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AN INNOVATIVE TECHNIQUE FOR REMOVAL OF FLUORIDE FROM DRINKING WATER

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ABSTRACT

High concentrations of fluoride in drinking water had caused widespread fluorosis. A simple, precise, rapid and reliable technique has been developed for removal of fluoride in drinking water. The innovative technique employs activated alumina for defluoridation of drinking water. Alumina is inert in nature, hence it is safe to use and handle. The innovation in regeneration of alumina makes the technique cost effective. The reliability of the newly developed technique has been established by analyzing spiked water samples of high concentrations of fluoride (upto 50 ppm) and levels of fluoride has been brought down to less than 1 ppm. The method is superior to currently employed techniques and is recommended to the laboratories where a huge volume of water is to be defluoridated.

Key words: Fluoride, Fluorosis, Water pollution, Activated alumina, Regenerative technique.

INTORDUCTION

High fluoride levels in drinking water has become a critical health hazard of this century as it induces intense impact on human health including skeletal and dental fluorosis. Fluoride in minute quantity is an essential component of normal mineralisation of bones and formation of dental enamel[1]. However, its excessive intake may result in slow, progressive crippling scourge known as fluorosis. The world health organisation (WHO) had recommended values of fluoride in drinking water: 0.1 to 0.5 ppm[2]. There is a minor aberration from this standard as U.S. standard recommends that the fluoride content in drinking water should be between 0.6 and 0.9 ppm. The bureau of Indian standard which is the main regulatory agency for drinking water in India specify that the maximum desirable limit of fluoride in drinking water is 0.5 ppm but in absence of alternatives, the maximum permissible limit is 1.5 ppm[3].

The flurosis is caused by oral intake of fluoride when drinking water contains more than the permitted concentration of fluoride. Fluorosis may be life threatening in particular fluoride affected area if proper defluoridation techniques are not employed to curtail the levels of fluoride in drinking water. In India, endemic fluorosis effects more than one million population and is a major problem in 17 of the 25 states. The most affected states in India are Rajasthan, Andhra Pradesh, Orissa, Gujarat, Madhya Pradesh and Chhattisgarh states[4]. Similar health problems due to high fluoride content in ground water have also been reported worldwide and it is estimated that around 260 million people are adversely affected in 30 countries

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of the world especially from China, Sri Lanka, Spain, Holland, Italy, Maxico and North and South American Countries[5].

Health impacts of fluoride

Fluoride being a highly electronegative element has extraordinary tendency to get attracted by positively charged ions like calcium. Hence, the effect of fluoride on mineralized tissues like bone and teeth leading to developmental alternations is of clinical significance as they have highest amount of calcium, hence they attract the maximum amount of fluoride that gets deposited as calcium-fluoroapatite crystals. About 95% of fluoride in the body is deposited in hard tissues and it continues to be deposited in calcified structure even after other bone constituents (Ca, P, Mg, carbonates and citrate) have reached the steady state. Due to such deposition, bones deformation causes irreversible damages.

The other problems associated with health impact of fluoride are generally overlooked because of the notion prevailing that fluoride only affects bones and teeth. Other problems arise due to the excessive intake of fluoride are fibre degeneration, low haemoglobin levels, deformaties in RBCS, excessive thirst, headache, skin rashes, nervousness, neurological manifestation, depression, gastro intestinal problems, urinary tract malfunctioning, nausea, tingling sensation in fingers and toes, repeated abortions, male sterility etc. It is also responsible for destruction of about 60 enzymes.

Factors affecting fluorosis

The severity of fluorosis is influenced by concentration of fluoride in water and period of its usage. Nutritional status and physical strain also play vital role in deciding total effects of fluoride pollution. A diet poor in calcium, for example, increases the body's retention capacity of fluoride[6]. Environmental factors include annual mean temperature, humidity, rainfall, tropical climate, duration of exposure etc. Besides, other factors such as pH in terms of alkalinity, age, calcium in diet, fresh fruits and vitamin-C reduces fluoride toxicity. Whereas, trace elements like molybdenum enhances the fluoride toxicity. Defluoridation of drinking water is the only pragmatic approach to solve the fluoride pollution problem as the use of alternate water sources and improvement of nutritional status of population at risk have their own limitations and are expensive affairs[7]. Generally, methods reported in literature are based on adsorption, ion exchange, precipitation and miscellaneous. All these methods, their principle of operation, advantages, disadvantages, limitations and applications have been critically reviewed[8,9]. Adsorption techniques are advantageous for defluoridation as the processes are capable of removing fluoride up to 90% and are cost effective[10-12]. However, these processes are highly dependent on pH and efficient at narrow pH range (pH between 5 and 6). High concentration of total dissolved solids (TDS) may pose fouling problems and also presence of sulfate, phosphate and carbonate results in ionic competition impairing the efficiency of the fluoride removal system. Ion exchange resins technology is advantageous as it retains the taste and colour of the treated water intact and is capable of removing 90 – 95% of fluoride[13]. Regeneration of resins generally pose problem as it leads to fluoride rich waste, which necessitates separate treatment before final disposal. The Nalgonda technique, which is a well established process and has been adopted in India and Tanzania[14,15]. The method comprises of addition, in sequence, of sodium aluminate or lime, bleaching powder and alum to the water samples, followed by flocculation, sedimentation and filtration. The technique can be used both for domestic as well as for community water supplies[7]. However, the process is not automatic. It requires a regular attendant for addition of chemicals and look after the treatment process. Requirement of large space for drying of sludge and maintenance cost are the other notable limitations. Bone, bone char and synthetic bone materials have shown good efficiency for curtailment of fluoride in water samples[16,17]. However, high cost, non-acceptability on moral and ethical grounds are the notable limitations.

