Investigation of Optimum Operating Parameters for Removal of Fluoride Using Naturally Available Geomaterial

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Abstract— **Drinking water is often the main source of fluoride intake by humans, especially in areas where their concentrations in groundwater and/or surface water is high. Endemic fluorosis is present in at least 20 states of India, affecting more than 65 million people including 6 million children. Fluoride ion (F) concentrations in India's groundwater vary widely, ranging from 0.01 mg/L to 48 mg/L. Defluoridation of ground water and supply of safe drinking water is the only immediate solution to this problem. The present investigation is an attempt towards a feasible solution. Batch adsorption studies were undertaken to assess the suitability of naturally available Bauxite as a geomaterial 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 1.8g/50mL, equilibrium was achieved in 90 minutes and enhanced adsorption was obtained at pH 6. Maximum fluoride removal was observed to be 94% at optimum conditions. Freundlich, Langmuir as well as Tempkin isotherms were plotted and kinetic constants were determined.**

Keywords— Adsorption, Bauxite, Fluoride, Freundlich isotherm, Langmuir isotherm, Tempkin isotherm.

I. INTRODUCTION

Water is frequently referred to as a universal solvent, because it has the ability to dissolve almost all substance; that comes in its contact. Some elements are essential in trace amount for human being while higher concentration of the same can cause toxic effects. Fluoride is one of them. Due to rapid urbanization and growth of modern industries (anthropogenic source of fluoride) as well as geo chemical dissolution of fluoride bearing minerals (natural source of fluoride), fluoride concentration is increasing in the environment including water resources.

The high concentration of fluoride in the drinking water leads to destruction of enamel of teeth and causes a number of conditions referred to collectively as fluorosis. The problem of high fluoride in groundwater has now become one of the most important toxicological and geo environmental issues in India. During the last three decades high fluoride concentration in water resources resulting in the disease called "Fluorosis" is being highlighted considerably throughout the world. Over the years rapid strides have been made in India to mould the availability of water to match country's manifold potable water demand. It is a conclusive fact that concentration between 0.6 to1.2 mg/L is essential to protect teeth decay, while higher concentration (beyond 1.5 mg/L) can cause teeth mottling and still higher concentration of fluoride may lead to different major health hazards.

Fluorosis has attained an alarming dimension all over the world. It is wide spread in certain developing countries like Kenya, China, Algeria, Argentina, Morocco, Senegal, Turkey and Thailand and also in developed countries like Japan and USA. In India, one of the serious health problems is prevalence of fluorosis. A report published by Rajiv Gandhi National Drinking Water Mission in 1983 identified 15 states including Delhi as endemic for fluorosis. Presently, 17 states which are endemic for fluorosis are: Andhra Pradesh, Karnataka, Tamil Nadu, Haryana, Maharashtra, Gujarat, Rajasthan, Kerala, J&K, Himachal Pradesh and Chandigarh states are also affected by fluorosis. The report states that an estimated 62 million people in India are affected with dental, skeleton /non skeleton fluorosis.

Human beings have been suffering fluorosis since ages. However, the cause of this disease is intake of high content of fluoride was ascertained only a few decades ago. Problem is increasing day by day as fluoride level is gradually getting higher than the prescribed maximum desirable limits. The fluoride level in water in India ranges from 2-29 ppm, where as the permissible level in drinking water according to WHO standard is 1.0-1.5 ppm. High incidence of endemic fluorosis in India is due to fact that large area of the country's water supplies is having high level of fluoride. In tropical countries, skeletal fluorosis occurs even with drinking low level of fluoride. Epidemiological observation revealed that nutritional status might influence chronic fluoride toxicity.

People are consuming fluoride in water up to 18 mg/l. It is easily absorbed by the body from contaminated drinking water. After absorption, fluoride ion is quickly distributed throughout the body, easily crossing the membranes and going into tissues. It accumulates in body due to high reactivity of fluoride ion with calcium of teeth and bones. It forms calcium fluorophosphates crystal and leaves unbound calcium in the

same tissue, which gets calcified and in turn results in stiffness of tissues and joints. This finally leads to skeletal fluorosis in later stage. That's why fluoride is called as bone seeking mineral and bones as sink for fluoride. About 90% of the fluoride retrieved in body is associated with calcified tissues.

A several conventional and advanced technique based on the various mechanisms like precipitation, membrane filtration, ion exchange and adsorption of fluoride removal are plasticized worldwide, but the major issues related to these techniques are their cost, applicable for large scale treatment plants, post treatment by product and their disposal problems and other unnoticed drawbacks leading to environmental issues. So there is stern need to find alternate treatment options, which provide hassle free application at rural level of developing countries.

