

*Development of a hybrid material for the removal of fluoride from water*

A

*Dissertation*

*Submitted in partial fulfillment*

FOR THE DEGREE OF

**MASTER OF SCIENCE IN CHEMISTRY**

Under The Academic Autonomy

of

NATIONAL INSTITUTE OF TECHNOLOGY, ROURKELA

By

Auroprasad Mohanty



Under the Guidance of

**Prof. R.K.Patel**

**DEPARTMENT OF CHEMISTRY**

**NATIONAL INSTITUTE OF TECHNOLOGY**

**ROURKELA – 769008(ORISSA)**



**NATIONAL INSTITUTE OF TECHNOLOGY  
ROURKELA**

**CERTIFICATE**

This is to certify that the thesis entitled, “Development of a hybrid material for removal of fluoride from water “submitted by Mr. Auroprasad Mohanty in partial requirements for the award of Master of Science Degree at the National Institute of Technology, Rourkela is an authentic work carried out by him under my supervision and guidance. To the best of my knowledge, the matter embodied in the thesis has not been submitted to any other University / Institute for the award of any Degree or Diploma.

Date

Prof. R.K.Patel (HOD)  
Department of Chemistry  
National Institute of Technology,  
Rourkela- 769008

TO My PARENTS

WHO HELPED ME THROUGH OUT

AND

TO MY TEACHER

WHO TAUGHT ME THE BEAUTY OF CHEMISTRY

## ACKNOWLEDGEMENTS

This thesis is the account of one year of devoted work in the field of Material Chemistry at the National Institute of Technology, Rourkela, India, which would not have been possible without the help of many.

A few lines are too short to make a complete account of my deep appreciation for my advisor Prof. R.K.Patel. I would like to thank him for his valuable guidance and constant encouragements which I have received during the last year.

I acknowledge my sincere regards to all staff's member, Department of Chemistry, NIT Rourkela for their dedication towards students.

I am also thankful to my lab mates Anil Kumar Giri, Ramesh Chandra Sahoo, who worked with me since last one year.

Last but not the least, I would like to record deep respect to my parents & friends for selflessly extending their support.

Date:

Auroprasad Mohanty

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## 1. Introduction

Over the last thirty years, the use of pure waters for drinking and other purposes have been the dominant concern along with the concern of better environment. The development of new technology has grown up steadily but water purification in the community level almost remains same. In years to come, water purification process will be a major challenge throughout the globe. In this context no significance breakthrough has been achieved. Ground water is one of the major sources of water for domestic purposes in India. It was believed that ground water is purer and safer than surface water due to earth covering which works as a natural filter. But it is not true. Few decades back, water was considered to be pure and unpolluted if it was odorless, free from turbidity and good from aesthetic point of view. But now, the whole concept of water pollution has changed. Even if the water is clear, it may be polluted. Besides that, the surface water is also contaminated by the effluents from industries, municipalities and other places. The contamination of hazardous anions, fluoride in particular and other anions like nitrate, sulphate etc in general, in ground water is a wide spread phenomenon which causes many health problem. Many domestic water purification processes are available but not suitable for rural people because of high cost and regular maintenance. So there exist a great gap between technology developed and its application where required. In terms of the magnitude of problem, this will be a small attempt for a big problem.

Fluoride related health hazards are a major environmental problem in many regions of the world. Literature review reveals that, India is among the 25 nations around the globe, where health problem occurs due to the consumption of fluoride-contaminated water. In India, 17 states have been identified as epidemic for fluorosis and Orissa is one of them. The fluoride contamination in Orissa is wide spread, where 10 district out of 30 have excess of fluoride in ground water. More than 60% of our fluoride demand is fulfilled by the consumption of drinking water. Excess of fluoride ( $>1.5$  mg/L) in drinking water is harmful to the human health. The physiological effects of fluoride upon human health have been studied since the early part of 20th century. Several reports and studies established both the risk of high fluoride dosing and the benefits of minimal exposure a. A low dose of fluoride was deemed responsible for inhibiting dental caries while a higher daily dose was linked to permanent tooth and skeletal fluorosis . Fluoride ingested

with water, goes on accumulating in bones up to the age of 55 years. At higher doses fluoride interfere with carbohydrates, lipid protein, vitamin, enzyme and mineral metabolism. Therefore, pre-concentration or removal of fluoride from aqueous solutions is a matter of great concern in analytical and environmental works. Determination of fluoride in drinking water has received a considerable attention, due to its detrimental effects on health.

Fluoride has two sources. It can appear “naturally” in water or it can appear as a toxic waste. Even where it does appear without any help from industry, it can cause problem. The earliest problems associated with toxic wastes involved those businesses manufacturing aluminum with the resulting wastes usually being sodium fluoride. In Britain, today, the most frequently used toxic waste product used for fluoridation comes from the phosphate fertilizer industry.

