Efficient Fluoride Removal by a Fixed-Bed Column of Self-Assembled Zr(IV)-, Fe(III)-, Cu(II)-Complexed Polyvinyl Alcohol Hydrogel Beads

Sai Kiran Mani and Rajni Bhandari*

ABSTRACT: Fixed-bed column adsorption studies are performed with metal-complexed polyvinyl alcohol (PVA) hydrogel beads to remove fluoride from groundwater. The fixed-bed column (bed height = 8 ± 0.2 cm) of copper–zirconium–PVA (PCZH), zirconium–PVA (PZH), and iron–zirconium–PVA (PFZH) hydrogel beads have equilibrium fluoride removal capacities of 17.26 ± 0.05, 31.67 ± 0.05, and 11.84 ± 0.05 mg g⁻¹ from a 10 ± 0.20 mg L⁻¹ fluoride solution of pH 6.5 maintained at a flow rate of 1 ± 0.01 mL min⁻¹. The breakthrough curves for fluoride adsorption are analyzed by non-linear empirical models of Thomas, Bohart–Adams, Yoon–Nelson, and semi-empirical bed depth service time models. The maximum fluoride adsorption capacities obtained from the Thomas model are 25.66 ± 0.05, 38.17 ± 0.05, and 13.75 ± 0.05 mg g⁻¹ for PCZH, PZH, and PFZH. Moreover, the column of PZH (bed height = 4 ± 0.2 cm) can remove about 1.67 ± 0.05 mg g⁻¹ of fluoride from the alkaline groundwater sample with high total dissolved solids containing 2.84 ± 0.20 mg L⁻¹ fluoride maintained at a flow rate of 0.5 ± 0.01 mL min⁻¹. The fluoride removal efficiency decreases marginally (<1 ± 0.02%) in the presence of interfering ions such as chlorides, sulfates, phosphates, bicarbonates, and nitrates. Furthermore, the fixed-bed column (bed height = 4 ± 0.2 cm) of PCZH, PZH, and PFZH remove 7.40 ± 0.05, 14.85 ± 0.05, and 6.53 ± 0.05 mg g⁻¹ fluoride, respectively, even after the third regeneration cycle. Additionally, the hydrogel beads are effective in the removal of arsenate (≤90 ± 0.02%) and chromate ions (≤96 ± 0.02%) from 100 ± 0.20 mg L⁻¹ solution in batch adsorption studies. Therefore, the hydrogel beads could be used as potent filters for the removal of fluoride, chromate, and arsenate ions from water.

1. INTRODUCTION

Groundwater is widely used for domestic needs. However, the presence of high fluoride content in groundwater is a matter of concern. Earth’s crust has about 625 mg kg⁻¹ of fluoride, which is mainly present in minerals such as fluorite, topaz, cryolite, amphiboles, sellaite, apatite, villiaumite, mica, and certain clays. The concentration of fluoride in groundwater also depends on lithology, residence time, seasonal changes, and local pollution caused mainly by anthropogenic sources such as industries, oil refineries, coal burning, or leakages in the aquifers. Fluoride contamination of groundwater is a global issue affecting several million populations of Asia, Africa, and United States of America.

In India, fluoride contamination is rampant in the southern and western regions encompassing the districts of Andhra Pradesh, Telangana, Kerala, Uttar Pradesh, Uttarakhand, Bihar, Jharkhand, and West Bengal. The fluoride concentration in groundwater varies from 0.6 to 7.8 mg L⁻¹ in these regions.6 The permissible limit of fluoride in drinking water is 1.5 mg L⁻¹ as per the World Health Organization and 1.0 mg L⁻¹ as per the Bureau of Indian Standards. Therefore, the development of efficient fluoride removal technologies is highly desirable. Several methods have been developed for fluoride removal from water, such as precipitation, ion exchange, reverse osmosis, adsorption, membrane filtration, and electrodialysis.
Table 1. Summary of Material Characteristics and Outcomes of Batch Fluoride Adsorption Studies of the Hydrogel Beads

| s.no. | experiment | PCZH | PFZH | PZH | instrumental technique used |
|-------|------------|------|------|-----|-----------------------------|
| 1     | physical profile of beads | swelling index | 199.44 ± 0.02% | 238.93 ± 0.02% | 243.51 ± 0.02% | analytical weighing balance |
|       | dimensions (diameter × height) | 3.6 ± 0.01 mm × 10 ± 0.01 mm | 3.6 ± 0.01 mm × 10 ± 0.01 mm | 4.0 ± 0.01 mm × 11 ± 0.01 mm | screw gauge |
| 2     | morphology | mesoporous surface | coarse surface with ridges | coarse mesoporous surface | scanning electron microscopy |
| 3     | porosity | average pore size (nm) | 0.55 ± 0.01 | 0.27 ± 0.01 | 0.68 ± 0.01 | Brunauer–Emmet–Teller surface analyser |
|       | pore volume (cm³ g⁻¹) | 5.35 ± 0.05 × 10⁻⁴ | 2.97 ± 0.05 × 10⁻⁴ | 5.22 ± 0.05 × 10⁻⁴ |
|       | surface area (m² g⁻¹) | 1.95 ± 0.02 | 2.15 ± 0.02 | 1.54 ± 0.02 |
| 4     | thermal stability | major weight loss due to disruption of cross-links (41.84 ± 0.02%) | major weight loss due to disruption of cross-links (43.09 ± 0.02%) | major weight loss on polymer degradation (40.5 ± 0.02%) |
| 5     | crystallinity of beads | crystallite size (nm) | 2.30 ± 0.01 | 1.65 ± 0.01 | 1.35 ± 0.01 | X-ray diffractometer |
|       | degree of crystallinity (%) | 22.00 ± 0.02% | 14.38 ± 0.02% | 17.93 ± 0.02% |
| 6     | adsorption thermodynamics | standard Gibbs free energy of adsorption, ΔG° (kJ mol⁻¹) | −37.13 ± 0.02 | −43.07 ± 0.02 | −43.48 ± 0.02 | ΔH° and ΔS° is calculated by Van’t Hoff equation |
|       | standard enthalpy of adsorption, ΔH° (kJ mol⁻¹) | −81.22 ± 0.02 | −48.30 ± 0.02 | −163.99 ± 0.02 |
|       | standard entropy of adsorption, ΔS° (J mol⁻¹ K⁻¹) | 274.99 ± 0.02 | 185.12 ± 0.02 | 572.42 ± 0.02 |
| 7     | batch fluoride adsorption studies | pH | 3.0 ± 0.2–9.0 ± 0.2 | 3.0 ± 0.2–9.0 ± 0.2 | 3.0 ± 0.2–9.0 ± 0.2 | bench-top meter with fluoride-ion-selective electrode |
|       | contact time | 6 ± 0.02 h–12 ± 0.02 h | 6 ± 0.02 h–12 ± 0.02 h | 6 ± 0.02 h–12 ± 0.02 h |
|       | initial fluoride concentration | 10 ± 0.2 mg L⁻¹ | 10 ± 0.2 mg L⁻¹ | 10 ± 0.2 mg L⁻¹ |
|       | ion interference (Cl⁻,NO₃⁻,HCO₃⁻, PO₄³⁻ and SO₄²⁻) | negligible | negligible | negligible |
|       | regenerability (% fluoride removal after the 10th cycle) | 97 ± 0.02 | 95 ± 0.02 | 99 ± 0.02 |
|       | metal leaching from the adsorbent | Cu²⁺ = 0.040 ± 0.030 mg L⁻¹ | Fe³⁺ = 0.230 ± 0.020 mg L⁻¹ | Zr⁴⁺ = 0.017 ± 0.002 mg L⁻¹ | inductively coupled plasma–mass spectrometry |
|       | | Zr⁴⁺ = 0.017 ± 0.002 mg L⁻¹ | | | |
Table 2. Parameters of Fixed-Bed Column Studies of Hydrogel Beads Obtained from the Breakthrough Curves

| Bed material | Flow rate (±0.01 mL min⁻¹) | Bed height (±0.2 cm) | EBCT (±0.02 min) | % fluoride removal (±0.05 mg g⁻¹) | φf (±0.06 mg g⁻¹) | qf (±0.02 mg) | qeff (±0.02 mg g⁻¹) |
|--------------|-----------------------------|----------------------|------------------|----------------------------------|------------------|--------------|------------------|
| PCZH         | 0.50                        | 5.73                 | 15.60            | 9.38                             | 0.10             | 0.18         | 0.38             |
|              | 1.00                        | 9.38                 | 27.60            | 17.38                            | 0.38             | 0.38         | 0.38             |
| Zr–PVA       | 0.50                        | 10.94                | 27.60            | 17.38                            | 0.38             | 0.38         | 0.38             |
|              | 1.00                        | 27.60                | 55.20            | 45.78                            | 0.38             | 0.38         | 0.38             |

- % fluoride removal: The percentage of fluoride removal from the solution.
- φf: Fluoride adsorption capacity.
- qf: Fluoride adsorption at equilibrium.
- qeff: Effective fluoride adsorption.

