

# Zirconium-based adsorbent and hydroxy-lapatite for the removal of fluoride from drinking water, Jagalur, Davangere, Karnataka, India

Raghu V<sup>1</sup> and Srinidhi R Kulkarni<sup>2</sup>

PhD scholar, Department of Civil Engineering, BIET Davangere<sup>1</sup>

Assistant Professor, Department of Chemical Engineering, BIET Davangere<sup>2</sup>

**Abstract:** Drinking fluoridated water is a big health concern in various nations. The current study focuses on fluoride removal by a) zirconium-impregnated hybrid anion exchange (HAIX-Zr) resin, b) synthetic hydroxyapatite (HAP), and c) co-precipitation with calcium and phosphate. Fluoride absorption by HAIX-Zr resin was fairly quick, with 60% elimination achieved in 30 minutes. Fluoride absorption by HAIX-Zr resin followed the pseudo-second order kinetic model, and adsorption data best suited the Freundlich isotherm. Fluoride removal ability of the resin reduced as pH and bicarbonate concentration increased. Continuous flow packed-bed studies with genuine groundwater were also carried out.

**Key words:** Groundwater, fluoride removal using Zirconium Synthetic hydroxy lapatite calcium and phosphate

## I. INTRODUCTION

Water is an essential natural resource required for sustaining all forms of life on earth. Water is regarded as a “human right” rather than a “human need”. Access to “closer and cleaner drinking water” is still a distant dream for about one-sixth of humanity on this planet (Ayoob et al., 2008). As of 2015, it was estimated that three out of ten people (2.1 billion) do not use a safely managed drinking water source (UNESCO, 2019). Around the world, 663 million people lack access to clean drinking water (UNICEF, 2016). After the addition of clean water and sanitation as a Sustainable Development Goal (SDG), there has been increasing global attention for solving water-related issues, especially in developing countries.

There are several organic and inorganic groundwater contaminants responsible for various water-borne diseases. Fluoride is one of the major inorganic contaminants of groundwater. Estimates suggest that around 200 million people from 25 nations around the globe are affected by the adverse effects of fluoride (Ayoob and Gupta, 2006). In India, groundwater, and around seventy million people are drinking water with fluoride concentrations more than the prescribed limit (Macdonald et al., 2011).

## II. OBJECTIVES OF THE STUDY

The current study sought to create a low-cost, long-term fluoride elimination technique. The following goals were envisioned:

- Investigate the efficacy of HAIX-Zr resin for fluoride removal
- Assess the efficacy of synthetic non-calcined HAP for fluoride removal
- Investigate fluoride removal by co-precipitation with calcium and phosphate
- Create a HAP-based household defluoridation unit these goals have been met through a number of batch and continuous flow column tests.

## III. MATERIALS AND METHODS

### Instruments Used

1.pH meter 2.Ion-selective electrode 3.Peristaltic pump 4.Electronic balance 5.Fluoride meter 6.Spectrophotometer 7.Conductivity meter 8.Inductively coupled plasma - atomic emission spectroscopy (ICP-AES) 9.Total Organic Carbon Analyzer

- HAP crystallite size was calculated using Scherrer equation (3.1) (Mostafa, 2005):  $L = K \cdot \lambda / \beta \cdot \cos \theta$
- The degree of crystallinity (crystalline fraction) of synthesized HAP was calculated using the equation reported by Landi et al. (2000) as:  $B002 \sqrt{Xc} = K$

IV. EXPERIMENTAL METHODS

All the experiments were conducted at room temperature unless otherwise specified.

1. Fluoride Removal by Hybrid Anion Exchange Resin (HAIX-Zr): Batch Studies

Sample water spiked with fluoride to determine the effects of different aqueous phase parameters such as pH, contact time, co-existing anions, 0 1000 2000 3000 4000 5000 6000 0 20 40 60 80 100 Intensity Angle 2θ FAP FAP FAP FAP 36 initial fluoride concentration, and temperature. The effect of pH was studied over the pH range 4-11. For adsorption kinetics, variation in fluoride concentration was observed over the contact time of 360 min, with an adsorbent dose of 1 g/L. Adsorption isotherm studies were conducted with different initial fluoride concentrations (3-20 mg/L).