Various treatment technologies, based on the principle of precipitation, ion exchange, electrolysis, membrane and adsorption process such as reverse osmosis, nanofiltration, electro dialysis and donnan dialysis have been proposed and is tested for removal efficiency of fluoride from drinking water as well as industrial effluent . Adsorption process involves the passage of the water through a contact bed where fluoride is removed by ion exchange or surface chemical reaction. Adsorption on activated alumina, alum, charcoal, agricultural waste and its ash has been reported. Among these technologies fluoride adsorption by hybrid material appeared to be an interesting process. Most of the available materials for defluoridation are expensive and technically non-feasible. Hence, the need to find locally available defluoridation media for safe and easy use at both household and community levels is desirable. The aim of this research was to evaluate the removal of fluoride ions from water by sorption behavior of fluoride in the hybrid material prepared by incorporating inorganic ion exchanger in a stable organic polymeric material as a function of pH of solution, concentration of adsorbate and temperature.

## **2. Review of Previous work**

In India various adsorbent like agricultural product, herbal product and various minerals are used to remove the anions and cations. The Nalgonda technique is one such process which is widely used for community defluoridation. But it has some disadvantages like high aluminum content in the treated water which has some adverse effect on human health. There is no standard method for removal of arsenic and other anions from water. In national level, various research

groups are working to prepare adsorbing material and subsequently using the material for removal of various hazardous anions and cations from the aqueous solution. Layered double hydroxides (LDHs) constitute a class of lamellar ionic compounds containing a positively charged metal hydroxide sheet compensated by a large number of exchangeable charge-balancing anionic and water molecules, which are present in the interlayer spaces. Due to the presence of large interlayer spaces and huge number of exchangeable anions are present. HTLcs as well as their calcined products exhibit huge anion exchange capacity (AEC) which is comparable to that of anion exchange resins. The high AEC of these materials help for adsorption of undesirable anions from contaminated water. Similarly the hybrid material possesses the mechanical strength provided by organic counterpart and ion exchange capacity by inorganic part.

Islam et al. evaluated the removal efficiency of fluoride from aqueous solution using quicklime. Their studies indicate that the adsorption process is chemisorption along with precipitation. Removal efficiency was found to be maximum when the initial fluoride concentration was high. Their technique of removal may be suitably employed to treat industrial effluent where the concentration of fluoride is high. But the removal of fluoride using quick lime cannot be used for domestic purpose, since it cannot bring fluoride concentration within permissible limit, and also increases the pH of the treated water.

Durmaz et al. proposed a new technique for the removal of fluoride from diluted solution with Neosepta AHA anion exchange membrane has been studied by Donnan dialysis. The effects of concentration, pH, and accompanying anion on feed phase and receiving phase composition were investigated. Neosepta AHA anion exchange membrane was used for the removal of fluoride and the flux of fluoride with respect to the concentration, pH, and the effect of the counter-ions ( $\text{HCO}_3^-$ ,  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ ) were obtained between 34-136.10<sup>-7</sup> (m.mol.cm<sup>-2</sup>.s<sup>-1</sup>). The effect of the fluoride flux increased with increasing of concentration on the feed phase. The flux of fluoride was found to be higher at higher pH in the feed phase. In addition, the accompanying counter-anions also influenced the flux of fluoride and the order of flux was founded as  $\text{HCO}_3^- > \text{Cl}^- > \text{SO}_4^{2-}$ . The removal of fluoride was attempted using natural materials such as red soil, charcoal, brick, fly-ash and serpentine and many more. Each material was set up in a column for a known volume and the defluoridation capacities of these materials were studied with respect to

time. There are many literatures available in the journal and internet but few important references related to project are presented.

### **3. AIM AND OBJECTIVES**

Water is one of the most important natural resources upon which all life process depends. Indiscriminate use and misuse of water is making it unfit for human consumption. A recent survey reveals that, 90% of water available contains many pollutants which cause number of health problems. The purification of water is a major challenge in future years to come. Hence an attempt has been made in the present work to prepare hybrid materials which can be utilized for the removal of fluoride and other anions from water. To achieve the desired result, this work has been started with the following objectives:-

- (1) To prepare a potential hybrid material incorporating organic and inorganic ion-exchanger.
- (2) To characterize the material by using the modern technique.
- (3) To explain the feasibility study on the removal of fluoride from water by column process.
- (4) To interpret the data to know the feasibility of the above study.

### **4. MATERIALS AND METHODS**

#### **4.1 Reagents:**

Zirconium oxychloride octahydrate, propanolamine and other chemicals were procured from E Merck, India. Standard solution of fluoride was prepared from weighed sodium fluoride and stored in polyethylene bottle. TISAB buffer solution was prepared by dissolving 58 g of sodium chloride, 4g of 1, 2-diaminocyclohexane tetra acetic acid (CDTA) and 57ml of glacial acetic acid in water and diluting to 500ml. After placing in a cold water bath, 5M sodium hydroxide was slowly added with stirring until the pH lies in the range 5.0-5.5 and diluted to 1L.

## 4.2 Apparatus Required:

Orion ion selective electrode was used to measure the pH and Orion 720 A+ ion analyzer was used to measure the fluoride concentration. Calibration was made in the range 0.1-10 ppm of F<sup>-</sup> by using known concentration of sodium fluoride standard.



Figure-1: Orion 720 A+ ion analyzer with Orion ion selective electrode

**Theory of Operation:** The fluoride electrode consists of a sensing element bonded into an epoxy body. When the sensing element is in contact with a solution containing fluoride ions, an electrode potential develops across the sensing element. This potential, which depends on the level of free fluoride ion in solution, is measured against a constant reference potential with a digital pH/mV meter or specific ion meter. The measured potential corresponding to the level of fluoride ion in solution is described by the Nernst equation.

$$E = E_o + S \log (A)$$

Where: E = measured electrode potential.

