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Removal of fluoride from drinking water by adsorption onto Activated Alumina and activated carbon.

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Abstract
The ability of activated alumina and activated carbon to remove Fluoride from aqueous solution has been investigated. The studies were carried out as functions of contact time, concentration and pH. The data indicate that activated alumina surface sites are heterogeneous in nature and that fits into a heterogeneous site binding model. The optimum pH for complete removal of Fluoride from aqueous solution were described. The rate of fluoride removal was rapid during several time intervals of time, and equilibrium was attained were described in detailed.

Key words: Defluoridation, Activated alumina, Activated carbon.

1. Introduction

Fluoride is a naturally occurring element in minerals, geochemical deposits and natural water systems and enters food chains through either drinking water or eating plants and cereals. Fluorine and its compounds are valuable and extensively used in industry such as production of high purity graphite, fertilizers, electrolysis of alumina, semiconductors, etc. Fluoride is beneficial in human body for the calcification of dental enamel and maintenance of healthy bones when present within the permissible limit. But when fluoride is present in excess of 1.5 mg/l, it causes molting of teeth and lesion of endocrine glands, thyroid, liver and other organs [1, 2]. Fluoride pollution has been observed in several minerals and chemical processes and in natural water systems over several regions like Asia, Africa, America, Europe, where the fluoride concentration can range from 0.01 to 3 mg/l in fresh water and 1–35 mg/l in ground water [3]. Due to high toxicity of fluoride to mankind, there is an urgent need to treat fluoride-contaminated drinking water to make it safe for human consumption.Adsorption [4, 5], ion exchange [6], precipitation [7] and electrodialysis [8] are named to be the most commonly used methods for the defluoridation of water. Among these methods, adsorption is the most widely used method for the removal of fluoride from water. Several techniques have been developed for removal of fluoride from drinking water by adsorption and precipitation processes.

Activated alumina [9], amorphous alumina [10], activated carbon [11], low-cost adsorbents such as calcite, clay charcoal, tree bark, saw dust, rice husk, ground nut husk [4, 5, 12–13] and rare earth oxides are found to be different materials that are used for defluoridation. However, limit for fluoride removal by most of them is greater than 2 mg/l so that they are not considered for the drinking water. The most important factors influencing adsorption are pH of water and the adsorbent.

The main objective of this investigation is to study the removal of fluoride from drinking water using activated alumina and activated carbon. The removal tests were carried out by varying contact times, at different pH, adsorbent dosage and fluoride concentration in water.

2. Materials

The ground water samples collected from Choutuppal, Nalgonda district, Telangana, contain about 8 ppm of fluoride concentration. In the process of evaluating the percentage of fluoride removal from the water samples, several chemicals and additives are used. Most of the chemicals used in this research work have been purchased from Sigma-Aldrich, Bangalore, India. Spadn's reagent and Zirconium chloride are the main reagents used in this study. The stock solutions were prepared by dissolving anhydrous NaF in distilled water.

3. Experimental Methodology

Activated carbon used for the tests was purchased from Sigma-Aldrich. Synthetic fluoride solutions were used for the adsorption experiments. Standard solution of 0.01 M sodium fluoride was prepared in de mineralized water and diluted to exactly 8 mg/L. A known amount of industrial grade activated carbon and fluoride solution were taken in a 100-mL stopper conical flask. The final volume was

made up to 50 mL with deionized water. It was uniformly agitated at constant speed in a thermostatic water bath at the designated temperature over a period of time and filtered on a Whatman No. 42 filter paper. The concentration of fluoride in the filtrate was determined by SPADNS method and the percentage of fluoride removed was calculated from the ratio of fluoride taken and that remaining in the solution. Alumina used for the tests was purchased from Sigma-Aldrich. Synthetic fluoride solutions were used for the adsorption experiments. Standard solution of 0.01 M sodium fluoride was prepared in de mineralized water and diluted to exactly 8 mg/L. A known amount of industrial grade alumina and fluoride solution were taken in a 100-mL stopper conical flask. The final volume was made up to 50mL with deionized water. Uniformly agitated at constant speed in a thermostatic water bath at the designated temperature over a period of time and filtered on a Whatman No. 42 filter paper. The concentration of fluoride in the filtrate was determined by SPADNS method and the percentage of fluoride removed was calculated from the ratio of fluoride taken and that remaining in the solution.

