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Studies on Fluoride Removal Using Adsorption Process

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Batch adsorption studies were undertaken to assess the suitability of commercially available activated charcoal to remediate fluoride-contaminated water. The effects of some of the major parameters of adsorption, viz. pH, dose of adsorbent, rate of stirring, contact time and initial adsorbate concentration on fluoride removal efficiency were studied and optimized. The optimum sorbent dose was found to be 2.0 g/100 mL, equilibrium was achieved in 120 minutes and enhanced adsorption was obtained at pH 2. Maximum fluoride removal was observed to be 94% at optimum conditions. Freudlich as well as Langmuir isotherms were plotted and kinetic constants were determined.

Key Words : *Fluoride, adsorption, activated charcoal, Freundlich isotherm, Langmuir isotherm*

Introduction

Fluoride is well recognized as an element of public health concern. Fluoride is present universally in almost every water (higher concentrations are found in ground water), earth crust, many minerals, rocks etc. It is also present in most of everyday needs, viz. toothpastes, drugs, cosmetics, chewing gums, mouthwashes, and so on. Though a small amount of it is beneficial for human health for preventing dental carries, it is very harmful when present in excess of 1 mg/L. World Health Organization (WHO) and IS : 10500 recommend that the fluoride content in drinking water should be in the range of 1-1.5 mg/L. An intake of more than 6 mg/d of fluoride results in multidimensional health manifestations, the most common being dental and skeletal fluorosis.[2] (Jamode *et al.*, 2004a)

The occurrence of high fluoride concentrations in ground water is a problem faced by many countries, notably India, Sri Lanka, China, the Rift Valley countries in East Africa, Turkey, and parts of South Africa. Fluoride epidemic has been reported in as many as 19 Indian states and Union Territories. India is one among the 23 nations in the world, where fluoride contaminated groundwater is creating health problems. The state of Art Report of UNICEF confirms the fluoride problem in 177 districts of 20 states in India. The high fluoride levels in drinking water and its impacts on human health have increased the importance of defluoridation studies (S. Chidambaram *et al*., 2003)[12]. The magnitude of the problem is sinking in and efforts are being made towards defluoridation of drinking water, combating the debilitating fluorosis and taking steps to prevent and control the disease. (G. Karthikeyan and A. S. Sundarraj, 2002)[10].

Nalgonda technique developed by NEERI is commonly preferred at all levels because of its low price and ease of handling (E. Dahi *et al.*, 1996)[9]. Various processes tried so far for the removal of excess fluoride from water are adsorption, ion exchange, precipitation, and membrane process. However, most of these methods have high operational and maintenance cost, low fluoride removal capacities, lack of selectivity for fluoride, undesirable effects on water quality, generation of large volumes of sludge and complicated procedures involved in the treatment. Adsorption is the process considered to be efficient to defluoridate the water. Researches were carried on different adsorbents, viz. activated carbon, processed bone char powder, activated alumina, magnesia, activated bauxite, fly ash, granular calcite, alum, lime, etc. (Choi 1979, Bhargava 1991, Killedar & Bhargava 1998a,b, and T. Wijesundara 2004)[5,7,8,13,14].

Batch studies were conducted to evaluate the feasibility of fluoride removal using activated charcoal under varying conditions and also to examine applicability of adsorption isotherm to fluoride removal on activated charcoal.

Materials and methods

Materials

All the reagents used for the present study were of GR grade from E. Merck Ltd. India. The stock solution of 100 mg/L fluoride was prepared by dissolving 221 mg anhydrous NaF in 1 litre of distilled water. This 1 mL of solution has 0.1 mg of fluoride. Fluoride standard solution was prepared by diluting 100 mL stock solution to 1000 mL distilled water. A calibration curve was prepared using standard solutions.

