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Use of Calcite for Defluoridation of Drinking Water in Acidic medium

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Abstract

A higher level of fluoride in drinking water poses serious health hazards to humans. Fluoride accumulates in bones and teeth in the form of fluorapatite which causes the bones to become brittle. Oral intake of fluoride higher than 1.0 to 1.5mg/L results in skeletal and dental fluorosis. Batch experiments were carried out to investigate the removal of fluoride from acid treated water by using calcite as the adsorbent. The effect of calcite dosage with different concentrations of acetic acid on defluoridation capacity was evaluated. The removal efficiency of fluoride increased with increase in the dose of calcite. Calcite is found to be a very low cost material and treating it with 0.05M acetic acid has resulted in increasing the defluoridation capacity to 75.6%. For a dosage of 7gm/l of calcite used for treating water with acetic acid the removal was 65.03% and the pH of treated water was observed to be 6.7 to 7.4 which makes it fit for drinking purposes. Results obtained depicted that the defluoridation is due to both adsorption and precipitation processes. It was found that the acidified water was neutralized by calcite and the pH of treated water was in the range of 6.7 to 7.4 after treatment. This study indicated that calcite is a very low cost adsorbent and can be used as a defluoridation agent.

Keywords: Fluoride, calcite, defluoridation, adsorbent.

Introduction

The presence of high fluoride concentrations in ground water resources is a major problem in almost 23 nations in the world including China, Canada, Sri Lanka, African subcontinent and India. UNICEF had reported that fluorosis is endemic in 177 districts of 20 states in India. WHO has set the permissible level for fluoride in drinking water to be upto 1.5 mg/L[1]. Fluoride is ingested is through water, food and air, water being the major source. Long-term consumption of fluoridated water has severe health impacts which can be categorized as follows: 1.5-4 mg/L causes dental fluorosis[2], >4 mg/L may promote both dental and skeletal fluorosis[3], while >10 mg/L may cause crippling fluorosis and some neurological damage[4] may also be encountered. Therefore, fluoride removal from potable water is a very important part of drinking water treatment. The general mechanism of action when fluoride enters in the body is shown in figure 1.

Several techniques have been employed for fluoride removal of potable water such as reverse osmosis[5], and nanofiltration[6]. It has been found that adsorption is a very potent technique for defluoridation of aqueous solutions[7,8,9]. Adsorbents like activated alumina have been used for the same purpose in commercial level[10]. Activated alumina which has a high potential for fluoride uptake is an expensive adsorbent, and must be regenerated using an alkaline solution. The capacity of activated alumina was found to be 3-6 mg F/g of alumina using batch experiments[10]. Using activated alumina for fluoride removal studies in a continuous flow fluidized system is a cost effective and efficient method but it has limitations due to the regeneration requirements of the spent adsorbent. Various natural-adsorbents such as activated rice husk[11], Montmorillonite clay[12], pumice stone[13], *Citrus limetta* fruit peel[14], neem and kikar bark[15] are also being studied for their potential as adsorbents for the removal of fluoride from drinking water. Defluoridation using bone char[16] is especially useful, locally available and quite effective but it is not universally accepted. Several precipitation methods using alum, lime and the Nalgonda process involve low costs but introduce residual aluminium in the treated water and is therefore not a safe process [17]. Other techniques such as Electro dialysis and reverse osmosis have very high costs. Calcium in the form of calcite[18], quicklime[19] and limestone[20] has been studied by some researchers for fluoride removal through adsorption process. The selection of the most suitable method is always made after considering the difficulties associated with the methods and cost of the process.

In the already established techniques for defluoridation, some technological as well as economic constraints are present. Since, calcium ions have a good affinity towards fluoride ions calcium based adsorbent such as calcite is a good alternative for defluoridation studies. This paper presents an attempt to remove fluoride by using a very low cost material (calcite) as adsorbent. The study shows the effect of calcite dosage on the fluoride adsorption characteristics and the effect of pre-acid treatment of fluoride water on the removal capacity.

