Enhanced fluoride adsorption and regeneration efficiency of cross-linker-free mesoporous hydroxyapatite/chitosan nanocomposites

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Abstract
The presence of F⁻ ions in water is either a helpful or harmful outcome, contingent upon the concentration level of the pollutant. In this work, hydroxyapatite/chitosan (HAp/CS) nanocomposites were prepared incorporating varying weight percentages of chitosan with HAp, using co-precipitation followed by lyophilization without employing any cross-linking agents for the adsorption of F⁻ ions. An increase in the concentration of chitosan in the HAp matrix significantly enhanced the colloidal stability, F⁻ ion adsorption capacity, and reduced the particle size (length 38% and width 86%) when compared to HAp. The respective maximum F⁻ adsorption capacity of HAp/CS1, HAp/CS2, HAp/CS3, and HAp/CS4 nanocomposites were 56 mg/g, 80 mg/g, 82 mg/g, and 100 mg/g at pH 7, which was considerably higher (10 times) than HAp when compared to other existing reports. The adsorption isotherm and kinetics of HAp and HAp/CS nanocomposite adsorbent confirmed the monolayer and strong chemisorption mechanisms. The surface morphology of the adsorbent after adsorption of F⁻ ions changed from rod to sphere along with an increase in particle size, as confirmed by HR-TEM. Moreover, FTIR and XPS analysis revealed the surface interaction between the adsorbent and F⁻ ions through ion exchange and electrostatic interaction, which lead to the formation of fluorapatite. HAp/CS4 showed 2.5 times higher sustainable regeneration efficiency (90% in 30 min) up to 7th cycle than HAp. Furthermore, the solution pH (5–7) of treated water was maintained at neutral pH after fluoride adsorption, rendering the water potable. Hence, these results demonstrate that chitosan plays a significant role in the removal of F⁻ ions and this composite is ideal for F⁻ ion adsorption applications.

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Graphical abstract

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Introduction

Today’s world encounters many kinds of environmental pollution due to rapid industrialization and urbanization. The degradable and non-degradable waste from industrial effluents such as arsenic, fluoride, copper, iron, mercury, and chromium are directly discharged into drinking water, thereby reducing freshwater retention [1]. Amidst this consequence, fluoride (F−) ions are one of the highly toxic environmental pollutants in water reservoirs, originating from natural and anthropogenic sources [2]. F− is essential for the human body, especially for children’s bone and teeth growth, and serves as a resistance against dental decay at 0.7 mg/L. Conversely, 80% of diseases are contracted through drinking water, and F− contamination accounts for 65% of skeletal and dental fluorosis incidences [3]. Based on health care and environmental concerns, the World Health Organization (WHO) advises that the amount of ionic F− present in drinking water shall not exceed 1.5 mg/L [4]. Nevertheless, most common water bodies exceed the standard limits due to the dissolution of F− ions from natural minerals such as fluorspar, cryolite, and fluorapatite [5]. Currently, there are many techniques for removing of F− ions from water, which include ion exchange [6], reverse osmosis [7], adsorption [8], membrane filtration [9], biological filtration [10], flocculation [11], and electrochemical method [12]. Adsorption is a profitable, easy-to-fabricate portable water purifying method, which involves a variety of low-cost adsorbents such as biopolymers [13], alumina [14], hydroxyapatite [15], and activated carbon [16]. Hydroxyapatite (Ca_{10}(PO_{4})_{6}OH_{2}) (HAp) matrix is an inorganic material comparable to natural bone and teeth, containing calcium and phosphate. Numerous works of literature on HAp have noted its extensive use in many implementations such as dental implants, gas sensors, drug
delivery, and wastewater treatment [17]. Generally, HAp has been widely used for the adsorption of F− ions due to the large number of hydroxyl groups, high surface area, biocompatibility, and porosity [18]. However, the use of HAp adsorbent in fixed-bed columns is not feasible due to the excessive pressure drop while applying on the field. To overcome this disadvantage, HAp requires the supplementation of polymers [19]. In recent decades, polymer-based nanocomposite materials have often been characterized by their ability to remove F− ions. Moreover, various natural polymers are available in the earth’s crust. One such natural polymer is chitosan (CS), extracted from the shells of crab and shrimp; it is the second most eco-rich and cost-effective material on Earth. Partial deacetylated chitosan consists of poly-β (1–4)2 acetamido-2-deoxy-D-glucose C backbone with amine and hydroxyl functional groups and has proven to be ideal for F− ion adsorption [20]. Long et al. prepared CS/Ag-HAp through micro-emulsion technique to remove the Cu(II) and rhodamine dye [21]. The HAp/chitosan layered composites was used by Chuan Jian Zhang et al. having high mechanical strength for the removal of Pb(II) ions [22]. Pereira et al. developed HAp/chitosan with cross-linking agents of glutaraldehyde for the adsorption of diclofenac [23]. The adsorption of Ni(II) ions was carried out by HAp/Fe3O4/CS synthesized from shrimp shells, slag, and bones using cross-linking regents [24]. Meenakshi et al. prepared the chitosan HAp by the calcination method for the adsorption of F− ions [25]. The Cr (VI) was adsorbed by the hydrothermally synthesized Sr-doped HAp nanorods was used [26]. Zhichao Yu et al. prepared MgO mesoporous nanofibers for the adsorption of fluoride and Congo red [27]. Overall, HAp-based chitosan nanocomposites are used for the removal of heavy metals, dyes, and pharmaceutical pollutants. Here, we have developed cross-linker-free mesoporous hydroxyapatite/chitosan nanocomposites that have not been reported for F− ion adsorption.