Different types of adsorbents are used for removal of fluoride from water. Researches were carried on different adsorbents such as, fly ash, red mud, zeolite, laterite, bone char, bentonite, activated alumina, activated carbon etc.

This present study deals with adsorption of fluoride on bauxite. Batch study were conducted to evaluate the feasibility of fluoride removal under the varying condition and also to examine the applicability of adsorption isotherms to fluoride removal on bauxite.

II. MATERIALS AND METHODOLOGY

A. Materials

The adsorbent used in this study was bauxite that was collected from Rawmin mining and industries Pvt.Ltd.Kolhapur in Maharashtra. It was washed several times to remove earthy matter, it was then air dried and ground manually to obtain desired particle sizes using different particle molecular sieves, namely 0.3mm, 0.3-0.5mm, 0.5-1.0mm, 1.0-1.4mm, 1.4-2.0mm. FTIR spectra of bauxite were obtained using ABB Bomem Fourier Transform Infrared Spectrometer FTIR 8400.

B. Preparation of synthetis fluoride solution and reagent

The synthetic fluoride solution and reagents are freshly prepared adopting the standard method of preparation prescribed by APHA [1]. The stock solution of 100 mgL^{-1} fluoride was prepared by dissolving 221 mg of anhydrous NaF in 1 L of distilled water. This 1 ml of solution has 0.1mg of fluoride. Fluoride standard solution was prepared by diluting 100 ml of stock solution to 1000 ml distilled water. Test solution of 3, 5,7,10 mg L^{-1} F^{-} was prepared from fresh stock solution. A calibration curve was prepared using standard solutions. SPAND solution is prepared by dissolving 958mg of SPAND in 500ml of distilled water.

C. Batch study

Batch experiments were performed for the determination of equilibrium time and selection of an isotherm. All the experiments were carried out in 100 mL glass jar with 50 mL test solution at room temperature (29±2°C). The jar, along with known volume of test solution of fixed concentration and 1.0 g of the adsorbent at neutral pH, was shaken in mechanical stirrer at 400 rpm to study the equilibration time for maximum adsorption of fluoride and to know the kinetics of adsorption process

The batch study was performed to determine the optimum condition and to study the effect of pH, adsorbent dose stirring rate, contact time and initial fluoride concentration on the test solution. The effect of pH on fluoride was studied by adjusting the pH of test solution using 0.5N HNO$_3$ or 0.1N NaOH on fixed quantity of adsorbent, while effect of adsorbent dose, stirring rate, contact time and initial fluoride concentration was studied by varying dose, stirring rate, contact time and initial fluoride concentration respectively. At the end of the desired contact time, the sample was filtered using Whatman no. 42 filter paper and the filtrate was analyzed for residual fluoride concentration by SPADNS method, spectrophotometrically.

(UV-VIS spectrophotometer: Model No.SL Elico, UV 210) at the wavelength of 570 nm described in the standard methods of examination of water and wastewater.

The percent removal of the fluoride was calculated as follow:

$$\% \text{ Removal} = \frac{Ci - Ce}{Ci} \times 100$$

Where, C$_i$ is the initial fluoride concentration (mg/l), C$_e$ is the equilibrium concentration of fluoride solution (mg/l).

III. 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 effect of pH, adsorbent dose, stirring rate, contact time and initial fluoride concentration 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 ^{o} C).

A. 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, 8 and 10 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 10 mg/L of fluoride solution for contact time of 60 min with a dose of 1.0 g/50 mL of bauxite. 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 87 % is achieved at pH 6. A decrease in the extent of removal of fluoride ions was observed at pH 2 and pH 10 of the solution. Therefore the pH which gave maximum fluoride removal was taken into the consideration for further studies. probable reason for low adsorption at pH 2 could be explained by the greater tendency of the fluoride to form aqueous protonated fluoride: thus, reducing the concentration of free fluoride available for precipitation with the Al^{3-} of the

gibbsite or adsorption into kaolinite layer structure through exchange with OH⁻, At high pH, the lower efficiency could be due to both Le Chatelier's principle and competitions. OH⁻ and F⁻ are isoelectronic with same charge and ionic radii. Higher the concentration of OH⁻, the more difficult it is for OH⁻ already attached to Al^{3-} to be replaced by F⁻ and go into solution.
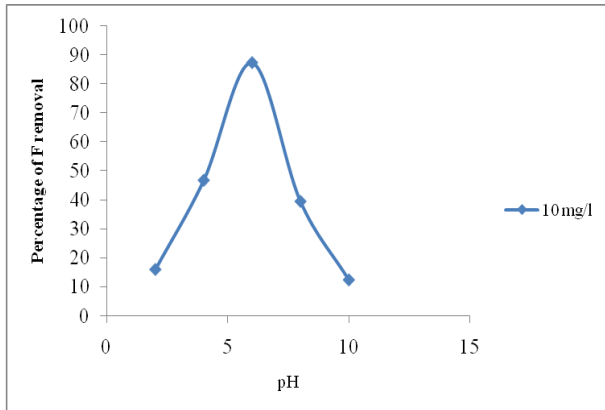