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The adsorbent used in the study was powdered activated charcoal (GR grade, E Merck). Dosing of adsorbent was done in wet basis through 5% slurry prepared in distilled water. The characteristics of powdered activated charcoal used are given in the **Table 1.**

Table 1 : Specifications of powdered activated charcoal

Sr. No.	Description	Value
1	Substances soluble in water	$\leq$ 1 %
2	Substances soluble in HCl	$\leq$ 3 %
3	Chloride	$\leq$ 0.2 %
4	Sulphates	$\leq$ 0.2 %
5	Heavy metals (as Pb)	$\leq$ 0.005 %
6	Iron (Fe)	$\leq$ 0.1 %
7	Adsorption	$\geq$ 180 mg/g
8	Loss on drying (120^0C)	$\leq$ 10 %
9	Residue on ignition (600^0C)	$\leq$ 5 %

Test solution of 5 mg/L F^- was prepared by adding appropriate quantity of NaF with tap water keeping in view that the maximum concentration of fluoride normally reported in fluoride affected areas is around 5 mg/L. The physio-chemical properties of the tap water are given in **Table 2.**

Table 2 : Physio-chemical properties of tap water

Parameter	Value
pH	8.4
Turbidity (NTU)	2.1
Total solids (mg/L)	171.0
Total alkalinity (mg/L)	140.69
Total hardness as $CaCO_3$ (mg/L)	121
Chloride (mg/L)	19.30
Fluoride (mg/L)	0.1

Equipment

Batch adsorption studies were conducted using Jar test apparatus (Scientific Corporation, India) equipped with stirring paddles with provisions for controlled mixing speed .A spectrophotometer (Systronics, portable) Model -169 was used to analyze fluoride content of water at a wavelength of 570 nm.

Test conditions

Measured volumes (1000 mL) of test samples were mixed using the Jar test apparatus in 1000 mL borosil beakers. After the addition of adsorbent in each beaker simultaneously, the content was mixed at 30 rpm for 60 min. At the end of the stirring period, the beakers were removed slowly from the jar tester platform and the contents of the beakers were allowed to settle for 2 min. After settlement of adsorbent, the supernatants were carefully decanted, filtered through 42 No. filter paper and analyzed for residual fluoride by SPADNS method using SPADNS solution and zirconyl acid reagent as per the procedure of Standard Methods for Examination of Water and Wastewater.

Results and discussion

Understanding of adsorption technique is possible with knowledge of the optimal conditions, which would herald a better design and modeling process. Thus, the effect of some major parameters like pH, contact time, dose of adsorbent and initial concentration of fluoride ions of the uptake on adsorbent materials were investigated from kinetic viewpoint. Adsorption studies were performed by batch technique to obtain the equilibrium data. All the experiments were conducted at room temperature (29 ± 0.5 °C).

Effect of pH

The pH of the aqueous solution is a controlling factor in the adsorption process. Thus, the role of pH at 2, 4, 6 and 8 was observed. The pH was maintained at desired value with ±0.2 by adding 0.5 N HNO_3 or 0.1 N NaOH with 1000 mL of prepared solution of 5 mg/L of fluoride solution for contact time of 60 min with a dose of 0.6 g/100 mL of powdered activated charcoal. The influence of pH on extent of sorption is shown in **Fig. 1.**

As depicted in **Fig. 1**, it was observed that the maximum adsorption of 85 % is achieved at pH 2. A decrease in the extent of removal of fluoride ions was observed with increase in the pH of the solution. One of the reasons for better adsorption at low pH values may be attributed to large number of H^+ ions present at these pH values, which in turn neutralizes the negatively charged OH^- ions on adsorbed surface thereby reducing hindrance to the diffusion of fluoride ions. At higher pH values, the reduction in adsorption may be possible due to abundance of OH^- ions causing increased hindrance to diffusion of fluoride ions. It was observed that the surface adsorbed anions favorably in low pH range due to the presence of H^+ ions, whereas the surface was active for the adsorption

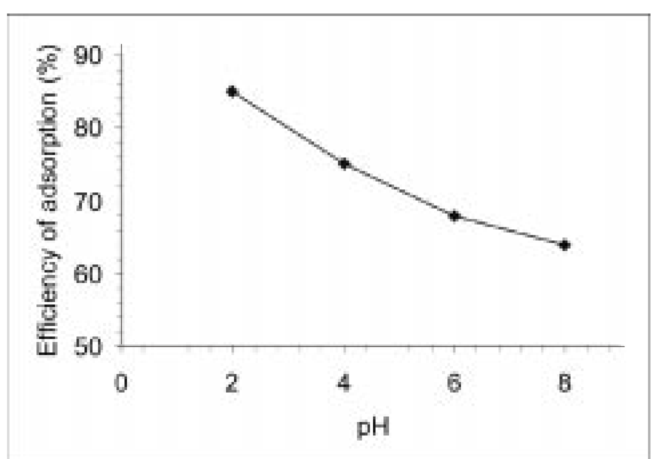

Fig. 1 : Effect of pH on fluoride removal
(Initial F^- Concentration of 5 mg/L; Adsorbent dose of 0.6 g/100 mL, contact time of 60 min. and stirring rate was 30 rpm.)

of cations at high pH values due to the accumulation of OH^- ions (Bhargava 1991, Jamode 2004a and A. K. Yadav 2005)[2,4,5]. Thus, pH of 2, which gave maximum fluoride removal, was taken into consideration for further studies.