Water is 1 mg L⁻¹, as per the Bureau of Indian Standards (BIS), while it is 1.5 mg L⁻¹ according to the World Health Organization (WHO). Ingestion of excess fluoride causes dental, skeletal, and non-skeletal fluorosis. Moreover, accumulation of fluoride in the body has adverse effects on the gastrointestinal, reproductive, and nervous systems.

There are several mitigation strategies used to curb the fluoride menace, namely, ion exchange, precipitation, adsorption, electrocoagulation, nanofiltration, and other membrane processes. Membrane filtration and electrocoagulation techniques are energy-intensive and have high maintenance costs. The membrane and electrodes used for the process need frequent replacement and are often costly. However, adsorption has attracted wide attention of researchers due to its cost-effectiveness, high selectivity, and good efficiency. In order to establish a contact between the adsorbate and the adsorbent, different adsorption techniques are used which include batch, continuous fixed-bed, continuous moving bed, continuous fluidized bed, and pulsed-bed adsorption. Though batch fluoride adsorption studies are effective in the optimization of various parameters, column fluoride adsorption studies are effective in proving the practical applicability of the adsorbents for water treatment. The adsorbent is tightly packed in a column, and the fluoride solution passes through it continuously at a fixed flow rate. This model is widely used in industries to treat a large quantity of pollutants. Thus, in the current work, fixed-bed adsorption studies are carried out with the metal ion-complexed PVA hydrogel beads for efficient fluoride removal to develop potent filters for defluoridation.

Although there are many reports on batch adsorption studies for fluoride removal, there are a few reports in literature about fixed-bed column studies as the process is time-consuming and requires a longer optimization time. Nevertheless, mathematical modeling of the fixed-bed column adsorption process reduces the time required for optimization of column parameters for efficient adsorption. Moreover, careful experimental design of different parameters involved in the study could be done by using a surface response methodology to make the process very efficient and to minimize the optimization time. So far, researchers have used clays, metal-loaded bio-sorbents, mixed metal oxides, and carbonaceous materials as adsorbents for the fixed-bed fluoride adsorption studies. However, the materials reported so far have not been effective in the defluoridation of groundwater due to high interference from other competing ions. Moreover, these adsorbents have good fluoride removal capacity predominantly at an acidic pH. To overcome these challenges, self-assembled zirconium (PZ), iron–zirconium (PFZH), and copper–zirconium (PCZh)–complexed PVA hydrogel beads are synthesized, which have good regenerability, wide pH applicability, and good selectivity for fluoride even for groundwater samples. In the current study, the fluoride adsorption efficiency by the fixed-bed column of cylindrical metal–PVA hydrogel beads is explored by experimental techniques. In addition, mathematical modeling of the breakthrough curve is done to obtain the parameters for fixed-bed column adsorption. To the best of our knowledge, this is the first study on a fixed-bed column of metal–PVA hydrogel beads for effective fluoride adsorption from the groundwater sample. Moreover, due to good anion binding ability of the hydrogel beads, they are also tested for the removal of potentially toxic metal ions like...
arsenic (V) and chromium (VI), which predominantly exist as AsO$_4^{3-}$ and CrO$_4^{2-}$, respectively, in aqueous solution.$^{19,20}$ Therefore, the hydrogel beads could be used for the effective removal of fluoride, arsenate, and chromate ions.

2. MATERIALS AND METHODS

2.1. Materials. Zirconium oxychloride octahydrate (ZrOCl$_2$$\cdot$8H$_2$O, 98%) and trans-1,2 diaminocyclohexane-$N,N,N,N$-tetraacetic acid monohydrate (CDTA monohydrate, 98%) were purchased from Sigma-Aldrich. Polyvinyl alcohol (molecular weight = 1,45,000; degree of hydrolysis = 98–99%), sodium fluoride (NaF, 99.99%), sodium hydroxide (NaOH, 99%), hydrochloric acid (HCl, 37–38%), acetic acid (CH$_3$COOH, 96%), copper sulfate pentahydrate (CuSO$_4$$\cdot$5H$_2$O, 99%), ferric nitrate nonahydrate [Fe(NO$_3$)$_3$$\cdot$9H$_2$O, 98%], glutaraldehyde [OHC(CH$_2$)$_3$CHO, 50 wt % solution in H$_2$O], and potassium chromate (K$_2$CrO$_4$, 98.5%) were procured from Merck, India. Sodium arsenate heptahydrate (Na$_2$HAsO$_4$$\cdot$7H$_2$O, 98%) was obtained from Loba Chemie.
Pvt. Ltd., India. All chemicals were of analytical grade and used without further processing. The solutions were prepared in Milli-Q water (Direct Q UV-8, 18 MΩ cm−1).

2.2. Synthesis of Metal-Ion–PVA Hydrogel Beads. The metal-ion–PVA hydrogel beads are obtained by simple one-pot synthesis. A 10 wt % (w/v) solution of PVA and 0.20 ± 0.02 mol L−1 of the metal salt with 20 ± 0.02 µL of 50 wt % (v/v) glutaraldehyde are added in a vial, and the solution is homogenized in a vortex shaker. The solution gelates and self-assembled cylindrical beads are formed on heating at 70 ± 2 °C. The hydrogel beads are washed and subjected to freeze–thaw cycles. Finally, the polymer hydrogel beads are dried at 90 ± 2 °C and used for column adsorption studies.

2.3. Optimization of Column Parameters. The physico-chemical characterization of the metal-ion-incorporated hydrogel beads is performed. The effects of pH, temperature, interfering ions, and initial fluoride concentrations on the batch adsorption process are optimized (Table 1). The experimental results of fluoride adsorption studies and the characterization of the hydrogel beads establish that fluoride uptake occurs mainly by chemical bonding, hydrogen bonding, and pore diffusion. The thermodynamic parameters of adsorption are computed from the adsorption equilibrium studies at 25, 35, and 45 °C.21,22 The standard Gibbs’s free energy of adsorption (ΔG°o) is calculated as

\[ \Delta G^o = -RT \ln K_c \]  

where \( K_c \) the dimensionless equilibrium constant, is obtained by converting Langmuir constant \( K_L \), which is given by eq 2.

\[ K_c = 55.5 \times 1000 \times K_L \times M_w \]  

where \( M_w \) is the molar mass of the analyte used in the study (i.e., NaF).

The standard enthalpy (ΔH°) and standard entropy (ΔS°) of adsorption are obtained from the van’t Hoff equation

\[ \ln K_c = -\frac{\Delta H^o}{R} \times \frac{1}{T} + \frac{\Delta S^o}{R} \]  

Figure 3. Non-linear mathematical model fit (Thomas, Bohart–Adams, and Yoon–Nelson) for the breakthrough curves of PCZH, PFZH, and PZH, variation in: (i) flow rate (a,c,e) and (ii) bed height (b,d,f).

Figure 4. BDST model: (a) PCZH, (b) PFZH, and (c) PZH.
Table 3. Mathematical Modeling of the Breakthrough Curves

| beads       | $N_{th}$ (±0.05 mg L$^{-1}$) | $k_{BDST}$ (±0.0001 L mg$^{-1}$ min$^{-1}$) | $R^2$ |
|-------------|-------------------------------|---------------------------------|-------|
| PCZH        | 67.04                         | 1.51 × 10$^{-2}$                | 0.95  |
| PFZH        | 57.67                         | 1.74 × 10$^{-2}$                | 0.99  |
| PZH         | 60.47                         | 3.47 × 10$^{-2}$                | 0.99  |

USA). Furthermore, for the fixed-bed column adsorption studies, parameters such as bed height and flow rate are optimized.

