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REMOVAL OF FLUORIDE FROM GROUNDWATER

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ABSTRACT

Batch experiments were performed using Activated Alumina as an adsorbent for initial fluoride concentrations in the range of 5-35ppm. It was found that the equilibrium data were explained better by Freundlich isotherm than Langmuir's. Column experiments were conducted with the same adsorbent using initial fluoride concentrations and Hydraulic retention time as variables. The removal efficiency of fluoride was found to be in the range of 88-98%. The reproducibility of experiments was checked and the error was found to be in the range of 2.6%-5.3% based on fluoride removal efficiency.

Keywords: Fluoride, adsorption, alkalinity, SPADNS and activated alumina.

INTRODUCTION

The presence of fluoride, in quantities in excess of limits is a serious matter of concern from a public health point of view. Like any other pollutant the fluoride pollution can also occur due to both natural and man made reasons. Fluoride in drinking water is known for both beneficial and detrimental effects on health. In India, it is generally prevalent in many federal states. Fluoride is beneficial when present in concentrations of 0.8-1.mg/l. Some people were found with the mottled enamel of the teeth when fluoride was present in potable waters in concentrations in excess of 1.5mg/l. Indian standards for fluoride in drinking water was given (Central Pollution Control Board, 1998) as 1mgF/l.

Skeletal fluorosis has been observed at concentrations beyond 3mg/l. According to WHO (Guidelines, 1984) for drinking water quality, the excessive limit for fluoride is fixed as 1.5mg/l, after which the water needs treatment for its removal. The fluoride content in the groundwater (tap water) of IIT Madras which was used in the experiments is found to be 0.3mgF^-/l, which is well within the limit.

Among the techniques for fluoride removal, activated alumina filtrations was the most effective method and it was generally considered to be combined ionexchange and physical adsorption (Singh and Maheswari, 2001). For neutral and acidic solutions, the adsorption capacities of fluoride by alumina were interfered by the presence of sulphate (Young and Hwei-Mei, 2002). The Langmuir and Freundlich isotherms can well describe the equilibrium behaviours of the adsorption processes.

Early saturation and lower fluoride removal were observed at higher flow rate and at higher concentrations and the pH was shown as a decisive parameter in fluoride removal (Subhashini and Pant, 2004). Some researchers (Subhashini and Pant, 2004) concluded that activated alumina was a suitable adsorbent for the removal of fluoride from drinking water and the removal of fluoride from aqueous solutions strongly depended on the contact time, pH of the solution and the adsorbent concentration.

The two step brushite saturation and apatite precipitation method (Larsen and Pearce, 2002) could also be employed for initial fluoride concentrations from 1 to 5ppm but the efficiency decreased when initial fluoride levels decreased.

A new technique (Lounici *et al.*, 2001) to regenerate AA saturated with fluoride ions based on the use of an electrochemical cell was reported. The advantage of this process was mainly its rapidity (6-15 min) to desorb fluoride. The efficiency of AA to remove fluoride from water strongly depended on the pH and the alkalinity of the raw water. Furthermore, some ions could interfere and reduce the defluoridation efficiency of AA.

The AA adsorption process was studied using six 2L capacity reactors for different pH values and different fluoride concentrations (Wu and Nitya, 1979). The results showed that the best efficiency of 78% was observed for pH of 5. Moreover, when [F^-] / AA ratio was reduced, the efficiency increased by 3%. It was also shown that fluoride removal obeyed Langmuir isotherm.

The experimental data (Young and Hwei-Mei, 2002) with different initial fluoride concentrations at pH of 6 and a temperature of 30^{o}C were fitted to Langmuir and Freundlich models with relatively good applicability. For initial fluoride concentration of 5ppm, the effect of flow rate was studied using 30ml/min and 20ml/min. The maximum percentage fluoride removal was 86% and 92% respectively. It was determined experimentally that the higher the temperature of calcination, the lower the adsorption capacity was found when bone char material was used as an adsorbent (Phantumvanit and Legeros, 1997). Clay minerals (Coetzee *et al.*, 2003) and their efficiency in defluoridation of raw waters containing 10ppm of fluoride ions were studied. Australian origin

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Bauxite clays gave 80% fluoride removal and bauxite consisting of amorphous aluminium trioxide showed 99% efficiency for initial fluoride concentrations of 10ppm and at a pH of 6.