The HAp/CS nanocomposites were synthesized, utilizing the co-precipitation technique followed by lyophilization. During freeze-drying, the material is in crystallite form, as pores on the surface of the adsorbent are created. This process facilitates higher ion adsorption efficiencies and faster rates of adsorption. The adsorption of F− ions has been studied under various adsorption parameters, viz. pH, initial concentration, presence of other co-anions, and contact time using the batch adsorption technique. The adsorption mechanisms of adsorbents were studied using kinetic models and adsorption isotherms. Furthermore, the adsorption mechanism of F− ions on an adsorbent surface was analysed using Fourier transform infrared spectroscopy (FTIR) and X-ray photoelectron spectroscopy (XPS). The main objective of this work is to improve the colloidal stability and F− ion adsorption capacity by incorporating CS in HAp/CS nanocomposites.

**Materials and methods**

**Materials**

HAp and HAp/CS nanocomposite adsorbents were prepared by precursors of calcium nitrate tetrahydrate (Ca(NO3)2.4H2O, Merck), diammonium hydrogen
phosphate ((NH₄)₂HPO₄, Merck), chitosan ((C₆H₁₁NO₄)ₙ at low molecular weight of 50–190 kDa, with ≥ 85% deacetylated Sigma-Aldrich), and acetic acid (CH₃COOH, Merck). For the batch adsorption studies, sodium fluoride (NaF, Merck), sodium nitrate (NaNO₃, Merck), sodium hydroxide (OH⁻, Merck), sodium chloride (NaCl⁻, Merck), sodium carbonate (Na₂CO₃²⁻, Merck), sodium sulphate (Na₂SO₄²⁻, Merck), and ammonium solution (NH₄OH, Merck) were used. All chemicals used in this study were of analytical grade with no further purification.

