

## ADSORPTION OF FLUORIDE BY GAMMA ALUMINA

C.R. Nagendra Rao \* and J. Karthikeyan \*\*

\* Professor & Head, National Institute of Technical Teachers Training & Research (Chennai), Hyderabad Extension Centre, Sanketika Vidya Bhavan, Mahavir Marg, Masb Tank, Hyderabad 500028.AP, India

\*\* Professor, Dept. of Civil Engineering, SVU College of Engineering, Tirupati 517502 AP, India

### ABSTRACT

The extent of problem of the excessive fluoride in drinking water is so serious that attracted the focus of many researchers and consequently many solutions for the problems were also suggested; but a simple to operate technology appropriate to rural areas has not yet been accomplished. Aluminum compounds are known to have high potential for removal of fluoride from water. In the present work, gamma Alumina, a purest form of alumina was investigated to assess its sorptive removal capacity of fluoride from water employing a synthetic fluoride solution of  $4 \text{ mg.L}^{-1}$ . The adsorbent exhibited rapid and high uptake of fluoride under experimental conditions. The effect of various parameters like contact time, pH, initial fluoride concentration and sorbent dose was investigated. About 85% removal was achieved in the first 10 minutes at a sorbent dose of  $8 \text{ g.L}^{-1}$ . Adsorption efficiency was found to be dependent on initial fluoride concentration and the sorption process followed BET model. The variation of pH over wide range i.e., up to pH 10 has insignificant effect on sorption but beyond the pH of 10, the effect was drastic. Among anions investigated for their effect on adsorption process, carbonates were most serious in reducing fluoride uptake capacity of the sorbent. Desorption studies with distilled water resulted in negligible desorption of fluoride from the adsorbent. Regeneration by alum solution was found to be more effective than other regenerants like HCl and NaOH etc. Cyclic regeneration with alum indicated the potential usefulness of the sorbent for nearly 10 cycles without significant loss of sorption capacity.

**Keywords:** Fluoride, Drinking water, gamma Alumina, adsorption, isotherm, regeneration

### INTRODUCTION

The concentrations of fluoride up to  $1.0\text{-}1.5 \text{ mg.L}^{-1}$  are beneficial as it helps calcification of dental enamel especially in young children, whereas excess concentration of fluoride causes dental and/or skeletal fluorosis (Paul and George, 1978). The excess fluoride related problems are endemic to India and many other parts

of the world. The detrimental effects of excessive fluorides prompted many workers to orient their efforts for development of an effective method for its removal.

Defluoridation of drinking waters is usually accomplished by either precipitation or by adsorption processes. Chemical precipitation methods including 'Nalgonda Technique' (Bulusu et. al., 1979), employing soluble metal salts are associated with certain problems which render them less attractive for field application like large quantities of chemical doses, alkaline pH of treated water, handling and disposal of large volumes of hazardous chemical sludge.

In this respect, adsorption and ion exchange processes appear to be a better alternative for field application.

Of many materials like Activated carbon (McKee and Jhonston, 1934), De-greased and alkali treated bone (Smith, H.V. and Smith, H.C., 1937) and bone char (Killedar and Bhargava, 1988a, 1988b), Anion and cation exchange resins (Bhakuni, 1970), Serpentine (Kulkarni and Nawlakhe, 1974) and activated alumina investigated for adsorption of fluoride, the successful demonstration of activated alumina was significant (Boruff, 1934, Fink and Lindsay, 1936, Swope and Hess, 1937); the fluoride removal capacity of activated alumina increases directly with fluoride concentration and inversely with pH of the water (Savinelli and Black, 1958).

Defluoridation by activated alumina is a preferred choice. Activated alumina is prepared through dehydration of  $\text{Al}(\text{OH})_3$  at high temperatures. Gamma alumina is the purest form of alumina and has reportedly superior sorption capacities but its preparation is difficult and hence not widely used. The objective of the present study is to investigate the effectiveness of gamma alumina for adsorption of fluoride from water. For this, batch sorption studies to investigate kinetics and equilibrium of sorption process, effect of other ions were all investigated and are presented herein.