$E_0$  = reference potential.

A = fluoride ion activity level in solution.

S = electrode slope (about 57 mV per decade)

The level of fluoride ion, A, is the activity.

### **4.3. Procedure:**

Fluoride was estimated by Orion ion selective electrode and Orion 720 A+ ion analyzer. Total ionic strength adjusting buffer (TISAB – III) solution was added to both samples and standards in the ratio 1:10. which regulates the ionic strength of samples and standard solutions. It also adjust the pH and avoid interferences by polyvalent cations such as Al(III), Fe(III) and Si(IV), which are able to complex or precipitates with fluoride and reduce the free fluoride concentration in the solution. The CDTA preferentially complexes with polyvalent cations present in water or aqueous solution (e.g.  $Si^{4+}$ ,  $Al^{3+}$  and  $Fe^{3+}$ ). The electrode is selective for the fluoride ion over other common anions by several orders of magnitude. One litre of 100 ppm NaF solution was prepared which was subsequently diluted to form 10, 20, 30, 40 ppm solution. These solutions were taken to calibrate the instruments.

### **4.4. Synthesis of the Ion-exchange Material:**

Zirconium (IV) oxide-propanolamine exchanger was prepared by mixing 0.2M aqueous solution of propanolamine with a 0.1 M zirconium oxychloride solution in the ratio of 1:1(v/v) at pH 3 with constant stirring for several hours. The desired pH was adjusted by adding dilute hydrochloric acid dropwise. The white gel so obtained was allowed to stand overnight at room temperature and then filtered, washed with demineralised water to remove excess reagents till the filtrate attains a pH value of 5 or 6, which was dried at 40°C. The product was broken into shining granules when immersed in water. The exchanger was then converted into  $H^+$  ions form by treating it to 1.0 M  $HNO_3$  for 24hr with occasional shaking. The  $H^+$  form exchanger was further converted into  $Ca^{++}$  form by treating it with calcium solution.

#### 4.5. Structure of Ion-exchanger material

The probable structure of the hybrid material was proposed based on elemental analysis data, molecular weight measurement, FTIR, TGA & DTA analysis. The detail of the above analysis could not be given because of some technical problem in the software. However the proposed formula of ZrO-PA exchanger is given in Fig.2.

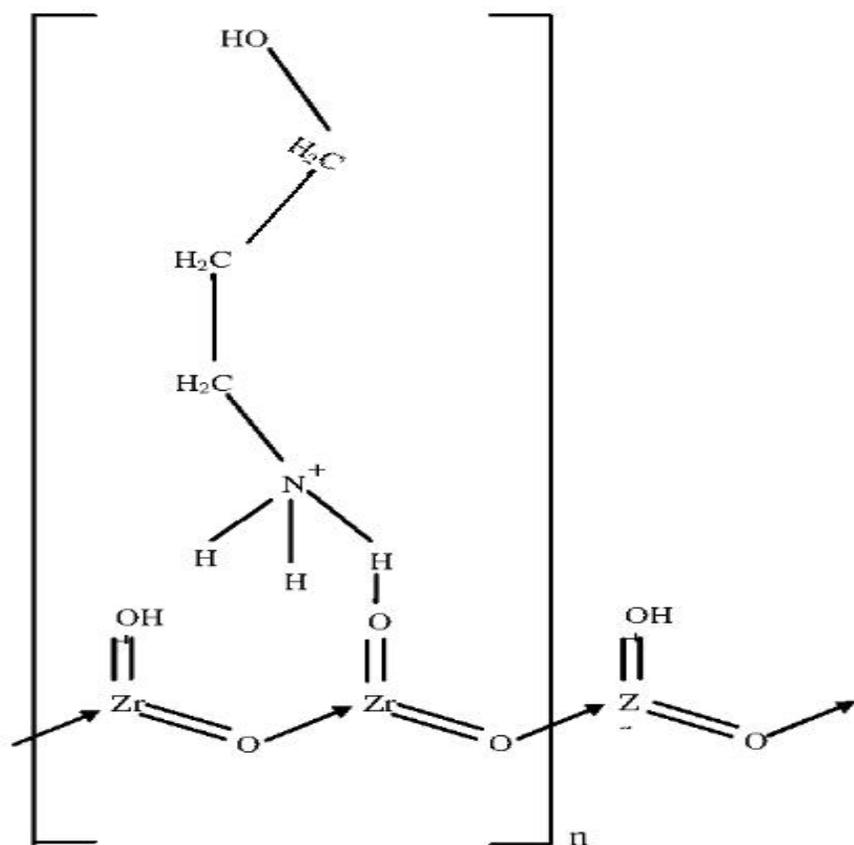


Fig.2: Structure of Ion-exchanger ZrO-PA

#### 4.6. Column Preparation and Ion Exchange Procedure:

The glass column containing a stopcock and a porous disk at the bottom with a glass wool support was 25cm long and 1.0cm in diameter. Then 1.0g of ZrO-PA exchanger was packed into the column. It was washed successively with water and acetone, respectively. The sample solutions of varying concentration were adjusted to pH 2 and passed through the column at a flow rate of 1-2 ml/min with the help of a peristaltic pump. After passing the solution, the

column was rinsed twice with water. The adsorbed fluoride on the column was eluted with 1.0 M HCl solution then analyzed for fluoride concentration by ion selective electrode.