2.3.1. Lab-Scale Fixed-Bed Column Adsorption Studies. Fabricated borosilicate glass columns with 1.3 cm inner and 1.5 cm outer diameters and lengths of 5 and 10 cm are used for the study. These dimensions are chosen to make a potent portable fluoride water filter for commercial applicability.23 The dried hydrogel beads are packed into the column and plugged with cotton on either side of inlet and outlet, for continuous flow fixed-bed studies. Columns with bed heights of 2 ± 0.2, 4 ± 0.2, and 8 ± 0.2 cm are chosen for the study. On passing the fluoride solution, the hydrogels swell up due to the high swelling ability, thereby reducing the void spaces in the column. As the hydrogels exhibit pH-independent behavior in a wide pH range (3.0 ± 0.2–9.0 ± 0.2), the column adsorption is carried out with a fluoride solution of pH 6.5 ± 0.2 (Table 1).18 The groundwater fluoride concentration is generally found to be 10 ± 0.20 mg L$^{-1}$ in India.1,2 Hence, for fixed-bed column adsorption, the influent fluoride concentration ($C_{in}$) is maintained at 10 ± 0.20 mg L$^{-1}$, and all the studies are conducted at 25 °C. Three different flow rates (0.10 ± 0.01, 0.50 ± 0.01, and 1.0 ± 0.01 mL min$^{-1}$) are maintained using a peristaltic pump (Ismatec Reglo ICC, Cole Parmer, Germany) with the fluoride influent pumped in the upward direction to avoid channeling.17 The adsorbent bed heights are fixed at 2 ± 0.02 cm (adsorbent dosage = 0.9 g), 4 ± 0.02 cm (adsorbent dosage = 1.8 g), and 8 ± 0.02 cm (adsorbent dosage = 3.6 g). Water is collected from the column outlet every hour, and the effluent fluoride concentration ($C_{out}$) is measured using a bench top meter with a fluoride-ion selective electrode (Orion A124, Thermo Fischer Scientific, USA) using TISAB II.24 The fluoride ion-selective electrode has a limit of detection of 0.02 mg L$^{-1}$ (10$^{-6}$ mol L$^{-1}$) and could be used in the temperature range of 0–80 °C. The reproducibility of data is ±2% on regular calibration, and the electrode has a linear range of operation for a slope between −54 and −60 mV. This is obtained by calibrating the electrode with three fluoride standards of a 10-fold difference in the concentration. The electrode could be used for the detection of the fluoride concentration as low as 0.02 mg L$^{-1}$.

2.4. Evaluation of the Breakthrough Curve. The performance of the column packed with PZH, PCZH, and PFZH beads are evaluated based on the breakthrough curves. Breakthrough curves are a plot of the ratio of effluent concentration to the influent concentration ($C_{out}/C_{in}$) versus time. The shape of the breakthrough curve and time required for breakthrough plays a significant role in interpreting the dynamic behavior of the column and improves the operational design. The steepness of the breakthrough curve also provides the information about the extent to which the adsorbent bed could be utilized.25

The column breakthrough time ($t_b$) is taken when $C_{out} ≤ 1.5$ ± 0.2 mg L$^{-1}$ and the saturation time ($t_s$) is chosen when the
The effluent concentration is 95% of the initial concentration (10 ± 0.2 mg L⁻¹). The effluent volume (\( V_{eff} \)) passing through the column is given by

\[ V_{eff} = Q \cdot t_e \]  

where \( Q \) is the flow rate (L h⁻¹) and \( t_e \) is the column exhaustion time.²⁷

The amount of fluoride in the column (\( m_{in,t} \) mg) at time, \( t \) (h), is given by

\[ m_{in,t} = C_0 Q t \]  

where \( Q \) is the flow rate (L h⁻¹) and \( C_0 \) is the initial concentration of the fluoride solution (mg L⁻¹).

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Figure 5. FT-IR spectra of polymer hydrogel beads before and after fluoride adsorption.

Scheme 1. Mechanism of Fluoride Adsorption by Fixed-Bed Column of Metal–PVA Hydrogel Beads

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Table 5. Evaluation of the Column Performance

| beads  | flow rate (±0.01 mL min⁻¹) | bed height (±0.2 cm) | DoSU (±0.02%) | SUR (±0.05 g L⁻¹) | number of bed volumes (±0.10) |
|--------|---------------------------|---------------------|--------------|--------------------|-----------------------------|
| PCZH   | 0.50                      | 2                   | 54.94        | 12.50              | 135.68                      |
|        | 0.10                      | 4                   | 56.93        | 6.52               | 52.01                       |
|        | 0.50                      | 4                   | 37.42        | 2.61               | 138.03                      |
|        | 1.00                      | 4                   | 28.03        | 1.53               | 241.83                      |
|        | 0.50                      | 8                   | 59.30        | 0.85               | 197.87                      |
| PZH    | 0.50                      | 2                   | 52.14        | 13.64              | 124.37                      |
|        | 0.10                      | 4                   | 22.07        | 11.53              | 29.40                       |
|        | 0.50                      | 4                   | 25.68        | 2.61               | 130.03                      |
|        | 1.00                      | 4                   | 5.82         | 1.43               | 237.44                      |
|        | 0.50                      | 8                   | 34.20        | 2.18               | 155.47                      |
| PFZH   | 0.50                      | 2                   | 61.71        | 18.75              | 90.45                       |
|        | 0.10                      | 4                   | 65.42        | 5.66               | 59.93                       |
|        | 0.50                      | 4                   | 38.05        | 3.00               | 113.07                      |
|        | 1.00                      | 4                   | 51.67        | 1.67               | 203.52                      |
|        | 0.50                      | 8                   | 55.09        | 2.03               | 166.77                      |
The amount of unadsorbed fluoride \((m_{\text{out},t}, \text{mg})\) at time, \(t\), is calculated by multiplying the area under the dimensionless curve with the initial concentration, \(C_0\), and the flow rate \((Q)\) is given by the equation

\[ m_{\text{out},t} = C_0 Q \int_0^t \left( \frac{C_t}{C_0} \right) dt \]  

(6)

The amount of fluoride adsorbed \((m_{\text{ads},t}, \text{mg})\) by the column is given by

\[ m_{\text{ads},t} = m_{\text{in},t} - m_{\text{out},t} \]  

(7)

The equilibrium uptake capacity \((q_e, \text{mg} g^{-1})\) by the column at saturation time \((t_s)\) is given by the equation

\[ q_e = \frac{m_{\text{ads},t}}{M} = \frac{C_0 Q \int_0^{t_s} \left( 1 - \frac{C_t}{C_0} \right) dt}{M} \]  

(8)

The uptake at breakthrough is given by

\[ q_b = \frac{m_{\text{ads},t_b}}{M} = \frac{C_0 Q \int_0^{t_b} \left( 1 - \frac{C_t}{C_0} \right) dt}{M} \]  

(9)

where \(M\) is the mass of the adsorbent in grams.\(^\text{23}\)

The fluoride adsorption efficiency of the column packed with hydrogel beads is given by

\[ \% \text{ Fluoride removal} = \frac{m_{\text{ads},t}}{m_{\text{in},t}} \times 100 \]  

(10)

The empty bed contact time (EBCT) of the column is defined as

\[ \text{EBCT} = \frac{\text{Bed volume(mL)}}{\text{Flow rate(mL min}^{-1})} \]  

(11)

The greater values of removal efficiency, breakthrough time, and saturation time indicate the good adsorption ability of the hydrogel beads packed in the column.

3. RESULTS AND DISCUSSION

The efficiency of fluoride removal is largely dependent on the bed height of the column and the flow rate of the analyte.\(^\text{9}\)

The nature of the breakthrough curve is understood by predicting the mass-transfer zone (MTZ) that exists in a fixed-bed column. This is given by the equation

\[ \text{MTZ} = \left( 1 - \frac{t_b}{t_s} \right) \times L \]  

(12)

where \(L\) is the length of the column, \(t_b\) is the breakthrough time, and \(t_s\) is the saturation time.

As a fluoride solution passes through the adsorbent in the column, in the upward direction, the adsorbent in the lower layers of the column adsorbs rapidly \((C_t/C_0 = 0)\). With time, the lower layers get saturated and adsorption occurs in the unadsorbed layers of the adsorbent and eventually, the column gets saturated \((C_t/C_0 = 1)\). Thus, at a particular initial concentration of the analyte, the rate at which the column saturates depends on the flow rate (Table 2). Moreover, the time required for column saturation also escalates on increasing the bed height (Table 2). The breakthrough curves are plotted with respect to time and treated effluent volume (Figures 1 and 2).

3.1. Effect of the Flow Rate on Fluoride Adsorption by Metal–PVA Hydrogel Beads. The fixed-bed fluoride adsorption by the hydrogel beads is studied at three different flow rates with a constant bed height of 4 ± 0.2 cm and an inlet fluoride concentration of 10 ± 0.2 mg L\(^{-1}\). It is observed that on increasing the flow rate from 0.10 ± 0.01 to 1 ± 0.01 mL min\(^{-1}\), the breakthrough and saturation time decrease.\(^\text{28}\) This is because the contact time of fluoride with the adsorbent decreases on increasing the flow rate (Table 2). Moreover, the fluoride removal efficiency is better for the hydrogel beads at a lower flow rate as fluoride gets sufficient time for interaction with the hydrogel beads. This also justifies the higher breakthrough time for PCZH, PZH, and PFZH at 46 ± 0.02, 26 ± 0.02, and 53 ± 0.02 h, at a flow rate of 0.10 ± 0.01 mL min\(^{-1}\) (Figure 1a,c,e). However, on increasing the flow rate, the equilibrium fluoride adsorption capacity and the treated effluent volume increases. This is because at a flow rate of 1 ± 0.01 mL min\(^{-1}\), more amount of fluoride passes through the column \((m_{\text{in}})\) and the fluoride adsorbed \((m_{\text{ads}})\) by the column increases (Table 2).\(^\text{25}\) The fluoride removal capacities are 31.67 ± 0.05 mg g\(^{-1}\) (PZH), 17.26 ± 0.05 mg g\(^{-1}\) (PCZH), and 11.84 ± 0.05 mg g\(^{-1}\) (PFZH) for an effluent flow rate of 1 ± 0.01 mL min\(^{-1}\). Hence, a greater volume of fluoridated water is treated at a higher flow rate (Figure 2). However, to facilitate sufficient adsorbent contact time with fluoride and to improve the fluoride removal efficiency, the flow rate of the analyte is fixed at 0.50 ± 0.01 mL min\(^{-1}\).