**Synthesis of Adsorbent**

HAp/CS nanocomposites were synthesized with the assistance of co-precipitation followed by the lyophilization technique. Briefly, a stochiometric molar ratio of Ca:P (1:0.6 M) was prepared individually in 100 ml of distilled water and stirred for 1 h. Next, chitosan (1 g) was dissolved with 1% of CH₃COOH to obtain a homogeneous gel formation. The polymer solution of CS was gradually blended with 100 mL of 1 M calcium nitrate solution, and this mixture was constantly stirred (300 rpm) at 303 K. Afterwards, the calcium nitrate solution containing CS was dropwise added to 100 mL of 0.6 M di-ammonium hydrogen phosphate solution. Meanwhile, the entire reaction was maintained at pH 10 using an ammonia solution. The resultant product was aged for 12 h at ambient temperature (303 K) and centrifuged with triple-distilled water. Finally, the collected nanocomposite precipitate was retained in the pre-freeze at – 20 °C for 8 h and dried at lyophilized (~110 °C) for 12 h to obtain a fine powder of HAp/CS1 nanocomposite adsorbent. A similar procedure that was followed for the other three concentrations of chitosan (x = 2; x = 3; x = 4) is referred to as HAp/CS2, HAp/CS3, and HAp/CS4. The schematic diagram representing the synthesized HAp/CS nanocomposites is shown in Fig. 1.

**Fig. 1** Schematic representation of HAp/CS4 nanocomposite synthesis process

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Batch adsorption study

The adsorption behaviour of F$^-$ ion onto the surface of HAp and HAp/CS nanocomposites of adsorbents was evaluated by the batch adsorption technique. Initially, 1000 mg/L of F$^-$ ion stock solution was formulated by dissolving 2.216 g of sodium fluoride (NaF) in triple-distilled water, and the desired amount of F$^-$ ion concentrations (50–500 mg/L) was serially diluted from the stock solution. The equilibrium adsorption capacity was analysed by varying the concentration (100–500 mg/L). The effects of F$^-$ ion solutions pH (3–12) was altered with the help of 0.1 M of NaOH and HCl. The effects of competing co-anions (NO$^3$-, OH$^-$, Cl$^-$, CO$_3^{2-}$, and SO$_4^{2-}$) and recycling efficiency were also examined. In brief, 20 mg of adsorbent was immersed in 20 mL of fluoride solution, and the mixtures were shaken at 200 rpm using a rotating shaker at an ambient temperature (303 K), and the adsorbed solution was collected at predetermined time intervals. After reaching the equilibrium adsorption time, the adsorbent was filtered and the residual F$^-$ ion concentration was tested using an Ex-Tech fluorimeter. Equation (1) is utilized to calculate the adsorption capacity of F$^-$ ions [28].

\[
(Q_e) = (C_o - C_f) \times (\frac{V}{M})
\]

where $C_o$ and $C_f$ denote the initial and final concentrations of F$^-$ ion (mg/L), $M$ is the weight of the HAp and HAp/CS nanocomposite adsorbents (mg), $V$ is the volume of the F$^-$ ion solution (mL), and $Q_e$ represents the adsorption capacity of the adsorbent (mg/g).

Characterization

The adsorbent structure was examined by X-ray diffractometer [PAN analytical] using Cu-K$_{α}$ radiation ($λ = 1.54$ Å) at $10° - 60°$ degree step size 0.02° per sec. The functional groups of adsorbents were confirmed through Fourier transform infrared spectroscopy (FTIR-7600, JASCO) by the KBR technique and measured from 4000 cm$^{-1}$ to 400 cm$^{-1}$. Surface morphology and elemental analysis of adsorbents were done using a high-resolution scanning electron microscopy (HR-SEM, FEI Quanta FEG 200) and high-resolution transmission electron microscopy (HR-TEM, Talos F200S), respectively. The pore size and specific surface area of adsorbents were measured through the Brunauer–Emmett–Teller (BET) isotherm model using a surface area analyser—TPD/TPR (model: Quanta Chrome). Furthermore, the surface elemental composition of the adsorbent was analysed by X-ray photoelectron spectroscopy (ULVAC-PHI, Inc; model: PHI5000 version probe III). The colloidal stability of the adsorbent was measured with the Zeta potential value using dynamic light scattering (DLS Malvern Zetasizer Nano-ZS). Ex-tech fluorimeter was used to quantify F$^-$ ion capacity, and the pH of the solution was analysed by an Eu-tech pH meter.
**Results and discussion**