In the present communication an innovative technique has been presented for defluoridation of drinking water employing activated alumina. Activated alumina is an aluminium oxide, which is highly porous and exhibits high surface area. It is worthwhile to mention here the crystal structure of alumina contains cation lattice in discontinuities giving rise to localized areas of positive charge. This property of alumina has been exploited in the development of present technique. Also, alumina has a high preference for fluoride compared to other anionic species because of high electronegativity of fluoride. Thus, alumina becomes an attractive adsorbent for curtailment of fluoride. Besides, alumina does not shrink, swell or soften nor disintegrate when immersed in water. These unique properities of alumina has given an impetus to develop an innovative technique for removal of fluoride in drinking water. Also, in the present work regeneration of alumina was carried out and thus the newly developed technique had become economical. The absence of corrosive and toxic fluids resulting in longer component life, higher overall efficiency and greater reliability are other notable advantages. Besides, the inert nature of alumina makes it suitable for safe and easy handling. Regenerative innovation had made the technique cost effective and therefore, recommended to the laboratories where defluoridation of drinking water is carried out.

EXPERIMENTAL

Material and methods

Activated alumina (I.P.C.L. CATAD Division, Thane) was utilized and the physicochemical properties of activated alumina are described in Table 1. Although, the granular alumina has advantage of being available in smaller sizes, making the internal active surface of alumina more rapidly available for containment of fluoride but to avoid pressure drop problem in a packed bed, spherical beads of activated alumina were preferred in the present studies.

Table 1: Physicochemical properities of activated alumina

S. No.	Characteristics	Value
1	Particle forms	Spheres
2	Particle size (mm)	2.5
3	Water adsorption capacity (% w/w)	21
4	Surface area (m^2/g)	232
5	Pore volume (cm^3/g)	0.42
6	Bulk density (g/cm^3)	0.80
7	Bed crushing strength (% w/w, min.)	92
8	Loss on attrition (max.)	0.20
9	Loss on ignition (250 – 1000^{o}C, %)	6.0

Pretreatment of activated alumina

A pretreatment of activated alumina was carried out by dipping activated alumina in 2.9% $Al_2(SO_4)_3.18H_2O$ for a period of one hour.

Column: A glass column of was employed for conducting the column studies. For uniform distribution of liquid glass bead were placed above the adsorbent.

Stock solution of fluoride

Stock solution of fluoride was prepared by dissolving 2.21 g (AR grade) sodium fluoride in 1000 mL of distilled water. The solution was further diluted appropriately for preparing standards of fluoride.

Ion selective electrode

Fluoride ion selective electrode of EUTECH Model No. 2100 alongwith pH meter was utilized for monitoring of levels of fluoride. The instrument was calibrated routinely by standard solution of fluoride.

Recommended procedure

Activated alumina (procurred from IPCL, CATAD Division, Rabale, Thane) was employed in the present studies. A stock fluoride solution of 50 mg F L^{-1} was prepared. A test fluoride solution of 10 mg F L^{-1} was prepared by appropriate dilution of stock solution. Batch sorption test were conducted to investigate the effect of controlling parameters. Activated alumina was packed in a glass column (ID 35 mm, bed length 320 mm) and water samples (spiked by adding standard solutions of fluoride) were passed through column maintaining constant flow rate. Effluent samples were collected at different time intervals and analysed for residual fluoride content by employing fluoride ion selective electrode. Normal precautions for trace analysis were taken through out.