3.2. Effect of Bed Height on Fluoride Adsorption by Metal–PVA Hydrogel Beads. The adsorbent bed height also plays a crucial role in designing the column for groundwater treatment. Raising the height of packed adsorbent in the column from 2 ± 0.2 to 8 ± 0.2 cm at 0.50 ± 0.01 mL min\(^{-1}\) flow rate brings about an increase in the column breakthrough time \((t_b)\), saturation time \((t_s)\), and

![Figure 6. Regeneration curves for the fixed-bed column adsorption: (a) PCZH, (b) PFZH, and (c) PZH.](https://pubs.acs.org/journal/acsodf)
treated effluent volume ($V_{eff}$), and MTZ (Table 2). Hence, the column efficiency depends on the adsorbent bed height. It is observed that the effective MTZ increases on raising the bed height in the fixed-bed column. The EBCT increases as the bed height is increased. EBCT of the column with bed heights, $2 \pm 0.2$, $4 \pm 0.2$ and $8 \pm 0.2$ cm are $5.31 \pm 0.03$, $10.62 \pm 0.03$ and $21.24 \pm 0.03$ min, respectively. It is observed that the fluoride removal efficiency of the column is higher for $8 \pm 0.2$ cm bed height as the adsorbate–adsorbent interaction is prolonged due to high EBCT (Table 2). Moreover, the column saturation time for PCZH ($47 \pm 0.02$ to $167 \pm 0.02$ h), PZH ($74 \pm 0.02$ to $255 \pm 0.02$ h), and PFZH ($39 \pm 0.02$ to $153 \pm 0.02$ h) when the bed height changes from $2 \pm 0.2$ to $8 \pm 0.2$ cm. This substantiates that the column with a greater bed height could be used for a longer period of time (Figure 1b,d,f).

Moreover, a larger effluent volume is treated and the efficiency of the column also improves at a bed height of $8 \pm 0.2$ cm (Figure 2b,d,f).

### 3.3. Column Adsorption Models

The breakthrough curves are analyzed using the three empirical kinetic models, namely, Thomas, Bohart–Adams, Yoon–Nelson, and a semi-empirical bed depth service time (BDST) model, to obtain different parameters for fixed-bed adsorption (Figures 3 and 4). These models are chosen specifically to obtain the maximum adsorption capacity and half-time of breakthrough of the column, to understand the mechanism of adsorption and efficacy of the column for fluoride removal. The empirical models can be mathematically simplified into the following non-linear expression, which is given by

\[
\frac{C_t}{C_0} = \frac{1}{1 + e^{(a-b)t}}
\]  

However, the parameters “a” and “b” are different in the models.

#### 3.3.1. Thomas Model

The Thomas model is based on the assumption that equilibrium adsorption data follows the Langmuir adsorption isotherm and obeys pseudo-second-order kinetics. The model assumes that the rate-limiting step is devoid of diffusion and axial dispersion.

The linear equation of the Thomas model is given by

\[
\ln \left( \frac{C_t}{C_0} - 1 \right) = \frac{k_{Th}q_e m}{Q} - k_{Th}C_0 t
\]  

where $k_{Th}$ is the Thomas rate constant (L mg$^{-1}$ h$^{-1}$), $C_0$ is the initial fluoride concentration (mg L$^{-1}$), $C_t$ is the fluoride concentration at any time, $t$ (mg L$^{-1}$), $q_e$ is the fluoride adsorbed per unit gram of the adsorbent (mg g$^{-1}$), $m$ is the mass of the adsorbent (g), and $Q$ is the flow rate of the adsorbent (L h$^{-1}$).

The non-linear equation of the Thomas model can be expressed in the form of eq 13, which is given as

\[
\frac{C_t}{C_0} = \frac{1}{1 + e^{\frac{k_{Th}q_e m}{Q} - k_{Th}C_0 t}}
\]  

The data obtained from the fixed-bed column studies are fitted in the Thomas model (Figure 3). Parameter $k_{Th}$ decreases with the increase in the flow rate (Table 3). This indicates that a fluoride uptake predominantly occurs by chemisorption. Moreover, the equilibrium adsorption data for hydrogel beads fit well in the Langmuir adsorption isotherm.
in the batch adsorption studies. The value of \( q_0 \) obtained from the Thomas model is in good agreement with the calculated equilibrium capacity, \( q_e \), indicating that this model best describes the dynamic behavior of the column.

3.3.2. Bohart–Adams Model. This model is based on the assumption that equilibrium does not occur instantaneously. The rate of adsorption is proportional to residual capacity of the adsorbent and concentration of the adsorbate. The linear equation of the Bohart–Adams model is given as follows:

\[
\ln \left( \frac{C_0}{C_t} - 1 \right) = \frac{k_{BA} N_0 L}{u} - k_{BA} C_0 t
\]  

(16)

The non-linear equation for the Bohart–Adams model is given by

\[
\frac{C_t}{C_0} = \frac{1}{1 + e^{(\ln(N_0/k_{BA}) - k_{BA} C_0 t)}}
\]  

(17)

where \( k_{BA} \) is the Bohart–Adams rate constant (L mg\(^{-1}\) h\(^{-1}\)), \( N_0 \) is the saturation concentration (mg L\(^{-1}\)), \( Z \) is bed depth of the column (cm), and \( F \) is the linear velocity (cm min\(^{-1}\)).

The fixed-bed column data are fitted in the Bohart–Adams model. It is observed that at a higher flow rate, the value of \( N_0 \) increases while \( k_{BA} \) decreases (Table 3). However, the value of \( N_0 \) decreases on raising the bed height, which implies that external mass transfer in the column adsorption process plays a role and the adsorption occurs slowly.

3.3.3. Yoon–Nelson Model. The Yoon–Nelson model is based on the assumption that the decrease in the adsorption rate depends on the probability of adsorption of the adsorbate. The linear equation of the Yoon–Nelson model is given as follows:

\[
\ln \left( \frac{C_0}{C_t} - 1 \right) = \frac{k_{YN} N_0 L}{u} - k_{YN} C_0 t
\]  

(18)

The non-linear equation for the Yoon–Nelson model is given by

\[
\frac{C_t}{C_0} = \frac{1}{1 + e^{(\ln(N_0/k_{YN}) - k_{YN} C_0 t)}}
\]  

(19)

where \( k_{YN} \) is the Yoon–Nelson rate constant (L mg\(^{-1}\) h\(^{-1}\)), \( N_0 \) is the saturation concentration (mg L\(^{-1}\)), \( Z \) is bed depth of the column (cm), and \( F \) is the linear velocity (cm min\(^{-1}\)).

The fixed-bed column data are fitted in the Yoon–Nelson model. It is observed that at a higher flow rate, the value of \( N_0 \) increases while \( k_{YN} \) decreases (Table 3). However, the value of \( N_0 \) decreases on raising the bed height, which implies that external mass transfer in the column adsorption process plays a role and the adsorption occurs slowly.

In the batch adsorption studies. The value of \( q_0 \) obtained from the Thomas model is in good agreement with the calculated equilibrium capacity, \( q_e \), indicating that this model best describes the dynamic behavior of the column.