**X-ray diffraction (XRD)**

The XRD patterns of HAp and HAp/CS nanocomposite samples are presented in Fig. 2a. The diffraction peaks of synthesized adsorbents HAp, HAp/CS1, HAp/CS2, HAp/CS3, and HAp/CS4 exhibited the hexagonal structure of HAp phase and were well matched with JCPDS card no: 09–0432 [29]. The peak intensity of HAp/CS nanocomposites slightly increased compared to HAp, revealing the orientated crystallization along c-axis. Tugha Basargan et al. observed the same in chitosan-containing hydroxyapatite composites [30]. Table 1 shows the average crystallite size

![Fig. 2](image-url)
of HAp, HAp/CS1, HAp/CS2, HAp/CS3, and HAp/CS4 computed using the Scherrer formula, and the respective corresponding values were found to be $12 \pm 1$ nm, $10 \pm 1$ nm, $8 \pm 1$ nm, $6 \pm 1$ nm, and $5 \pm 1$ nm. The increasing chitosan concentration reduced the crystallite size of the nanocomposite compared to HAp [31]. Furthermore, the crystalline phase of HAp is not influenced by the incorporation of chitosan, due to the strong electrostatic interaction between HAp and chitosan. Figure 2b confirms that the XRD pattern of F$^-$ adsorbed HAp-F, HAp/CS1-F, HAp/CS2-F, and HAp/CS4-F concurred with JCPDS card no (FA): (03–0736) [32]. Besides, the diffraction peaks of all adsorbed adsorbents became narrow and sharp, indicating an increase in the crystallite size. It could be attributed to the replacement of adsorbent active sites of hydroxyl ions (OH$^-$) by F$^-$ ions through the ion exchange process, thereby leading to the formation of fluorapatite [Ca$_{10}$(PO$_4$)$_6$F$_2$]. There was no significant change in the crystallite size of HAp-F compared to pre-adsorbed F$^-$ ions (Table 1). F$^-$ adsorbed nanocomposites of HAp/CS1-F (20%), HAp/CS2-F (100%), HAp/CS3-F (166%), and HAp/CS4-F (260%) showed higher crystallite size. Sandeep et al. reported an increase in the crystallite size of the adsorbent (Fe-HAp), in the case of arsenic adsorption [33].

### Table 1: Crystallite size of the adsorbents

| Sample code before adsorption | Crystalline size (±1 nm) | Sample code after adsorption | Crystalline size (±1 nm) |
|-----------------------------|-------------------------|------------------------------|-------------------------|
| HAp                         | 12                      | HAp-F                        | 11                      |
| HAp/CS1                     | 10                      | HAp/CS1-F                    | 12                      |
| HAp/CS2                     | 8                       | HAp/CS2-F                    | 16                      |
| HAp/CS3                     | 6                       | HAp/CS3-F                    | 16                      |
| HAp/CS4                     | 5                       | HAp/CS4-F                    | 18                      |

**Fourier transform infrared spectroscopy (FTIR)**

FTIR spectra of the synthesized HAp and HAp/CS nanocomposites are depicted in Fig. 2c. In HAp and HAp/CS adsorbents, the bands at 3451 cm$^{-1}$, 1614 cm$^{-1}$ and 630 cm$^{-1}$ are attributed to the stretching and bending modes of OH$^-$ group, respectively [34]. The stretching vibration of CO$_3^{2-}$ was observed at 861 cm$^{-1}$ and 1446 cm$^{-1}$ due to the absorption of atmospheric carbon dioxide [35]. The bands around 454–560 cm$^{-1}$ are related to the bending vibration of PO$_4^{3-}$. The appearance of asymmetric stretching mode of PO$_4^{3-}$ was observed at 1019 cm$^{-1}$ [36]. For HAp/CS nanocomposites, the presence of N–H bending vibration of CS was confirmed at 1585 cm$^{-1}$, where a reduction in intensity occurred with an increase in the concentration of CS, stabilizing the electrostatic interaction between HAp and CS [37]. Following the F$^-$ ion adsorption, the FTIR spectra of HAp-F, HAp/CS1-F, HAp/CS2-F, HAp/CS3-F, and HAp/CS4-F show the non-existence of hydroxyl and carbonate groups. In contrast, the presence of sharp intensity of stretching and bending vibrations was also observed in the PO$_4^{3-}$ band (Fig. 2d). These changes confirm the ion exchange process between the functional groups of adsorbents and F$^-$ ions [38].
Moreover, the peaks of the amine group were absent, indicating the electrostatic interaction of F⁻ ions on the HAp/CS nanocomposite surface. The above-mentioned mechanisms reveal the formation of fluorapatite.