Percentage fluoride removal and adsorption capacity per gram of adsorbent  $q_e$  (mg/g) were calculated by given as: % removal =  $((C_o - C_e) / C_o) \times 100$   $C_o$  = initial fluoride concentration

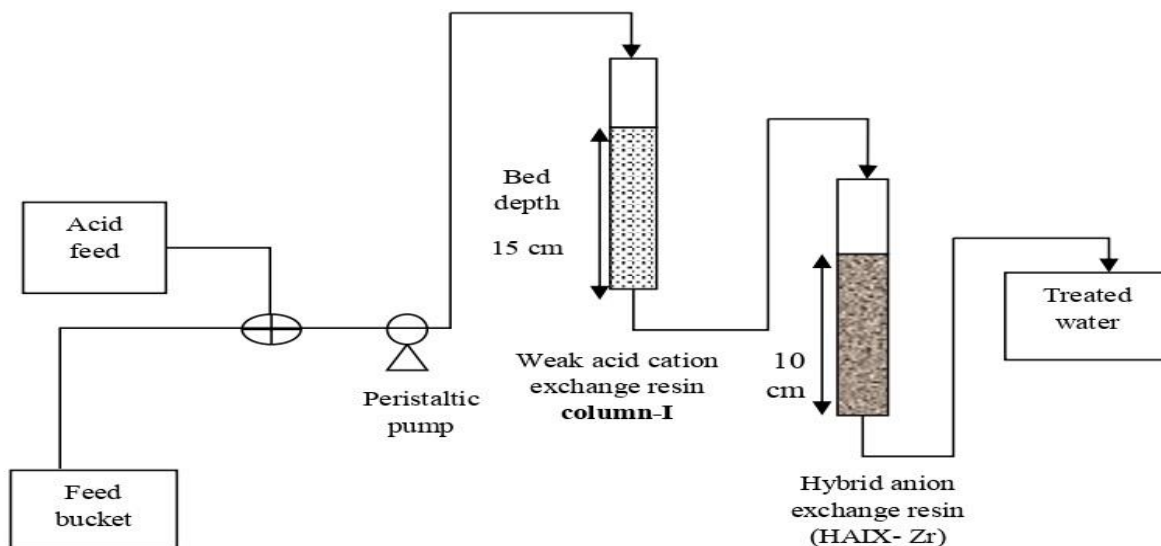
$$q_e = ((C_o - C_e) / m) \times V$$

$C_e$  = Equilibrium fluoride concentration  
 $m$  = mass of adsorbant  $V$  = volume of solution

In these experiments, the concentration of these co-ions was varied up to 100 mg/L.

2. Fluoride Removal by Hybrid Anion Exchange Resin (HAIX-Zr): Continuous Flow Packed-Bed Studies

In actual field conditions, a fixed-bed mode of operation is preferred over batch mode. Therefore, continuous flow fixed bed reactor studies were also conducted. Regeneration of fluoride-loaded HAIX-Zr resin was conducted by passing the mixture of 3 % NaOH and 3 % NaCl (W/W) solution. The regenerate solution was passed through the fluoride-loaded resin bed at the flow rate of 1.5 mL/min using a peristaltic pump. Samples taken at column outlet were analysed for fluoride concentration after dilution.



3. Fluoride Removal by HAP: Batch Studies

HAP dose was kept constant at 1 g/L. The initial pH of samples was set to 7±0.1 using diluted HCl or NaOH. Samples were taken at a predefined time interval and were filtered through 0.2 µm nylon filter. as pH, fluoride, phosphate, and calcium. In the following subsection, methodologies adopted for various batch experiments conducted to evaluate fluoride removal by HAP have been mentioned.

**4. Effect of HAP’s Ca/PHAP Molar Ratio and Amended Aqueous Calcium on Defluoridation**

Batch trials were carried out at room temperature using a 60 rpm end-over-end rotor. A dosage of 1 g/L HAP was utilised. For the studies, HAPs with Ca/PP molar ratios of 1.64 and 1.70 were utilised. 100 mg of HAP was accurately weighed and placed to HDPE bottles containing 100 mL of simulated fluoride solution.

**5. Effect of HAP’s Calcination Temperature on Fluoride removal**

The fluoride removal ability of HAP dried at 80°C and calcined at 300, 600, and 800 °C with and without modified aqueous calcium was investigated. CaCO<sub>3</sub> was used to make a 10 g/L calcium stock solution.

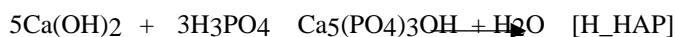
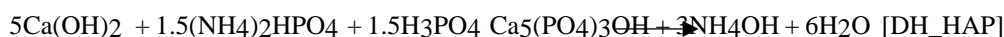
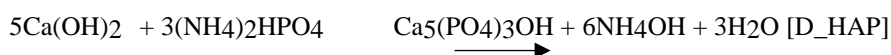
**6. Fluoride Removal by HAP in Simulated Groundwater**

