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**FLUORIDE REMOVAL USING ZR LOADED A500P IN COMPARISON WITH ACTIVATED ALUMINA**

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**Abstract**

Fluoride contamination of groundwater, both anthropogenic and natural, represents a major problem. A500P anion exchanger was loaded with Zr ions and precipitated with sodium hydroxide followed by thermal treatment at 60 °C to form Zr oxide in hydrated phase. Fluoride removal by using Zr loaded A500P in comparison with activated alumina was investigated by batch studies from solutions with fluoride concentration 5 mg/L at different experimental conditions. The results indicate that fluoride adsorption occurs immediately over the entire surface of A500P Zr loaded resin, after shaking for 6 h to reach equilibrium, as well as activated alumina. The obtained data indicated the relatively high removal activity of Zr loaded A500P when compared with activated alumina. Furthermore, the investigation of the effect of competitive species such as  $\text{SO}_4^{2-}$  and  $\text{PO}_4^{3-}$  indicate that both sulphate and phosphate strongly affect the rate of fluoride removal which completely suppressed by reaching 1000 ppm and 1 ppm dose from sulphate and phosphate, respectively. The variation of pH in 2-10 range indicates that the rate of fluoride removal is inversely proportional to pH. Furthermore, the lower pH shows the higher removal capacity.

**Keywords;** A500P, Zr oxide,  $\text{SO}_4^{2-}$ ,  $\text{PO}_4^{3-}$  and pH change

**Introduction**

Recently, fluoride was commonly thought to be removed from solution by precipitation in calcite systems. However, in 2003, Fan et al. [1] published a paper suggesting that sorption of fluoride onto calcite can occur. This paper considering a much larger range of concentrations, examined the impact of pH and competition of oxyanions on the system, and considers evidence for sorption when precipitation of fluoride is known to occur at fluoride concentrations in groundwater range up to 160 mM (3000 mg/L). Elevated concentrations can also occur through the natural dissolution of fluoride-bearing minerals in bedrock and soil. Many researchers [2-9] have used adsorption onto activated alumina or ion exchangers [10] to remove fluoride from solution, while others [11-18] have used various forms of lime [ $\text{Ca}(\text{OH})_2$ ,  $\text{CaO}$ ,  $\text{CaCO}_3$ ] or other calcium salts to increase calcium activity in solution, thereby removing fluoride by precipitation as fluorite ( $\text{CaF}_2$ ). These

techniques have advantages and disadvantages. For example, adsorption onto activated alumina requires  $\text{pH} < 7.0$  before any real gains are made, but decreasing solution pH greatly increases the amount of aluminum species released into solution to potentially dangerous levels and frequent regeneration of sorption sites is required. The major disadvantages of precipitation methods are the difficulty in obtaining equilibrium fluoride concentrations less than  $0.42\text{mM}$  because of solubility constraints and pH above 9, which is unacceptable for some regulatory authorities.

Calcite has been suggested as a fluoride removal medium by many authors. Pickering and co-workers [15, 19, 20] concluded that fluorite precipitation was the main mechanism of fluoride removal because the mass of fluoride lost from solution was independent of the weight of calcite present. Reardon and Wang [11] employed data from column experiments to conclude that fluoride removal was achieved by dissolution of calcite and subsequent precipitation of  $\text{CaF}_2$ . However, the hypothesis that precipitation of  $\text{CaF}_2$  is the only method of fluoride removal is inconsistent with the known behavior of calcite exposed to other ions. For example, calcite can also adsorb metal ions such as cadmium [21, 22], manganese [23], and zinc [24] as well as phosphate [25], with the degree of adsorption being pH-dependent.

Yang et al. (13) expanded on work done by Glover and Sippel [14] and Simonsson [12] to include the effect of competing anions ( $\text{SO}_4^{2-}$  and  $\text{PO}_4^{3-}$ ) on fluoride removal by calcite and found decreased fluoride removal in their presence. In addition, sulfate and phosphate were removed even when solutions of their respective calcium salts were under saturated. Yang and colleagues could not explain their removal by precipitation but did not consider the possibility of adsorption.