### Table 7. Physico-Chemical Analysis of Groundwater Before and After Fluoride Adsorption

| parameter     | before adsorption | after adsorption |
|---------------|-------------------|------------------|
| pH (±0.01)    | 8.12              | 7.10 7.20 6.72   |
| TDS (±2 mg L\(^{-1}\)) | 1100              | 245 257 290      |
| hardness (±0.01 mg L\(^{-1}\)) | 856.00            | 821.76 770.40 719.04 |
| Na\(^+\) (±0.01 mg L\(^{-1}\)) | 308.10            | 299.70 304.81 288.80 |
| K\(^+\) (±0.01 mg L\(^{-1}\)) | 3.38              | 3.26 3.35 3.11   |
| Mg\(^{2+}\) (±0.01 mg L\(^{-1}\)) | 618.60            | 540.30 575.20 402.70 |
| Ca\(^{2+}\) (±0.01 mg L\(^{-1}\)) | 856.65            | 721.65 590.05 714.89 |
| conductivity (±0.001 mS cm\(^{-1}\)) | 0.070             | 0.063 0.061 0.061 |
| fluoride (±0.01 mg L\(^{-1}\)) | 2.84              | 0.00 0.00 0.00   |

Table 8. Parameters of Fixed-Bed Column Studies for Fluoride Adsorption by Hydrogel Beads Obtained from Breakthrough Curves in the Presence of Interfering Ions

| beads  | flow rate (±0.01 mL min\(^{-1}\)) | bed height (±0.2 cm) | \( m_0 \) (±0.02 mg) | \( m_{0,b} \) (±0.02 mg) | \( t_b \) (±0.02 h) | \( t_s \) (±0.02 h) | \( \theta_0 \) (±0.05 mg g\(^{-1}\)) | \( \theta_b \) (±0.05 mg g\(^{-1}\)) | \( V_{ef} \) (±0.03 mL) | EBCT (±0.02 min) | MTZ (±0.02 cm) | DoSU (±0.02%) | SUR (±0.05 g L\(^{-1}\)) | % fluoride removal (±0.02%) |
|--------|---------------------------------|---------------------|---------------------|---------------------|---------------------|---------------------|---------------------------------|---------------------------------|---------------------|---------------------|-----------------|----------------|----------------|----------------|----------------|
| PCZH   | 0.50                            | 2                   | 12.60               | 7.24                | 10                  | 36                  | 8.05                            | 5.06                            | 1260                | 5.31               | 1.44            | 62.88          | 3.00            | 57.46          |
| PZH    | 0.50                            | 2                   | 24.68               | 12.75               | 11                  | 60                  | 14.17                           | 6.15                            | 2040                | 5.31               | 1.63            | 52.55          | 2.72            | 51.64          |
| PFZH   | 0.50                            | 2                   | 10.80               | 5.38                | 6                   | 30                  | 5.98                            | 3.45                            | 1080                | 5.31               | 1.60            | 57.67          | 5.00            | 49.83          |

Figure 7. (a) Borosilicate-column packed with PFZH beads, (b) laboratory-scale column setup, (c) ion-interference studies, and (d) non-linear model fit (Thomas, Bohart–Adams, and Yoon–Nelson) for breakthrough curves of groundwater sample.
adsorbate and the occurrence of breakthrough at the adsorbent, which is given by the linear equation

$$\ln \left( \frac{C_0}{C_t} - 1 \right) = k_{YN} \tau - k_{YN} t$$  \hspace{1cm} (18)

The Yoon–Nelson model could be written in a non-linear mathematical form given by

$$\frac{C_t}{C_0} = \frac{1}{1 + e^{(k_{YN} \tau - k_{YN} t)}}$$  \hspace{1cm} (19)

where $k_{YN}$ is the Yoon–Nelson rate constant coefficient and $\tau$ is the time required for 50% breakthrough.14

On fitting the data in the Yoon–Nelson model, it is observed that the value of $\tau$ reduces at a higher flow rate (Table 3). This is because the breakthrough is attained faster due to reduction in the EBCT.23 It is observed that $k_{YN}$ is inversely related to the bed height.14 The column with a greater bed height has a longer saturation time as indicated by a higher value of $\tau$ for PCZH ($\tau = 116 \pm 0.02$ h), PZH ($\tau = 164 \pm 0.02$ h), and PFZH ($\tau = 113 \pm 0.02$ h) (Table 3).

### 3.3.4. Bed Depth Service Time Model

The efficiency of the column depends on its ability to provide clean water for a longer duration. The service time of the column for a specific bed height is determined using the BDST model (Figure 4). The model assumes that the rate of adsorption depends on the interaction between the adsorbent and the unused adsorbent in the column bed.9 This model was initially proposed by Bohart and Adams and later modified by Hutchins.31 The model is based on the linear relationship between the bed height and service time of the column. This is based on the assumption that the adsorbate is directly adsorbed onto the adsorbent, there is a negligible contribution by intraparticle diffusion or mass transfer. The BDST model is given by the equation

$$t = \frac{N_0}{C_0 F} Z - \frac{1}{k_{BDST} C_0} \ln \left( \frac{C_0}{C_t} - 1 \right)$$  \hspace{1cm} (20)

where $t$ is the time at which breakthrough is attained (min), $F$ is the linear flow velocity (cm min$^{-1}$), $N_0$ is the adsorption capacity of the bed in mg L$^{-1}$, $Z$ is the bed depth (cm), and $k_{BDST}$ is the rate constant (L mg$^{-1}$ min$^{-1}$). The bed saturation capacity obtained from the BDST model indicates that PCZH removes a greater amount of fluoride compared to other hydrogel beads (Table 4).

### 3.4. Mechanism of Fluoride Adsorption

Adsorption equilibrium of the adsorbate in aqueous medium and the solid adsorbent in a fixed-bed column is generally attained due to axial dispersion, intra-particle diffusion resistance (pore and surface diffusion) and film resistance.14 This can be explained by considering the following stages of adsorption: (1) fluoride is transported from the bulk solution into an immobile layer of ions surrounding the hydrogel beads by advective transport or axial dispersion to the hydrogel beads, (2) fluoride can penetrate through the immobile layer to reach the adsorbent surface sites, (3) adsorption can occur by the binding of fluoride to the specific sites of the adsorbent, and (4) the fluoride can also diffuse into the pores of the hydrogel beads by intraparticle diffusion. The rate of fluoride removal by hydrogel beads is dependent on one or more of these commonly reported phenomena.32 In batch adsorption studies, stage 1 and stage 2 can be neglected as the adsorbent is stirred vigorously. However, in the fixed-bed column adsorption studies, stage 1 and 2 also play a role in the rate-determining step especially for the column of a greater bed height.35 The binding of fluoride to the metal-incorporated PVA hydrogel beads may occur by electrostatic interaction, hydrogen bonding, and pore diffusion.18 FT-IR analysis of spectra of the metal-incorporated hydrogel beads, post-fluoride adsorption, proves the existence of the interaction between fluoride and hydrogels (Figure 5). In the FT-IR spectrum of metal–PVA hydrogel beads, characteristic peaks of PVA such as the O–H, C–H, C=O, and C–O are present.33 The peak corresponding to the O–H$_{\text{in}}$ is observed at 3429 cm$^{-1}$ in the FT-IR spectra. This can be attributed to the M–OH and the free –OH groups present in the polyvinyl alcohol of the hydrogel beads.14 The slight broadening of the O–H$_{\text{in}}$ peaks could be due to the hydrogen-bonded interaction existing between PVA chains.34–37 The peak at 1630 cm$^{-1}$ corresponds to the stretching of the C=C groups formed due to the heat treatment of the hydrogel beads during the synthesis.18 The semi-crystalline nature of PVA in the hydrogel beads is confirmed by the appearance of a peak around 1100 cm$^{-1}$ due to C=O$_{\text{ar}}$ in the metal–PVA hydrogel beads. The presence of the acetal group is confirmed by the appearance of a peak at 1020 cm$^{-1}$, which is due to the cross-linking of PVA with glutaraldehyde.39 Apart from this, the characteristic peaks in the region 450–850 cm$^{-1}$ are attributed to the existence of M–O bonds.40,41 The peaks at 801 and 466 cm$^{-1}$ are due to the presence of Zr–O bonds in PZH, PFZH, and PCZH beads.42 The peak for Fe–O in PFZH beads appears at 663 cm$^{-1}$, whereas the peak at 666 cm$^{-1}$ is due to the Cu–O bond in PCZH beads.41,43,44 After fluoride adsorption, the peaks in the FT-IR spectra of the hydrogel beads shift to a higher frequency with reduced intensity, indicating the interaction of fluoride with the metal ions.42 The Zr–O peaks in the spectrum of PZH beads shift to 817 and 478 cm$^{-1}$. After fluoride adsorption, the Zr–O peaks in PFZH shift to 817 and 478 cm$^{-1}$. The Fe–O peak is shifted to 670 cm$^{-1}$ in the spectrum of PFZH. A peak appears at 678 cm$^{-1}$ in the spectrum for PCZH beads post-fluoride adsorption. These changes can be taken as the evidence of fluoride binding to the metal ions because the M–F

### Table 9. Parameters of the Fixed-Bed Column of Hydrogel Beads for Fluoride Adsorption Obtained from Breakthrough Curves for Groundwater Sample

| beads   | flow rate (±0.01 mL min$^{-1}$) | bed height (±0.2 cm) | $m_u$ (±0.02 mg) | $m_{ads}$ (±0.02 mg) | $h_b$ (h) | $t_s$ (h) | $q_t$ (±0.05 mg g$^{-1}$) | $q_b$ (±0.05 mg g$^{-1}$) | $V_{eff}$ (±1 mL) | $MTZ$ (±0.02 cm) | $DoSU$ (±0.02%) | $SUR$ (±0.05 g L$^{-1}$) | % fluoride removal (±0.02%) |
|---------|---------------------------------|----------------------|-----------------|---------------------|----------|---------|-----------------|------------------|-----------------|----------------|----------------|------------------|----------------------|-------------------------|
| PCZH    | 0.50                           | 4                    | 5.70            | 2.71                | 34       | 57      | 1.50            | 1.12             | 2010            | 10.62          | 1.61            | 76.67            | 1.76                  | 47.44                   |
| PZH     | 0.50                           | 4                    | 5.28            | 3.01                | 41       | 58      | 1.67            | 1.39             | 1860            | 10.62          | 3.72            | 85.74            | 1.46                  | 56.92                   |
| PFZH    | 0.50                           | 4                    | 3.49            | 1.39                | 15       | 36      | 0.77            | 0.44             | 1230            | 10.62          | 2.33            | 61.23            | 4.00                  | 40.10                   |
absorptions generally occurring in far IR regions are undetectable by the FT-IR spectrophotometer.\(^4\)