Only analytical chemicals were used. All spectrophotometric measurements were made on Chemito 2500UV-Visible Spectropho-tometer using quartz cells of 10-nm. The pH of the solutions at the beginning and end of the experiments were measured, and the average values were reported. All pH measurements were made by an Elico Digital pH meter (model L1 120) using a combined glass electrode (model CL 51). The pH meter was calibrated with Orian Standard buffers before any measurement. The amount of fluoride removed during the process was monitored by using UV-Visible Spectrophotometer (Analytic Jena SPEKOL 1200) at variable periods of time

The experimental parameters examined were fluoride concentration, dosage of industrial grade alum, and pH.

4. Results and Discussion

4.1.Defluoridation using activated carbon

As already stated, the adsorption techniques are the best for effective defluoridation of contaminated water as they are cheap in operational cost. Carbon is also a natural resource available at all times to apply over industrial scales. The activated carbon has widespread industrial and domestic applications. The carbon was dried at 60^{o}C for 24 h. The sample was further sieved to 100 mm particle size and stored in airtight containers until further use.

The process of defluoridation is affected by several parameters like concentration, pH, dosage and reaction time. The following results illustrate the impact of all these reactive parameters to defluoridation process using carbon.

Removal of fluoride as a function of dosage (industrial grade alum) is shown below.

4.1.1.Effect of Dosage and Time

The variations in fluoride removal percentage with respect to time was shown in Fig. 1. It was clear that with a fixed amount of carbon, the amount of fluoride decreases with time. The changes or the increments in the amount of carbon used did not effect the fluoride removal (i.e., the amount of fluoride adsorbed per gram of carbon). Optimal defluoridation was observed at 40 min of time. The effect of dosage over defluoridation was evaluated at different dosage levels of carbon .i.e starting from 2 g/L, several dosages like 3, 4, 5 g/L were also tested for their defluoridation capability.

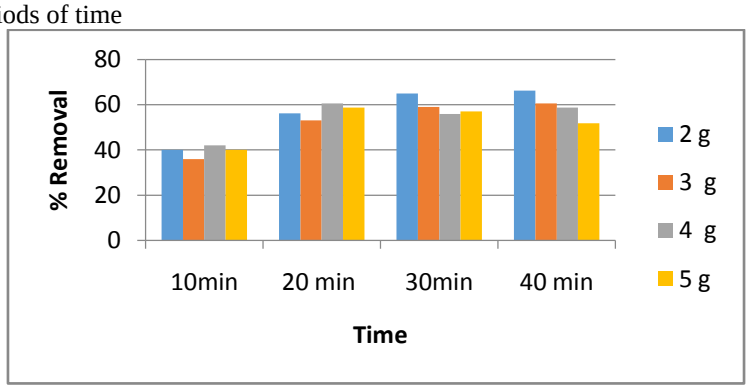

Fig.1.Effect of dosage and time on defluoridation using carbon

From the above Fig.1. it was clear that the extent of defluoridation increased with time, i.e. starting from 10 min of time the amount of defluoridation increased to 20 min and then to 30 min and 40 min. The optimal removal was observed at 40 min of time. The experiments were carried out over several dosage levels starting from 2g/L. It was clear that the best defluoridation was observed with a dosage of 2g/L of carbon.

For an initial carbon dosage of 2 g/L the defluoridation was found to be 40%, 56 %, 65%, 66% and 88% at respective times of 10 min, 20 min, 30 min and at 40 min periods. In the case of 3 g/L dosage, the extent of defluoridation was found to be

36%, 53%, 59% and 60 % of respective time periods. At an initial dosage of 4 g/L of carbon, the results were very interesting and noticeable as the extent of defluoridation was found to be 46%, 60%, 56% and 58%, respectively, at 10, 20, 30 and 40 min time periods. In case of 5g/L, dosage the results were quite miserable as the extent of defluoridation was found to be 40 %, 58%, 57% and 51%, respectively, at 10, 20, 30 and 40 min of time.