**High-resolution scanning electron microscopy (HR-SEM)**

Figure 3.1 displays the HR-SEM micrograph of HAp, HAp/CS1, HAp/CS2, HAp/CS3, and HAp/CS4 nanocomposite adsorbents. Figure 3.1a shows uniformly distributed rod-like morphology of HAp nanoparticles with dimensions of 95 × 45 nm. There was no change in morphology with an increase in CS incorporation (1%, 2%, 3%, and 4%), and the respective particle size of HAp/CS1 (88 × 20 nm), HAp/CS2 (30 × 10 nm), HAp/CS3 (27 × 10 nm), and HAp/CS4 (25 × 8 nm) is lower than HAp (Fig. 3.1b–e). The morphology of the F⁻ ion adsorbed samples, viz. HAp-F, HAp/CS1-F, HAp/CS2-F, and HAp/CS3-F, was rod-like with respective average particle size of 100 × 40 nm, 50 × 20 nm, 50 × 15 nm, and 65 × 15 nm (Fig. 3.1f–i). HAp/CS4-F shows the morphological transformation from rod to a sphere (90 ± 2 nm) compared to pre-adsorbed sample HAp/CS4 (Fig. 3.1j). These remarkable changes indicate that the HAp/CS4 contained amine groups, smaller particle size, greater specific surface area, and good colloidal stability, which resulted in more active sites for F⁻ adsorption. Based on this factor, F⁻ ions fully adhered to the surface-active site of HAp/CS4 through the ion exchange and surface complexation process than other nanocomposites. The EDAX spectra of HAp, HAp/CS1, HAp/CS2, HAp/CS3, and HAp/CS4 nanocomposite adsorbents are shown in Fig. 3.2a–e, confirming the presence of Ca, P, C, and O. Also, it confirms the adsorbed F⁻ ion on the adsorbent surface as indicated in Fig. 3.2f–j. Furthermore, the elemental mapping of pre- and post-F⁻ ion adsorption samples shows the uniform distribution of Ca, P, C, O, and adsorbed F⁻ ion on the adsorbent surface (Fig. 3.3).

**High-resolution transmission electron microscopy (HR-TEM)**

HR-TEM images of HAp and HAp/CS4 nanocomposite adsorbents displayed the rod-like morphology as shown in Fig. 4a–b. The average particle size of HAp and HAp/CS4 is 110 × 40 nm and 30 × 10 nm, respectively. LI Xiangnan et al. have developed 100 × 200 nm core shells of HAp/CS nanocomposites using a surfactant (Span85) [39]. Yue Liao et al. have prepared the mesoporous hydroxyapatite/chitosan nanorods prepared using cross-linking agent glutaraldehyde with 20–30 nm in width and 50–100 nm in length [40]. In comparison with the above work, the particle size of HAp/CS4 nanocomposites was reduced. This was attributed to an increase in CS concentration with the HAp matrix, which resulted in a significant decrease in the particle size of adsorbent without the presence of surfactant and cross-linker agents. In Fig. 4c–d, after adsorption of F⁻ ions, HAp-F shows rod-shaped morphology, while the HAp/CS4-F adsorbent were spherical, as confirmed by the HR-SEM (Fig. 3j). The particle size of HAp-F is 70 × 10 nm, and the average diameter of Hap/CS4-F is approximately 20 ± 3 nm. In addition,
the interplanar spacing distance measured from the lattice fringes of Hap, Hap/CS4, Hap-F, and Hap/CS4-F was 0.284 nm, corresponding to the Hap phase of the (002) plane (Fig. 4e–h). Furthermore, the SAED pattern of Hap, Hap/CS4, Hap-F, and Hap/CS4-F adsorbents having the two lattice planes (211) and (002) correspond to the interplanar spacing distance at 0.28 nm and 0.34 nm, respectively (Fig. 4i–l).
X-ray photoelectron spectroscopy (XPS)