#### 4.7. Sample Preparation and Sorption Procedure:

In order to study the adsorptive capacity of ZrO-PA exchanger in Ca ion form, the batch method was used. 0.5 g exchanger was added to 50 ml of aqueous solution containing fluoride ion at various concentration (0.1 to 20 ppm) in a 100ml polythene flask and was shaken in a thermostat water bath at 20, 30, 40 and 50<sup>0</sup> C for 6h. The ion exchanger was then removed by filtration. The concentration of the analyte ion in the filtrate was determined using ion selective electrode. The sorption capacity (mmol/g dries exchanger) and percent uptake for the sorption of fluoride ion was calculated by the following equation using the analysis data presented in table-2:

Percent uptake (U%) = conc. of F<sup>-</sup> ion in the exchanger phase/initial conc. of F<sup>-</sup> in water \*100.

## 5. Results and discussion

### 5.1. Characterization of the sorbents

Fig.s a and b depict the FTIR spectra of ZrO-PA and fluoride treated ZrO-PA, respectively. The band at 3427 cm<sup>-1</sup> denotes NH stretching vibrations and the band at 1633 cm<sup>-1</sup> denotes C=O stretching vibrations. The slight broadening of band at 3405 cm<sup>-1</sup> in the fluoride sorbed ZrO-PA may be taken as an indicative of hydrogen bonding between the sorbent and the fluoride. The other data could not be presented due to problem in software.

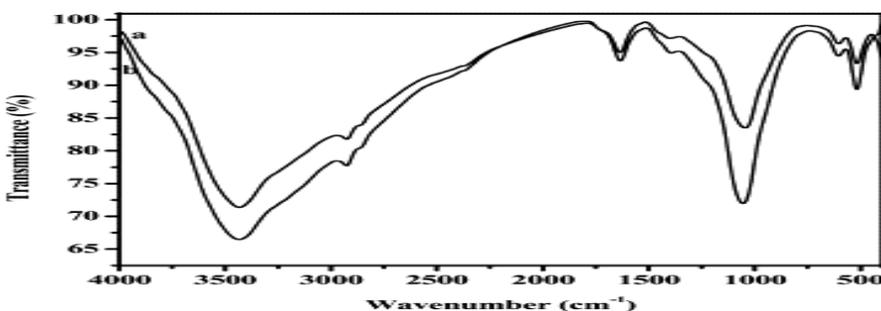


Fig.2. FTIR spectra of (a) ZrO-PA and (b) fluoride-sorbed ZrO-PA.

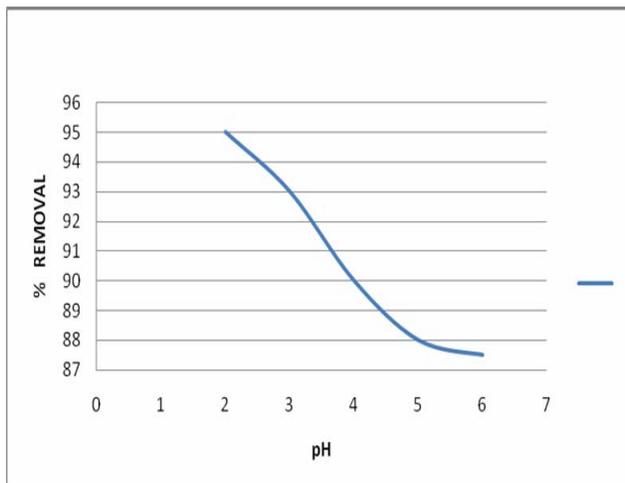
## 5.2. Effect of pH

The sorption capacities of ZrO-PA exchanger in  $\text{Ca}^{2+}$  form for fluoride ion in batch process at  $30^{\circ}\text{C}$  are 0.82, 0.75, 0.58, 0.54 and 0.40mmol g dry exchanger at pH 2,3,4,5, 6 respectively. The percentage removal of fluoride with respect to different pH is represented in table-1. The percentage removal at different pH was also depicted in graph -1,2,3,4, From the above data and figure, it reveals that sorption capacity decreases regularly with increasing pH which indicates the stability of  $\text{CaF}^+$  ion at low pH value. The exchange material in  $\text{Ca}^{2+}$  form has been taken for further studies in acidic media due to its higher selectivity towards fluoride ions. The volume of the buffer solution had no much influence on sorption.