4.1.2.Effect of pH on defluoridation using activated carbon

As already illustrated, the pH of the solution strongly impacts the extent of adsorption of anions. So it was required to establish the impact of pH on the extent of defluoridation. Hence the removal of fluoride was studied at different pH values ranging from 5 to 9. The results are presented in Fig.2, The maximum removal was observed at a pH value of 7.

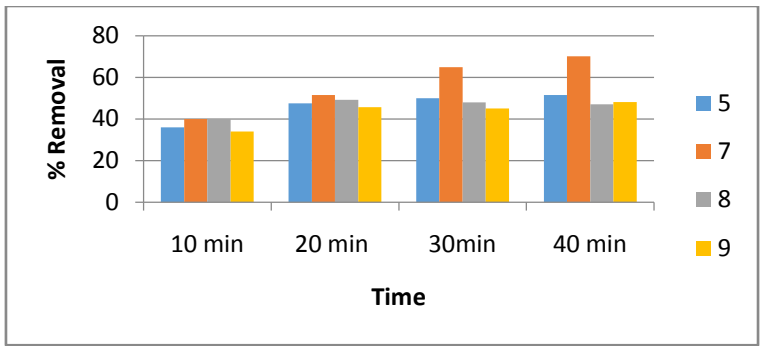

Fig. 2. Effect of pH on defluoridation using activated carbon

From the above results it was clear that maximum defluoridation was obtained in 40 min of time. Defluoridation was strongly impacted by the pH of the solution even after using the activated carbon as the adsorbent. Experiments were carried out at various pH levels from 5 to 7, 8 and 9. At an initial pH at 5, the extent of defluoridation was found to be about 36%, 47%, 50% and 51%, respectively, at 10, 20, 30, 40 min of reaction time. At an initial pH of 7 the extent of defluridation was found to be 40%, 51%, 65% and 70%, respectively, at 10, 20, 30 and 40 min of time. At an initial pH of 8, the extent of defluoridation at different intervals of time was found to be about 40%, 49%, 48% and 47%, respectively, at 10, 20, 30, 40 min of reaction time. When the pH of the medium was 9 the extent of defluridation was found to be 34%, 45%, 45% and 48 %, respectively, at of 10, 20, 30 and 40 min of time.

4.1.3.Effect of fluoride Concentration on defluoridation using Activated carbon

Several parameters influenced the defluoridation process, but the amount of fluoride present in water has always been the key parameter since most of the methodologies have their limitations in defluoridationat various fluoride concentrations. The experiments were carried out at different fluoride concentration levels from 2 ppm to 10 ppm levels. The following Fig.3. give a brief illustration of the impact of fluoride concentration over alum dosage.

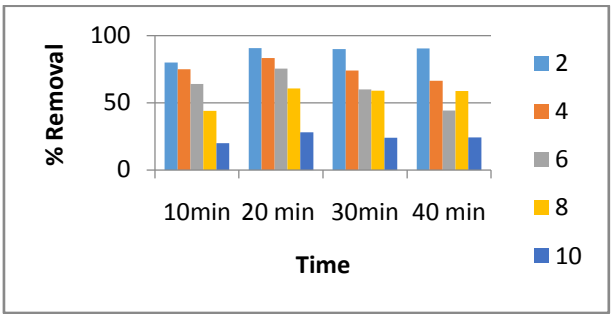

Fig.3. The effect of fluoride concentration over defluoridation

From the above Fig.3. it was clear that optimal defluoridation was observed at a dosage of 2g/L and at about 40 min of time at 2 ppm of fluoride in water. However, this particular dosage showed different percentages of removal of fluoride at different time periods. To evaluate the efficiency of this methodology the dosage of 2g/L was selected and it showed different defluoridation contents at different periods of time.

At an initial fluoride concentration of 2 ppm, defluoridation was found to be about 80%, 90%, 90% and 91% respectively at 10, 20, 30 and 40 min of reaction time. However, at an initial fluoride concentration of 4 ppm, defluoridation was observed to be about 75%, 83%, 74% and 66%, respectively, at 10, 20, 30 and 40 min of reaction time. In case of initial fluoride concentration 6 ppm, defluoridation was about 64%, 75%, 60% and 44%, respectively, at 10, 20, 30 and 40 min of reaction time. In the case of

initial fluoride concentration of 8 ppm, defluoridation was found to be about 44%, 60%, 59% and 58%, respectively, at 10, 20, 30 and 40 min of reaction time. But at an initial fluoride concentration of 10 ppm, the defluoridation was found to be about 20%, 28%, 24% and 24%, respectively, at 10, 20, 30 and 40 min of reaction time.