Fig. 1. Effect of pH on fluoride removal

B. Effect of adsorbent dose

Studies on effect of adsorbent doses were conducted by varying adsorbent doses between 0.2 to 2.4 g/50 mL. The pH was maintained at 6, while initial fluoride ion concentration was fixed at 10 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 bauxite was efficient for 69.99 % removal of fluoride ions at the lowest dose of 0.2 g/50 mL and 91.86 % at maximum dose of 2.4 g/50 mL respectively, at room temperature of 29 ± 0.5°C. There was found less significant fluoride ion removal after applying dose of 1.8 g/50 mL and hence this dose was selected for further studies.

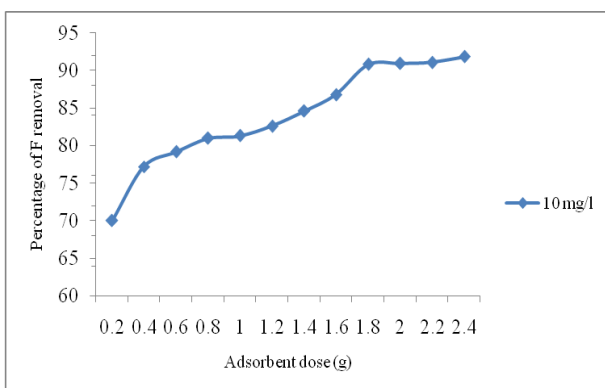Fig. 2. Effect of Adsorbent dose (g) on fluoride removal

C. Effect of stirring rate

Studies on the effect of stirring rate were conducted by varying speeds from 50 to 400 rpm, at optimum pH of 6 with adsorbent dose of 1.8 g/50 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.

The removal is 67.5% at 50 rpm and attains 79.9% at 400 rpm. The percentage adsorption is less at lower stirring rate and increases with the stirring rate up to 300 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 300 rpm does not show any significant increase and hence stirring rate of 300 rpm was considered for further study.
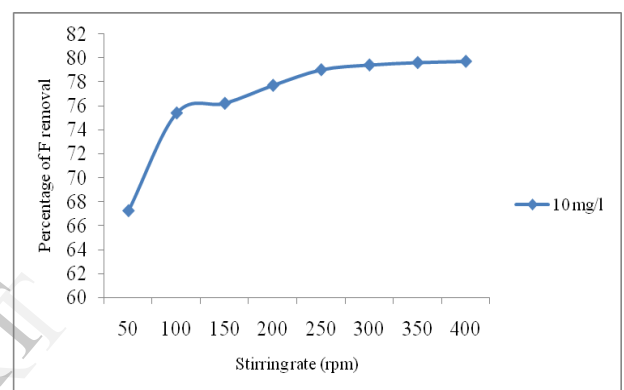

Fig. 3. Effect of Stirring rate on fluoride removal

D. Effect of contact time

Contact time plays a very important role in adsorption dynamics. The effect of contact time on adsorption of fluoride onto bauxite is shown in Fig.4. Batch adsorption studies using the concentrations 3.0, 5.0, 7.0 and 10.0 mg/L of fluoride solution and with 1.8g/50 mL of the adsorbent at pH of 6 with particle size of 0.3-0.5mm were carried out at constant stirring rate of 300 rpm.

Referring to the Fig. 4. Shows progression of adsorption reaction and the percentage removal of fluoride for different contact times. It is found that at each concentration, there is an increase in the percentage of fluoride removal 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. All the curves have similar shapes, only differing in the extent of adsorption. With the increase in fluoride concentration from 3

to 10mg/l the percentage of fluoride removal decreases from 93.8-83.6% and curve gradually attains equilibrium after 90min. As there was no significant increase in % fluoride removal after 90 minutes, so equilibrium time of 90 minutes was chosen and this was employed in all subsequent experiment.