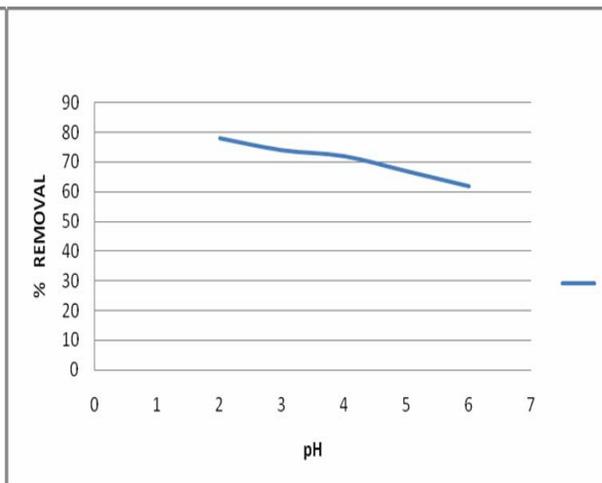
Table1: Percent Removal of fluoride at different pH

Initial Loading in ppm	Percent Uptake of fluoride				
	pH 2	pH 3	Ph 4	pH 5	pH 6
01.0	98±1	95±2	96±2	98±2	97±2
01.0	95±2	93±2	90±1	93±2	87.5±1
10.0	77±2	74±1	72±2	67±2	63±2
20.0	66±2	63±2	59±1	55±2	49±2

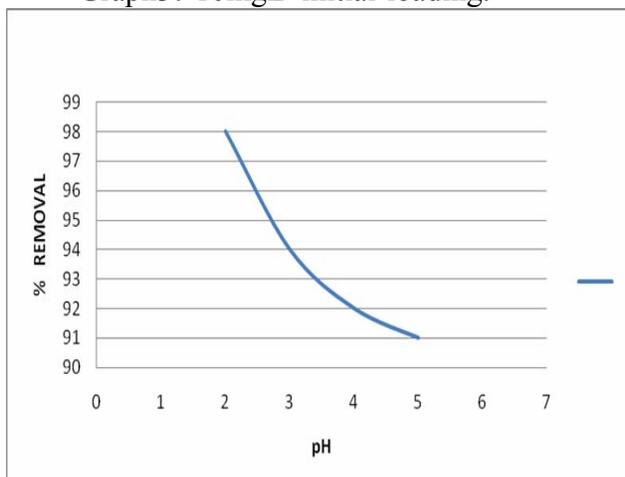
Graph1: 0.1mgL<sup>-1</sup> initial loading.



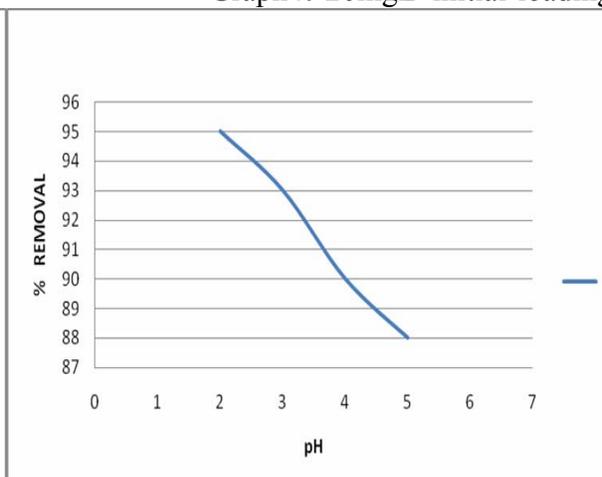
Graph2: 1mgL<sup>-1</sup> initial loading.



Graph3: 10mgL<sup>-1</sup> initial loading.



Graph4: 20mgL<sup>-1</sup> initial loading.



### 5.3. Effect of temperature

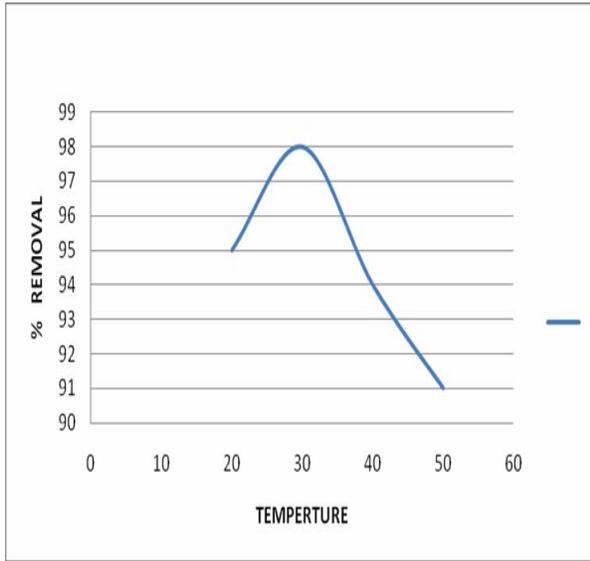
From the previous study it is ascertained that the maximum removal was achieved at pH 2. Hence pH 2 is maintained for further studies. The percentage removal study was carried out at different temperature from 20° C to 50° C with a variation of initial loading of F- from 0.1 to 20 ppm. The data of these studies are represented in table 2. The percentage removal at different temperature was also depicted in graph -5,6,7,8 . It is observed that a temperature of 30° C is optimum for maximum uptake. The exchanger shows a decreasing trend above and below this temperature. The expected capacity trend, which was expected to be better at high temperature is altered. Again this order of uptake is pH dependent and it decreases with increasing pH values of

solutions. When the effect of concentration is studied at 30°C, the exchanger in Ca<sup>2+</sup> form exhibits strong sorption ability, particularly in low concentration region. This may be attributed to small particle size with large surface area, where a chemical reaction is more favourable and stable. The small size of the fluorine atom causes it to be saturated quickly with electron density on the surface of zirconium oxide and propanolamine. Furthermore, the highest electronegativity of fluorine combined with its small size results in a much greater reactivity