Moreover, the pore volume for the hydrogel beads is comparatively smaller indicating that intraparticle diffusion does not play a predominant role in enhancing the fluoride removal capacity. Besides, the breakthrough curve shows a steep increase, initially. This indicates that fluoride adsorption before the breakthrough occurs rapidly due to the availability of greater adsorbent sites (Scheme 1). After the breakthrough, the fluoride adsorption might occur by physisorption and pore diffusion. The adsorption of fluoride at this stage may be controlled mainly by the mass-transfer process involving the movement of fluoride ions into these pores.\(^4\) Therefore, the overall rate of fluoride adsorption slows down as confirmed by the low value of the rate constant obtained by fitting the breakthrough curves in the column adsorption models (Table 3).

However, the evidence of spontaneity of the fluoride adsorption on hydrogel beads is obtained by calculating the standard Gibbs free energy (Table 1). The \(\Delta G^\circ\) of the adsorption process is \(-37.13 \pm 0.02\), \(-43.48 \pm 0.02\), and \(-43.07 \pm 0.02\) kJ mol\(^{-1}\) for PCZH, PZH, and PFZH. The high negative value of standard Gibbs free energy and the enthalpy indicates chemisorption of fluoride on hydrogel beads.\(^8,21,47\) Hence, based on the column adsorption models, analysis of the breakthrough curves and the thermodynamics of adsorption, it is proved that the fluoride adsorption to the hydrogel beads occurs mainly by chemisorption.

### 3.5. Column Performance Indicator

The performance of the column is evaluated based on the degree of sorbent used (DoSU), sorbent usage rate (SUR), and the number of bed volumes processed.

The DoSU during the adsorption is the ratio of fluoride uptake at the breakthrough (\(q_b\)) to the fluoride uptake at equilibrium (\(q_e\)), which is given by the equation

\[
\text{DoSU} = \frac{Q_b}{Q_e} \quad (21)
\]

In addition, the SUR is defined as the unit mass of the adsorbent (\(M\) in g) required to obtain a clean effluent before the breakthrough (\(V_b\) in L) which is given by

\[
\text{SUR} = \frac{M}{V_b} = \frac{M}{Q_b} \quad (22)
\]

Another, important parameter is the number of bed volumes processed by the column, which is given by the equation

\[
\text{Number of bed volume} = \frac{\text{Volume treated at breakthrough}(V_b)}{\text{Volume of adsorbent bed}} \quad (24)
\]

The higher value of DoSU indicates that the adsorbent used for column adsorption has good fluoride removal efficiency at the breakthrough. Similarly, a lower value of SUR implies that lesser amount of the adsorbent is required to treat contaminated water. The higher value of bed volumes signifies that the column can be used for the treatment of a larger volume of contaminated water.\(^4\)
The degree of sorbent usage is higher for the column of smaller bed height and lower flow rate. However, the degree of sorbent usage is enhanced for a column of greater bed height, even at a higher flow rate, as more adsorbent sites are available for adsorption. Among the hydrogel beads, PCZH exhibits the highest DoSU implying good fluoride removal efficiency before the breakthrough.

On increasing the bed height, the SUR decreases, which implies that a lower adsorbent dosage is required for obtaining clean water at a greater bed height. For PCZH, PZH, and PFZH beads, the SUR for a bed height of 8 cm is 0.85 ± 0.05, 2.18 ± 0.05, and 2.03 ± 0.05 g L⁻¹, while fluoride removal efficiencies are 74 ± 0.02%, 62 ± 0.02%, and 61 ± 0.02%, respectively (Tables 2 and 5). Moreover, the SUR are 1.58 ± 0.05 (PCZH), 1.43 ± 0.05 (PZH), and 1.67 ± 0.05 g L⁻¹ (PFZH) at a flow rate of 1 mL min⁻¹, while a larger adsorbent dosage is required to treat 1 L of fluoride-containing water at a lower flow rate.

The number of treated bed volumes depends mainly on the flow rate of the fluoride solution. Increasing the column bed height at a constant flow rate does not bring about a drastic change in the treated bed volume. However, on the flow rate from 0.10 ± 0.01 to 1 ± 0.01 mL min⁻¹ increases the number of processed bed volumes increase from 5.2 ± 0.10 to 214.83 ± 0.10 for PCZH, from 29.40 ± 0.10 to 237.44 ± 0.10 for PZH, and 59.93 ± 0.10 to 203.52 ± 0.10 for PFZH. The number of bed volumes processed by the column of PCZH with a bed height of 4 ± 0.2 cm at a flow rate of 1 ± 0.01 mL min⁻¹ is the highest, which implies that PCZH could be used for treating a larger volume of water.

### 3.6. Adsorbent Regeneration

The economic viability of the adsorbent is determined by its reusability. In the column adsorption studies, the fixed-bed column is recharged by eluting with 0.10 ± 0.02 mol L⁻¹ HCl for 2 ± 0.02 h at a flow rate of 1 ± 0.01 mL min⁻¹ (Figure 6). PFZH retains 51 ± 0.02% efficiency while PCZH and PZH have 54 ± 0.02% and 46 ± 0.02% fluoride removal efficiency after the third regeneration cycle (Table 6). This shows that fluoride adsorption in the continuous flow system might require a longer regeneration time. However, the calculated value of equilibrium adsorption capacity does not change significantly on reusing the hydrogel beads as the time required for the saturation of the column is less affected on regeneration (Table 6). This shows that the hydrogel beads have good regenerability.

### 3.7. Practical Applicability of Metal–PVA Hydrogels for Water Treatment

The metal-incorporated hydrogel beads exhibit good selectivity toward fluoride. A simulated solution containing 10 ± 0.2 mg L⁻¹ fluoride and 100 ± 0.2 mg L⁻¹ of interfering ions such as nitrates, chlorides, phosphates, bicarbonates, and sulfates is fed into a column of 2 ± 0.2 cm bed height containing 0.90 ± 0.01 g of hydrogel beads maintained at a flow rate of 0.50 ± 0.01 mL min⁻¹ (Figure 7c). Generally, these ions compete for the adsorbent sites and lower the fluoride removal efficiency of the adsorbent. However, in the case of the hydrogel beads, the fluoride removal efficiency decreases marginally even in the presence of interfering ions. The fluoride removal efficiency is lowered by < 1 ± 0.02% in the simulated solution containing interfering ions when compared with a column subjected to a feed solution containing only 10 ± 0.20 mg L⁻¹ fluoride (Tables 2 and 8). The fluoride removal capacity of the column follows the order: PZH (14.17 ± 0.05 mg g⁻¹) > PCZH (8.05 ± 0.05 mg g⁻¹) > PFZH (5.98 ± 0.05 mg g⁻¹). However, PCZH has good fluoride removal efficiency at the breakthrough as DoSU is the highest (62.77 ± 0.02%). This indicates that the column containing PCZH reduces the fluoride content of water containing interfering ions below the permissible limit for a longer duration. However, a slight decrease in the column breakthrough time, saturation time, and treated effluent volume is observed for all the hydrogel beads in the presence of interfering ions.