Effect of adsorbent dose

Studies on effect of adsorbent doses were conducted by varying adsorbent doses between 0.2 to 2.4 g/100 mL. The pH was maintained at 2, while initial fluoride ion concentration was fixed at 5 mg/L and contact time was kept as 60 minutes.

The response of adsorbent dose on the removal of fluoride is presented in **Fig. 2.** The observations reveal that an increase in the adsorption occurs with the corresponding increase in the amount of adsorbent. The increase in the removal efficiency with simultaneous increase in adsorbent dose is due to the increase in surface area, and hence more active sites were available for the adsorption of fluoride. The results showed that activated carbon was efficient for 83 % removal of fluoride ions at the lowest dose of 0.2 g/100 mL and 92.4 % at maximum dose of 2.4 g/100 mL respectively, at room temperature of 29 ± 0.5°C. There was found less significant fluoride ion removal after applying dose of 2.0 g/100 mL and hence this dose was selected for further studies.

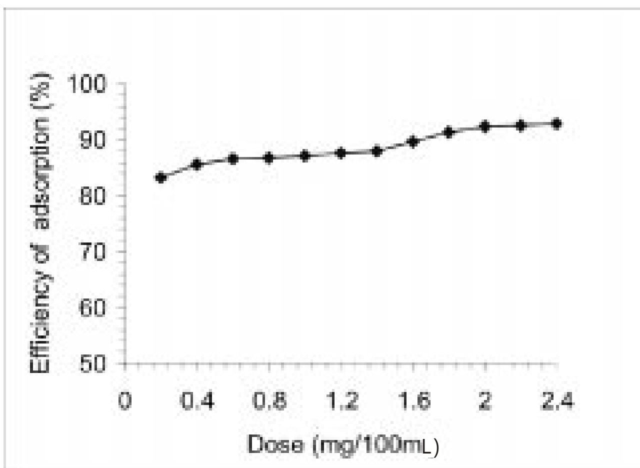

Fig.2 : Effect of adsorbent dose on fluoride removal
(Initial F^- Concentration of 5 mg/L; Contact time of 60 min.; pH 2.0 and stirring rate of 30 rpm)

Effect of stirring rate

Studies on the effect of stirring rate were conducted by varying speeds from 20 to 150 rpm, at optimum pH of 2 with adsorbent dose of 2 g/100 mL and contact time of 60 minutes. The influence of stirring rate on the extent of adsorption is shown in **Fig. 3.**

It reveals that fluoride removal is a function of stirring rate. At a given time, fluoride removal increases with the increase in the rate of stirring (Killedar and Bhargava, 1993)[6].

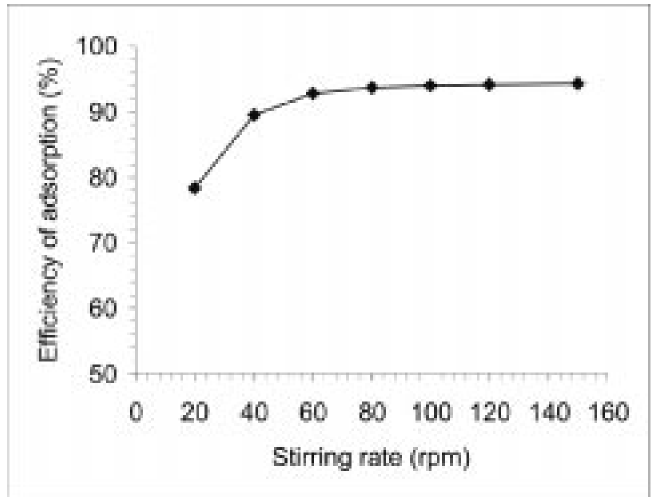

Fig. 3 : Effect of stirring rate on fluoride removal
(Initial F^- Concentration of 5 mg/L; Adsorbent dose of 2 g/100 mL;Contact time of 60 min.; pH 2.0)

The removal is 78.4% at 20 rpm and attains 96.8% at 150 rpm. The percentage adsorption is less at lower stirring rate and increases with the stirring rate up to 60 rpm and thereafter remains more or less constant. The reason for the increase in efficiency is that at higher speeds better contact between the adsorbent and adsorbate is possible. The adsorption extent for stirring rate of 60 rpm does not show any significant increase and hence stirring rate of 60 rpm was considered for further study.