The reduction of fluoride concentrations from 5-20ppm to less than 1.5ppm was obtained when treating 1L of water and using 120-240g of fired clay chips (*Moges et al.*, 1996). A packed column of clay pot was saturated with 285mg fluoride/kg of adsorbent when passing 20L of water (10ppm of fluoride) through it. The column defluorinated 6L of tap water containing 10ppm fluoride to less than 1.5 ppm.

Experiments were carried out by using a very cheap adsorbent hydroxyapatite (Ying *et al.*, 2001) and these results were compared with the results of the experiments carried out with activated alumina and bone charcoal and found that synthetic hydroxyapatite had a better removal capacity than these materials.

In Agra city (India) groundwater containing 0.8-4.9ppm of fluoride was treated by activated charcoal(AC) prepared from wheat husk or alum treated fly ash(ATF) obtained from a thermal power plant(Singh *et al.*, 2000). A removal efficiency of 90.7% was observed using 2g of AC/100mL groundwater and a 68.6% fluoride removal was obtained with 3g ATF/100ml groundwater. Both root and shoot parts of Eichhornia plants were used (Dahiya *et al.*, 2000) to remove fluoride from 2.5ppm solutions. Eichhornia roots managed to remove less than 62% of the fluoride and shoots had 74% removal efficiency.

MATERIALS AND METHODS

Some researchers (Lounici *et al.*, 2001) have concluded that fluoride removal by AA was the result of an ion exchange occurring as follows:

$$AlOH(s) + F^- \rightarrow AlF(s) + OH- \quad (1)$$

$$AlOH_2(s) + F^- \rightarrow AlF(s) + H_2O \quad (2)$$

$$AlOH(s) + 2F^- \rightarrow AlF_2^- + OH- \quad (3)$$

In the above equations, (s) represents the solid phase.

Characteristics of Activated Alumina adsorbent

The adsorbent used for the present study has a surface area and pore volume as given in Table 1.

Equilibrium Studies

50ml of synthetically prepared fluoride solution of required concentrations (in the range of 5 to 35ppm) were added to 1g of Activated Alumina adsorbent in a conical flask. After shaking in a shaker, a sample was taken from each conical flask. The mixture was filtered (using a Whatman No.42 filter paper of pore size 1µm,ashless type) and the filtrate containing the fluoride was analysed in a UV visible spectrophotometer (Model No.UV265FS, Shimadzu, Japan) at a wavelength of 570nm. Prior to this, a calibration curve was prepared and used for determining the fluoride concentrations.

Column experiments

As shown in the figure 1, a glass column of 3.3cm in diameter and 50cm in height having the volume of around .0004274m^3 was packed with 397g of Activated Alumina adsorbent and supported with the help of a stand. With the help of a peristaltic pump, the feed solution was introduced to the top of the column. The feed solution ran through the bed and the samples were collected at the effluent end of column. The peristaltic pump was used to maintain the required HRT. A sample volume of 5ml was collected at required time intervals in a sample beaker. The collected sample solution was taken in a test tube and it was diluted to 50 ml. 10ml of SPADNS reagent was added to that and thoroughly mixed. After the adsorption, the effluent fluoride concentrations were determined. Fluoride removal % was calculated according to the formula given below.

Amount of fluoride removed (%) =

$$\frac{\text{Initial Conc. of } F^- - \text{Final Conc. of } F^-}{\text{Initial Conc. Of } F^-} \times 100$$

The experiments were conducted in a similar manner for 3 different HRT's and different initial fluoride concentrations.

Analytical Techniques

pH measurements were made using a digital pH meter (Model No. D1 7007, Digison Electronics, Hyderabad). The alkalinity determinations were made by titrimetric method. Fluoride concentration determinations were done by UV visible spectrophotometer. All the chemicals used were AR grade. Sodium fluoride was used to prepare synthetic fluoride solutions of different concentrations.