Recipe of various synthetic groundwater matrices

Components (mg/L)	Synthetic Groundwater			DI
	A	B	C	
F	9.89	9.96	9.79	10.1
Ca <sup>2+</sup>	139.6	24.59	14.93	0
Mg <sup>2+</sup>	162.45	13.16	1.6	0
SiO <sub>2</sub>	34.4	45	54.2	0
HCO <sub>3</sub> <sup>-</sup>	1439.6	512.4	1195.6	0
SO <sub>4</sub>	1.7	15.5	20.8	0

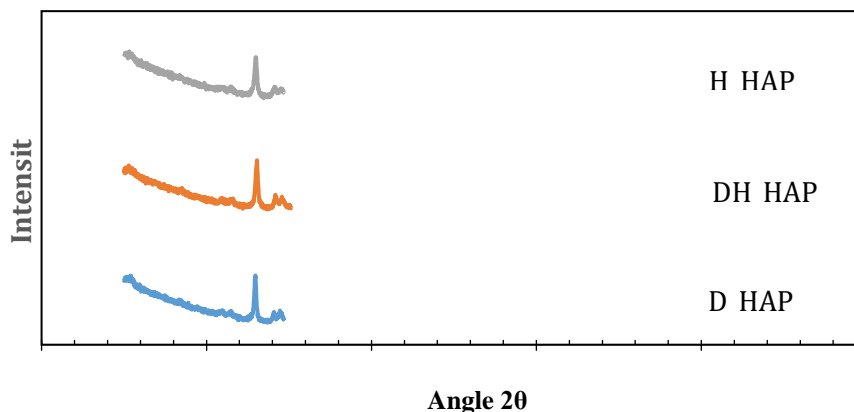
**7. Fluoride Removal by HAPs Synthesized under Different Reaction Conditions**

Batch experiments were conducted to evaluate the fluoride removal using HAPs prepared with three different methods. Different proportions of DAP and phosphoric acid were used, which are shown in following reaction conditions:



The synthesized HAPs were characterized using XRD pattern. The crystalline peaks at 2θ

= 26, 32, 32.3, 33.2, 34.3, and 46.8° were compared and agreed with synthetic HAP (reference no.- 00003-0747 X’Pert software). The prepared HAPs were evaluated for dissolution and fluoride removal capacities through batch experiments.



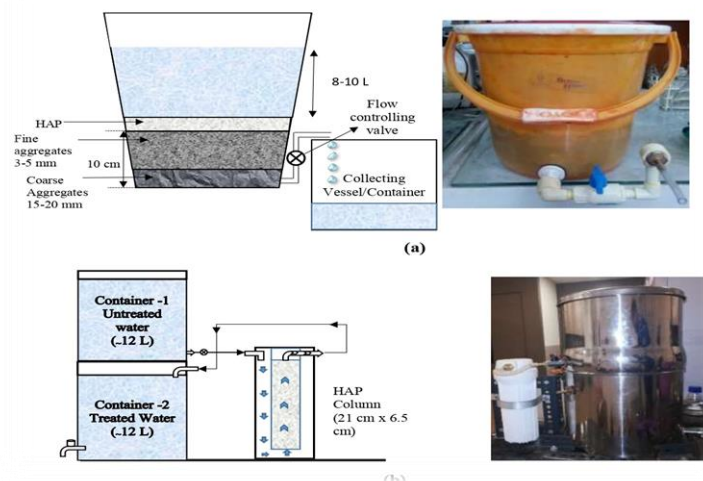
XRD pattern of HAPs synthesized with different methods

**8. Fluoride Removal by Co-precipitation with Calcium and Phosphate: Batch Studies**

Using normal calcium phosphate and fluoride solutions, a synthetic solution containing calcium (55 mg/L and 100 mg/L), phosphate (25 mg/L), and fluoride (5 mg/L) was created. Samples were collected at predetermined intervals and filtered through a 0.2 m nylon filter before being evaluated for different water quality parameters. Solids retained above the filter were examined using XRD and XPS at the end of the tests. The effect of seeding (FAP) was investigated by adding 0.1 g/L FAP to the sample solution. The effect of pH was studied at controlled pH levels of 6, 7, and 8.5. Bicarbonate concentrations of 50 mg/L, 100 mg/L, and 200 mg/L were used to test the impact.