## **EXPERIMENTAL METHODOLOGY**

### **Materials**

The gamma alumina, used as a sorbent, was obtained from BHEL-Electroplating division of Bangalore, India. The material received was in the form of fine crystals.

Standard fluoride adsorbate solutions were prepared by dissolving appropriate amount of reagent grade NaF in distilled water. A stock solution of  $100 \text{ mg.L}^{-1}$  fluoride was first prepared and all working solutions were prepared by appropriate dilution of freshly prepared stock solution with distilled water. All experiments were conducted at room temperature (26-30°C).

A SYSTRONICS 105 Spectrophotometer was used for analysis of fluoride concentration using SPADNS method, outlined in 'Standard Methods for Examination of Water and Wastewater (APHA, AWWA, WEF, 1995).

## **Experimentation**

Agitated non-flow batch adsorption experiments were conducted to study the effect of controlling parameters like contact time, sorbent dosage, pH, etc. on sorptive uptake of fluoride by gamma alumina employing a bottle – point method wherein each observation (point on the graph) was obtained from an individual bottle. A number of identical samples of bottles were employed as duplicates. To a 50 ml of test fluoride solution of 4 mg. L<sup>-1</sup> fluoride taken in a bottle (Tarson's PP specimen bottle), pre calculated quantity of sorbent was added and mixed on a rotary shaker at 35-40 rpm for varying time intervals.

To determine the equilibrium sorption time, samples were withdrawn after desired contact time of 5, 10, 15, 30, 60, 120, 180, 240 and 300 minutes. The sorbent was separated from solution by vacuum filtration using Whatman 40 ashless filter paper and the filtrate was analyzed for residual fluoride concentration.

The effect of pH on fluoride removal was studied by adjusting the pH of the test solution to initial pH of 3.0, 4.5, 6.0, 8.0, 9.5, 11.0 and 12.0.