RESULTS AND DISCUSSION

Effect of contact time on defluoridation

For sorption studies, contact time is one of the most important parameters as it decides the efficiency of the system. The studies on the contact time revealed as the contact time increases, % removal increases rapidly, but gradually approaches to constant value exhibiting the attainment of equilibrium. The sorption reaction depicted in Fig. 1 indicates that it follows a pattern of the three phases. First phase is the rapid phase where the rate of removal is very rapid and this had occurred in initial 20 minutes. This may perhaps due to instantaneous sorption reaction in which fluoride ions were adsorped rapidly on to the surface of the activated alumina due to specific chemical interaction (or affinity) and due to diffusive and other driving forces. In the second phase, the rate of sorptive uptake decreased due to lesser sorption as a result of migration of fluoride ions from the film/boundary layer to interior pore/capillary surfaces. In the third phase i.e. after 80 minutes, the rate of removal levels off significantly, this had denoted attainment of equilibrium and this may perhaps due to non-availability of sorption sites. As there was no significant increase in % removal of fluoride after 80 minutes. An equilibrium time of 80 minutes was taken and this was employed in all subsequent experiments.

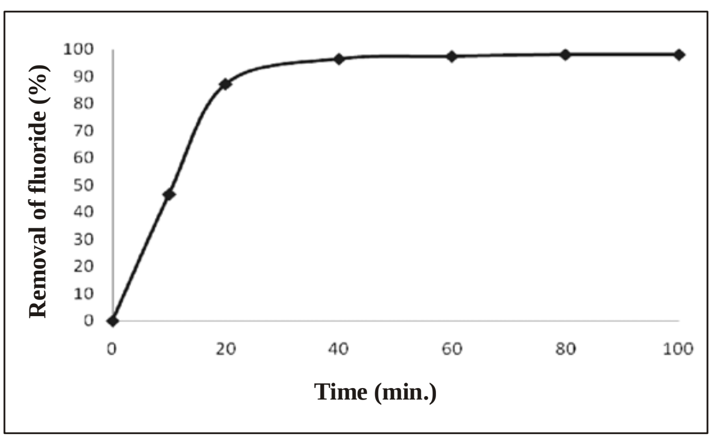

Fig. 1: Effect of contact time

Effect of pH on defluoridation

The influence of pH on removal of fluoride was conducted employing test solution adjusted the pH ranging between 2 and 10.5 (Fig. 2). The results obtained clearly indicates that as the pH of the test fluoride solution is increased from 3 to 7, removal of fluoride remains almost constant at around 90 to 95% but drastically reduce to 70% at pH 9. This drastic reduction in removal with increasing pH is the characteristics of anions sorption with a distinctive sorption edge. The pH sorption edge is narrow pH region often about 2 pH unit wide in which sorption behavior changes dramatically. In the present studies, the decrease in sorption rate was observed by increasing pH above 7.5 indicating pH-sorption edges characteristics of anionic sorption i.e., nearly complete removal at low pH to no removal at higher pH value. This indicates the formation of ligand like complexes whose tendency to sorb decreases with increasing pH[18]. Higher removal at lower pH values may be attributed due to surface reactions of the type ion exchange, and/or hydrolysis occurring simultaneously leading to the change in the electrokinetic properties of the surface of activated alumina resulting in reduction of the negative charges at the surface of activated alumina, which in result enhances the sorption of negatively charged fluoride ion[19].

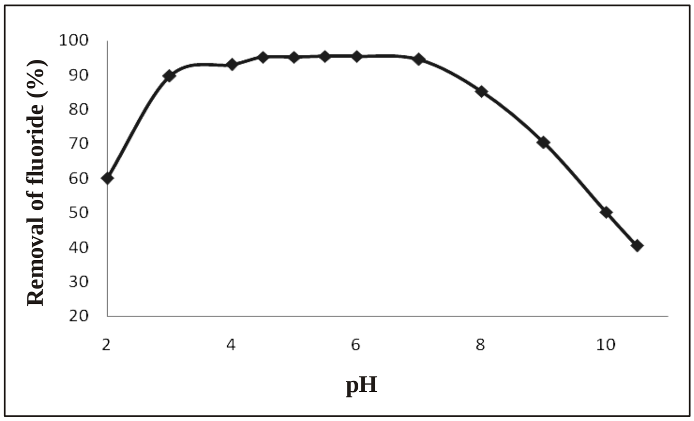

Fig. 2: Effect of pH

Effect of dose of activated alumina

The effect of dose of activated alumina was studied and results are presented in Fig. 3. The results indicates that fluoride uptake increased as the dose of activated alumina is increased from 2.5 g L^{-1} to 20 g L^{-1}. The reason for this is obvious at the higher dose of adsorbant, more sorbent surface will be available for sorption reaction and this results in higher removal. It may also be observed that initially the removal of fluoride increases as the dose is increased, but beyond certain dose range, there is no significant increase in removal. This may be due to exhaustion i.e., non – availability of fluoride ions or even due to non sorbability of fluoride ions as a result of sorbent-sorbate interaction.