Effect of contact time

Studies on the effect of contact time were conducted by varying it from 30 to 150 minutes, keeping adsorbent dose of 2.0 g/100 mL, pH of 2 and stirring rate of 60 rpm.

Fig. 4 shows the progression of adsorption reaction and the percentage removal of fluoride for different contact times. It is found that the removal of fluoride ions increases with increase in contact time, but after some time, it gradually approaches a constant value, denoting attainment of equilibrium. Further increase in contact time does not increase uptake due to deposition of fluoride ions on the available adsorption sites on adsorbent material. The changes in the extent of removal might be due to the fact that initially all adsorbent sites were vacant and the solute concentration gradient was high. Later, the fluoride uptake by adsorbent decreased significantly, due to the decrease in the number of adsorption sites. Decreased extent of adsorption, particularly towards the end of experiment, indicates the possible monolayer of fluoride ions on the outer surface, pores of the adsorbent and pore diffusion onto inner surface of adsorbent particles through the film due to continuous mixing maintained during the experiment (A. K. Yadav *et al.*, 2005)[4].

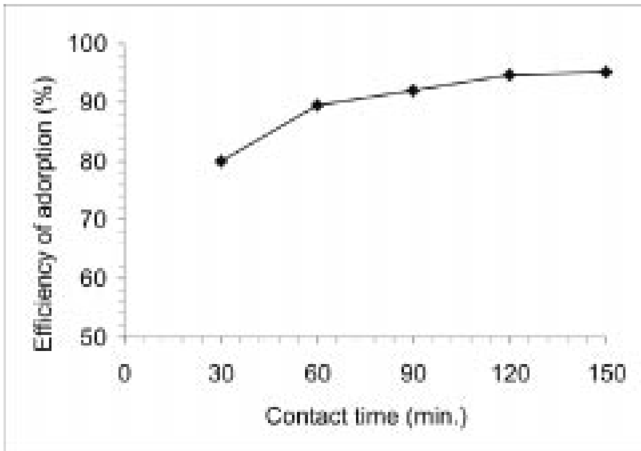

Fig. 4 : Effect of contact time on fluoride removal
(Initial F^- Concentration of 5 mg/L; Adsorbent dose of 2g/L 100mL; Stirring rate 60 rpm; pH 2.0)

It was assumed that the equilibrium time is that at which curves appear nearly asymptotic to the time axis. In the present case, the equilibrium time was obtained at 120 min and hence considered for further study.

Effect of initial fluoride concentration

Studies on the effect of initial fluoride concentration were conducted by varying it from 5 to 25 mg/L keeping adsorbent dose of 2.0 g/100 mL, pH of 2, stirring rate of 60 rpm and contact time of 120 minutes.

Fig.5 indicates that the percentage removal of fluoride ion decreases with increase in initial fluoride ion concentration. The percentage removal of fluoride was observed to be 94% at 5 mg/L and 70% at 25 mg/L. This is probably due to the fact that for a fixed adsorbent dose, the total available adsorption sites are limited, thereby adsorbing almost the same amount of fluoride, a decrease in percentage of removal of fluoride corresponding to an increased initial fluoride ion concentration was observed.

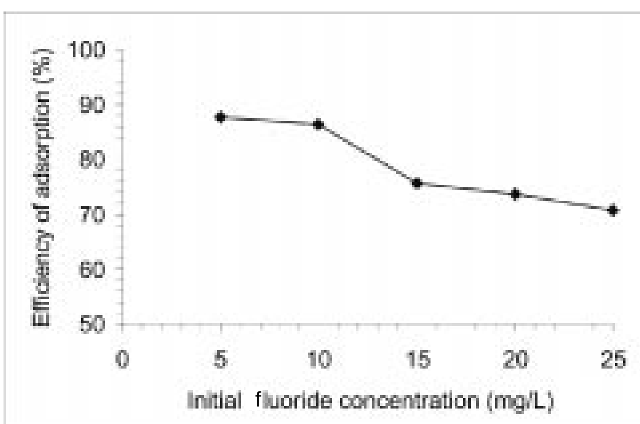

Fig. 5 : Effect of Initial F^- concentration on fluoride removal
(Adsorbent dose of 2g/100mL; Stirring rate 60rpm; pH 2.0; Contact time of 120 min.)