In the present work, we have utilized the filtering characteristics of Zr oxide by coating Zr oxide on A500P resin. This Zr modified material was used for the removal of fluoride ions from drinking in batch systems as well as column run and the results were compared with those using activated alumina. The performance of the fluoride removal was investigated as a function of initial fluoride concentration and amount of adsorbent.

## **Experimental**

All chemical reagents used in this work were of analytical grade (AR). Activated alumina], sodium hydroxide, zirconium oxychloride and sodium fluoride were purchased from Sigma–Aldrich Chemicals.

To prepare the adsorbent, 20 gm of A500P was treated with 8% zirconium oxychloride and the mixture was shaken for 24 hr at room temperature. The obtained material was washed and treated with 5 % solution of NaOH to precipitate Zirconium as Zirconium hydroxide and then dried at 60 °C overnight.

Adsorbent characterization was accomplished by means of X-ray diffraction (XRD, Bruker axs, D8 advance diffractometer, Billerica, USA) analysis and Scanning Electron microscope (SEM, JEOL JSM-6360A, equipped with EDX system JED-2300).

Fluoride, sulfate and phosphate measurements were carried out using ion chromatography (Dionex Ion Pac(R) attached with SRC18 column with eluent consisted of 2:7 sodium carbonate: sodium bicarbonate mixture, and the flow rate was 1.2 ml/min. In all cases, air was bubbled through the reaction mixture to ensure a constant dissolved O<sub>2</sub> concentration.

All batch equilibrium experiments were carried by mixing 200 ml F<sup>-</sup> solution at natural pH and different pH as well as different doses of Zr loaded A500p, activated alumina, sulfate and phosphate. The equilibrium concentrations were determined using IC, after filtration.

The amount of adsorbate F<sup>-</sup> per gram of adsorbent (Q<sub>ads</sub> mol/ g) and the maximum number of adsorbed molecules Q<sub>max</sub> was determined according to the derived Langmuir equation after linearization:

$$Q_{ads} = \frac{Q_{max} K_{ads} C_{eq}}{K_{ads} C_{eq} + 1} \quad (1)$$

The Freundlich parameters K and n were calculated classically using the results in all the studied of concentrations ( $C_{eq} = K C_o^n$ )

Fixed bed column runs were carried out using a glass column (11 mm in diameter), constant-flow stainless steel pumps, and an ISCO fraction collector. Exhausted A500P loaded with Zr was regenerated using 0.5 % NaOH.

## Results and Discussion.

### *Characterization of Zr loaded A500P*

The XRD diffractogram of the ion exchange (A500P) sample which has been modified with Zr oxide is presented in Fig. (1b) compared with that of the parent A500P in Fig. (1a). The data obtained indicated that the hybrid ion exchange (HIX)

samples possess an amorphous structure due to the absence of any diffraction line characteristic of the crystalline phase and/or Zr-oxide species. This may be due to that the formed Zr-oxide particles are smaller than the detection limit of the instrument and located in the nano range which cannot be detected by XRD.

Fig. 2 shows the SEM micrograph of A500P ion exchange particles modified with Zr cations. A number of macropores in the sizes of 20–300  $\mu\text{m}$  can be readily observed. The obtained SEM picture for hybrid ion exchange particles and the close physical observation suggest that the zirconium oxide agglomerates are accessible to dissolved solutes through a network of pores.

### Adsorption of fluoride over Zr loaded A500P

Since the rate of removal of pollutants depends on the amount of adsorbed ions, a series of experiments were carried out by batch test to study the adsorption of  $\text{F}^-$  on Zr-A500P surface at different doses of the catalyst (0.05, 0.1, 0.15 and 0.2 g/l). It was found that an equilibrium adsorption of a Langmuir type was observed.