**9. Development of HAP based Household Defluoridation Unit (HDU)**

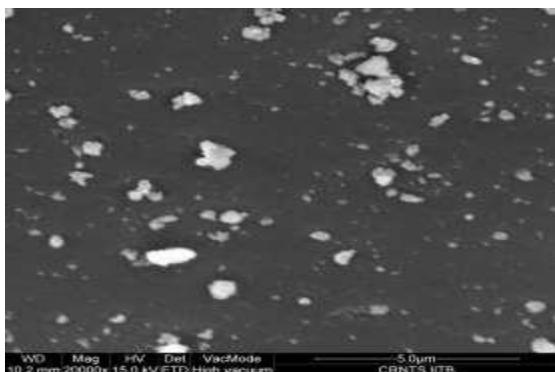
Figure (a) shows a schematic of the HDU developed using HAP particles and aggregates of different sizes. The original HDU design consisted of a 16 liter bucket, leaving a volume of 8–10 liters after the introduction of aggregates and HAP particles (Fig. a). Bucket filter outlet fittings were made of chlorinated polyvinyl chloride (CPVC). At the bottom of the bucket, a 10 cm thick layer of aggregate of different sizes with a size of 10-15 mm was placed followed by a layer of 3-5 mm thick aggregate. Approximately 268 g of 1.18-2 mm HAP particles were spread over the agglomerates followed by 222 g of 0.5-1.18 mm HAP particles. The total dried depth of the HAP layer was (approximately) 2.5 cm and the dry volume of the particles was 1 liter. The developed bucket filter was tested in real field conditions (Davangere, Karnataka, India). Fluorinated water from Tank 1 enters the outer chamber of the treatment unit and then her HAP column inside. Water flow in the HAP column is from bottom to top. After passing through the HAP column, the treated water exits the treatment unit and is sent to tank 2 for storage prior to use. HAP particles with sizes ranging from 0.355 mm to 1 mm were loaded into the treatment unit.



Schematic of household defluoridation unit (a) older design having HAP bed above the layer of aggregates (b) improvised design with HAP column separated from storagetanks

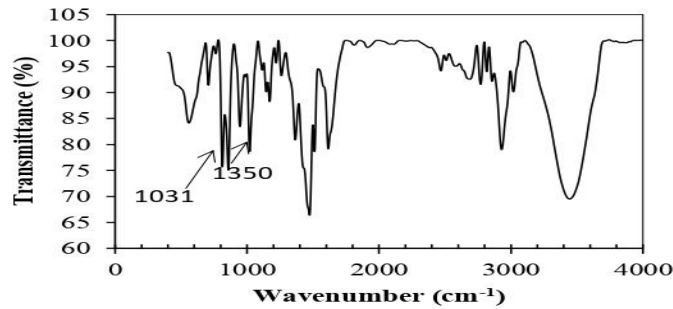
**V. RESULTS AND DISCUSSION**

**1. Fluoride Removal using Zirconium Impregnated Anion Exchange Resin (HAIX-Zr)**

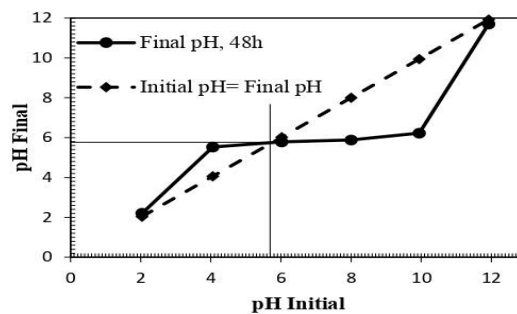


Element	Weight %
Carbon	16.55
Oxygen	2.58
Zirconium	61.19
Chloride	19.68

Figure: Scanning electron microscope (SEM) images with EDX analysis of HAIX-Zrresin



FTIR spectrum of hybrid anion exchange resin (HAIX-Zr)



The  $pH_{pzc}$  of HAIX-Zr resin, 0.01 M NaCl as background electrolyte concentration

Comparison of defluoridation capacity of various adsorbents at circum-neutral Ph

Adsorbent	Particle size (mm)	Dose (g/L)	Initial F <sup>-</sup> conc. (mg/L)	pH	Contact time (h)	Capacity (mg/g)	References
Granular zirconium-iron oxide	1-1.5	5	10	7±0.2	10	2	Dou et al., 2011
Manganese oxide impregnated activated alumina	0.096 (d50)	8	25	6.5	3	2.875	Tripathy et al., 2006
Magnesium substituted hydroxyapatite	<0.425	1	5.5	7±0.5	24	2.636	Garg & Chaudhari, 2012
Manganese oxide coated alumina	0.5-0.6	5	11.14	7±0.2	3	1.863	Maliyekkal et al., 2006
Activated alumina	0.5-0.6	5	11.14	7±0.2	10	1.488	Maliyekkal et al., 2008
Lanthanum incorporated chitosan beads	-	1.5	5.34	7±0.2	24	3.2	Bansiwal et al., 2009
Hydroxyapatite	0.6-0.84	3	5	6	23	1.534	Jiménez-Reyes & Solache-Ríos, 2010
HAIX-Zr	1-2	1	10	7±0.1	3	8.43	Present study

**2. Continuous Flow Packed-Bed Column Studies**

Fluoride concentration in the groundwater sample was  $2.6 \pm 0.2$  mg/L, which is more than the WHO guideline value (1.5 mg/L F<sup>-</sup>) and Indian fluoride standards (1 mg/L F<sup>-</sup>).