E. Effect of initial fluoride concentration

Studies on the effect of initial fluoride concentration were conducted by varying it from 3 to 15 mg/L keeping adsorbent dose of 1.8 g/50 mL, pH of 6, stirring rate of 300 rpm and contact time of 90 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 96.2% at 3 mg/L and 78.22% at 15 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.
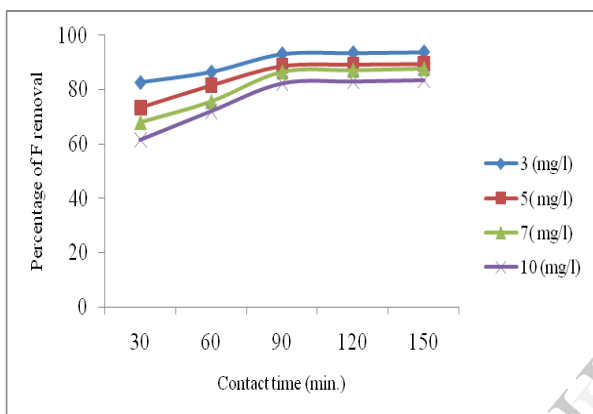
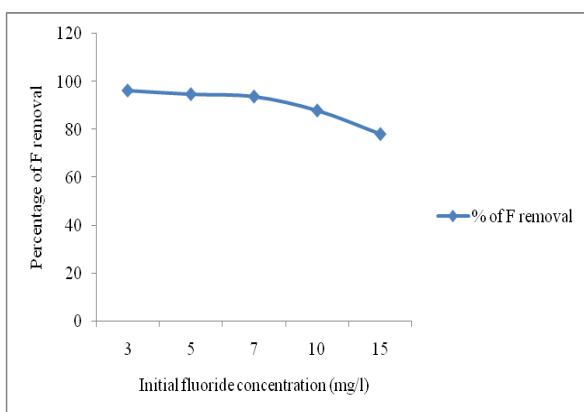

Fig. 4. Effect of Contact time (min.) on fluoride removal

Fig. 5. Effect of Initial fluoride conc. on fluoride removal

F. Sorption mechanism

Adsorption isotherm helps in determining the feasibility of bauxite for treating fluoride ion in water. Freundlich, Langmuir and Tempkin isotherms were plotted to provide deep insight to the adsorption of fluoride on bauxite. The isotherm not only provides the general idea of the effectiveness of the bauxite in removing fluorides, but also

indicates the maximum amount of fluoride ions that will be adsorbed by the bauxite. 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. Freundlich Isotherm: The general form of Freundlich isotherm is given in the following equation.

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

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

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

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) and K_f and $1/n$ are the Freundlich constants.

As shown in Fig. 6, Freundlich isotherm was plotted with log q_e vs. log C_e From the graph, the value of K_f is 0.2202 and $1/n = 1.470$, and thus, Freundlich isotherm is-

$$q_e = 0.2202 * C_e^{1.470}$$

A smaller value of $1/n$ points out a better adsorption mechanism and formation of relatively stronger bond between adsorbate and adsorbent. If $1/n < 1$, bond energies with surface density, if $1/n > 1$, bond decreases with surface density and if $1/n = 1$ all surface sites are open in order to generate the equilibrium data C_e (mg/L). The different adsorbent doses are applied to confirm the applicability of Freundlich isotherm.

Langmuir Isotherm: Langmuir isotherm is based on the assumption that point of valance exists on the surface of the adsorbent and that each of these site is capable of adsorbing one molecule. It is assumed that the adsorption sites have equal affinities for molecules of adsorbate and that the presence of adsorbed molecules at one site will not affect the adsorption of molecules at an adjacent site.
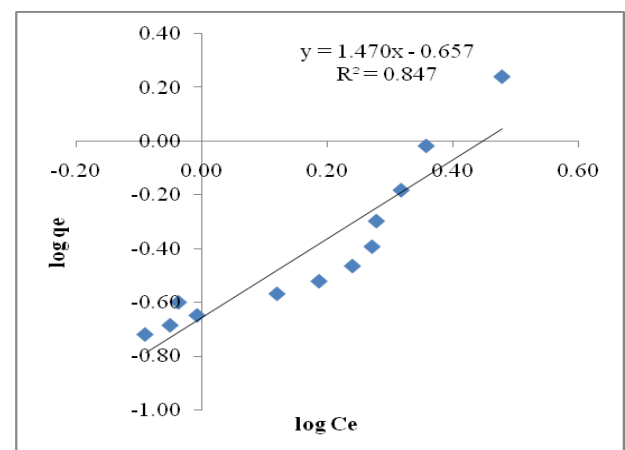