According to the Langmuir model, the coverage  $\Theta$  varies as

$$\Theta = \frac{Q_{\text{ads}}}{Q_{\text{max}}} = \frac{CKC_{\text{eq}}}{1 + CKC_{\text{eq}}} \quad (2)$$

Where:  $Q_{\text{ads}}$  is the number of adsorbed molecules at the adsorption equilibrium,  $Q_{\text{max}}$  is the maximal adsorbable quantity,  $K$  is the Langmuir adsorption constant of  $\text{F}^-$  on Zr-A500P and activated alumina and  $C_{\text{eq}}$  the concentration of  $\text{F}^-$  at the adsorption equilibrium (Fig. 3).

$$\frac{1}{Q_{\text{ads}}} = \frac{1}{Q_{\text{max}}} + \frac{1}{Q_{\text{max}}KC_{\text{eq}}} \quad (3)$$

Equation (3) represents the linear transformation of Eq. (2) which is expressed by the following equation:

Therefore, a linear relation between  $1/Q_{\text{ads}}$  and  $1/C_{\text{e}}$  can be obtained with an intercept =  $1/Q_{\text{max}}$  and a slope =  $1/Q_{\text{max}}K$ , where the values of  $Q_{\text{max}}$  and  $K$  can be calculated from the linear relation shown in Fig. 4. The data obtained indicate that the value of  $K=0.54$  and  $Q_{\text{max}}= 2.14 \text{ mg F}^-/\text{g resin}$ .

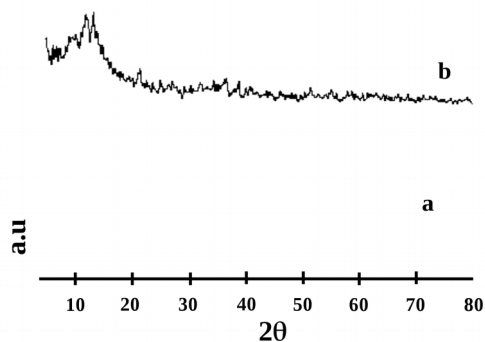


Fig. 1 XRD patterns of different cations modified HIX a) A500P b) Zr-A500P

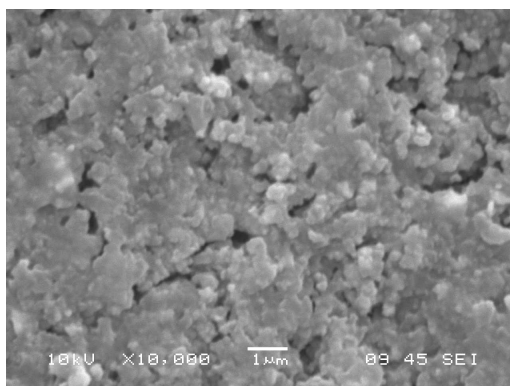


Fig. 2. Scanning Electron Micrograph of the Zr modified polymeric material (A500P)

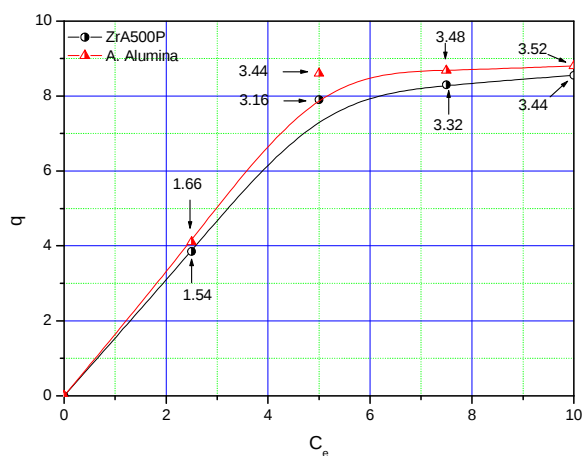


Fig. 3. The Langmuir model for F<sup>-</sup> adsorption over Zr-A500P and activated alumina