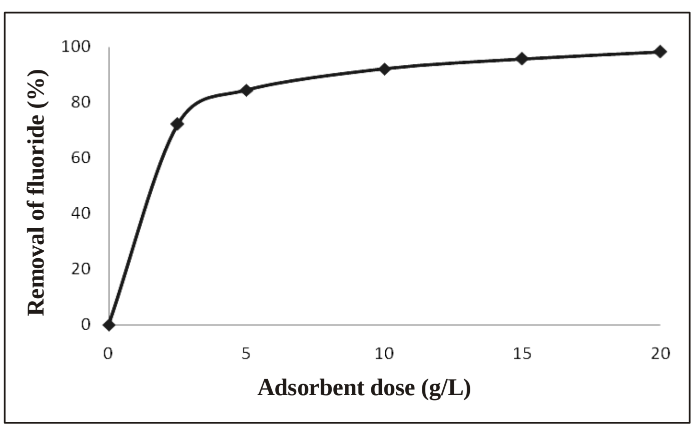

Fig. 3: Effect of dose of activated alumina

Interference effect

The effect of diverse ions on the containment of fluoride were conducted. The results are shown in the Table 2. The studies revealed that there was no significant effect of cations on the recovery of fluoride except nickel had marginal effect on the recovery of fluoride although it was well within the stipulated value of fluoride in drinking water.

Table 2: Effect of diverse ions

Ion	Added as	Final fluoride level (ppm)
F^-	NaF	0.66
Fe^{3+}	$Fe(NO_3)_3 . 6H_2O$	0.68
Ni^{2+}	$Ni(NO_3)_2 . 6H_2O$	0.88
Cd^{2+}	$Cd(NO_3)_2 . 6H_2O$	0.64
Pb^{2+}	$PbCl_2$	0.62
Ba^{2+}	$Ba(NO_3)_2$	0.67
Zn^{2+}	$Zn(NO_3)_2 . 6H_2O$	0.65
Mg^{2+}	$Mg(NO_3)_2 . 6H_2O$	0.60
Mn^{2+}	$Mn(NO_3)_2 . 6H_2O$	0.56
Cr^{3+}	$Cr(NO_3)_3 . 9H_2O$	0.77

Blank: 10 ppm fluoride at inlet, Diverse ions added: 100 ppm
Volume of sample: 1000 mL, pH: 7.0 ± 0.1

Regeneration of exhausted activated alumina

Regeneration of exhausted activated alumina is a notable advantage of this innovation. The regeneration makes the technology very economical. Extensive studies were carried out using different regenerates, namely, alum, hydrochloride and sulphuric acids and sodium hydroxide. The results clearly revealed that an excellent efficiency could be achieved by combining 1% sodium hydroxide with 0.5 N sulphuric acid. A simple dip regeneration appears to be appropriate as it is convenient for laboratory as well as field purposes. The procedure adopted for this purpose was simply transfer the exhausted sorbent into a nylon bag, dip the bag in 10 L, 1% sodium hydroxide for 8 to 10 hours (or overnight) with intermittent stirring. The sorbent was subsequently washed with water to remove excess alkali. Subsequently, the sorbent bag was dipped into 10 L of 0.5 N sulphuric acid for 8 to 10 hours. This was followed by washing with normal water till the pH ~ 6 was achieved. Thus regenerated activated alumina was ready for the next cycle of operation. It has been observed that thus regenerated activated alumina showed less than 20% loss during 10 defluoridation cycles. Thus, the novelty of regeneration was successfully proved.

Disposal of spent regenerants

The disposal of the spent regenerants is one of the most important factors, otherwise, the fluoride removed will again reenterd in the water system. The regeneration process of activated alumina generates spent alkali, acid and high fluoride contents. Methods employed for spent regenerants disposal can be classified into following three categories.

- The addition of excess of calcium chloride to spent alkali regenerant to precipitated fluoride and then mix the supernatant with acid regenerant.
- Simple mixing of spent alkali/acid regenerants.
- Mixing alkali/acid regenerants and using additives like alum or lime to remove fluoride as well as to improve settling properties of the sludge.

The third category gave promising results and more than 85% fluoride could be removed. The sludge was collected periodically and used for making the bricks for construction purpose.

CONCLUSION

Activated alumina after pretreatment with aluminium sulphate has given promising results for removal of fluoride from drinking water. An adsorption capacity of regenerated activated alumina was found to be 4.06 g/Kg at pH 7. It has been observed that the adsorption capacity of activated alumina is strongly dependant on the flow rate, inlet fluoride ion concentration and bed length and the fluoride removal is greater under condition of high contact time and lower concentration of fluoride. The regeneration of activated alumina bed was investigated and results revealed excellent performance of regenerated activated alumina for removal of fluoride in drinking water. This innovation of regeneration makes the system economical on one hand and also avoid the logistic requirement of changing the adsorbent after every cycle of saturation on the other hand. Hence, activated alumina sorbent clearly seems to be viable option for defluoridation methods due to its significant specific sorption.

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