

3 Utilization of Zeolite Adsorbent for Defluoridation of Drinking Water

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Abstract

The presence of Fluoride ions in drinking water in concentration more than 1.5mg/lit is injurious to health. For this reason its removal is very essential from potable water. This paper describes the use of Zeolitic adsorbent (scolecite) from Ahmednagar (Pune) area in India, for separation of fluoride ions from the water. Fluoride ions are found to be retained on the zeolite bed while many other ions migrated either partially or completely. Worldwide drinking water is greatly contaminated with fluoride ions in certain areas. This idea can be developed on large scale for the removal of fluoride from drinking water.

Keywords: Fluoride, Defluoridation, Zeolite, Drinking water, Scolecite.

Introduction

Fluoride is an essential constituent for the prevention of cavities formation in the teeth and provides strength to the skeletal system. We get fluoride usually from the natural water supplies and also from some dietary sources. According to WHO guidelines 2011 the normal concentration of fluoride for human beings is 1.5mg/lit. It has been observed that low calcium and high bicarbonate alkalinity favor high fluoride concentration in ground water (Bulusu et. al-1980., Meier et al. - 1992) Now a day due to the growing use of fluoride in industries and dental health products the concentration of fluoride in the environment is increasing .This causes increase in the concentration of fluoride in drinking water and other sources.

According to UNICEF official position (Water front 1999) on water fluoridation, fluorosis is endemic in at least 25 countries across the globe. The total number of people affected is not known, but a conservative estimate would number in the tens of millions. In 1993, 15 of India's 32 states were identified as endemic for fluorosis. In Mexico, 5 million people (about 6% of the population) are affected by fluoride in groundwater. Fluorosis is prevalent in some parts of central and western China. Worldwide instances of fluorosis due to drinking water are on the rise. Despite this serious raise in consequences of excessive fluoride in drinking water, there is a lack of full awareness on it. Great efforts are therefore required to support more research for the irradiation of this problem.

Excessive fluoride in drinking water may cause molting of teeth or dental fluorosis, which causes discoloration of enamel layer (Choubisa et.al-1996), this discoloration may be in the form of spots or horizontal streaks and chipping of teeth in children in severe cases. Bone fluorosis is noticed while concentration of fluorides exceeds 1.5 mg/lit.



Photographs showing Dental fluorosis and skeletal fluorosis



Photograph showing children affected from skeletal fluorosis M.P. (INDIA).

Beside dental and skeletal fluorosis, excessive fluoride may lead to muscle fiber degeneration, low hemoglobin levels, abnormalities in RBC's, headache, nervousness, depression, gastrointestinal problems, nausea, urinary tract disorders, tingling sensation in fingers and toes. Male sterility etc.

So, it is necessary to remove fluoride from drinking water in order to prevent dental, skeletal fluorosis and other disorders. Fluoride poisoning caused due to drinking water can be prevented or minimized by using alternate water sources, or by removing excessive fluoride from it. The process of removing fluoride from water is called defluoridation. Water supplies can be treated to remove fluoride in two ways, flocculation and adsorption.

Defluoridation of drinking water is the only practicable option to overcome the problem of excessive fluoride in drinking water, where alternate source is unavailable. Extensive research has been done on various methods for removal of fluoride from water and waste water. These methods are based on the principles of adsorption (Raichur et al.-2001), ion-exchange (Singh et.al-1999), precipitation – coagulation (Saha et.al-1993, Reardon-2000) membrane separation process (Amer et.al-2001, Dieye et.al-1998) electrolytic defluoridation (Mameri et.al-2001), electro dialysis (Hichour et.al-1999, Hichour et.al-2000) Etc.