Furthermore, the efficiency of the fixed-bed column of PCZH, PZH, and PFZH is checked for its practical applicability by subjecting it to a continuous feed of the groundwater sample collected from the Anantapur district of Andhra Pradesh, India (Figure 5). The physico-chemical analysis of the groundwater is done before and after adsorption (Table 7). The concentrations of K⁺, Mg²⁺, Ca²⁺, and Na⁺ are estimated by microwave-assisted atomic emission spectroscopy (MP–AES 4200, Agilent, USA). The fixed-bed column adsorption of fluoride by the hydrogel beads shows promising results (Tables 7–9). About 57 ± 0.02% of fluoride is removed from the groundwater by PZH beads. The degree of sorbent usage is 86 ± 0.02% for PZH, while it is 77 ± 0.02% and 61 ± 0.02% for PCZH and PFZH beads which implies that the column could be used effectively for defluoridation of groundwater (Table 9). Mathematical models (Thomas, Bohart–Adams, and Yoon–Nelson) are used for the analysis of the breakthrough curve (Figure 7d). The equilibrium fluoride capacity calculated from the Thomas model is well correlated with the results obtained from the fixed-bed column adsorption studies (Table 10). The time required for 50% saturation of the column is PZH (48 ± 0.02 h) > PCZH (41 ± 0.02 h) > PFZH (14 ± 0.02 h). Likewise, the saturation concentration...
Table 11. Comparison of the Performance of the Adsorbents Reported in Literature for Fixed-Bed Fluoride Adsorption Studies with the Current Work

| Material                  | pH     | Initial bed exhaustion (mg L⁻¹) | Bed height (cm) | Flow rate (mL min⁻¹) | Initial cation removal (mg g⁻¹) | Recovery (mg g⁻¹) | Regeneration efficiency (%) | Regenerating agent | e⁻⁻ capacity (mg L⁻¹) | e⁻⁻ capacity (mg L⁻¹) | Regeneration cycle | e⁻⁻ capacity (mg L⁻¹) |
|---------------------------|--------|-------------------------------|-----------------|----------------------|-------------------------------|-----------------|-----------------------------|-------------------|----------------------|---------------------|-----------------|-------------------|
| Kanuma mud               | 5−7    | 4.35                          | 10              | 10                   | 1.39                          | 0.95            | 50                          | 0.1 mol L⁻¹ NaOH  | 3       | 74 ± 0.02%         | 74 ± 0.02%         | 250              | 95 ± 0.02%         |
| Tinospora cordifolia      | 5−7    | 3.5                           | 4               | 1                     | 0.18                          | 0.16            | 99                          | 0.1 mol L⁻¹ HCl   | not reported | 77 ± 0.02%         | 77 ± 0.02%         | 450              | 90 ± 0.02%         |
| NA                        | 5−7    | 3.5                           | 1                | 5                    | 0.02                          | 0.02            | 96                          | 0.1 mol L⁻¹ HCl   | not reported | 90 ± 0.02%         | 90 ± 0.02%         | 0.2 mil L⁻¹      | 93 ± 0.02%         |
| PFZH                      | 5−7    | 3.5                           | 5               | 20                   | 1.66                          | 1.66            | 92                          | 0.1 mol L⁻¹ HCl   | not reported | 96 ± 0.02%         | 96 ± 0.02%         | 300              | 93 ± 0.02%         |
| PCZH                      | 5−7    | 3.5                           | 2               | 30                   | 0.02                          | 0.02            | 88                          | 0.1 mol L⁻¹ HCl   | not reported | 88 ± 0.02%         | 88 ± 0.02%         | 100              | 93 ± 0.02%         |
| PZH                       | 5−7    | 3.5                           | 10              | 10                  | 1.66                          | 1.66            | 92                          | 0.1 mol L⁻¹ HCl   | not reported | 92 ± 0.02%         | 92 ± 0.02%         | 100              | 92 ± 0.02%         |

**a** NA = Data not available.

## 3.8. Comparative Assessment of Fluoride Adsorbents for Fixed-Bed Column Studies

Polyvinyl alcohol is an environmentally benign and economically viable polymer. Metal ions and glutaraldehyde are reacted with PVA to obtain self-assembled hydrogel beads by one-pot synthesis. The metal–PVA hydrogel beads are more efficient in bringing about defluoridation of water when compared to the other adsorbents, which are used for fixed-bed adsorption studies, as reported in the literature (Table 11). These hydrogel beads remove fluoride at a wide pH range of 3−9, while most of the adsorbents exhibit good defluoridation capacity only at acidic pH. Moreover, the metal ions are bound to the PVA matrix, which prevents secondary contamination of the treated water (Table 1). The fixed-bed column of bio-based adsorbents have shown good fluoride removal efficiency from solutions containing higher initial fluoride concentrations. These adsorbents remove fluoride effectively at a greater flow rate. However, the adsorbents reported in literature have been used only for the removal of fluoride from simulated water samples (Table 11). Because the fixed-bed columns of metal–PVA hydrogel beads are used at a lower flow rate of 1 mL min⁻¹, the columns have a high exhaustion time for a bed height of 4 cm. Moreover, the fixed-bed columns of metal–PVA hydrogel beads are also effective in the removal of fluoride from alkaline groundwater. This proves that metal–PVA hydrogel beads can be used for the defluoridation of groundwater.

## 4. CONCLUSIONS

Defluoridation by a continuous-flow fixed-bed column of PCZH, PZH, and PFZH indicate that the hydrogel beads could be used to develop potent fluoride filters. The breakthrough time of the column nearly tripled on increasing the adsorbent bed height from 2 ± 0.2 to 8 ± 0.2 cm at a constant flow rate. The hydrogel beads have a good fluoride removal efficiency [PCZH (74 ± 0.02%), PFZH (61 ± 0.02%)].
indicate that chemisorption predominates the adsorption applications. Furthermore, PFZH indicates that these metal-complexed hydrogel beads have the removal capacities of 8.05 ± 0.2 mg L⁻¹ for PCZH, PZH, and PFZH, respectively, from a 10 ± 0.20 mg L⁻¹ fluoride solution containing interfering ions such as nitrates, bicarbonates, sulfates, phosphates, and chlorides. Thus, the hydrogel beads exhibit good selectivity toward fluoride. Additionally, the column of hydrogel beads effectively removes fluoride even from the groundwater sample and has good reusability. Moreover, PFZH exhibits removal efficiencies of 99 ± 0.02% (CrO₄²⁻), 92 ± 0.02% (AsO₄³⁻), and 96 ± 0.02% (F⁻) from a solution containing 100 ± 0.2 mg L⁻¹ of chromate and arsenate ions and 10 ± 0.2 mg L⁻¹ of fluoride ions in batch adsorption studies. This indicates that these metal-complexed hydrogel beads have the ability to simultaneously remove arsenate, chromate, and fluoride anions from water and have potential industrial applications.

### Author Information

**Corresponding Author**

Rajni Bhandari – Department of Chemistry, Sri Sathya Sai Institute of Higher Learning, Anantapur 515001, India; orcid.org/0000-0003-4894-3238; Phone: +91 9490044014; Email: rajnibhandari@sssihl.edu.in

**Author**

Sai Kiran Mani – Department of Chemistry, Sri Sathya Sai Institute of Higher Learning, Anantapur 515001, India

Complete contact information is available at: https://pubs.acs.org/10.1021/acsomega.2c00834

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### References

1. Ali, S.; Fakhri, Y.; Golbini, M.; Thakur, S. K.; Alinejad, A.; Parsheh, I.; Shekhar, S.; Bhattacharya, P. Concentration of Fluoride in Groundwater of India: A Systematic Review, Meta-Analysis and Risk Assessment. *Groundw. Sustain. Dev.* 2019, 5, 100224.

2. Samal, A. K.; Mishra, P. K.; Biswas, A. Assessment of Origin and Distribution of Fluoride Contamination in Groundwater Using an Isotopic Signature from a Part of the Indo-Gangetic Plain (IGP), India. *HydroResearch* 2020, 3, 75–84.

3. Mani, S. K.; Bhandari, R.; Nehra, A.; Manohar, C. S.; Belliraj, S. K. Zirconium–Cerium and Zirconium–Lanthanum Complexed Polyvinyl Alcohol Films for Efficient Fluoride Removal from Aqueous Solution. *J. Dispersion Sci. Technol.* 2021, 42, 1–16.

4. Suthasri, V.; Sudharsan Reddy, Y. Hydrogeochemical Evaluation of Groundwater in and around Lakkireddipalli and Ramapuram, Y.S.R District, Andhra Pradesh. *HydroResearch* 2019, 2, 85–96.

5. Dhillon, A.; Kumar, D. Evaluation of a Nanoporous Adsorbent for the Removal of Health-Hazardous Fluoride Ions from Aqueous Systems. *J. Mater. Chem. A* 2015, 3, 4215–4228.

6. Dhillon, A.; Soni, S. K.; Kumar, D. Enhanced Fluoride Removal Performance by Ce–Zn Binary Metal Oxide: Adsorption Characteristics and Mechanism. *J. Fluorine Chem.* 2017, 199, 67–76.

7. Kumar, H.; Patel, M.; Mohan, D. Simplified Batch and Fixed-Bed Design System for Efficient and Sustainable Fluoride Removal from Water Using Slow Pyrolyzed Okra Stem and Black Gram Straw Biochars. *ACS Omega* 2019, 4, 19513–19525.

8. Loganathan, P.; Vigneswaran, S.; Kandasamy, J.; Naidu, R. Dethiodurification of Drinking Water Using Adsorption Processes. *J. Hazard. Mater.* 2013, 248-249, 1–19.

9. Patel, H. Fixed-Bed Column Adsorption Study: A Comprehensive Review. *Appl. Water Sci.* 2019, 9, 1–17.

10. Xu, Z.; Cai, J.-g.; Pan, B.-c. Mathematically Modeling Fixed-Bed Adsorption in Aqueous Systems. *J. Zhejiang Univ., Sci.*, A 2013, 14, 155–176.

