DEFLUORIDATION PROPERTIES OF ACTIVATED ALUMINA

G Karthikeyan', B V Apparao and S Meenakshi
India

SUMMARY: Laboratory studies were conducted to assess the chemical behaviour of activated alumina as a defluoridating material by the batch equilibration method. Defluoridation is found to require a minimum of 20 minutes contact time. The capacity is found to be between 3 mg/g in alkaline water and 20 mgF/g in acidic water. At pH 7, the defluoridation capacity was found to be 5.6 mg/g. The capacity decreases with increased bicarbonate concentration, but is found to be independent of the presence of other anions like chloride and sulphate. The saturated medium could be regenerated by 2 % hydrochloric acid, 2 % sodium hydroxide or 1 % sulphuric acid. The fluoride removal obeyed Langmuir's adsorption isotherm indicating that the forces of adsorption are governed by chemi-sorption.

Key words: Activated alumina; Alumina; Fluoride; Defluoridation capacity; Batch equilibration; Regeneration; Sorption mechanism.

INTRODUCTION

Defluoridation of water is one of the alternatives already adopted for provision of safe drinking water in some fluorotic areas. A large number of materials have been identified as potential defluoridating materials, functioning through ion exchange, adsorption and chemical processes. Each method has its limitations as well as its merits.

Activated alumina is one of the most popular and cost effective materials used for defluoridation of water.[1-6] However very little information is available about the chemical behaviour of activated alumina in the defluoridation process. This study is carried out to establish the dependence of various factors governing the defluoridation property of activated alumina. The effect of different parameters on the defluoridation capacity has been experimentally verified. Based on the results a plausible mechanism of the fluoride removal by activated alumina is proposed.

MATERIALS AND METHODS

Defluoridation experiments using activated alumina LR grade supplied by s.d. Fine Chemicals Pvt. Ltd., Boisar, India were carried out by batch equilibration method. Besides the determination of defluoridation capacity of activated alumina, the effect of the variables such as contact time, particle size and other parameters like pH, concentration of fluoride ion, temperature and the presence of chloride, sulphate and bicarbonate ions were experimentally verified.

The concentration of fluoride was measured using expandable ion analyser EA 920, the fluoride ion sensitive electrode 9409 and the reference electrode (all Orion USA make).[7] The pH measurements were done using an analog pH meter 324 of Systronics India make. The concentrations of chloride and bicarbonate ions were determined by the standard titrimetric method.[8] The concentration of sulphate ion was determined by turbidimetric method using Spectronic 20 spectrophotometer (Bausch and Lomb).[8]

* *Department of Chemistry, Grandhigam Rural Institute, Grandhigam 624 302, Tamil Nadu, India. E-mail: gricc@dindgul.tn.nic.in*

Regeneration experiments were carried out using regenerants like hydrochloric acid, sulphuric acid and sodium hydroxide.

Defluoridation capacity of activated alumina was calculated in mg F per g by dividing the amount of removed fluoride by the added amount of the medium.

The effect of contact period on the efficiency of activated alumina was determined by keeping the following parameters constant:

- The particle size
- pH at 7.0
- The fluoride ion concentration of raw water sample at 10 mg/L
- The concentration of chloride, sulphate, and bicarbonate ions as nil.

Activated alumina of different particle sizes were prepared using scientific test sieves of ELITE scientific instruments Co., Bombay. The experiments were conducted by keeping the concentration of fluoride at 10 mg/L, in the absence of chloride, sulphate, and bicarbonate ions. Temperature was retained at 30°C and the pH was maintained at 7. The effect of pH on the defluoridation capacity was determined at the following five pH levels viz., 3, 5, 7, 9, and 12. All weighings were carried out using a Mettler AE 240 electronic balance having an accuracy of 0.02 mg.

RESULTS AND DISCUSSION

Contact time, particle size and temperature. The defluoridation capacity of activated alumina reached saturation after a period of 20 minutes. That is, the minimum period of contact required for maximum defluoridation is 20 minutes. There is an increase in the defluoridation capacity with a decrease in the particle size as expected, since the process is governed by adsorption. The defluoridation capacity of activated alumina is independent of temperature.

Effect of fluoride and other ions. The adsorption of fluoride on activated alumina obeyed Langmuir's adsorption isotherm indicating that the forces of adsorption are governed by chemi-sorption.

Chloride and sulphate ions have very little effect on the fluoride removal capacity of activated alumina, whereas bicarbonate ions behave differently. Figure 1 shows the influence of bicarbonate ions. Activated alumina adsorbs bicarbonate ions also in addition to fluoride. The observed dependence of bicarbonate ions on the defluoridation capacity of the material is due to the specificity factor, which distinguishes between fluoride and other ions such as chloride and sulphate besides bicarbonate. The adsorption of anions by activated alumina takes place in the following order:

$$F^- >> OH^- >> HCO_3^- >>> Cl^- = SO_4^{2-}$$

Effect of pH. Figure 2 shows the marked dependence of pH on the defluoridation efficiency of the adsorbent. At pH 7, it has the defluoridation capacity of 5.6 mg F^-/g activated alumina which increased nearly four times to a value of 20.4 mg F^-/g at pH 3. It decreases to 3.0 mg F^-/g activated alumina at higher alkaline range. It is worth noticing the extremely high defluoridation capacity at pH 3, a property, which could make activated alumina a very promising material. The reasons for this marked influence of pH are discussed in detail in the later part of this paper.

