Removal of Fluoride Ion from Aqueous Solution

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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.*

I. 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 mineralization 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 organization (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 fluorosis 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 of the world especially from China, Sri Lanka, Spain, Holland, Italy, Maxico and North and South American Countries5.

II. HEALTH AFFECTS

Fluoride in drinking water is beneficial at low concentrations, but presents health concerns at higher concentrations [19]. There are many sources of fluoride in the diet. Dentists apply fluoride to teeth; some municipal water systems add fluoride to the water supply; and some toothpastes have fluoride as an additive; and some foods also have elevated fluoride such as fish and tea. The Centers for Disease Control (CDC) have recommended 1.0 to 1.2 milligrams per liter (mg/L) as the optimum beneficial concentration of fluoride in drinking water for dental protection in state of New Hampshire. At higher concentration however, there are health concerns. The US EPA has developed standards that limit the presence of fluoride in public drinking water supplies. These health standards are called maximum contaminant levels (MCLs). In addition, there are non-health related standards (that relate to aesthetics) called secondary maximum contaminant levels (SMCLs) which pertain to fluoride. These important ranges of fluoride in drinking water are explained below.

2.1 Fluoride concentration of approximately 1.1 mg/L

Fluoride has been shown to reduce tooth decay in children if they receive an adequate level. The optimal concentration, as recommended by CDC for New Hampshire, is approximately 1.1 mg/L. (1.1 mg/L is the same as saying 1.1 parts per million parts (ppm)). Below 0.5 mg/L there is little tooth decay protection. Above 1.5 mg/L, there is little additional tooth decay benefit.

2.3 Fluoride concentration over 2.0 mg/L

In the range of 2.0-4.0 mg/L of fluoride, staining of tooth enamel is possible. EPA categorizes staining as an aesthetic concern, and thus only requires that customers of public water systems be notified of the elevated fluoride level. EPA does not require fluoride removal when the concentration exceeds 2.0 mg/L but is less than 4.0 mg/L. Approximately 5% of New Hampshire bedrock wells have fluoride that exceeds 2.0 mg/L.

2.4 Fluoride concentration over 4.0 mg/L

At concentrations above 4.0 mg/L, studies have shown the possibility of skeletal fluorosis as well as the staining of teeth. In its most severe form, skeletal fluorosis is characterized by irregular bone deposits that may cause arthritis and crippling when occurring at joints. EPA recognizes skeletal fluorosis as a health concern, and thus requires that public water systems not only **notify** their customers, but also **treat** the water to lower the fluoride concentration. Less than 1% of New Hampshire bedrock wells have fluoride that exceeds 4.0 mg/L of fluoride. Specific health questions concerning fluoride's effects should be directed to a physician or dentist. For general health information concerning fluoride, please call the Environmental Health Risk Assessment Bureau of the New Hampshire Division of Public Health Services at 271- 4608.

III. 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 fluoride6. 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 fluoride13. 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 Tanzania1 [4, 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 costs, non-acceptability on moral and ethical grounds are the notable limitations.

IV. METHODS TO REDUCE FLUORIDE IN YOUR WATER SUPPLY

Commonly used domestic defluoridation processes various defluoridation methods are used for removal of fluoride from drinking water. These exiting methods for defluoridation of drinking water is expensive, slow, in efficient, unhygienic and highly technical.

[1] Nalgonda technique (Flocculation and Sedimentation)
[2] Activated alumina process (Adsorption)
[3] KRASS Process
[4] Other processes (Bio-remedial, Ion exchange, R.O. etc.)

4.1 New defluoridation method by- green chemical approach

A comparative study of degree of toxicity of NaF, NaSiF6, CaF2, CaSiF6, MgF2, ZnF2, AlF3 and CuF2 showed that calcium and aluminum fluoride are less toxic than other fluoride3. Therefore, in present paper authors used aluminum oxalate as defluoridation agents in soil pots and developed a new defluoridation method. The following investigations were conducted to find out the fluoride minimizing capacity of aluminum oxalate in the water samples kept in the soil pots.