11. Askari, M.; Salehi, E.; Ebrahimi, M.; Barati, A. Application of Breakthrough Curve Analysis and Response Surface Methodology for Optimization of a Hybrid Separation System Consisting of Fixed-Bed Column Adsorption and Dead-End Depth Filtration. *Chem. Eng. Process.* 2019, 143, 107594.

12. Chen, N.; Zhang, Z.; Feng, C.; Li, M.; Chen, R.; Sugira, N. Investigations on the Batch and Fixed-Bed Column Performance of Fluoride Adsorption by Kanuka Mud. *Desalination* 2011, 268, 76–82.

13. Sarkar, M.; Banerjee, A.; Pramankic, P. P.; Sarkar, A. R. Design and Operation of Fixed Bed Laterite Column for the Removal of Fluoride from Water. *Chem. Eng. J.* 2007, 131, 329–335.

14. Tariq, M.; Farooq, U.; Athar, M.; Salman, M.; Tariq, M.; Shahida, S.; Farooqi, Z. H. Fluoride Removal Using Simple Protonated and Xanthate Modified Protonated Ficus Religiosa Branch Powder in a Fixed-Bed Column. *Desalin. Water Treat.* 2019, 150, 204–212.

15. Paudyal, H.; Pangeni, B.; Inoue, K.; Kawakita, H.; Ohbo, K.; Alam, S. Adsorptive Removal of Fluoride from Aqueous Medium Using a Fixed Bed Column Packed with Zr (IV) Loaded Dried Orange Juice Residue. *Bioresour. Technol.* 2013, 146, 713–720.

16. Ghoraï, S.; Pant, K. K. Investigations on the Column Performance of Fluoride Adsorption by Activated Alumina in a Fixed-Bed. *Chem. Eng. J.* 2004, 98, 165–173.

17. Mohan, S.; Singh, D. K.; Kumar, V.; Hasan, S. H. Effective Removal of Fluoride Ions by RGO/ZrO2 Nanocomposite from Aqueous Solution: Fixed Bed Column Adsorption Modelling and Its Adsorption Mechanism. *J. Fluorine Chem.* 2017, 194, 40–50.

18. Mani, S. K.; Bhandari, R.; Nehra, A. Self-Assembled Cylindrical Zr (IV), Fe (III) and Cu (II) Impregnated Polyvinyl Alcohol-Based Hydrogel Beads for Real-Time Application in Fluoride Removal. *Colloids Surf., A* 2021, 610, 125751.

19. Andjelkovic, I.; Tran, D. N. H.; Kabiri, S.; Azari, S.; Markovic, M.; Losic, D. Graphene Aerogels Decorated with n-FeOOH Nanoparticles for Efficient Adsorption of Arsenic from Contaminated Waters. *ACS Appl. Mater. Interfaces* 2015, 7, 9758–9766.

20. Rajak, J. K.; Khandelwal, N.; Behera, M. P.; Tiwari, E.; Singh, N.; Ganie, Z. A.; Darbha, G. K.; Abdulahpur Monikhi, F.; Schäfer, T. Removal of Chromate Ions from Leachate-Contaminated Groundwater Samples of Khan Chandpur, India, Using Chitin Modified Iron-Enriched Hydroxyapatite Nanocomposite. *Environ. Sci. Pollut. Res.* 2021, 28, 41760–41771.

21. Patel, H. Comparison of Batch and Fixed Bed Column Adsorption: A Critical Review. *Int. J. Environ. Sci. Technol.* 2021, 1–18.

22. Tran, H. N.; You, S. J.; Hosseini-banghearei, A.; Choa, H.-P. Mistakes and Inconsistencies Regarding Adsorption of Contaminants from Aqueous Solutions: A Critical Review. *Water Res.* 2017, 120, 88–116.
Chatterjee, A.; Schiewer, S. Biosorption of Cadmium(II) Ions by Citrus Peels in a Packed Bed Column: Effect of Process Parameters and Comparison of Different Breakthrough Curve Models. Clean: Soil, Air, Water 2011, 39, 874–881.

24. Water Environment Federation, American Public Health Association. Standard Methods for the Examination of Water and Wastewater, 19th ed.; Greenberg, A. E., Ed.; American Public Health Association: Washington DC, USA, 1995; Vol. 142.

Han, R.; Wang, Y.; Zhao, X.; Wang, Y.; Xie, F.; Cheng, J.; Tang, M. Adsorption of Methylene Blue by Phoenix Tree Leaf Powder in a Fixed-Bed Column : Experiments and Prediction of Breakthrough Curves. Desalination 2009, 245, 284–297.

Rout, P. B.; Bhunia, P.; Dash, R. R. Evaluation of Kinetic and Statistical Models for Predicting Breakthrough Curves of Phosphate Removal Using Dolochar-Packed Columns. J. Water Process. Eng. 2017, 17, 168–180.

Song, W.; Xu, X.; Tan, X.; Wang, Y.; Ling, J.; Gao, B.; Yue, Q. Column Adsorption of perchlorate by Amine-Crosslinked Biopolymer Based Resin and its Biological, Chemical Regeneration Properties. Carbohydr. Polym. 2015, 115, 432–438.

Patel, H. Batch and Continuous Fixed Bed Adsorption of Heavy Metals Removal Using Activated Charcoal from Neem (Azadirachta Indica) Leaf Powder. Sci. Rep. 2020, 10, 16895.

Naja, G.; Volesky, B. Behavior of the Mass Transfer Zone in a Biosorption Column. Environ. Sci. Technol. 2006, 40, 3996–4003.

Ranganath, S.; Sandagopalan, M. S. G.; Nakkere, E.; Selvaraju, N. Adsorption of Hexavalent Chromium from Synthetic and Electroplating Effluent on Chemically Modified Swietenia Mahagoni Shell in a Packed Bed Column. Environ. Monit. Assess. 2016, 188, 411.

Chu, K. H. Breakthrough Curve Analysis by Simplistic Models of Fixed Bed Adsorption : In Defense of the Century-Old Bohart-Adams Model. Chem. Eng. J. 2020, 380, 122513.

Choy, K. K. H.; Ko, D. C. K.; Cheung, C. W.; Porter, J. F.; McKay, G. Film and Intraparticle Mass Transfer during the Adsorption of Metal Ions onto Bone Char. J. Colloid Interface Sci. 2004, 271, 284–295.

Perez, M. N.; Stylios, G. K.; Liang, Y.; Ouyang, F.; Cai, Y. Low-Temperature Synthesis of Novel Polyvinylalcohol (PVA) Nanofibrous Membranes for Catalytic Dye Degradation. J. Cleaner Prod. 2020, 262, 121301.

Velasquez-jime, L. H.; Hurt, R. H.; Matoes, J.; Rangel-mendez, J. R. Zirconium – Carbon Hybrid Sorbent for Removal of Fluoride from Water : Oxalic Acid Mediated Zr (IV) Assembly and Adsorption Mechanism. Environ. Sci. Technol. 2014, 48, 1166–1174.

Chandrakala, H. N.; Rajamar, B.; Shavakumaraiah, G. M.; Madhu, G. M.; Siddaramaiah. Preparation of Polyvinyl Alcohol – Lithium Zirconate Nanocomposite Films and Analysis of Transmission, Absorption, Emission Features, and Electrical Properties. J. Phys. Chem. C 2013, 117, 4771–4781.

Maity, N.; Barman, S.; Minenkov, Y.; Ould-Chikh, S.; Abou-Hamad, E.; Ma, T.; Qureshi, Z. S.; Cavallo, L.; D’Elia, V.; Gates, B. C.; Basset, J.-M. A Silica-Supported Monoalkylated Tungsten Dioxo Complex Catalyst for Olefin Metathesis. ACS Catal. 2018, 8, 2715–2729.

Maity, N.; Barman, S.; Abou-Hamad, E.; D’Elia, V.; Basset, J.-M. Clean Chlorination of Silica Surfaces by a Single-Site Substitution Approach. Dalton Trans. 2018, 47, 4301–4306.

Zhang, H.; Zhang, J. The Preparation of Novel Polyvinyl Alcohol (PVA)-Based Nanoparticle/Carbon Nanotubes (PnP/CNTs) Aerogel for Solvents Adsorption Application. J. Colloid Interface Sci. 2020, 569, 254–266.

Figueiredo, K. C. S.; Alves, T. L. M.; Borges, C. P. Poly (Vinyl Alcohol) Films Crosslinked by Glutaraldehyde Under Mild Conditions. J. Appl. Polym. Sci. 2008, 111, 3074–3080.

An, Y.; Han, W.; Han, J.; Zhao, G.; Zhou, S.; Zhang, X. Synergistic Effect on the Mechanical Behaviors of Ternary Graphene Oxide-Zirconium Diboride-Poly (Vinyl Alcohol) Papers. Mater. Des. 2016, 112, 275–281.