Several adsorbent materials have been tried in the past to find out an efficient and economical defluoridating agent. Activated alumina, activated carbon, activated alumina coated silica gel, calcite, activated saw dust, activated coconut shell carbon and activated fly ash ground nut shell, coffee husk, magnesia, serpentine, tricalcium phosphate, bone charcoal, activated soil sorbent, carbon, defluoron-1, defluoron-2 etc are different adsorbents materials reported in the literature (Muthukumaran et.al-1995, Min et.al 1999, Wang et.al-2001, Navaet.al-2003, Padmavathy-2003). The most commonly used adsorbents are activated alumina and activated carbon.

Activated alumina technique for defluoridation is being propagated in several villages by the voluntary organizations funded by UNICEF or other agencies to provide safe drinking water. The fluoride removing efficiency of activated alumina gets affected by hardness and surface loading (the ratio of total fluoride concentration to activated alumina dosage). The process is pH specific so pH of the solution should be between 5.0-6.0 because at pH > 7.0 silicate and hydroxide became stronger competitor of fluoride ions for exchange sites on activated alumina and at pH < 5.0, activated alumina gets dissolved in acidic environment leading to

loss of adsorbing media (Thergaonkar et.al-1987, Bishop et.al-1978). But the process is highly selective and it has very low adsorption capability, pretreatment and acidification is required. Its effectiveness for removal of fluoride becomes less after each regeneration.

McKee and Johnston 1934 investigated the use of powdered activated carbon for fluoride removal and achieved good results. The process is dependent on pH and yields good results at pH 3.0 or less. For this reason pH adjustment is required and the use of the material becomes expensive.

The literature survey has indicated that by the use of each of the above- mentioned techniques removal of fluoride can be done only under specified conditions and the suitability of a particular process will differ from place to place. This study and the remarkable tendency of zeolites of adsorption and ion exchange inspired us to undertake the present investigation to find out some utilities of zeolites for chromatographic work and how these properties can be used for removal of fluoride from drinking water. It is worth mentioning here that scolecite (a zeolite) has been used as a sorbent for the first time in the history of defluoridation.

Experimental

Materials- The scolecite sample used for chromatographic studies was obtained from Ahemadnagar near Pune, Maharashtra India. Scolecite is a tectosilicate mineral belonging to the zeolite group; it is a hydrated calcium silicate $\text{CaAl}_2\text{Si}_3\text{O}_{10}\cdot 3\text{H}_2\text{O}$. Only minor amounts of sodium and traces of potassium substitute for calcium (Gaines et al -1997).



Photograph showing natural scolecite cluster.

Method-

TLC has been performed at room temperature (28-30°C) using scolecite as adsorbent material with samples containing various cations and anions including

fluoride ion in order to check their migratory aptitude over the sorbent. All the samples were prepared in distilled water and same was also used as a developing solvent. It took hardly 10 minutes for the development of the plate.

I Preparation of the plate- Approximately 3 gm of finely powdered scolecite (zeolite) was taken in a dry beaker and mixed with approximately 2ml of distilled water to make slurry. The mixture was stirred with the help of a glass rod until uniform slurry free from bubbles has been formed. The slurry was poured in clean and dried plates in a uniform manner. The thickness of the layer was about 1 mm. The plate was dried in air for 5-10 minutes and then activated in a hot air oven at 110°C for about an hour.

II Preparation of solutions- All the samples were prepared in distilled water containing the corresponding ion. The chromatogram was developed with distilled water as a developing solvent.

10 ml of 100 ppm solutions of individual cations and anions have been prepared in the following manner:

- a) Solution of Copper ion: 2.51 mg of copper sulphate was weighed and dissolved in 10 ml of distilled water to make a clear solution.
- b) Solution of Lead ion: 1.82 mg of Lead acetate was weighed and dissolved in 10 ml of distilled water to make a clear solution.
- c) Solution of Nickel ion: 6.72 mg of Ammonium Nickel Sulphate was weighed and dissolved in 10 ml of distilled water to make a clear solution.
- d) Solution of Magnesium ion: 4.95 mg of Magnesium Sulphate was weighed and dissolved in 10 ml of distilled water to make a clear solution.
- e) Solution of Fluoride ion: 2.21 mg of Sodium Fluoride was weighed and dissolved in 10 ml of distilled water to make a clear solution.
- f) Solution of Chloride ion: 1.64 mg of Sodium Chloride was weighed and dissolved in 10 ml of distilled water to make a clear solution.
- g) Solution of Bromide ion: 1.5 mg of Potassium Bromide was weighed and dissolved in 10 ml of distilled water to make a clear solution.
- h) Solution of Iodide ion: 4.25 mg of Potassium Iodide was weighed and dissolved in 10 ml of distilled water to make a clear solution.
- i) Solution of Sulphate ion: 1.25mg of Magnesium Sulphate was weighed and dissolved in 10 ml of distilled water to make a clear solution.