Chemical characteristics of real-life groundwater sample from Jagalur village in Davandere Karnataka

Parameter	Value
pH	6.5-6.8
Alkalinity as CaCO <sub>3</sub>	600 mg/L
Hardness as CaCO <sub>3</sub>	200 mg/L
TDS	1137 mg/L
Fluoride concentration	$2.6 \pm 0.2$ mg/L

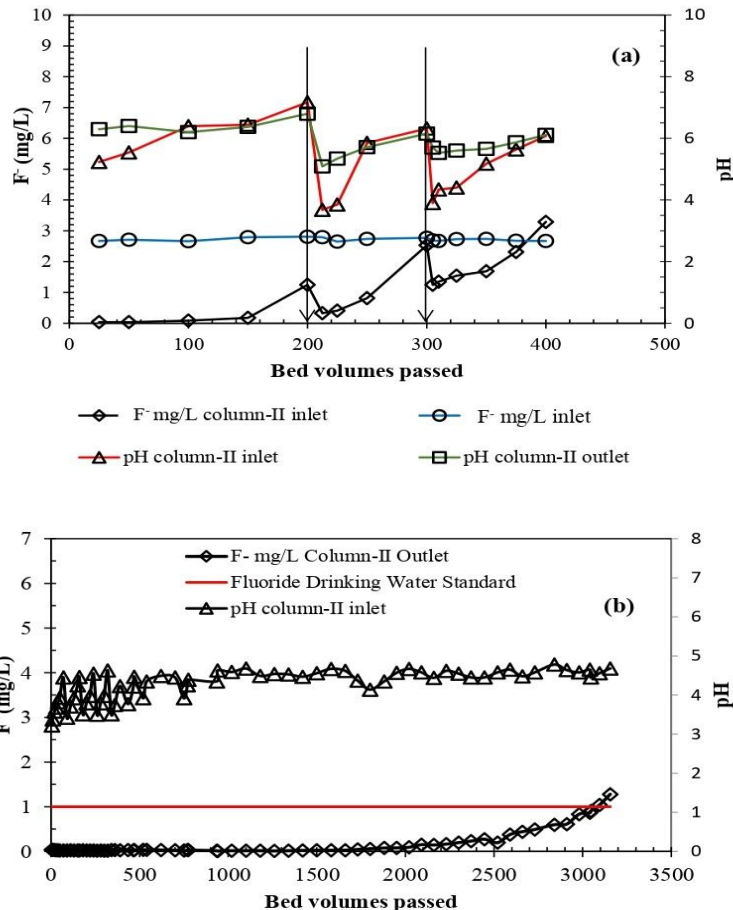
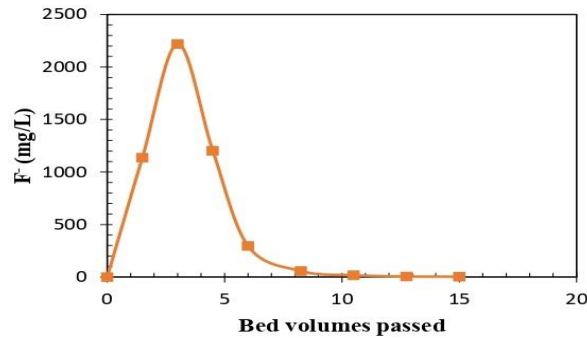


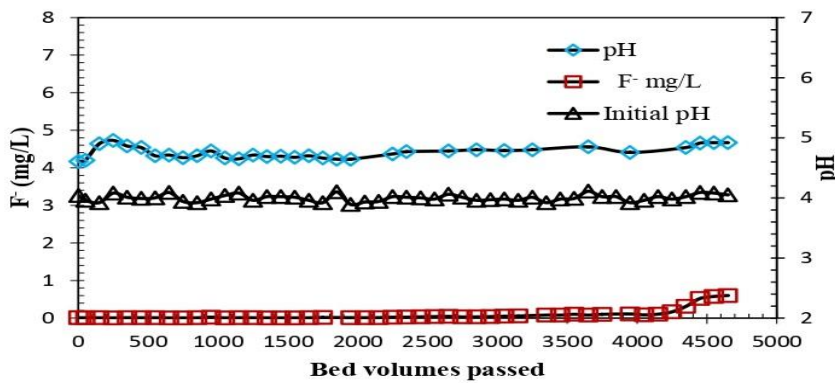
Figure: (a) Variation of pH and fluoride at column-2 for run-1, vertical arrows indicate regeneration of INDION 236 resin (b) Run-2, pH of the inlet water sample entering HAIX-Zrcolumn was decreased