4.2 Determination of different physical and chemical parameters of water samples

The pH, TDS and Al ion concentration were determined by the standard procedures. Result of these parameters shows that the values of all parameters in water samples are in their desirable limits.

4.3 Preparation of soil pots

Four soil pots (A, B, C and D) were prepared after incorporation of aluminum oxalate (2 g., 4 g., 6 g and 8 g.) in 500 g. of soil respectively as shown in flow chart given below2,5-7.

4.4 Determination of fluoride concentration

Fluoride concentration of untreated sample and the treated fluoride water samples was determined as per the standard procedure by ion selective method by Orion 720+ after time interval of 3, 24, 48 and 72 hours. Results are given in Fig. 1.

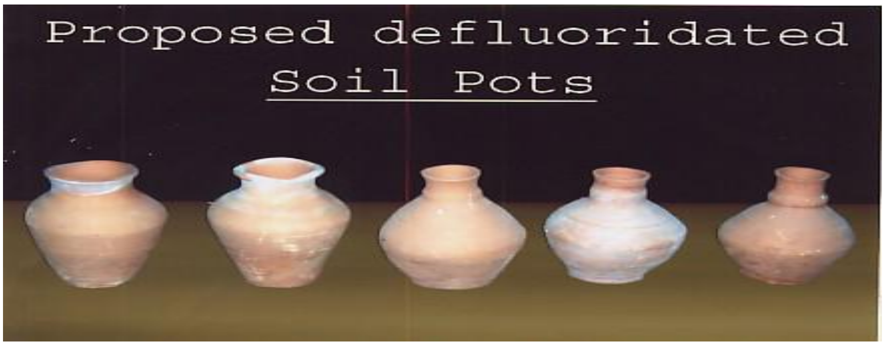


Fig. 1: Proposed soil pots

Investigation pertaining to the effect of increasing of aluminum oxalate in the soil pot on the fluoride concentration in Fig. 2 shows that the fluoride concentration of water sample (10 mg/L fluoride) decreases in the all soil pots with increasing amounts of aluminum oxalate at contact time periods. It is noticed that soil pot No-1 (having 2 g C6Al2O12), decreases the fluoride concentration of the water sample about 20% but in case of soil pot No. 3 (having 6 g C6Al2O12), the concentration of fluoride decreases about 70% at time interval 72 hours. This can be explained on the basis of surface chemistry. It is a general phenomena of surface chemistry that more the surface area of adsorbent more the adsorbate are adsorbed on the surface of adsorbent to form a unimolecular layer (Langmuir isotherm limitation) of adsorbent during chemsorption process. Result shows that a certain amount of aluminum oxalate reduces the fluoride concentration in the water sample.