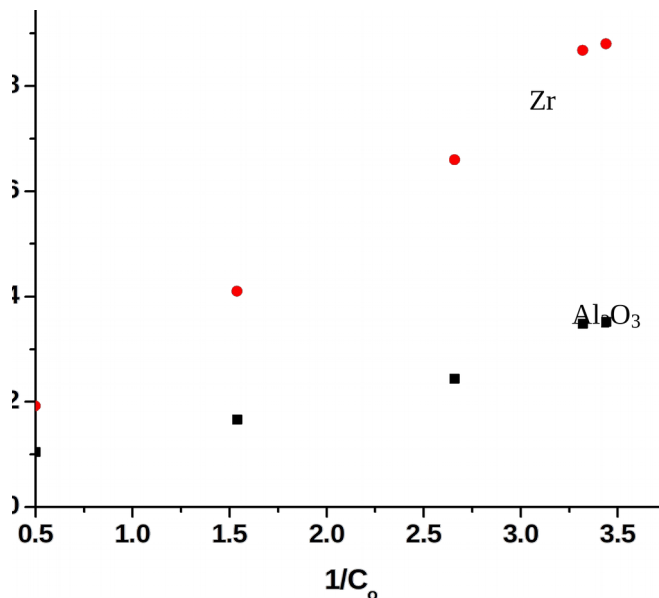


Fig. 4. The linear transformation Langmuir model for F<sup>-</sup> adsorption over Zr-A500P and activated alumina

#### *Effect of competitive anions on fluoride removal*

#### *Effect of adsorbent doses*

The data obtained indicate the relative similarity among Zr-A500P and activated alumina upon variation of adsorbent doses as depicted in Fig. 5.

#### *Effect of pH.*

Batch tests demonstrate that the amount of fluoride removed is dependent on pH. The results are shown in Fig. 6 for Zr-A500P and activated alumina with initial F<sup>-</sup> concentration of 6 mg/L over the pH range 2.0-10. The Figure shows a good removal of 50 and 40% at neutral pH for Zr-A500P and activated alumina, respectively. Furthermore, the data also demonstrate that equilibrium fluoride concentration is directly proportional to pH so that it is possible to decrease fluoride concentrations to any level by selecting the appropriate [H<sup>+</sup>]/[F<sup>-</sup>] ratio. The slow rate of reaction at higher pH could reflect OH<sup>-</sup> competition with F<sup>-</sup> for surface adsorption sites

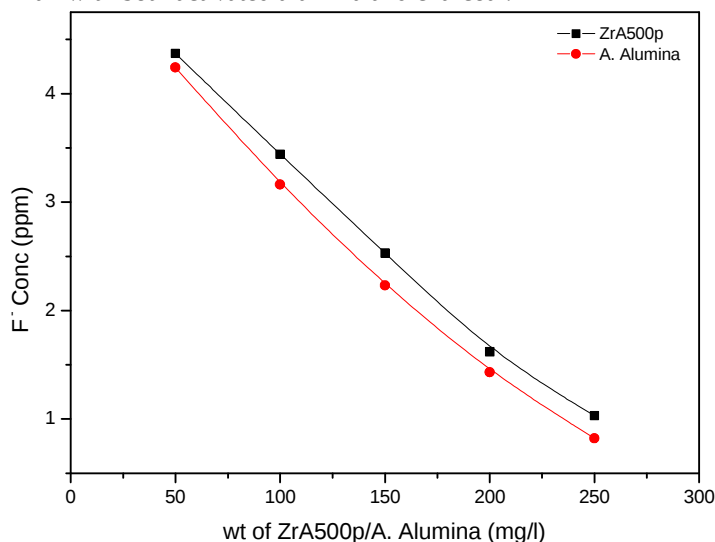
The data obtained for the effect of pH during the column run indicate also that pH 5.5 is the most efficient one for the removal of F<sup>-</sup>. Fig. 7 shows that F<sup>-</sup> start breakthrough after about 300 bed volumes at pH 5.5 whereas, at pH 7.5, F<sup>-</sup> broke through immediately at the beginning of the column run.