Regeneration. Results of elution capacity using sulphuric acid, hydrochloric acid and sodium hydroxide indicate that 2 % hydrochloric acid, 2 % sodium hydroxide and 1 % sulphuric acid are good regenerants.

Defluoridation mechanism. Defluoridation by activated alumina is explained in terms of adsorption of fluoride ions at the activated alumina/solution interface. Stern model of the alumina/solution interface is shown in Figure 3 and the mechanism of adsorption by activated alumina is explained on the basis of the double layer theory.

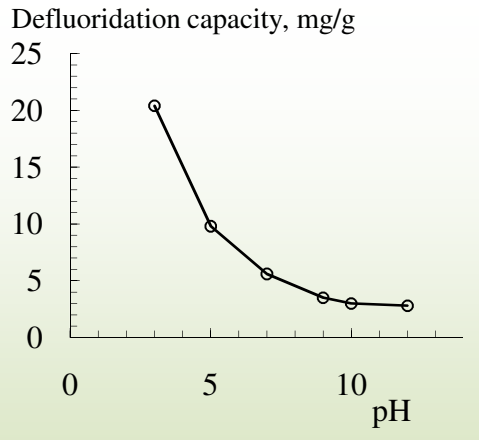

FIGURE 1. Defluoridation capacity of activated alumina at various pH values of the environment

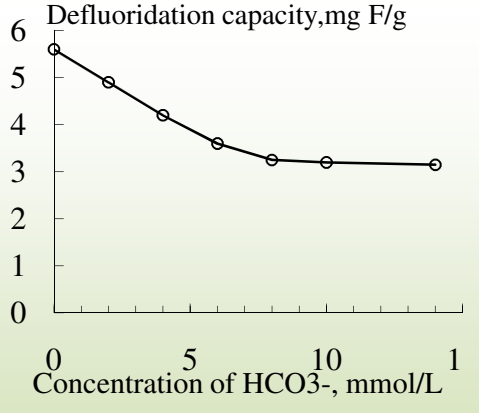

FIGURE 2. Defluoridation capacity of activated alumina at various concentration of bicarbonate ion.

The zero charge potential for activated alumina is at pH 9 and the surface charge of activated alumina may be controlled by the potential determining ion. The potential determining ion in this case is the hydrogen ion.[9,10] This means that when the concentration of hydrogen ion is greater, i.e. if the pH is less than 9, the alumina surface acquires a positive charge and this surface adsorbs negatively charged fluoride ions from the solution. Therefore at low pH range the positive charge on the surface of activated alumina increases and adsorption of fluoride becomes more pronounced.

Thus one type of the force responsible for adsorption of fluoride on activated alumina is certainly the columbic forces between the positively charged aluminium oxide and negatively charged fluoride ions. Nevertheless, the charge alone does not determine the adsorption process in the double layer. Another factor responsible is the specificity. This 'specificity' factor distinguishes between the fluoride and two ions, chloride and sulphate. The charged aluminium oxide favours fluoride ion and hence there is no adsorption of chloride and sulphate ions. However, activated alumina also adsorbs bicarbonate ions to some extent though the order is $F^- > HCO_3^-$. This is probably the reason for the decrease in the defluoridation capacity of activated alumina at increased concentrations of bicarbonate ions.

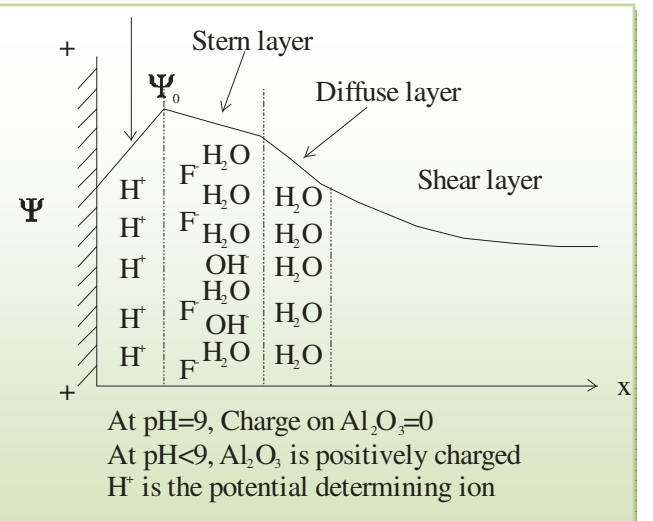

FIGURE 3. Model of the double layer between alumina/solution interface.

At pH greater than 9, when the activated alumina acquires a negative charge, there is still sufficient defluoridation capacity which cannot be explained in terms of forces of chemi-sorption. Fluoride removal by activated alumina may be purely governed by physi-sorption at higher pH ranges. In fact adsorption through van der Waals type of forces may be taking place to some extent throughout the pH range. This argument is supported by the fact that the defluoridation capacity is reached only after a minimum of contact time of 20 minutes. Chemi-sorption also starts taking place with decreasing pH and the extent of chemi-sorption increases at a much higher rate. This explains the very steep increase of defluoridation capacity of activated alumina from pH 5 to pH 3. When fluoride is eluted by 2 % sodium hydroxide solution the activated alumina acquires a very high negative charge and the adsorbed fluoride ions are repelled from the surface and are diffused into sodium hydroxide solution.

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