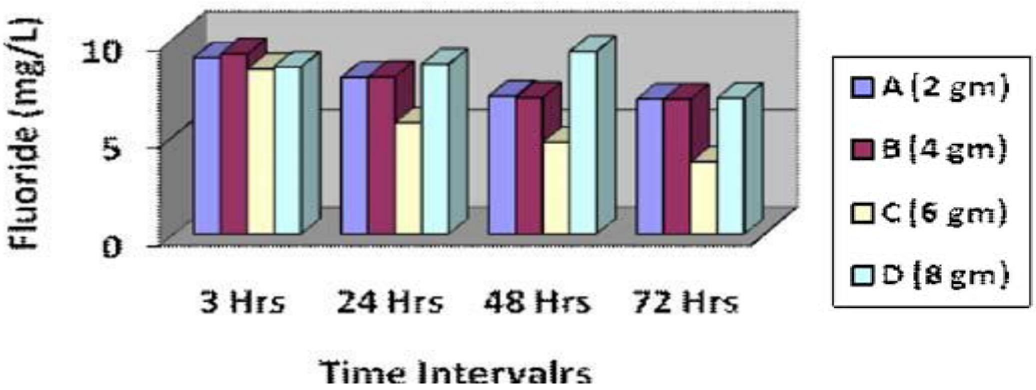
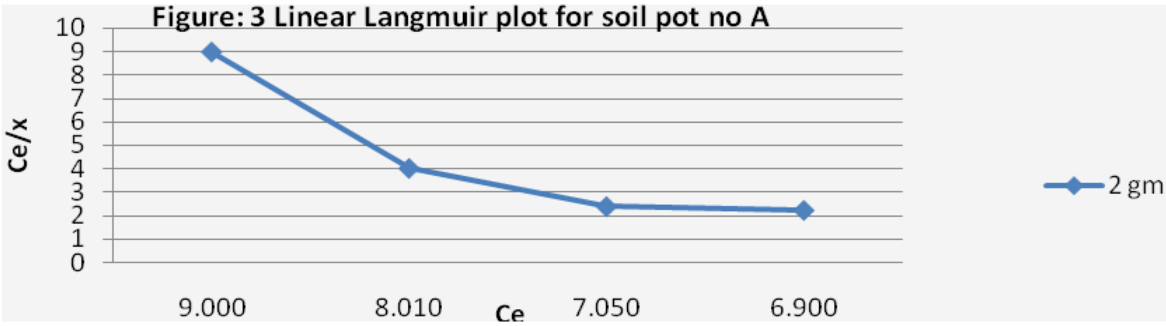
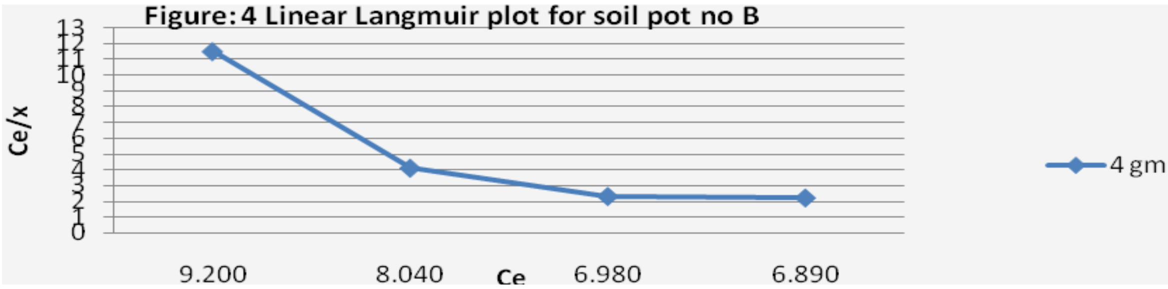
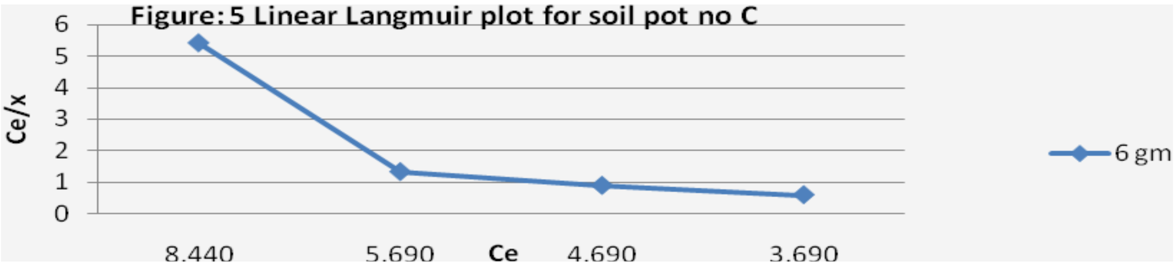