Material and Methods

Materials: Calcite was obtained from Chanda Minerals, Alwar, and Rajasthan, India and sieved to 300 BSS, mesh size. The chemical composition of calcite is given in table 1.

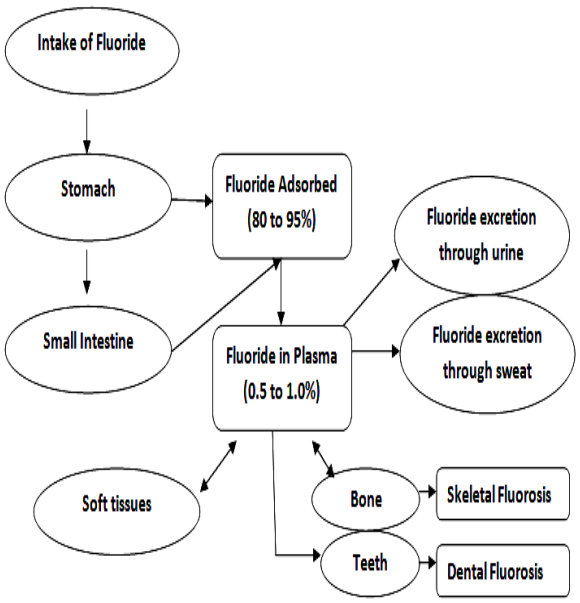

Figure-1
General mechanism of fluoride in body

Table-1
Chemical composition of calcite

S.no.	Composition	Percentage present
1.	$CaCO_3$	90% to 97%
2.	MgO	1.5% to 2.5%
3.	Silica	1 % to 3.5%

Standard solution of fluoride (1000 mg/L) was prepared by dissolving NaF (E-merck, Mumbai, India) deionized water and diluted as needed. All chemicals used in the study were of analytical grade. For adjusting pH dilute solutions of 0.1 N NaOH and HCl were used and a pH meter (Orion 2 star pH benchtop) was used for measurement purpose. Batch studies were conducted to determine the effect of calcite dosage and concentration of acid treated with. The experiments were carried out at room temperature (25±2˚C).

Fluoride analysis: The treated solution was filtered using Whatman filter paper No. 42 and the filtrate obtained was analyzed for residual fluoride concentration by using an Ion Selective Electrode (Thermo scientific Orion Versa 5 star). The calibrations were done using fluoride standards of 0.1, 1.0 and 10.0mg/L. To avoid any kind of interference with the electrode, an ionic strength fixer and buffer TISAB-II solution was added in 1:1 proportion to the sample.

Adsorbent dosage: Batch studies were done with calcite dosage of 3.0, 5.0, 7.0, 11.0, 13.0 and 15.0g/L and initial fluoride concentration of 10mg/L was used for optimizing the adsorbent dosage. The samples were kept in orbital shaker (Remi CIS24BL) at a speed of 200 rpm for 180 min, after which it was filtered out by Whatman filter paper No.42 and analyzed for fluoride ions. The data obtained in batch studies was used to calculate the percentage of fluoride removed by calcite adsorbent by using the following expression:

$$Percentage\ Removal = \frac{(C_e - C_o)}{C_e} X\ 100 \quad (1)$$

where C_e (mg/L) is the residual fluoride ion concentration and C_o (mg/L) is the initial concentration of fluoride ion in solution.

Acid treatment of water: Glacial acetic acid was used for acid treatment of water at different concentrations of 0.01M, 0.025 M, 0.05 M, 0.75 M and 0.10 M. Acid treatment was done to generate high amount of calcium ions which will help in lowering the fluoride ion concentration in solution. The samples were stirred in orbital shaker at a speed of 200 rpm for 180 min for proper contact between acidified water and calcite. The adsorbent dosage used was 7g/L for all samples.

Results and Discussion

Defluoridation experiments were being conducted in batch mode for varying adsorbent dosages and varying acid concentration for studying the adsorption process. The effects of the varying parameter on the adsorption capacity had been discussed below.