4.2.Defluoridation using Activated alumina

From the above experimental results of the adsorption techniques it was clear that these methods were considered to be the best methods for effective defluoridation of contaminated water as they are cheap in operational cost. Neutral alumina can also be used as an adsorbent for defluoridation and the methodology is known as chemical coagulation technique. Alumina has great significance in various industrial applications. Alumina was found to have widespread industrial and domestic applications. It was oven dried at 60^{o}C for 24 h. The sample thus was further sieved to 200 mesh particle size and stored in airtight containers until further use.

As mentioned earlier, defluoridation was clearly effected by various reactive parameters like concentration, pH, dosage and reaction time. The impact of all these parameters towards defluoridation was studied with the following results.

4.2.1.Effect of Dosage and Time

The relationship between the alumina dosage and time, and fluoride removal was shown in Fig. 4. It was clear that with higher amounts of alumina dosage, the amount of fluoride decreases with time. Experiments were performed starting from an initial dosage of 1 g/L and later extended to various levels of 1.5, 2, 3, 4, 5 and 8 g/L dosages. Optimal defluoridation was observed at 40 min of time.The following table represents the impact of reaction time and dosage on the defluoridation process. It was clear from the results that the extent of defluoridation increased with the increase in the alumina dosage. Right from 1 g/L initial dosage defluoridation increased at 1.5 g/L and later it increased to 2,3,4,5 and 8g/L dosages.

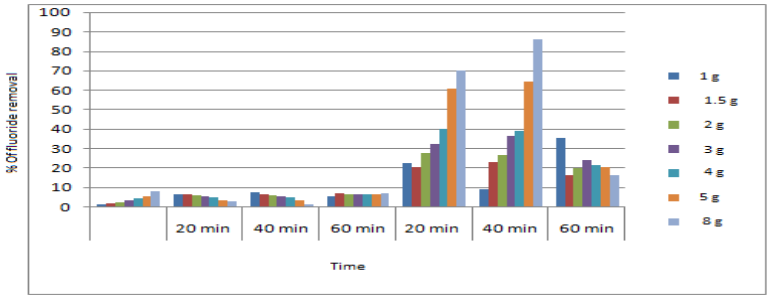

Fig. 4. Effect of dosage and time on defluoridation using alumina

From the above Fig. 4. it was clear that the extent of defluoridation increased with time, i.e. starting from 10 min of time the amount of defluoridation increased to 20 min and then to 30 min and 40 min as in case of activated carbon. The optimal removal was observed at 40 min of time. The experiments were carried out over several dosage levels starting with 1g/L. From an initial carbon dosage of 1 g/L the defluoridation was found to be 22%, 8 % and 35% at 20 min, 40 min and 60 min of time. In the case of 1.5 g/L dosage the extent of defluoridation was found to be 20 %, 23%, 16 % at respective time periods.

At an initial dosage of 2 g/L of alumina, the extent of defluoridation was found to be 27%, 26% and 19%, respectively, at 20, 40 and 60 min time periods. In the case of 3g/L dosage the extent of defluoridation was found to be 32 %, 36 % and 23%, respectively, at 20, 40 and 60 min of time. At 4g/L of initial dosage, the defluoridation levels were found to be 39%, 38% and 21%, respectively, at 20, 40 and 60 min time lags. At 5g/L of initial dosage the defluoridation levels were found to be 60%, 64% and 20% respectively at 20, 40 and 60 min time lags. And in case of a dosage of 8g/L the results are very interesting and they are noticed to show a defluoridation of 70%, 86% and 16%, respectively, at 20,40 and 60 min time, was observed.

4.2.2.Effect of pH on defluoridation using alumina:

PH of the medium strongly influenes the extent of defluoridation, so that the reliability of the individual methods has to be evaluated for affective defluoridation on various pH levels. Defluoridation was calculated at various pH levels starting with 4, and applied over several solutions containing pH values of 5,6 and 8. The strength of the hydroxide ions that increased in the medium, effected defluoridation as the ions acted strongly in competition with the fluoride. The results are presented in Figure.5.