**3. Regeneration of Fluoride Loaded HAIX-Zr Resin**

Regeneration of HAIX-Zr resin was performed using a mixture of 3% NaOH and 3% NaCl solution. The regenerant solution was passed through the fluoride-loaded resin bed at a 1.5 mL/min flow rate using a peristaltic pump. shows in figure the variation of fluoride



Variation of fluoride coming out of HAIX-Zr bed during regeneration, flow rate = 1.5 mL/min



HAIX-Zr resin performance for fluoride removal after regeneration

#### 4. Kinetics of Fluoride Removal by Synthetic HAP

The kinetics of fluoride uptake onto HAP was evaluated with 5 mg/L initial fluoride. Figure as in shows the variation of water quality parameters with 5 days (7200 min) of contact time.

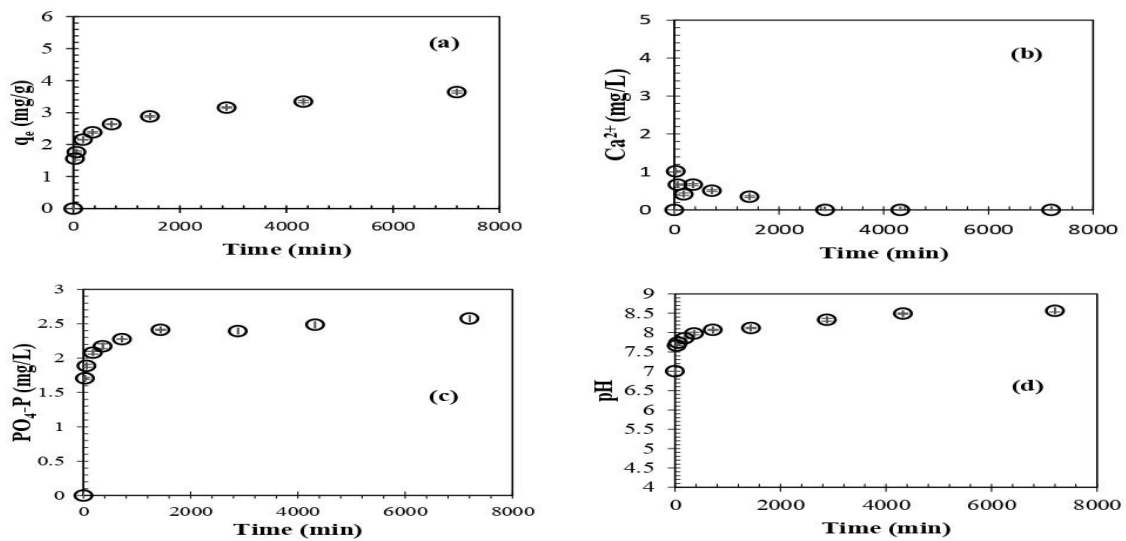


Figure: Variation of water quality parameters with contact time (a) fluoride (b) calcium (c) Phosphate, and (d) pH, HAP dose 1g/L, Ca/PHAP = 1.64

**5. Fluoride Removal by HAP in Simulated Groundwater**

groundwater matrices containing fluoride vary significantly in terms of the presence of other co-ions. groundwater chemistry comprising high alkalinity and low calcium concentrations typically favours the dissolution of fluoride-bearing minerals. . To prepare simulated groundwater, salts of calcium(CaCO<sub>3</sub>) and magnesium (MgCO<sub>3</sub>) were dissolved by passing CO<sub>2</sub> gas to replicate groundwater conditions.

Variation of treated water quality parameters with change in HAP dose for each synthetic groundwater matrix

Ground water matrix	HAP Dose (g/L)	pH (mg/L)	Ca <sup>2+</sup> (mg/L)	PO <sub>4</sub> -P (mg/L)	Mg <sup>2+</sup> (mg/L)
A (Ca <sup>2+</sup> =139.6 mg/L, Mg <sup>2+</sup> = 162.45 mg/L, HCO <sup>-3</sup> = 1439.6 mg/L)	1	6.77	99.41	0.13	159.6
	3	6.73	88.79	0.23	154.48
	5	6.73	83.59	0.44	155.62
B (Ca <sup>2+</sup> =24.59 mg/L, Mg <sup>2+</sup> = 13.16 mg/L, HCO <sup>-3</sup> = 512.4 mg/L)	1	6.40	15.05	0.68	12.53
	1.5	6.5	14.87	1.16	12.4
	3	6.39	11.38	1.76	11.41
	5	6.4	10.73	2.85	10.8
C (Ca <sup>2+</sup> =14.93 mg/L, Mg <sup>2+</sup> = 1.6 mg/L, HCO <sup>-3</sup> = 1195.6 mg/L)	1	6.64	5.82	1.40	1.88
	1.5	6.63	4.57	2.25	1.84
	3	6.65	3.61	4.26	1.83
Distilled water spiked with fluoride only	1	8.05	BDL	2.27	-
	1.5	8.3	BDL	3.11	-
	3	8.41	BDL	5.01	-
	4	8.58	BDL	5.91	-
	5	8.35	BDL	6.46	-