Effect of adsorbent dose: The effect of adsorbent dose on removal of fluoride using calcite as adsorbent is shown in figure 2, in which percent fluoride removal is plotted against adsorbent dose. Adsorbent dose of 7.0g/L was used to carry out further studies, since it showed lowest residual fluoride concentration. It was observed that percentage removal of fluoride increased with the increase in adsorbent dose initially and then decreased. It is well known that calcite can precipitate as well as adsorb fluoride. Due to acid treatment calcium ions get released into water and are precipitated as calcium fluoride. As this occurs, new active sites form on surface of calcite and fluoride ions get adsorbed onto them. The following reaction shows the reaction of calcite ($CaCO_3$) and sodium fluoride.

$$CaCO_3 + 2\ NaF \rightarrow CaF_2 + Na_2CO_3$$

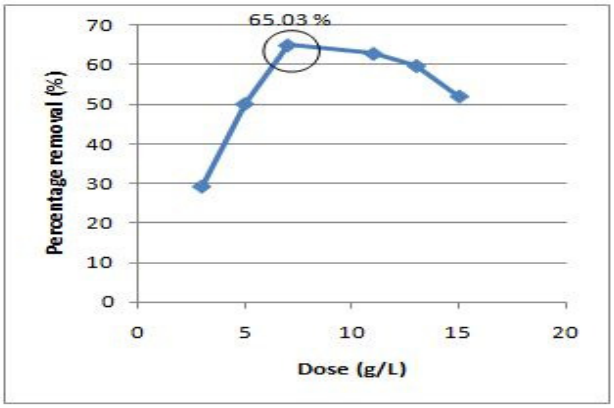

Figure-2
Effect of calcite dose on fluoride removal without acid treatment

Effect of acid concentration on removal efficiency: The effect of removal capacity of calcite at different concentrations of acetic acid is shown in figure 3. Results depict that acetic acid at concentrations of 0.05M and 0.025M was able to remove 75.6% and 64.9% of fluoride. Other concentrations of acetic acid were less effective in removing fluoride from water, therefore not studied further.

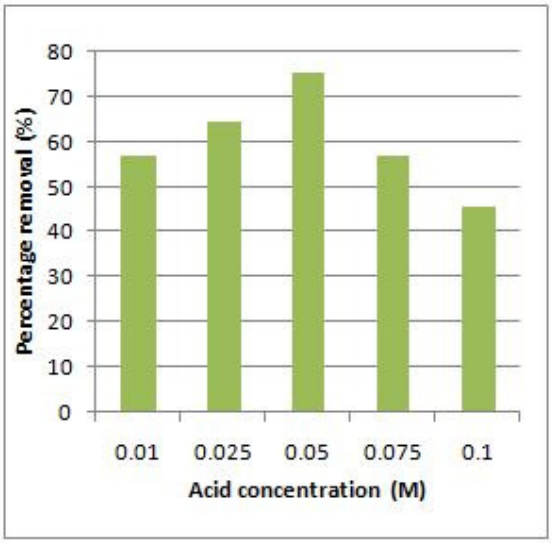

Figure-3
Effect of acid concentration on fluoride removal

Effect of contact time: The dependence of fluoride removal on contact time with calcite was determined by measuring the remaining fluoride ions concentration in samples withdrawn at an interval of 30 minutes up to 3 hours. Acetic acid concentrations of 0.025M and 0.05M were used for the study since among other concentrations of acid used they gave best results. The results are presented in figure 4. The removal rate of fluoride is rapid, but it gradually decreases with time until it reaches equilibrium. Rate of fluoride removal was higher when the process started due to larger surface area of calcite being available for the adsorption of fluoride ion. It can be noted that, since active adsorption sites are limited, fluoride uptake by the adsorbent surface is rapid initially then slows down. The removal of fluoride was found to increase with increasing contact time till 3 hours, and then it gradually decreased for both 0.025M and 0.05M of acidified fluoride sample solutions.