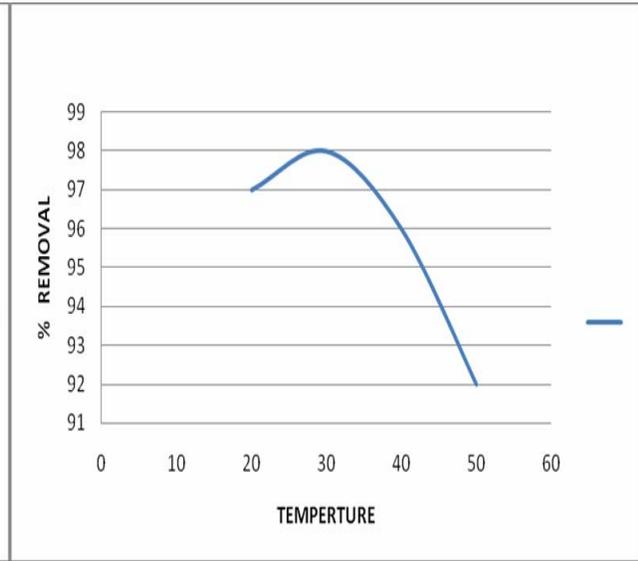
Table 2: Percent uptake of F<sup>-</sup> Ion on ZrO-PA at Different Temperature

Temperature	Initial Loading in ppm	pH 2	pH 3	pH 4	pH 5	Ph 6
20°C	00.1	95±1	93±2	92±2	91.5±4	92±2
	01.0	97±1	96±3	95±2	94±2	95±2
	10.0	95±1	93±2	92±1	91.5±2	94±3
	20.0	85±1	79±3	78±1	76±3	75±3
30°C	00.1	98±3	97±3	96±1	96.5±2	95±2
	01.0	98±1	98±2	97.5±1	97±2	97.5±3
	10.0	98±2	97±3	96±1	95±2	94±1
	20.0	94±1	90±2	88±2	82±1	81±2
40°C	00.1	94±2	95±2	96±1	94±2	93.5±1
	01.0	96±2	99±2	97±2	96±2	95±2
	10.0	92.5±2	94±1	93±1	92±2	94±1
	20.0	86±2	84±1	94±2	85±2	83±2
50°C	00.1	91±2	93±1	99±2	90±2	90±1
	01.0	92±2	95±2	96±2	95±2	92±2
	10.0	90±2	84.5±2	85±2	83±1	84±2
	20.0	80±2	79.5±2	77±1	75±3	74±2

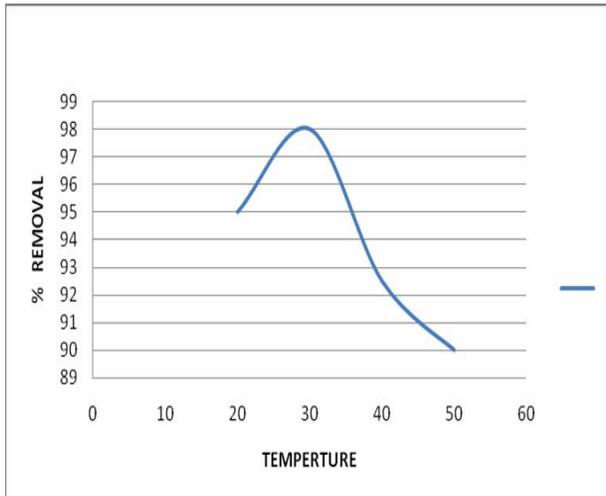
Graph5: 0.1mgL<sup>-1</sup> initial loading.



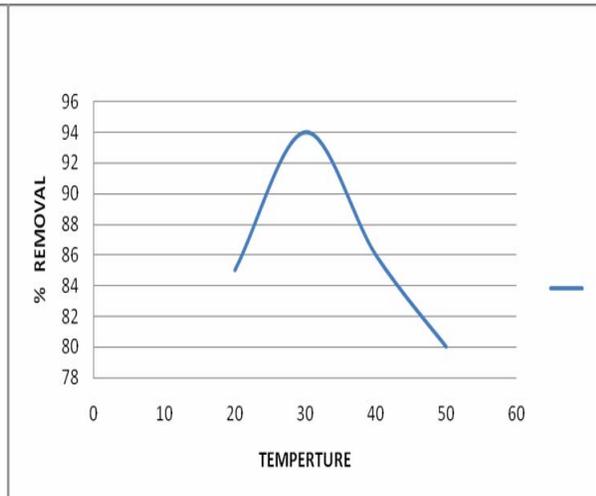
Graph6: 1mgL<sup>-1</sup> initial loading.



Graph7: 10mgL<sup>-1</sup> initial loading



Graph8: 20mgL<sup>-1</sup> initial loading.