Fig. 6. Freundlich Isotherm

The Langmuir equation is commonly written as:

$$qe = abCe/(1 + bCe)$$

The linear form of Langmuir isotherm can be expressed as:

$$1/qe = (1/a) + (1/abCe)$$

Where, q_e is the amount adsorbed (mg/g) and 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 and 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 2.368 and 0.09 respectively. Thus, the Langmuir equation for defluoridation using bauxite becomes
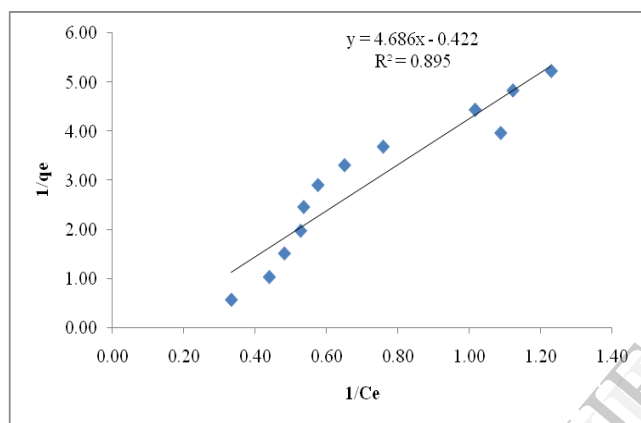
$$qe = 0.2132Ce/(1 - 0.09Ce)$$

Fig. 7. Langmuir Isotherm

Tempkin isotherm: The Tempkin isotherm contains a factor that explicitly takes in account adsorbing species-adsorbate interactions. This isotherm assumes that (i) the heat of adsorption of all molecules in the layer decreases with coverage due to adsorbate-adsorbent interaction, and (ii) adsorption is characterized by a uniform distribution of binding energies, up to some maximum binding energy. The Tempkin isotherm is represented by the following equation:
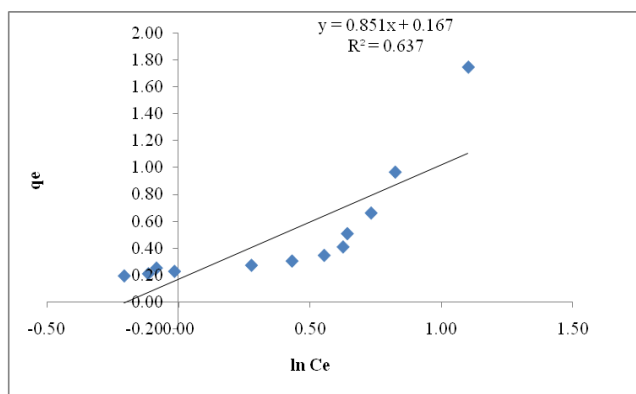

Fig. 8. Tempkin Isotherm

$$q_e = RT/b \ln(K_T C_e)$$

The linear form of the Tempkin isotherm is expressed as follows.

$$q_e = B_1 \ln K_T + B_1 \ln C_e$$

Where, $B_1 = RT/b$

Where, q_e and c_e have the same meaning as noted previously and the other parameters are called the Temkin constants. R universal gas constant (8.314 J mol^{-1} K^{-1}), T is temperature in (K). The plot of q_e versus log c_e will generate a straight line shown in fig. 8. The Temkin constants B_1 and K_T can be calculated from the slope and intercept of the linear plot.

Thus, the Tempkin equation for defluoridation using bauxite becomes

$$q_e = 0.851 \ln (1.2167C_e)$$

IV. CONCLUSION

Based on these studies, it is concluded that bauxite can be fruitfully utilized for the removal of fluoride. This suggests that raw bauxite can be used for defluoridation to treat water in high fluoride areas. The high defluoridation capacity of bauxite is attributable to gibbsite and kaolinite minerals. Precipitation of AlF_3 is thus predicted to be the fluoride removal mechanism with the gibbsite while exchange of OH groups in the gibbsite layer of the kaolinite with F$^-$ ions occurs in the kaolinite component of the defluoridation material.

The uptake of fluoride ions is possible between pH of 4.0 and 8.0; however, pH of 6 gives maximum fluoride removal. The percentage of fluoride removal was found to be a function of adsorbent dose and only increase defluoridation efficiency up to a dose of 1.8 g/50 ml at a given initial solute concentration. The percentage of fluoride removal was found to be increased with increase in 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 bauxite reveals that the equilibrium data fits better to Langmuir isotherm than Freundlich and Tempkin isotherm.

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