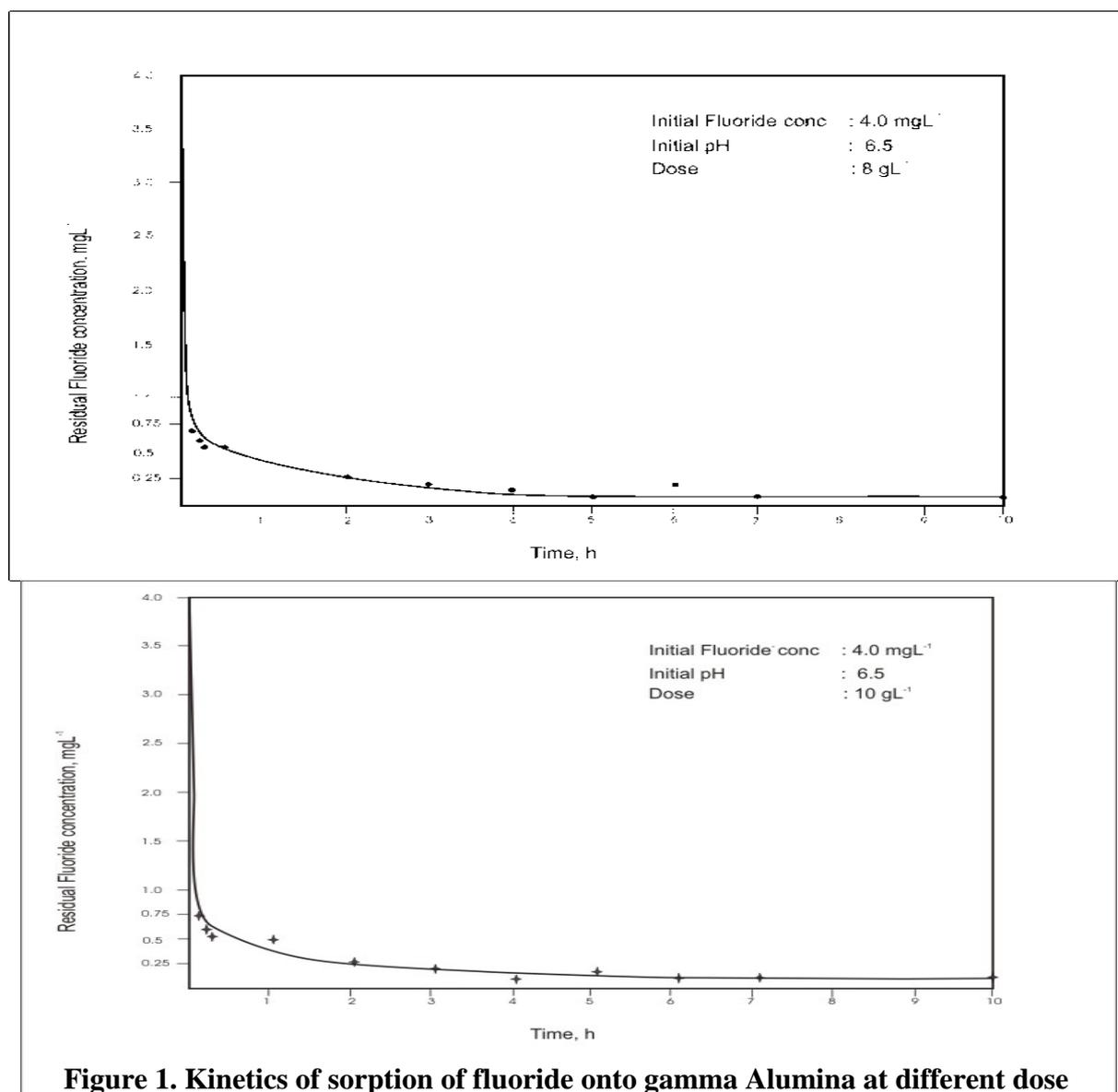
Desorption studies were conducted by dispensing loaded adsorbents in distilled water, agitated for equilibrium time and the supernatant analysed for acquired concentration of fluoride. For regeneration tests the sorbents were separated after sorption and then air dried for 24 hours.

In order to delineate the type of sorption, surface or pore diffusion, interruption studies were conducted during the present investigation. For this, first the sorbent was added to a test fluoride solution taken in a specimen tube and mixture was agitated as done in case of kinetics experiment. Aliquots of samples were withdrawn at various contact periods, the sorbent was separated from solution and the filtrate was analyzed for residual fluoride concentration. The sorbent samples thus separated from the fluoride solution at equilibrium period were air dried, till the material was completely dry. Air dried sorbents were again introduced (at the dosages same as before interruption) to test fluoride solution taken in a specimen tube and mixture was agitated as under the same conditions employed during pre-interruption to adsorption. Aliquots of samples were withdrawn at various contact periods, and analyzed for residual fluoride concentration.

## RESULTS AND DISCUSSION

### Kinetics of Sorption Reaction

Kinetics of sorptive uptake of fluoride was investigated employing two different doses of gamma alumina of 8 and 10 g.L<sup>-1</sup>. Kinetics of sorption indicating time dependency of sorptive uptake of fluoride by gamma Alumina is portrayed in Figure 1.



**Figure 1. Kinetics of sorption of fluoride onto gamma Alumina at different dose**

The data fits well into a sigmoid type curve with an initial steep sorption phase wherein almost 80-90% of removal is accomplished within 15 minutes of contact mainly due to strong interactive forces that are chemical (molecular) in nature. With prolonged contact time, sorption reduces gradually and eventually reaches a stationary level (of sorption) denoting completion of sorption reaction as either due to exhaustion of surface sites or sorbate molecules or inhibition of sorption interaction.

To analyze rate of fluoride sorption reaction, the kinetic data was analyzed using Lagergren equation, Pseudo Second order equation and Thomas equations. The sorption data is further processed to find the rate constant and coefficient of correlation,  $r^2$  and are given in Table 1.