In case of 0.05M acidified sample the residual fluoride concentration decreased from 3.41 to 2.88mg/l in 3 hours while in case of 0.025M acidified sample it decreased from 3.45 to 3.00 in the same time period. This shows that at higher concentration of acid the fluoride removal rate is higher and faster.

pH of water: The optimum pH will vary in different supplies, but is often in the range 6.5 to 9.5 (WHO 1996). pH of water treated with calcite was observed to be 6.7 to 7.4 which makes it fit for drinking purposes as shown in figure 5.

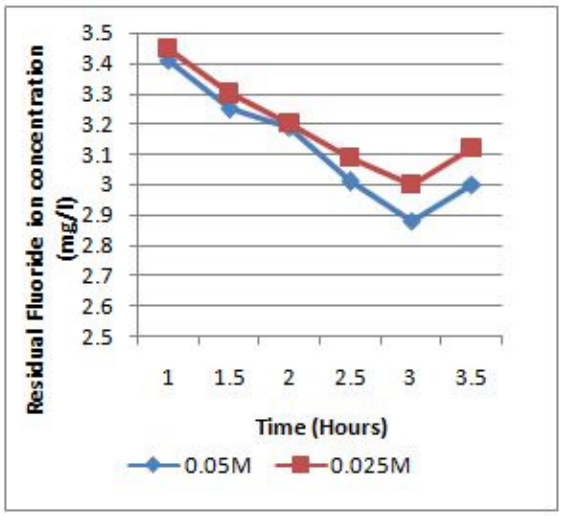

Figure-4
Effect of contact time on fluoride removal at acetic acid concentrations of 0.025M and 0.05M

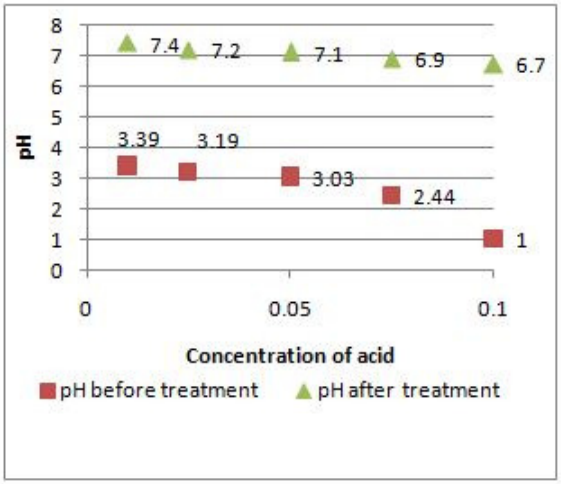

Figure-5
pH of water before and after treatment with calcite

Conclusion

Calcite is found to be a very low cost material and treating it with 0.05M acetic acid has resulted in increasing the defluoridation capacity to 75.6%. A dosage of 7g/L of calcite was used for treating fluoridated water without treating with acetic acid and the removal was 65.03% and the pH of treated water was observed to be 6.7 to 7.4 which make it fit for drinking purposes. Due to acid treatment more calcium ions got dissolved in the solution thus providing large number of adsorption sites for fluoride. While studying the effect of contact time on fluoride removal at acetic acid concentrations of 0.025M and 0.05M it was observed that when a higher concentration of acid is used the fluoride removal rate is higher as well as faster. The results demonstrate that calcite can be used as an economic solution for defluoridation of water.

Further research is needed to improve its properties and increase the removal capacity.

References

1. World Health Organization, Guidelines for drinking water quality, 3rd Edition, WHO, Geneva, **(2004)**

2. Aoba T. and Fejerskov O., Dental fluorosis: chemistry and biology, *Crit. Rev. Oral. Biol. Med.,* **13(2),** 155-170**(2002)**

3. Teotia M., Teotia S. P. S. and Kunwar K. B., Endemic skeletal fluorosis, *Arch. Dis. Child.,* **46(249),** 686-691**(1971)**

4. Sharma J. D., Sohu D. and Jain P., Prevalence of neurological manifestations in a human population exposed to fluoride in drinking water, *Fluoride,* **42(2),** 127-132**(2009)**

