teeth: Biochemical and scanning electron microscopic studies. *Current Science*, 77, 1677-1680.
- Turner, B.D., Binning, P. and Stipp, S.L.S. 2005. Fluoride removal by calcite: evidence for fluoride precipitation and surface adsorption. *Environmental Science and Technology*, 39, 9561-9568.

*Received: 1st March 2023*

*Accepted: 13th May 2023*