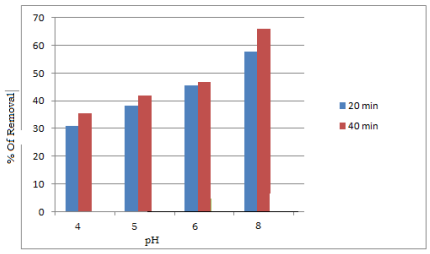

Fig.5. Effect of pH on defluoridation using alumina

From the above results it was clear that maximum defluoridation was obtained at 40 min of time. Defluoridation was strongly impacted by the pH of the solution. Experiments were carried out at various pH levels starting with 4 and then with 5, 6 and 8. At an initial pH of 4, the extent of defluoridation was found to be about 31% and 35%, respectively, at 20 and 40 min of reaction time. At an initial pH of 5 the extent of defluridation was found to be 38 % and 42%, respectively, at 20 and 40 min of time. At an initial pH of 6, the extent of defluoridation at different time intervals of time was found to be about 45% and 46%, respectively, at 20 and 40 min of reaction time. When the pH of the medium was 8 the extent of defluridation was observed to be 58% and 66%, respectively, at 20 and 40 min of time.

4.2.3.Effect of fluoride concentration on defluoridation using alumina:

Several parameters that affected the defluoridation process were described in detail. Any defluoridation methodology must produce optimal results over different concentrated levels of fluoride containing aqueous waste, since the amount of fluoride present in water has always been the key parameter.

In order to avoid possible limitations, defluoridation methodology was effectively applied over several fluoride concentrations from 2, 4, 6, 8 and 10ppm levels of fluoride. The following Fig.6. provide a brief account of the results.

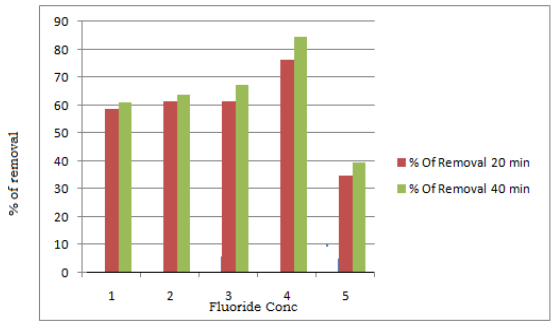

Fig. 6. The effect of fluoride concentration over defluoridation using alumina.

From the earlier experiments it was clear that the optimal removal was obtained at an initial dosage of 8 g/L of alumina. The concentrations of fluoride were recorded at a fluoride concentration of 2 ppm, the fluoride removal was 59% and 61%, respectively, at 20 and 40 min of time periods. When the initial fluoride concentration was 4 ppm, defluoridation was calculated as 61% and 64%, respectively, at 20 and 40 min of time. At an initial fluoride concentration of 6 ppm the extent of defluoridation was found to be 61 and 67%, respectively, at 20 min and 40 min. At 8 ppm of initial fluoride concentration the extent of removal was found to be 76% and 84%, respectively, at 20 and 40 min of time. At 10 ppm of fluoride concentration the effective defluoridation calculated to be 35% and 39%, respectively, at 20 and 40 min of time.

5. Conclusion

All the experiments were carried out using variable fluoride dosages, and optimal results were obtained at an initial fluoride concentration of 8 ppm. Optimal defluoridation was observed at 40 min, when the equilibrium was attained and after that no considerable defluoridation was observed. The best alum dosage for optimal defluoridation was found to be 8g/ liter and the higher the dosage the highest will be defluoridation. The optimal defluoridation was observed at an initial fluoride concentration of 8 ppm. The optimal pH condition for the best defluoridation was found to be 8. By activated carbon, optimal defluoridation was observed at 40 min, when the equilibrium was attained and after that no considerable defluoridation was observed. The best alum dosage for optimal defluoridation was found to be 2g/ liter and there was no use of increasing the dosage of carbon. Optimal defluoridation was observed at an initial fluoride concentration of 2 ppm. At higher fluoride concentrations this method was not found to be much effective for defluoridation. The optimal pH condition for defluoridation was found to be 7. The coexisting ions sulfate, nitrate and chloride highly impacts defluoridation process.

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