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Geochemical Study of Ground Water of Sanganer Area of Rajasthan (India) and Different Methods to Mitigate Fluoride Problem

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Abstract: An extensive geochemical study of 25 villages ground water was done. Analysis of groundwater samples shows a vast change in groundwater quality of Sanganer area of Jaipur district. One of the most relevant causes is the seepage of effluents of dyeing and printing industries of Sanganer area or due to other relevant causes. The potability of ground water is going to be deteriorated. There is a severe fluoride problem too. 75% of the villagers are suffering from dental fluorosis and skeletal fluorosis. The fluoride concentration is ranging between 1.5 ppm and 16.5 ppm.The problem of fluoride is so severe that younger generation is going to be impotent. Nalgonda technique and FUC technique have been used for mitigation of fluoride and fluoride concentration has been reduced from 16 ppm to 2 ppm by using this technique. But its removal is very time consuming and use of alumina is not good for health. NF membrane technology can remove over 95% fluoride from ground water in a single operation. NF membranes were not affected by source water composition. Therefore it is suggested that NF membranes could be used in any type of water.

Key words: Ground water, seepage, dental fluorosis, FUC technique, Nalgonda technique, activated alumina, NF45 nanofiltration membrane.

Introduction

The problem of high fluoride concentration in ground water resource has become an important health related geoenvironmental issue in some areas. India is among the 23 nations around the globe where health problems are occurring due to consumption of fluoride contaminated ground water. Rajasthan with a surface area of 342,000 sq. km is the largest state in India, contributing 10.41% of the area and 5.5% of the national population but has only 1% of the country's water resources. Jaipur has been quoted as one of the examples of the ancient town planning; however, it has fallen victim of multifold urbanization.

Jaipur has also been identified as one of the fastest growing urban centres in the third world. Over-exploitation of groundwater resources to meet the growing domestic, industrial and agricultural demand has led to severe crisis manifested in terms of depletion in availability and quality deterioration. Although the water resources related problems in Jaipur district are many, the present paper focuses on the fluoride distribution in the area and defluoridation methods. Although fluoride can be removed by various type of processes such as absorption processes (using activated alumina, etc.) and membrane processes (nano filtration and reverse osmosis), coagulation still play an important role in the removal of fluoride. However, little information has been known concerning the effectiveness of DOWS, USA. NF45 membrane will be very fruitful in removal of fluoride. Nalgonda technique has its good and ill effect.

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Experiment

Samples were collected from the wells the inhabitant of the Sanganer tehsil are using. The samples were collected according to the specification of APHA. The samples sites have been shown in graph (Bar Diagram) (Figure 1). The samples were analysed by methods described in APHA.

Result and Discussion

The fluoride concentration of different villages has been shown in the graph. Villagers have been told regarding the fluoride problem. They said that every one is suffering from either dental fluorosis, skeletal or gut fluorosis. The problem is so severe that younger generation is going to be impotent.