Reproducibility study

Certain numbers of experiments were repeated at random under identical conditions for initial concentrations of 5, 15 and 20ppm at HRT's of 0.402hr, 0.567hr, 0.799hr and 1.729hr respectively. The percentage deviations of repeated values of fluoride removal efficiency against original fluoride removal efficiency values were reported in %. The error % was found to be in the range of 2.6-5.3%.

RESULTS AND DISCUSSIONS

Batch experimental results

Based on the batch adsorption data at varying initial fluoride concentrations and at an adsorbent loadings (20g/l), the equilibrium data obtained were fitted to Freundlich isotherm equation:

$$\log(x/m) = \log k + 1/n \log C_e$$

where **k** and **1/n** are freundlich constants related to adsorption capacity and adsorption intensity respectively, **Ce** is the effluent concentration , **x** is the amount adsorbed and **m** is the unit mass of adsorbent. The data fit is shown in fig. 2. The values of ‘**k**’ and ‘**n**’ are found to be $0.39*10^{-7}$g/g and 0.2 respectively. The data fit to Langmuir isotherm equation was found to be unsatisfactory and hence not reported. Perhaps this system does not obey langmuir isotherm equation.

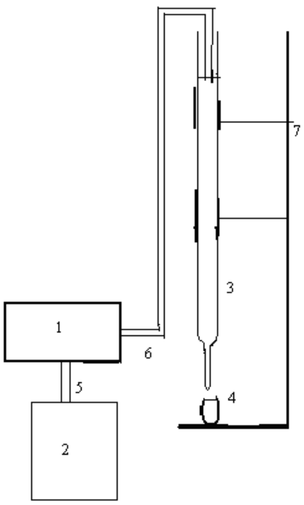

Fig. 1. Experimental set up: 1. Peristaltic pump, 2. water vessel, 3. glasscolumn, 4. sample beaker, 5. inlet, 6. outlet, 7. stand.

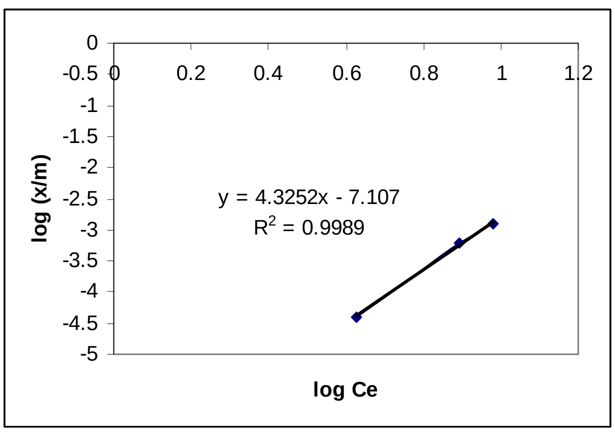

Fig.. 2. Freundlich plot for adsorption of fluoride.

Column experimental results

In the column experiments, a typical variation of % of fluoride removal against time is shown in fig.3, for a HRT of 1.73hrs and at an influent fluoride concentration of 5ppm. From this graph (Fig. 3), the maximum fluoride removal could be noted as about 96%. Similar plots were prepared for other HRT values at the same concentration of 5ppm and maximum values were noted. From the raw experimental data, maximum fluoride removal values obtained at a constant influent fluoride concentration (5ppm) were plotted against HRT and the typical variation is shown in fig. 4. From this plot, it can be observed that at HRT’s higher than 1hr, the maximum fluoride removal remained practically constant.

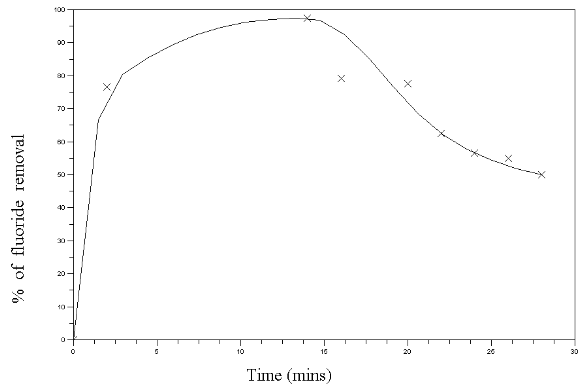

Fig.. 3. Plot of % of fluoride removal vs Time for a HRT of 1.73hrs at an influent fluoride concentration of 5ppm.