### ***Effect of Sulphate and Phosphate***

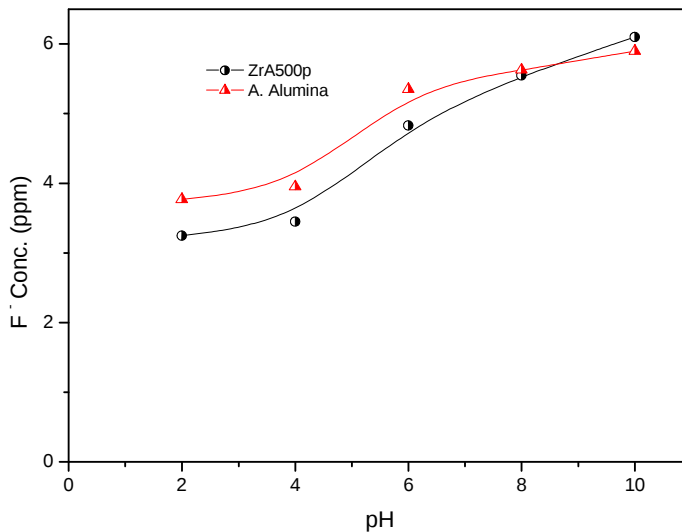
The investigation of competition of SO<sub>4</sub><sup>2-</sup> (120 - 1000 mg/L) and PO<sub>4</sub><sup>3-</sup> (0 - 1 mg/L) was carried out in batch and the obtained data are illustrated in Figs. 8&9. The data indicate that at lower concentrations of SO<sub>4</sub><sup>2-</sup> and PO<sub>4</sub><sup>3-</sup> the rates of F<sup>-</sup> removal are very high. Furthermore, upon increasing the concentration of both SO<sub>4</sub><sup>2-</sup> and PO<sub>4</sub><sup>3-</sup> the removal rate decreases and completely suppressed at 1000 mg/L SO<sub>4</sub><sup>2-</sup> and 1 mg/L PO<sub>4</sub><sup>3-</sup>.

### ***Column run***

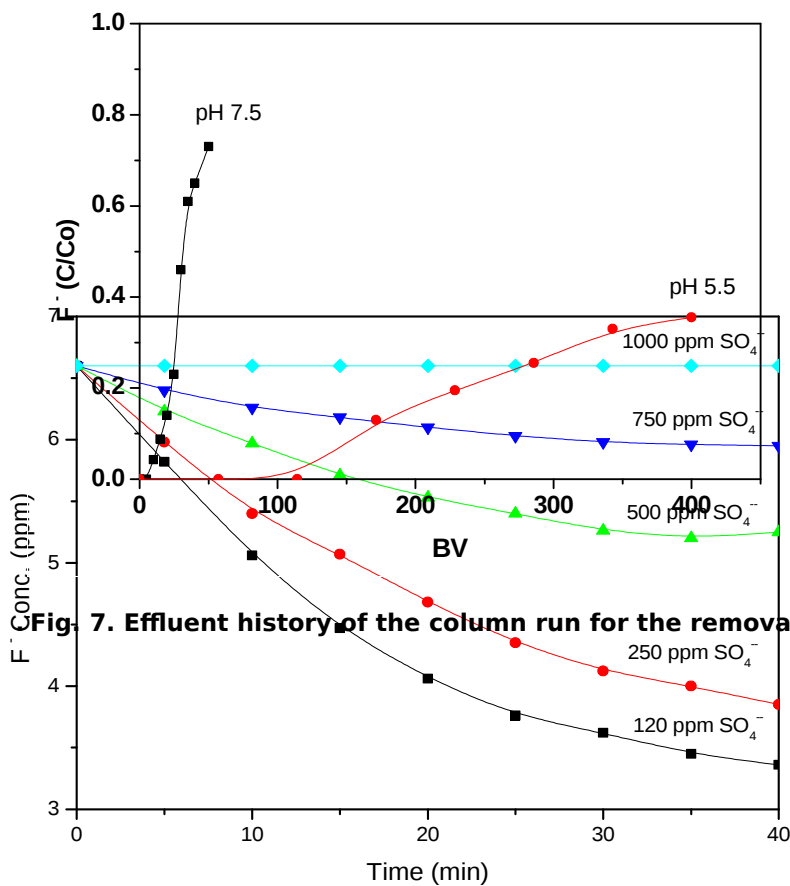
After commencing of the optimum condition for F<sup>-</sup> removal column runs were carried with Zr-A500P and activated alumina in comparison with charcoal as one of the oldest techniques used for F<sup>-</sup> removal. The data depicted in Fig. 10 shows the effluent history of the column run for the removal of F<sup>-</sup>. It is clear that F<sup>-</sup> breakthrough starts showing up after the passing of about 100 bed volumes for Zr-A500P cycle whereas, it starts break through immediately at beginning of the column run with both activated alumina and charcoal.