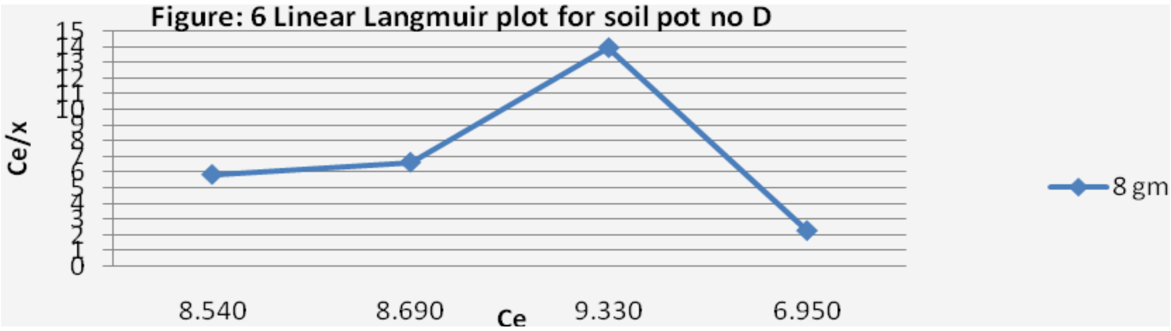
Fig. 2: Concentration of fluoride ions in different soil pots

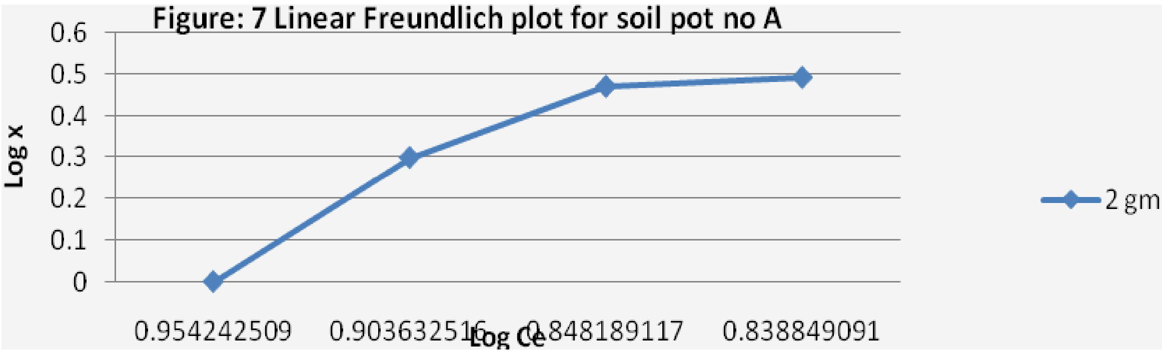
The removal of fluoride from water sample (10 mg/L) is expected due to the formation of polyhydroxide aluminum complex (e.g. [Al(H2O)3(OH)3] [Al(H2O)2(OH)4] etc.) with fluoride and adsorption of fluoride on polymeric aluminum oxalate. The linear Langmuir plots between Ce/x and Ce are shown in the Fig. 3-6. The linear Freundlich isotherm models are shown in the Fig. 7-10 by plotting log x/log Ce. The constant values of the both isotherms for each soil pot are given in the Table 1. It is observed from the curves and the correlation coefficient data that the fluoride adsorption follows neither Langmuir isotherm nor Freundlich isotherm in a perfect way. However, it follows Langmuir isotherm in a better way. The value of n is always less then unity, which indicates that, none of the soil pots have completely energetically homogeneous surface. This can be explained that all the four soil pots are associated with certain amounts of aluminum oxalate at certain specific sites having different activation energy. The adsorption involves attractive electrostatic interaction between the negative sites created by the ionization of the sodium fluoride and the positively charged Al3 cations.