**Table 1. Rate Parameters and Correlation Coefficients**

S. No.	Parameters	Value		
		Lagergren equation	Pseudo Second order equation	Thomas equation
1	Coefficient of correlation	0.196	0.999	0.935
2	Rate constant	0.004	0.96	0.03

### Equilibrium of Sorption Reaction

Isothermal equilibrium studies were conducted employing different initial fluoride concentrations of 2, 4, 6, 8, 10, 12, 16 and 20  $\text{mg.L}^{-1}$  and 8  $\text{g.L}^{-1}$  of sorbent. Experimental results along with experimental conditions are presented in Table 2.

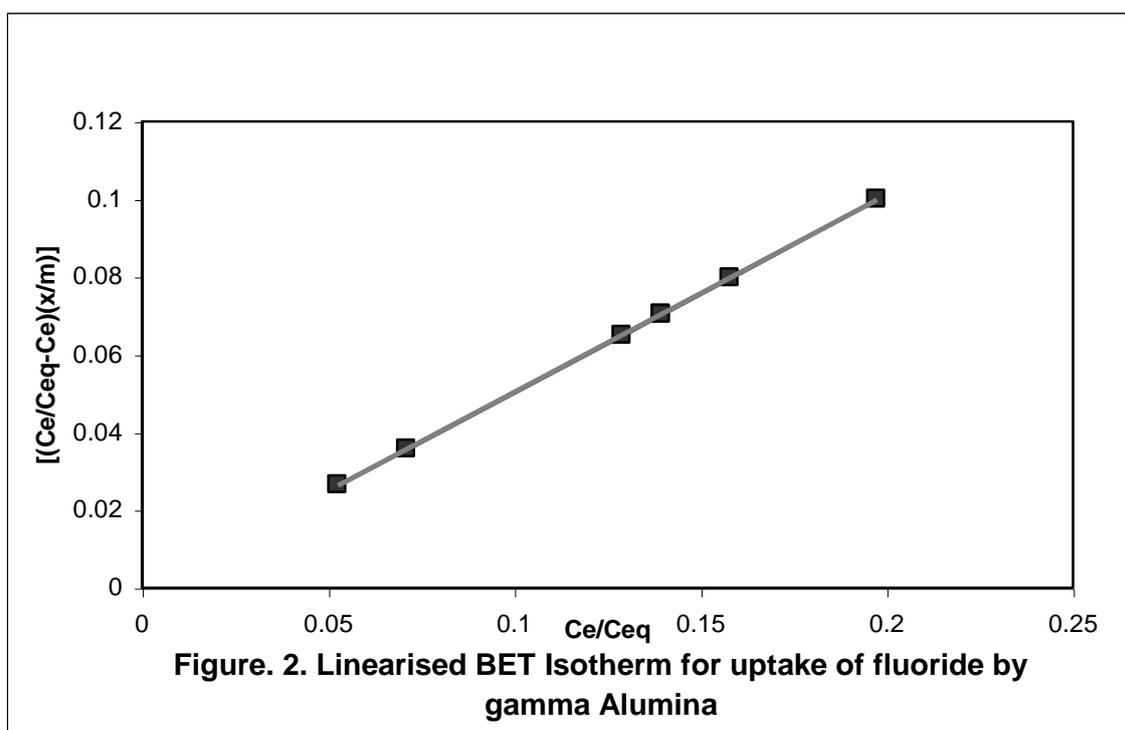
**Table 2. Sorption equilibria with estimated isotherm parameters for gamma Alumina**

Initial $\text{F}^-$ conc. ( $C_o$ ) mg/L	Residual $\text{F}^-$ conc. ( $C_e$ ) mg/L	$\text{F}^-$ Uptake, ( $C_o - C_e$ ) mg/L (x)	$q_e = x/m$
2.0	0.24	1.76	0.22
4.0	0.40	3.6	0.45
6.0	0.69	5.31	0.66
8.0	0.78	7.22	0.90
10.0	1.21	8.79	1.10
12.0	1.40	10.6	1.33
16.0	2.92	13.08	1.64
20.0	2.94	17.06	2.13
Experimental Conditions: Sorbent mass (m): 8.0 $\text{g.L}^{-1}$ , pH: 6.7, Contact time : 3hr			

It follows from the above table that the amount of fluoride uptake, and  $q_e$  i.e. uptake per unit weight of sorbent increased with increase in initial fluoride concentrations.