Comparison of experimental and theoretical service time values with change inflow rate (Bed Depth 21±0.5, F = 5 mg/L)

Flow rate (mL/min)	Theoretical service time (h)	Experimental service time (h)
3	10.34	8.95 ±0.35
5	2.87	4.55 ±0.35

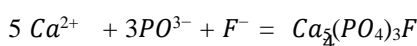
Comparison of theoretical and service time value, with change in initial fluoride concentration (Bed depth 14±0.5)

Initial concentration (mg/L)	Theoretical service time (h)	Experimental service time (h)
3	28.61	23.6 ±0.84
7	6.81	5.3 ±0.14

**6. Fluoride Removal by Co-precipitation with Calcium and Phosphate**

**a) Fluoride Removal by Co-precipitation with Excess Calcium (Ca/F = 9.5) and Phosphate (P/F = 6)**

The fluoride removal process was defined by the reaction (Deng et al., 2016):





$$K_{sp} = [Ca^{2+}]^5[PO_4^{3-}]^3[F^-] = 10^{-55.71} \text{ (at } 25^\circ\text{C)}$$

(When  $Ca^{2+}$ ,  $PO_4^{3-}$  and  $F^-$  in a solution are supersaturated,  $Ca(PO_4)F$  will precipitate.

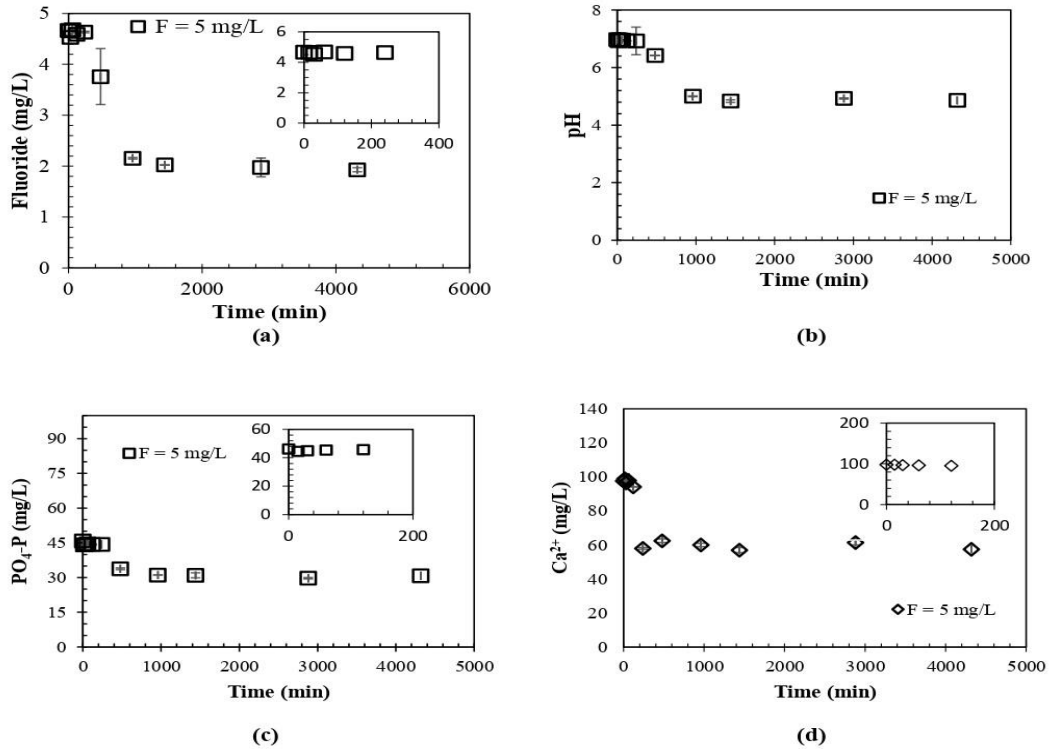


Figure: Variation of water quality parameters (a) fluoride (b) pH (c) phosphate, and (d) calcium (fluoride concentration over 72 h of contact time; initial Ca/P molar ratio of FAP =  $1.65 \pm 0.1$ ; initial pH =  $7 \pm 0.1$ )