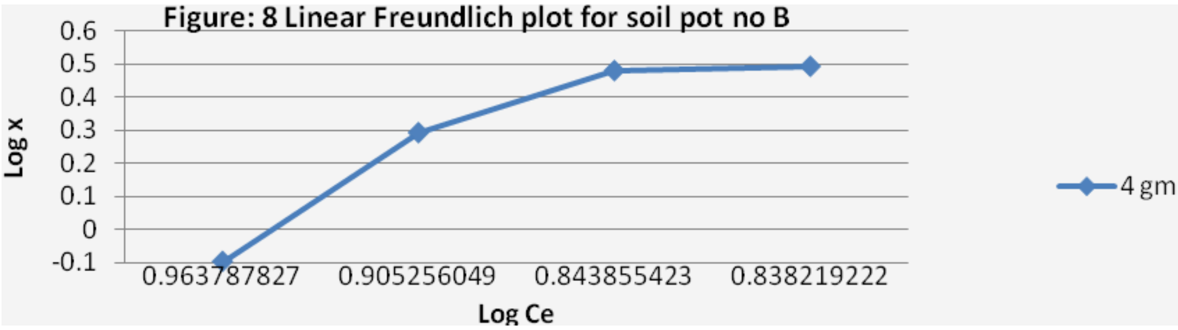


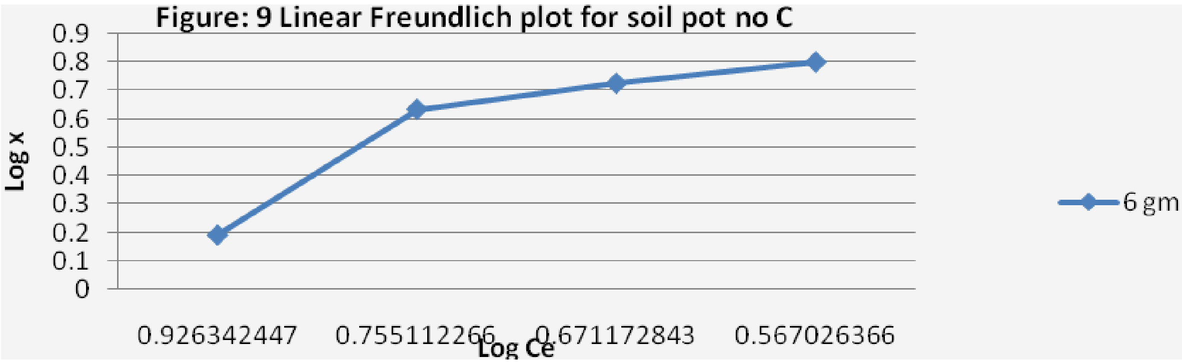












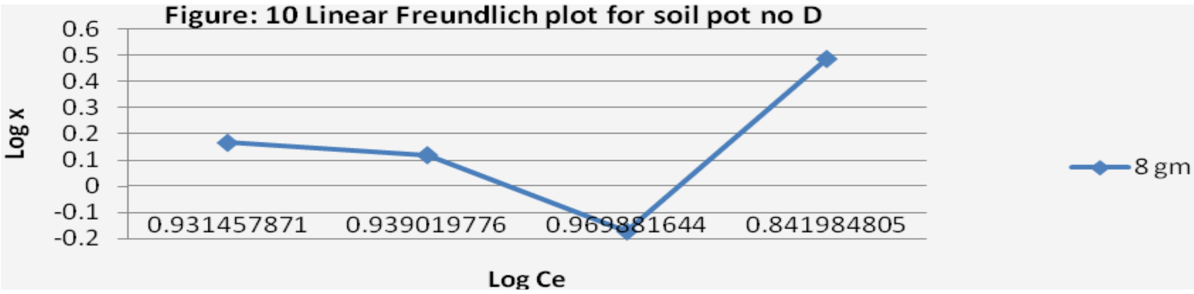


Table 1: Langmuir and Freundlich equation constants for adsorption of fluoride ions on different soil pots.

Soil Pots No.	C6Al2O12 in soil pots (g/500 g soil)	Langmuir equation constants		Freundlich equation constants	
		xm (mg/g)	k	N	kf
1	2g	0.487075	-0.17016	-3.82577	3.736795
2	4g	0.46465	-0.16922	-4.07778	3.954843
3	6g	1.807318	-0.36847	-1.5051	1.736619
4	8g	0.203617	-0.13747	-6.16173	5.881287

V. 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 avoids 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.

[1] Adsorption isotherm of fluoride ions follows the mixed model of the Langmuir and Freundlich isotherm. The adsorption does not depend on the BET surface area of the pots and takes place on certain specific site.

[2] Aluminum oxalate can be used as defluoridating agent in soil pots without effecting the environment as a Green Chemical Approach.

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