Sorption mechanism

Adsorption isotherm helps in determining the feasibility of activated carbon for treating fluoride ion in water (Y. C. Wu, 1979)[15]. Freundlich and Langmuir isotherms were plotted to provide deep insight to the adsorption of fluoride on activated carbon. The isotherm not only provides the general idea of the effectiveness of the activated carbon in removing fluorides, but also indicates the maximum amount of fluoride ions that will be adsorbed by the activated carbon. However, adsorption isotherms are equilibrium tests and thus do not indicate the actual performance of the adsorbent.

The Freundlich equation is basically empirical but is often useful as a means for data description. It generally agrees quite well with the Langmuir equation and experimental data over moderate ranges of concentration.

The general form of Freundlich isotherm is given in the following equation :

$$q_e = K_f\, C_e^{1/n} \qquad (1)$$

The linearised Freundlich adsorption isotherm is given in the following equation :

$$\log (q_e) = \log K_f + 1/n \log C_e \qquad (2)$$

Where

q_e is the amount of F^- ions adsorbed per unit weight of adsorbents (mg /g)

C_e is the equilibrium concentration in solution (mg/L)

K_f and 1/n are the Freundlich constants

Freundlich isotherm was plotted with log q_e vs. log C_e as shown in **Fig. 6.** From the graph, the value of K_f is 0.312 and 1/n= 0.5215, and thus the Freundlich isotherm is,

$$q_e = 0.312{*}C_e^{0.5215}$$

A smaller value of 1/n, points out a better adsorption mechanism and formation of relatively stronger bond between adsorbate and absorbent (R. Mehrotra *et al.*, 1999)[11].

Langmuir isotherm is valid for single-layer adsorption. It is based on the assumption that all the adsorption sites have equal affinity for molecules of the adsorbate and there is no transmigration of adsorbate in the plane of the surface.

The Langmuir equation is commonly written as :

$$q_e = abC_e / (1+bC_e) \qquad (3)$$

The linear form of Langmuir isotherm can be expressed as:

$$1/q_e = (1/a) + (1/abC_e) \quad s \qquad (4)$$

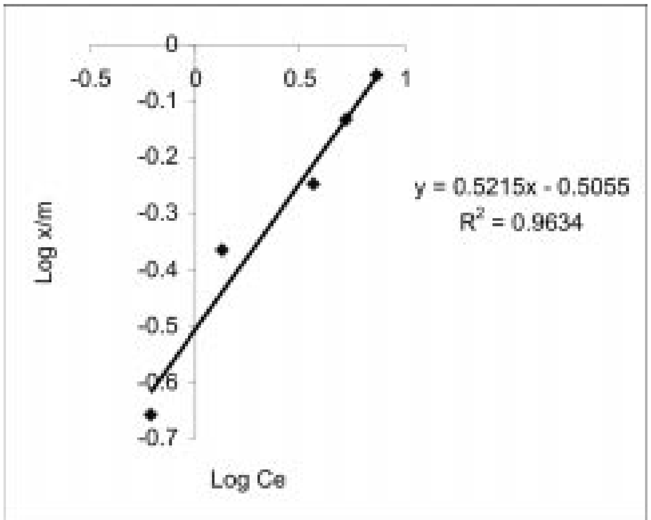

Fig. 6 : Freundlich isotherm

Where, q_e is the amount adsorbed (mg/g)

C_e is the equilibrium concentration in solution (mg/L)

a is number of moles of solute adsorbed per unit weight of adsorbent in forming a monolayer on the surface

b is a constant related to energy

Langmuir isotherm was plotted with $1/q_{e\ Vs}$ $1/\ C_e$ as shown in **Fig. 7.** The constants of Langmuir isotherm a and b are found to be 1.076 and 0.429 respectively. Thus, the Langmuir equation for defluoridation using activated carbon becomes

$$qe = 0.462C_e / (1 + 0.429\ C_e)$$

Conclusion

Based on these studies, it is concluded that activated charcoal can be fruitfully utilized for the removal of fluoride. The uptake of fluoride ions is possible between pH of 2.0 and 8.0, however, pH of 2 gives maximum fluoride removal since neutralization of OH^- ions by large number of H^+ ions takes place at less pH values. The percentage of fluoride removal was found to be a function of adsorbent dose and contact time at a given initial solute concentration. The removal increased with time and adsorbent dose, but with higher initial solute concentration decreased with time and adsorbent dose. The present study on defluoridation using activated carbon reveals that the equilibrium data fits better to Langmuir isotherm than Frendulich isotherm.