Similar observations have been reported elsewhere (Choi and Chen, 1979, Muthukumaran, 1995). The increase in amounts of fluoride uptake by unit weight of sorbent with increase in initial fluoride concentrations is perhaps due to sorbate concentration gradient, which is the driving force for intraparticle transport which facilitates diffusion of sorbate molecule to the surface sites for ultimate attachment (Karthikeyan, 1982).

The experimental data of equilibrium sorption were fitted to the linear form of three widely used isotherm equations namely, Langmuir, Freundlich and BET isotherm equations. From an analysis of coefficient of correlation ( $r^2$ ) and standard error of estimate, it is found that the equilibrium sorption data fits best into the BET adsorption isotherm equation which reflects apparent multilayer adsorption on a more or less homogeneous surface of uniform energy levels. Linearized BET isotherm is shown in Fig. 2. Sorption capacity and sorption intensity were estimated and are given in Table 3.



**Table 3. Estimated Sorption capacities and coefficients of correlation ( $r^2$ ) for various equilibrium models**

Sorbent	Model	Slope	Intercept	$r^2$
Gamma alumina	Langmuir	1.0204	0.0337	0.96
	Freuindlich	0.7748	0.0443	0.97
	BET	0.51	0.0004	1

Equilibrium adsorption data is also used to draw saturation for equilibrium sorption of fluoride onto gamma Alumina. Sorption isotherm/saturation curve thus obtained from the equilibrium adsorption data of gamma alumina resemble Type IV curve of BET classification (Brunauer et al., 1938 and 1940).

### **Effect of Dosage on Sorption reaction**

The effect of dosage of gamma alumina on removal of fluoride was conducted employing sorbent dosages ranging from 4 gL<sup>-1</sup> to 20gL<sup>-1</sup>. Distribution coefficient  $K_D$  that reflects the ability of binding of the surface and which is dependent as pH and type of the surface was calculated for fluoride - gamma alumina system at pH 6.5. The values of  $K_D$  increased with increasing sorbent dosage.

### **Evaluation of Rate Limiting Step**

In a well agitated system, adsorption processes involve movement/migration of sorbate molecule across the interface (film diffusion) and/or diffusion into the pores (pore diffusion) and one of these may control the overall rate and amount of sorption and eventually becomes rate controlling step. Then a linear plot of  $t^{0.5}$  versus fluoride sorbed per unit weight of gamma Alumina has to pass through the origin and the rate parameter ( $K_p$ ) of the intraparticle diffusion may be obtained from the slope of the above plot (Weber, 1972, Alexander and Mc Kay, 1977, Mc Kay et. al. 1980). A plot of graph of  $t^{0.5}$  Vs fluoride uptake by gamma Alumina is drawn to obtain the rate parameter ( $K_p$ ) of the intraparticle diffusion and further reckoned that intraparticle diffusion is the operative mechanism influencing the process of sorption though, some resistance is experienced by the sorbate molecules due to diffusion through the surface film (boundary layer) and a majority of fluoride uptake occurs rapidly by external mass transfer.

### **Interruption Studies**

To further delineate the type of sorption i.e. film diffusion or pore diffusion, studies like interruption in contact between the sorbate and sorbent (interruption studies) was conducted. Gamma Alumina exhibited a significant enhancement in sorptive uptake of 36.5 mg/g (77%) after interruption. The enhancement in sorption after recontact is perhaps due to migration of sorbate molecules into the inner pore surfaces, thus vacating and there by making available these sites for sorption. This phenomenon clearly indicates that pore diffusion is taking place which is in agreement and further validate kinetic data which corroborate pore diffusion to be rate limiting.