#### 5.4. Effect of other anions on the Sorption of F<sup>-</sup> on ZrO-PA

In potable water, the common anion like SO<sub>4</sub><sup>2-</sup>, Cl<sup>-</sup>, NO<sub>3</sub><sup>2-</sup> are usually present. In order to know the effect of this ion on the sorption of F<sup>-</sup>, these studies were made by taking anions like SO<sub>4</sub><sup>2-</sup> & Cl<sup>-</sup> along with F<sup>-</sup>. The same column method is used for selective recovery. The effect of SO<sub>4</sub><sup>2-</sup> & Cl<sup>-</sup> on the sorption on fluoride was presented in table-3. The concentration of these ions was found significantly low in the F<sup>-</sup> solutions giving a suitable determination and potential

application to water sample. The reaction mechanism is supposed to be intraparticle diffusion control.

Table 3: Effect of other anions on the sorption of F<sup>-</sup> on ZrO-PA

Anion (added as NH <sub>4</sub> salt)	Concentration (mgL <sup>-1</sup> )	Recovery (%)
Cl <sup>-</sup> (NH <sub>4</sub> Cl)	500	99± 2
SO <sub>4</sub> <sup>-</sup> (NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub> )	500	97± 2

### 5.5. Recovery of F<sup>-</sup> ion from water samples

In order to estimate the accuracy of the method and to achieve practical applications, different amounts of fluoride ions 1, 5, 10, 20 mg F<sup>-</sup> were added to 500ml of drinking water collected from the institute campus. The same procedure in experimental section was followed. The analytical data of this experiment was presented in table-4 The recovery values were higher than 97% which confirm the accuracy of the proposed procedure and the effectiveness of ZrO-PA exchanger in Ca<sup>2+</sup> form to remove fluoride from drinking water.

Table -4: Recovery of F<sup>-</sup> Ion from water sample

Water samples from the campus		
Amount F <sup>-</sup> added (mgL <sup>-1</sup> )	Found(mgL <sup>-1</sup> )	Recovery (%)
1.0	1.7± 0.2	99± 1
5.0	6.0± 0.3	98± 1
10	11.3± 0.5	98 ±1
20	21± 0.2	97 ±2

### 5.6. Adsorption isotherms

To quantify the sorption capacity of the sorbent studied for the removal of fluoride, the two most commonly used isotherms, namely Freundlich and Langmuir isotherms have been adopted.

#### 5.6.1. Freundlich isotherm

The Freundlich isotherm in its linear form is represented by

$$\log q_e = \log k_F + \frac{1}{n} \log C_e \quad (1)$$

where  $q_e$  is the amount of fluoride adsorbed per unit weight of the sorbent (mg/g),

$C_e$  is the equilibrium concentration of fluoride in solution (mg/L),

$k_F$  is a measure of adsorption capacity and  $1/n$  is the adsorption intensity.

The Freundlich isotherm constants  $1/n$  and  $k_F$  were calculated from the slope and intercept of the plot  $\log q_e$  vs  $\log C_e$  and are presented in Table 1. The values of  $1/n$  lying between 0 and 1 and the  $n$  values lying in between 1 and 10 indicate the conditions favorable for adsorption. The higher  $n$  values indicate the applicability of Freundlich isotherm.

Table 4. Freundlich and Langmuir isotherms of the ion exchangers

Temp. (K)	Freundlich isotherm					Langmuir isotherm					
	$1/n$	$N$	$k_F$ (mg/g) $1/n$ (L/mg)	$R$	$\chi^2$	$Q^\circ$ (mg/g)	$b$ (L/g)	$R_L$	$R$	$\chi^2$	
293	0.748	1.337	0.579	0.998	2.8 E-4	7.752	0.067	0.713	0.972	4.8 E-4	
303	0.674	1.484	0.706	0.987	3.8 E-4	6.289	0.101	0.623	0.978	7.3 E-4	
313	0.615	1.626	0.838	0.997	4.7 E-4	5.618	0.136	0.551	0.980	1.1 E-3	

### 5.6.2. Langmuir isotherm

The Langmuir isotherm in its linear form is represented by  $\frac{C_e}{q_e} = \frac{1}{Q^\circ b} + \frac{C_e}{Q^\circ}$ .

where  $Q^\circ$  is the amount of adsorbate at complete monolayer coverage (mg/g) and gives the maximum sorption capacity of sorbent,

$b$  (L/mg) is Langmuir isotherm constant that relates to the energy of adsorption.

The Langmuir constants  $Q^\circ$  and  $b$  were calculated from the slope and intercept of the plot  $C_e/q_e$  versus  $C_e$  respectively and the values are presented in Table1. There is an increase in  $Q^\circ$  values with increase in temperature which indicates sorption capacity increases with rise in temperature which in turn suggests the mechanism of fluoride removal by the sorbent is mainly due to chemisorption. The higher  $r$  values indicate the applicability of Langmuir isotherm.

The feasibility of the isotherm can be tested by calculating the dimensionless constant separation factor or equilibrium parameter  $R_L$  is expressed as

$$R_L = \frac{1}{1 + bC_0} \quad (3)$$

where  $b$  is the Langmuir isotherm constant and  $C_0$  is the initial concentration of fluoride (mg/L). The  $R_L$  value at different temperatures studied were calculated and are given in Table1. The  $R_L$  values lying between 0 and 1 indicate the conditions favourable for adsorption.

## 5.7. Thermodynamic treatment of the sorption process

Thermodynamic parameters associated with the adsorption viz., standard free energy change ( $\Delta G^\circ$ ), standard enthalpy change ( $\Delta H^\circ$ ) and standard entropy change ( $\Delta S^\circ$ ) were calculated for ZrO-PA as follows.