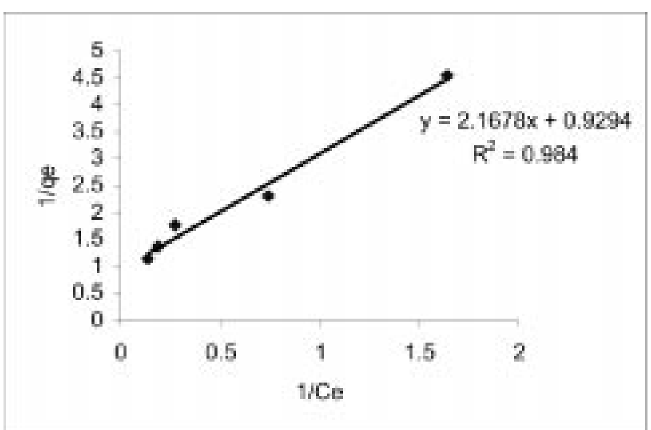

Fig.7 : Langmuir isotherm

References

1. APHA, AWWA, Standard Methods for the Examination of Water and Wastewater,19th Edition, Washington, DC (1995)
2. A. V. Jamode, V. S. Sapkal and V. S. Jamode, Defluoridation of Water Using Inexpensive Adsorbents, *J. Indian Institute of Science*, **84**, 163-171 (2004a)
3. A. V. Jamode, V. S. Sapkal and V. S. Jamode, Adsorption Kinetics of Defluoridation Using Low Cost Adsorbents, *J. Adsorption Science & Technology*, **22 (1)**, 65-73 (2004b)
4. A. K. Yadav, C. P. Kaushik, A. K. Haritash, A. Kansal and Neetu Rani, Defluoridation of Groundwater Using Brick as an Adsorbent, *J. Hazardous Materials* (2005) (Artical in press)
5. D. S. Bhargava and D. J. Killedar, Batch Studies of Water Defluoridation Using Fishbone Charcoal, *J. Water Pollution Control Federation*, **63(6)**, 848-858 (1991)
6. D. J. Killedar and D.S.Bhargava, Effect of Stirring Rate and Temperature on Fluoride Removal by Fishbone Charcoal, *Indian Journal of Environmental Health*, **35(2)**, 81-87 (1993)
7. D. J. Killedar and D. S. Bhargava, An Overview of Defluoridation Methods (Part-I), *Journal IPHE*, **1**, 21-29 (1998a)
8. D. J. Killedar and D. S. Bhargava, An Overview of Defluoridation Methods (Part-II), *Journal IPHE*, **2**, 78-82 (1998b)
9. E. Dahi, F. Mtalo, B. Njau and H. Bregnhj, Defluoridation using Nalgonda Technique in Tanzania, 22nd WEDC Conference, New Delhi (1996)
10. G. Karthikeyan and A. S. Sundarraj, Defluoridation Processes, www.twadboard.com/photos/nletjune 02_08.pdf

11. R. Mehrotra, B. S. Kapoor and B. Narayan, Defluoridation of Drinking Water Using Low Cost Adsorbent, *Indian J. Environmental Health*, **41(1)**, 53-58 (1999)

12. S. Chidambaram, A. L. Ramnathan and S. Vasudevan, Fluoride Removal Studies in Water Using Natural Materials, *Water SA*, **29(3)**, 339-343 (2003)

13. T. Wijesundara, Low Cost Defluoridation of Water Using Broken Bricks, 30th WEDC International Conference Vientiane, Lao PDR (2004)

14. W. W. Choi and Y. Chen, The removal of Fluoride from Waters by Adsorption, *J. AWWA*, **71(10)**, 562- 569 (1979)

15. Y. C. Wu and A. Nitya, Water Defluoridation with Activated Alumina, *J. Environmental. Engg*., **105 (2)**, 357-367 (1979)