5. Sehn. P., Fluoride removal with extra low energy reverse osmosis membranes: three years of large scale field experience in Finland, *Desalination,* **223(1),** 73-84**(2007)**

6. Tahaikt M., El Habbani R., Ait Haddou A., Achary I., Amor Z., Taky M., and Elmidaoui A., Fluoride removal from groundwater by nanofiltration. *Desalination*, **212(1),** 46-53**(2007)**

7. Thavamani S. S. and Rajkumar R. Removal of Cr(VI), Cu(II), Pb(II) and Ni(II) from Aqueous Solutions by Adsorption on Alumina, *Res. J. Chem. Sci* ., **3(8)**, 44-48**(2013)**

8. Al-Mamun M., Poostforush M., Mukul S.A. and Subhan M.A. Comparison studies of Adsorption Properties on Ni(II) Removal by Strong and Weak acid Cation-exchange Resins, *Res. J. Chem. Sci* ., **3(3)**, 34-41**(2013)**

9. Karthika C and Sekar M. Comparison studies of Adsorption Properties on Ni(II) Removal by Strong and Weak acid Cation-exchange Resins, *Res. J. Chem. Sci* .,**3(3),** 65-69**(2013)**

10. Tang Y., Guan X., Su T., Gao N. and Wang J., Fluoride adsorption onto activated alumina: Modeling the effects of pH and some competing ions. *Colloids. Surf A.*, **337(1),** 33-38,**(2009)**

11. George, S., Pandit, P., and Gupta, A. B., Residual aluminium in water defluoridated using activated alumina adsorption–Modeling and simulation studies, *Water Res.*, **44(10),** 3055-3064**(2010)**

12. Malay D.K, and Salim A.J., Comparative Study of Batch Adsorption of Fluoride Using Commercial and Natural Adsorbent, *Res. J. Chem. Sci* ., **1(7)**, 68-75 **(2011)**

13. Tor A., Removal of fluoride from an aqueous solution by using montmorillonite. *Desalination,* **201(1),**267–276,**(2006)**

14. Asgari G., Roshani, B., Ghanizadeh, G. The investigation of kinetic and isotherm of fluoride adsorption onto functionalize pumice stone, *J. Hazard. Mater.*, **217,**123-132**(2012)**

15. Dwivedi S., Mondal P. and Balomajumder C., Removal of Fluoride using *Citrus limetta* in batch Reactor: Kinetics and Equilibrium Studies, *Res. J. Chem. Sci* ., **4(1)**, 50-58**(2014)**

16. Kumar S., Gupta A., and Yadav J. P., Fluoride removal by mixtures of activated carbon prepared from Neem(*Azadirachta indica*) and Kikar*(Acacia arabica*) leaves. *Indian, J. Chem. Technol.*, **14(4),** 355-361**(2007)**

17. Ma W., Ya F., Wang R., and Zhao Y. Fluoride removal from drinking water by adsorption using bone char as a biosorbent, *Int. J. of Environ. Technol. and Manag.,* **9(1),** 59-69**(2008)**

18. George S., Pandit P., Gupta A.B. and Agarwal M., Modeling and Simulation studies for Aluminium-Fluoride Interactions in Nalgonda Defluoridation Process, *Chem. Prod. and Process. Model.,* **4(1),(2009)**

19. Turner B.D. Binning P., Stipp S.L.S., Fluoride removal by calcite: evidence for fluorite precipitation and surface adsorption, *Environ. Sci. Technol.,* **39(24) ,** 9561–9568, **(2005)**

20. Islam M. and Patel R.K., Evaluation of removal efficiency of fluoride from aqueous solution using quick lime, *J. Hazard. Mater.*, **143(1) ,**303–310, **(2007)**

21. Jain S. and Jayaram R.V. Removal of fluoride from contaminated drinking water using unmodified and aluminium hydroxide impregnated blue lime stone waste, *Sep. Sci. Technol.*, **44(6)** ,1436–1451, **(2009)**