The change in standard free energy of sorption is given by

$$\Delta G^\circ = -RT \ln K_0 \quad (5)$$

where  $K_0$  is the sorption distribution coefficient,  $\Delta G^\circ$  is the standard free energy change of sorption (kJ/mol),  $T$  is the temperature in Kelvin and  $R$  is the universal gas constant (8.314 J mol<sup>-1</sup> K<sup>-1</sup>). The sorption distribution coefficient ( $K_0$ ) was determined from the slope of the plot  $\ln(q_e/C_e)$  against  $C_e$  at different temperatures and extrapolating to zero  $C_e$  according to Khan and Singh method .

The sorption distribution coefficient can be expressed in terms of  $\Delta H^\circ$  and  $\Delta S^\circ$  as a function of temperature,

$$\ln K_d = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT}, \quad (6)$$

where  $\Delta H^\circ$  is the standard enthalpy change (kJ/mol) and  $\Delta S^\circ$  is standard entropy change (kJ/mol K). The values of  $\Delta H^\circ$  and  $\Delta S^\circ$  can be obtained from the slope and intercept of a plot of  $\ln K_0$  against  $1/T$ . The calculated thermodynamic parameters are presented in Table 2.

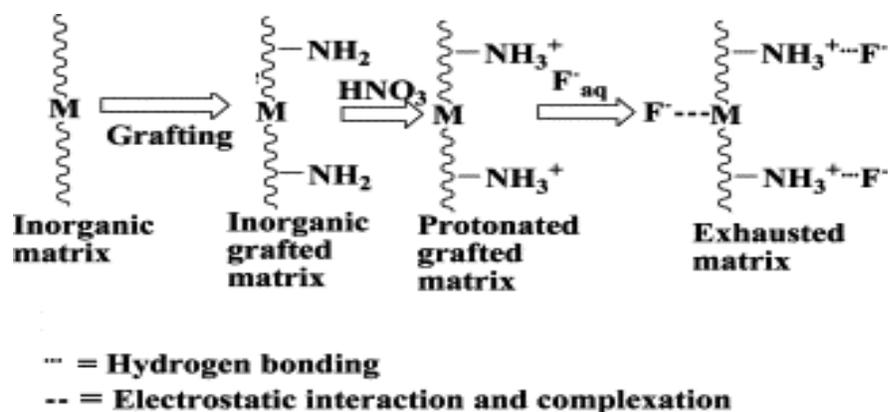
Table 5. Thermodynamic parameters for sorption of fluoride on ion exchangers at different temperatures

Sorbents	$\Delta G^\circ$ (J mol <sup>-1</sup> )			$\Delta H^\circ$ (kJ mol <sup>-1</sup> )	$\Delta S^\circ$ (J mol <sup>-1</sup> K <sup>-1</sup> )
	293 K	303 K	313 K		
ZrO-PA	-7885.94	-7278.27	-6885.29	23.55	51.82

The negative values of  $\Delta G^\circ$  confirm the spontaneous nature of sorption of fluoride ion by exchangers. The positive value of  $\Delta S^\circ$  which is a measure of randomness at solid/liquid interface indicates the fluoride sorption is irreversible and stable. The positive values of  $\Delta H^\circ$  for all the exchangers on fluoride sorption confirm the endothermic nature of sorption process.

## 5.8. Mechanism of fluoride removal

The fluoride removal by the sorbents appears to be controlled by both adsorption and ion-exchange mechanism as shown below. In fluoride solution, the F<sup>-</sup> ions get adsorbed onto the sorbent surface. In acidic medium, where the concentration of H<sup>+</sup> ion is high, the sorbent surface acquires positive charge which in turn attracts more fluoride ions by means of hydrogen bonding and hence there is a significant increase in DC at lower pH. As the pH increases surface slowly acquire negative charges which would repel fluoride ions and hence the fluoride removal by electrostatic attraction is ruled out in alkaline medium. The removal of fluoride may also be controlled by ion exchange with phosphate ions in addition to electrostatic attraction. Further the metal ions in the respective inorganic matrix could remove fluoride by means of both electrostatic interaction and complexation mechanism.



## 6. CONCLUSION

From the above studies, it is indicated that the adsorption process is chemisorption along with precipitation. Removal efficiency was found to be maximum when the initial fluoride concentration was high, hence this technique of removal may be suitably employed to treat industrial effluent where the concentration of fluoride is high. But the removal of fluoride using ZrO-PA cannot be used for domestic purpose, since it cannot bring fluoride concentration within permissible limit, and also increases the pH of the treated water. However, these methods can be optimized further by adding to other binding materials and can be formed into column, the study of which is in progress.

## 7. FUTURE WORK

The human curiosity to know the unknown things are the fundamental basis for scientific development. Based on the finding of present investigation, the following suggestions may be made for future studies:-

- (1) The hybrid material is considered as the next generation material which may be synthesized in nano-range.
- (2) The property in nano-range can be compared with the established property.
- (3) The surface area can be increased by some technique.
- (4) To improve the properties of the hybrid material as ion-exchanger.
- (5) A potable filter can be designed incorporating the results of above studies.

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