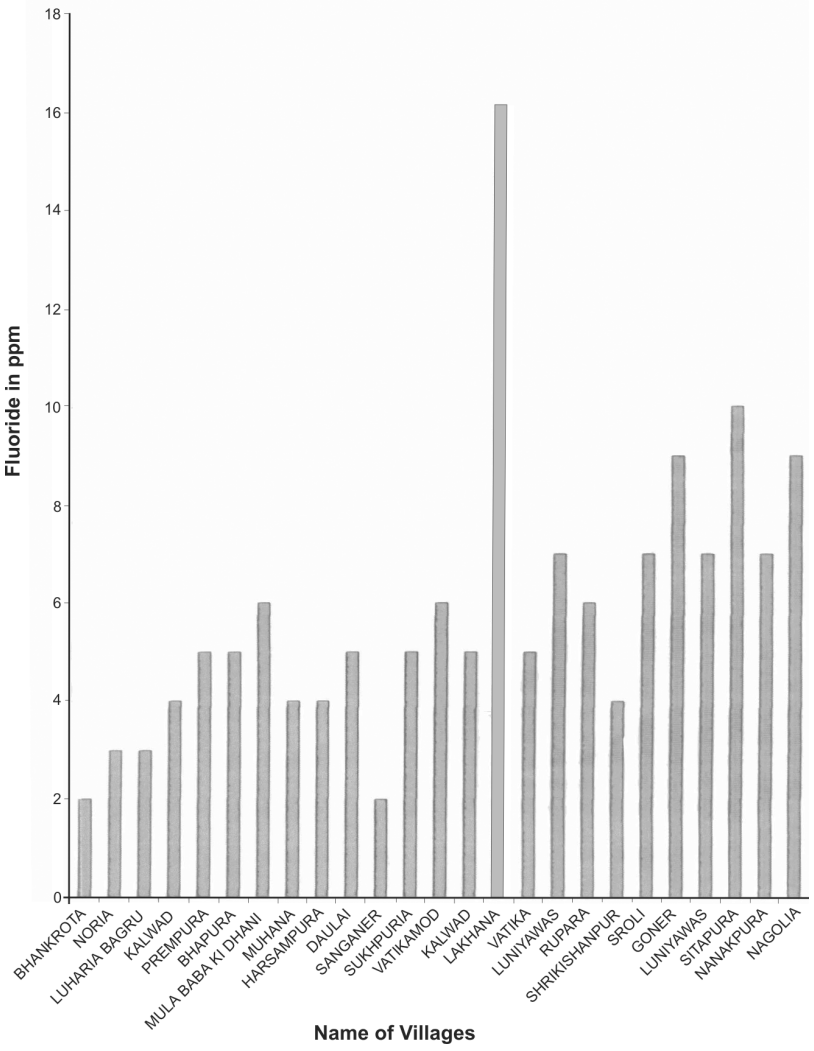

Figure 1: Maximum fluoride prone area of Sanganer tehsil of Jaipur.

Causes of Fluoride: Due to Lithology

This may be due to a specific fluoride mineral such as mica (thin shining flakes and amphiboles-elongated thin minerals common in many hard rocks). Most of the wells showing high values are located in hard rocks region. Fluorite mineral when reacts with water it dissociate to

$$CaF_2 \rightarrow Ca^{++} + 2F^-$$

releasing F^- ion in H_2O. Geological Survey of India has studied the lithology of the area and found the presence of fluorite mineral in the tehsil.

The interaction of fluoride and phosphorous in water and biotic system is striking through reaction such as

$$Ca_{10}\,(PO_4)_6\,(OH)_2 + 2F^- \rightarrow Ca_{10}\,(PO_4)_{\mathbf{6}}\,F_2$$

indicating to the incorporation of some amount of fluoride in bones along with phosphorus. Since it gives an excellent fit, in nature also a reaction similar to bone fixation is followed. When water with excess fluoride is used, it starts replacing the phosphorus in bones leading to weakening of the bones and fluorosis occur. Since most phosphate minerals such as appetite contains some amount of fluoride as per the above reaction, use of phosphate fertilizers lead to accumulation of excess of fluoride in soils that may eventually get into the ground water as well as soil run off to surface waters. This eventually ends up in the food chain through agricultural activities where the suitability of fluoride rich waters may be restricted. Removal of excess of fluoride is done by the general reaction

$$Al\,(OH)_3 + 3F^- \rightarrow Al\,F_3 + 3OH^-$$

Since aluminum and fluoride has great affinity.

Due to Pollution

As the printing and dyeing industries of Sanganer tehsil of Jaipur district is of world fame, one of the important reason for increasing fluoride concentration may be the use of artificial dyes instead of natural colours. The 500 small scale dyeing and printing units discharge their effluents in the Amanishah nala and the ground water of the Sanganer tehsil gets contaminated or polluted due to seepage from the polluted water. Farmers of the area are using polluted water for irrigation purpose since long.

Methods of Fluoride Removal (FUC = Fluoride up-take method)

It is probably a kind of ion exchange process in which hydroxyl ions are substituted by fluoride ions.

$$Al(OH)_3 + 3F^- \rightarrow AlF_3 + 3OH^-$$

The effect of hydroxyl ion concentration or the pH on the exchange process becomes clear from the above equilibrium equation. When the hydroxyl ion concentration is increased, the equilibrium reaction moves towards the left and fluoride ions are mobilized. From the above mechanism two points emerges:

(i) pH of activated alumina as supplied should not exceed 8.0 (10% w/w suspended in water)

(ii) Defluoridation capacity of activated alumina decreases with increasing pH or total alkalinity of the influent water. This also explains the different defluoridation capacity observed with water at different places in the country.

Methods of Testing FUC

(a) Washing of Activated Alumina

One kg of AA, taken in the nylon bag (300 mesh), was dipped in a plastic bucket containing 10L of raw water. AA in the bag was manually agitated. This procedure was repeated thrice with fresh raw water. Activated alumina was then transferred to a PVC column for determining FUC. Heat is liberated when activated alumina comes in contact with water. This may lead to disintegration of activated alumina particles.

Further AA samples can also have very fine particles. This may lead to very high Aluminium in treated water in the first defluoridation cycle. Washing procedure, described above is to minimize aluminum level in treated water.

(b) Experimental Setup

(i) One kg of AA was taken in a PVC column having following specification:
Height = 60 cm, I.D = 6.00 cm
Raw water characteristics: Natural ground water spiked with 10 mg/L as $CaCO_3$ Sulphate = 55 mg/L

(ii) FUC determination: 10 L of raw water was taken in a 12 L plastic bucket with a flow control device. Raw water was passed through the column containing 1 kg of AA at a flow rate of 40 mL/min. The flow rate gave an approximate empty bed retention time of 25 min. About 30 L of raw water was passed through the column during the day. Minimum of two-hour rest period was given between each run (i.e. after passing 10 L raw water). This is to stimulate the field conditions, as domestic defluoridation unit is expected to be used under similar conditions. Treated water samples were collected after every 20 L for the analysis of fluoride.