**b) Effect of pH on Fluoride Removal by Co-precipitation with Calcium and Phosphate**

The possible reason for the phenomenon is when  $HPO_4^{2-}$  or  $H_2PO_4^-$  releases  $PO_4^{3-}$  to form HAP or fluorapatite (FAP),  $H^+$  ions increase in the aqueous phase, hence decreasing the pH. Also, there is a possibility of formation of HAP first, followed by subsequent fluoride uptake by HAP. In the formation of HAP  $[Ca_5(PO_4)_3OH]$ ,  $OH^-$  ion is consumed from the aqueous phase, which could also be the reason for the decrease in pH. This indicates that at higher pH, along with FAP formation, HAP formation may also take place due to a higher concentration of  $OH^-$  ions. Similarly, calcium uptake was higher in the case of pH 7 and 8.5, least in the case of uncontrolled pH (Figure).

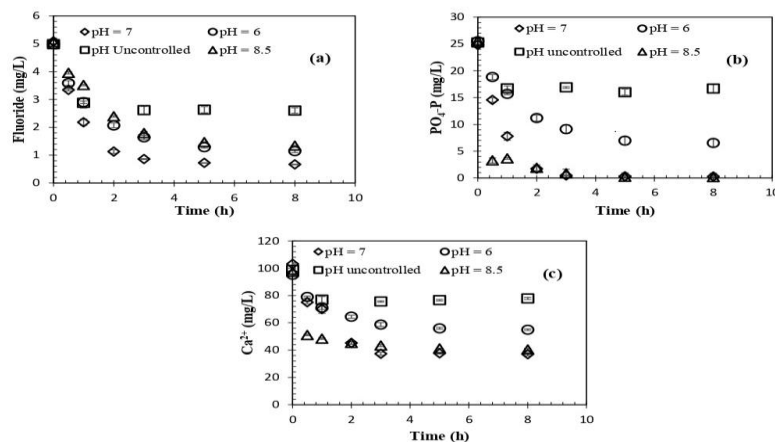


Figure: Variation of water quality parameters with change in pH, (a) fluoride (b) phosphate, and (c) calcium

**Table 1:** Water quality parameters of treated water from filter unit, the values shown are average of filters units for Jagalur

Village	No. of person drinking water from filter units	Water quality parameter in treated water	No. of days of filter run										
			2	25	28	31	34	37	45	50	55	60	65
Jagalur	14	Fluoride	0.17	0.24	0.18	0.19	0.12	0.25	0.27	1.05	0.91	0.15	0.57
		Phosphate	NA	0.05	0.02	0.04	0.62	0.03	0.07	1.49	0.52	0.72	2.47
		pH	NA	7.59	7.70	7.72	7.69	7.59	7.73	7.49	7.63	7.53	7.57

### CONCLUSIONS

Fluoride removal using HAIX-Zr resin

- At neutral pH ( $7 \pm 0.1$ ), the defluorination capacity of HAIX-Zr resin was higher than other adsorbents commonly used for fluorine removal (described in the literature).
- Increased aqueous pH and the presence of bicarbonate reduce the defluorination capacity of HAIX-Zr resins.
- Fixed-bed column studies have shown that a two-column design in which the sample water is passed through a cation exchange resin before his HAIX-Zr can effectively remove fluoride from real groundwater.
- Under the experimental conditions tested, one cycle of the sorbent used can treat approximately 3000 bed volumes of groundwater.
- In addition, the system can effectively remove excess dissolved solids (TDS) from brackish groundwater.
- HAIX-Zr-Resin is therefore committed to providing clean drinking water to fluoride-affected areas

### Fluoride removal by co-precipitation with calcium and phosphate

- Fluoride removal by co-precipitation with calcium and phosphate is kinetically slow, with nucleation of fluoroapatite (FAP) being the rate-limiting step. This can be catalyzed by adding FAP as a seed.
- In coprecipitation experiments, higher fluoride removal was observed at pH 7 compared to pH 6 and 8 for the conditions evaluated.
- Under the experimental conditions tested, the presence of bicarbonate increased the removal of fluoride by coprecipitation up to bicarbonate concentrations of 100 mg/L. A further increase in bicarbonate concentration (200 mg/l) decreased the fluoride removal efficiency.
- The presence of HAP and calcium carbonate ( $\text{CaCO}_3$ ) enhanced fluoride removal by co-precipitation with calcium and phosphate. However, in systems containing  $\text{CaCO}_3$ , FAP seeds were required to initiate the formation of FAP nuclei.
- Developed household defluoridation system can effectively remove fluoride from drinking water. Other water quality parameters (pH, calcium, TDS) were also below standard values.
- Therefore, the developed domestic defluoridation system shows promise in providing clean drinking water to the affected areas

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