## **Desorption and Regeneration Studies**

An adsorbent would be cost and energy effective if it can be reused. This is possible if the sorbent surface could be renewed or regenerated by desorbing the sorbed sorbate. Desorption experiments were conducted by suspending air dried sorbents in distilled water, 0.1N HCl, 0.1N NaOH and 1% alum solution respectively. It follows from these results that 1% alum solution is a better regenerant. Further, cyclic regeneration studies were conducted to find capacity loss in each cycle and overall loss of sorption capacity. Cyclic loading (sorption) and unloading (desorption/regeneration) studies were conducted with 1% alum solution for ten cycles and the results are analysed. The analysis indicated that the sorbent can be used effectively regenerated eight to nine times with amount adsorbed remaining fairly constant following each regeneration.

## **Influence of Chemical Parameters**

Fluoride in water occurs in association with several other chemical constituents and therefore removal of fluoride from water by adsorption depends on their interaction with the sorbate, sorbent and the solute. Some parameters that are of importance from engineering perspective are pH, presence of other ions (both anions and cations) and their combined effect.

### **pH of Water**

The pH of ground water though seldom is found too acidic or too alkaline. However, for a better understanding of the mechanism of fluoride uptake, sorptive uptake was investigated at pH varying from 3 to 11. As pH is increased from 3.0 to 4.0 removal increases from 84% to 98% and remains fairly constant upto pH 7.0 and gradually decreases to 83% at pH 10.0 and reduces to 64% at 11.0. The results indicate the usefulness of the sorbent over a wide range of pH that is normally encountered in real field conditions.

### **Effect of Other Ions**

Test fluoride solution was spiked with anions like sulphates, chlorides, carbonates and bicarbonates at concentrations midway between permissible limits and tolerance limits stipulated for drinking water (BIS 10500) and subjected to equilibrium sorption studies. From the results it is observed that the presence of anions, in general, has a negative influence on sorptive uptake of fluoride by gamma Alumina. The order of effect of anions on uptake of fluoride by gamma alumina, in general is carbonates > bicarbonates > sulphates > chlorides.

## Combined Effect of Other Ions

Ground waters contain a variety of anions, cations and other aggregate compounds in addition to fluoride. Therefore, to simulate real field water, local ground water was spiked with fluoride and subjected to equilibrium adsorption studies. The results of studies indicate that presence of other ions and aggregate compounds reduced sorptive uptake of fluoride considerably perhaps due to their combined effects.

## CONCLUSIONS

The present study involved investigation for fluoride uptake capacity of high purity Gamma alumina. The results have indicated high potential of the sorbent under study for fluoride sorption from synthetic solution. Some of the significant conclusions that may be drawn from the present study are:

- Batch sorption kinetics indicates considerable instantaneous removal within a few minutes of contact and is followed by a relatively slow up take till complete removal or saturation.
- Isothermal equilibrium sorption data suggest that sorption reaction follows the BET isotherm model involving multiplayer sorption. Desorption with distilled water and regeneration by 1% alum solution indicate strong sorbent-sorbate bonding and the sorption reaction to be of the type chemisorption.
- The fluoride uptake by gamma alumina initially increased with increase in pH from 3.0 to 4.0 removal increases from 84% to 98% and remains fairly constant upto pH 7.0. The results indicate the usefulness of the sorbent over a wide range of pH that is normally encountered in real field conditions.
- The presence of anions, in general, has a negative influence on sorptive uptake of fluoride by gamma Alumina. The order of effect of anions on uptake of fluoride by gamma alumina, in general is carbonates > bicarbonates > sulphates > chlorides.
- The results of studies indicate that presence of other ions and aggregate compounds reduced sorptive uptake of fluoride considerably perhaps due to their combined effects. This needs further investigation to eliminate the effect of carbonates in the tap water.
- Results of cyclic regeneration with alum indicated the potential usefulness of the sorbent for nearly 10 cycles without significant loss of sorption capacity.

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