III Application of spot-

A baseline about 2cm from the bottom of plate was drawn with pencil. The spots were applied with help of capillary tube of approximate volume of 1-2 micro liters. It was then dried in air for about 15-20 minutes.

III Development of Chromatogram:

The chromatogram was developed in ascending manner by immersing the plate in a developing solvent (distilled water) to a depth of approximately 0.5cm in a 250 ml beaker. The beaker was covered with a watch glass. Development was allowed to proceed till the solvent front nearly reaches the top. The plate was removed from the chamber and allowed to dry in air and then in hot air oven for about 15-20 minutes at 70° – 80° C.

Results and Discussion

It appeared from the results that all the cations (copper, lead, nickel, magnesium) and anions (chloride, bromide, iodide, sulphate) migrated from their spotting point and their characteristic Rf values have been observed. The Rf values showed that out of the all cations and anions under experimentation only fluoride ion was retained at the spotting point and didn't show any migration on scolecite plate.

The spots were then located by different locating reagents as described below:

- a) Location of Copper: A red brown spot appeared when sprayed with potassium ferrocyanide solution.
- b) Location of Lead: A yellow spot appeared when sprayed acidified potassium chromate.
- c) Location of Nickel: A scarlet red spot appeared when sprayed with Dimethyl Glyoxime.
- d) Location of Magnesium: A scarlet spot appeared when sprayed with alkaline titan yellow.
- e) Location of Fluoride: A light yellow spot appeared when sprayed with zirconium Alizarin lake solution.
- f) Location of Chloride: A white spot appeared when sprayed with silver nitrate solution.
- g) Location of Bromide: A light yellow spot appeared when sprayed with silver nitrate solution.
- h) Location of Iodide: A pale yellow spot appeared when sprayed with silver nitrate solution.
- i) Location of Sulphate: A white spot appeared when sprayed with acidified barium chloride solution.

It is found that the fluoride ion has been retained on the scolecite plate. The reason for this retention of fluoride is the structural characteristics of scolecite. Scolecite's structure has a typical zeolite openness about it that allows large ions and molecules to reside and actually move around inside the overall framework. The structure contains open channels that allow water and large ions to travel into and out of the crystal structure. The retention depends on the size of the molecules which is controlled by the size of these channels, the scolecite acting as a chemical sieve. In the crystal structure of Scolecite there are aligned chains of silicate tetrahedrons which produces the needle-like crystals and the cleavage results from the weaker bonds between the chains.

We get inspired to use scolecite for defluoridation because of usual partition adsorption and ion exchange

properties of it and above all that it contains calcium which may interact with fluoride ions to form CaF_2 which is insoluble in water and therefore there is a possibility that it can be retained. The relative cheapness of natural zeolite deposits as compared with the cost of synthetic molecular sieves is also a positive factor as far as further development of the procedure is concerned.

Conclusion

The above results indicate that the naturally occurring scolecite is having fluoride retaining properties and can be applied for the defluoridation of drinking water. This method is innovative and materials of abundant natural occurrence are used for improving the water quality. This method also does not require any specified condition and can be applied under normal conditions. If method is further developed successfully with scolecite, it can be applied with other zeolites that are having natural occurrence. The zeolite adsorbent can be used as a column material and if required synthetic methods can be developed such as membranes (zeolite membranes) etc.

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