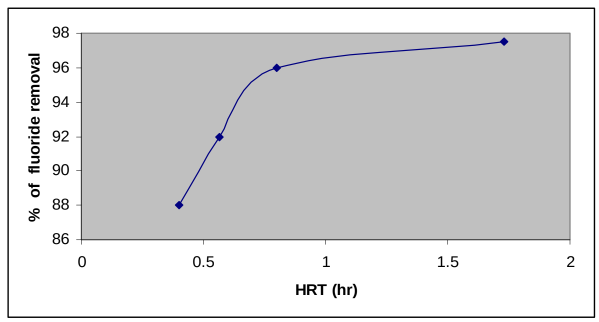

Fig.. 4. Plot of maximum fluoride removal values vs HRT for an initial fluoride concentration of 5ppm.

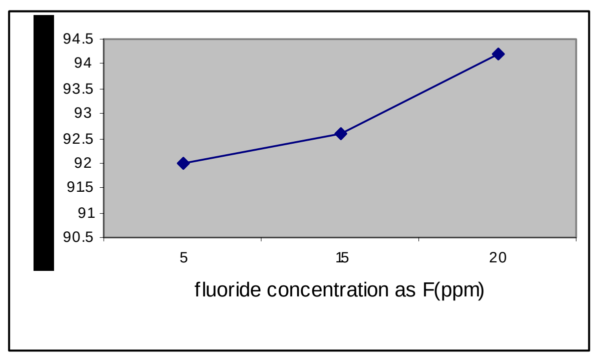

Fig.. 5. Plot of maximum fluoride removal values vs fluoride concentration for a HRT of 0.567hr.

A study has been carried out on the fluoride removal in a packed column of Activated alumina by (Talnikar *et al.*, 2004) and they observed that 5% - 94% fluoride removal under two experimental conditions, using synthetic and subsoil waters.

A study has been carried out on the defluoridation technique at household level using activated alumina as an adsorbent by (Banuchandra and Selvapathy, 2000) and they reported the residual fluoride concentrations in the range of 0.875mg/l – 1.03mg/l corresponding to contact times of 0.5-1.5hr respectively. They have studied the initial fluoride concentrations in the range of 0.8-1.2mg/l whereas for the present investigation, the range is 5-20mg/l.

Another study on the defluoridation using activated alumina as an adsorbent by (Subhashini and Pant, 2004) in the range of fluoride concentrations 2.5-14mg/l, reported a maximum removal of 69.25%.

At a HRT of 0.567hrs, the maximum fluoride removal values were plotted against increasing influent fluoride concentrations in fig.5. It can be observed that as the influent fluoride concentration increases, the maximum fluoride removal values are increasing.

Table 1. Characteristics of AA adsorbent.

S. No	Property	Value
1.	Bulk Density	1.07kg/m^3
2.	Pore Volume	0.29960177cm^3/g
3.	Surface Area	231.52 m^2/g

CONCLUSIONS

Activated alumina is a suitable adsorbent for the removal of fluoride from drinking (ground) water. Based on the batch experiments, the obtained data were fitted to the Freundlich isotherm equation and it was found that this equation fitts better than the Langmuir's equation. The Freundlich constant 'n' and the intercept 'k' value were found to be 0.2 and $0.39*10^{-7}$ g/g respectively. The results showed that at HRT's higher than 1hr, the maximum fluoride removal values remained practically constant for any particular influent fluoride concentration. The maximum fluoride removal values showed an increasing trend with increasing influent fluoride concentrations at any particular HRT. The reproducibility experiments showed that the error % was very much in a reasonable (2.6%-5.3%) range.

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Abbreviations and notations:
HRT – Hydraulic Retention Time
WHO – World Health Organisation
AA – Activated Alumina
SPADNS – 2-(p-sulphophenylazo)-1,8-dihydroxynaphthelene-2,6-disulphonicacid trisodium salt.
IIT - Indian Institute of Technology
ARgrade - Analytical Reagent grade
Conc. – Concentration