(iii) Fluoride and Aluminium Analysis: Fluoride concentration in raw water as well as treated water was analysed by using Orion fluoride specific electrode with Orion meter.

(iv) Aluminum was determined by colorimeter using ferrochrome cyanide R as per the procedure described in standard methods. Column was operated till the treated water fluoride level was 1.5 ppm. Volume of the raw water passeing through the column up to this point was noticed. Average concentration of the fluoride in treated water up to this volume was taken, as 0.75-mg/L. volume as initially treated water fluoride concentration will be low.

$$\text{Calculation of FUC} = \frac{(FCI - FCT) \times V}{W},$$

where FCI = fluoride concentration in inlet (Raw water), FCT = fluoride concentration in treated water, V = Volume of water passed through the column up to the fluoride concentration of 1.5 mg/L and W = Wt of activated Alumina, therefore

$$\text{FUC} = \frac{(10.5 - 0.75) \times 280 \text{ L}}{1 \text{ kg}} = 2730 \text{ mg/kg AA.}$$

Aluminum: With the washing procedure described above, aluminium concentration was below 0.1 mg/L throughout the defluoridation cycle.

Hence activated alumina is so far the best option for defluoridation of drinking water.

In our samples the fluoride concentration is reduced from 8.0 to 1.5 ppm with the help of FUC method.

Activated Alumina Uptake Method

Activated alumina effectively removes fluoride from drinking water. Alumina can be prepared in granular form for column operations. Removal of fluoride is not affected by the presence of the other anions in the ground water.

Table 1: Effect of concentration of fluoride on its uptake by alumina (static experiment)

Strength of fluoride solution (ppm)	*Uptake of fluoride by 1 gm. of alumina (mg)*
4	0.2
10	0.6
20	1.0
40	1.6
60	3.0
80	3.5
100	6.0

Solution added 100 ml
Activated alumina used 1 gram in each flask

Ground water containing 10 ppm of fluoride was passed through a column containing 20 gram of alumina. Out of 65 mg of fluoride 59.30 mgF was taken up by the alumina. This corresponds to an uptake of 2.96 mgF/ gram of alumina. The presence of other anions have not diminished the absorption capacity of alumina; on the other hand the value is higher. This may be due to the increased height of the bed. Thus alumina seems to be an effected fluoride-absorbing agent. Activated alumina effectively removes fluoride from ground water. Alumina can be prepared in granular form suitable for column operations. Removal of fluoride is not affected by the presence of other ions.

The Nalgonda Technique

In the Nalgonda Technique two chemicals, alum (aluminium sulphate) and lime are added to and rapidly mixed with the fluoride contaminated water. Induced by subsequent gentle stirring, "cotton wool"-like flocks develop (aluminum hydroxide) and are subjected to removal by the simple setting. The main contents of the fluoride are removed along with the flocks, probably due to combination of sorption and ion exchange with some of the produced hydroxide groups. It is simply a co-precipation. In present experiment fluoride concentration has reduced from 16 to 2.0 ppm in three operations.

Removal of Fluoride through Nano Filtration Membrane

There is a possibility of treating highly fluorinated ground water using a polyamide nanofiltration membrane. My personal view is based on the phenomenological model of Spiegler, Kedem and Katchalsky under a dilute solution condition but neglecting the charge carried by membrane used (denoted NF45 from Dow, USA). Selective defluoridation can be attained using NF membrane. It will be based on predominantly solution mass transfer.

As expected, the permeability is lower for fluorine and higher for iodine and the NF 45 membrane. Other halide ions preferentially retains chlorine showing one more time that fluorine. According to Pontalier et al., hydration can be considered as a force—the force necessary to extract the solute from the solvent to push it into the pores. In this way it requires more energy to extract F^- and to push it into the pores in comparison with Cl^-, although this hypothesis is very difficult to confirm. The use of NF deals the possibilities of treating highly fluorinated ground water using NF. The approach is based on the phenomenological model of Spiegler, Keedem and Katchalsky under dilute solution conditions and neglecting the charge carried by the membrane used (NF45 from DOW, USA).

The possibility of defluoridation totally depends upon the phenomenological parameters: the membrane reflection coefficient and Ps (the solute permeability). The phenomenological parameter can be linked to the hydration energy of halide ions. The solute permeability appeared to be linked to a kind of electrolyte.

Conclusions

Extensive geochemical study of 25 villages shows that there is an acute fluoride problem in Jaipur district. Though defluoridation methods used are of immense importance, further work has to be done on NF45 membrane, so that usual activated alumina method and Nalgonda technique could be changed for defluoridation in the area concerned or internationally NF 45 nano-filtration membrane can be used and excessive use of aluminium which is dangerous to human consumption can be controlled.

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