**.Fig. 5. Effect of adsorbent doses on the F<sup>-</sup> uptake**



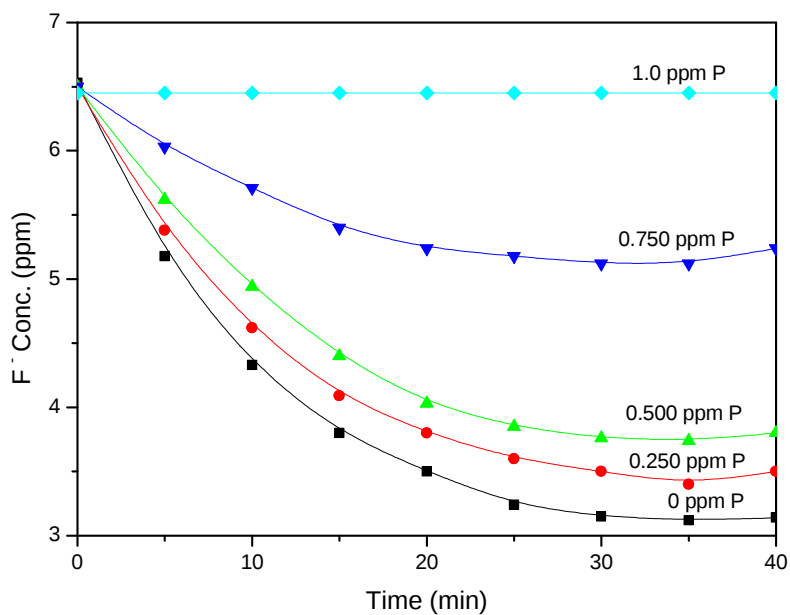
**.Fig. 6. Effect of pH on the F<sup>-</sup> uptake**



**Fig. 7. Effluent history of the column run for the removal of F**



.Fig. 8. Kinetics of sulfate effect on the removal of F



.Fig. 9. Kinetics of sulfate effect on the removal of F

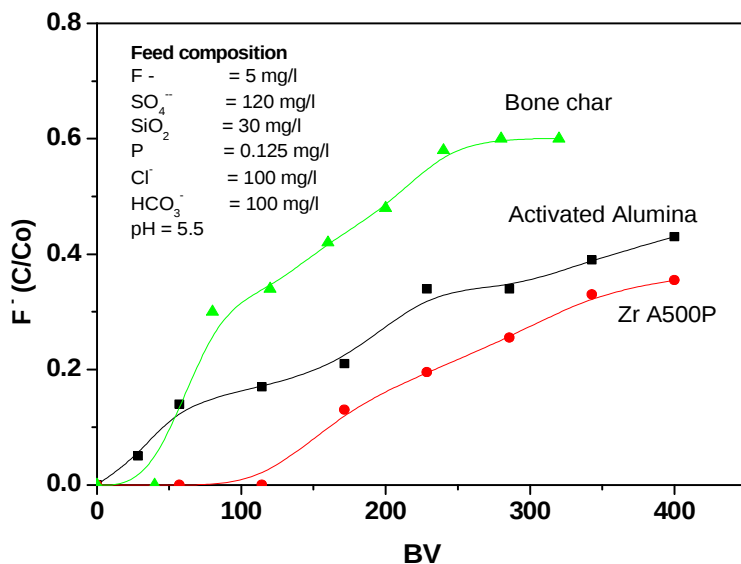


Fig. 10. Effluent history of the column run for the removal of F<sup>-</sup> over Zr-A500P, activated alumina and bone charcoal

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