XPS survey spectra displaying the presence of elements such as Ca, P, O, N, C, and adsorbed F⁻ ions on the surface of the HAp/CS nanocomposite are shown in Fig. 5a-b. The adsorbed F⁻ ions of peak F 1 s occurred at 685 eV (Fig. 5c) [41].
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The spectra of N 1 s in Fig. 5d that comprised of two peaks with binding energies 399.3 eV and 400.8 eV correspond to NH$_2$ and NH$_3^+$, respectively, confirming the presence of an amine group [42]. Figure 5e reveals that the Ca 2p spectra of HAp/CS4 composites deconvoluted into two peaks due to the spin–orbit rotation of Ca 2p$_{3/2}$ and Ca 2p$_{1/2}$ at respective binding energies of 347.37 eV and 350.41 eV. Similarly, P 2p spectra in Fig. 5f split into two, with peak positions of 2p$_{3/2}$ and 2p$_{1/2}$ at 133.52 eV and 132.53 eV, respectively. After F$^-$ ion adsorption, there was a slight shift towards the higher binding energies in Ca 2p and P 2p of HAp/CS4-F due to the electrostatic and ion exchange processes (Fig. 5g-h) [43]. O 1 s peak for HAp/CS4 represents three states: anion oxide (O$^{2-}$), surface hydroxyl group (OH$^-$), and adsorbed water (H$_2$O), which correspond to 531.94 eV, 531.08 eV, and 532.90 eV, respectively. In HAp/CS4-F, the binding energies of 531.03 eV (O$^{2-}$) and 531.31 eV (H$_2$O) indicate a slight change in F$^-$ ion adsorption. Besides, the hydroxyl group OH$^-$ noticeably decreased towards the lower binding energies (from 531.08 eV to 529.64 eV), demonstrating that the ion exchange process between hydroxyl and fluoride ions (OH$^-$–F$^-$), as shown in Fig. 5i-j [44]. The peak of C 1 s in Fig. 5k is deconvoluted into three peaks at C–C/C–H, C–N, and C–OH, corresponding to the 284.45 eV, 285.8 eV, and 288.05 eV, respectively. As mentioned in Fig. 5l, after F$^-$ ion adsorption, a slight shift can be observed in C–N (from 285.8 eV to 287.80 eV) and C–OH (from 288.05 eV to 287.48 eV) peaks due to the replacement of F$^-$ ions through the ion exchange reaction. This change in peak placement promotes the formation of fluorapatite (Ca$_{10}(PO_4)_6F_2$) on the HAp/CS4 surface, as confirmed by FTIR analysis.

Fig. 5 XPS spectrum of synthesized and fluoride adsorbed nanocomposites of: a–b survey spectra of HAp/CS4 and HAp/CS4-F; c F 1 s spectrum; d N 1 s spectrum; e–f before Ca 2p and P 2p spectrum; g–h after Ca 2p and P 2p spectrum; i–j before and after O 1 s spectrum; k–l before and after C 1 s spectrum.
Brunauer–Emmett–Teller analysis (BET)

The nitrogen adsorption and desorption studies of HAp, HAp/CS1, HAp/CS2, HAp/CS3, and HAp/CS4 composites are presented in Fig. 6a. The hysteresis loop of the synthesized adsorbents indicates the type IV isotherms that exhibit an ink bottle-shaped mesoporous structure due to capillary condensation [45]. The specific surface area of HAp, HAp/CS1, HAp/CS2, HAp/CS3, and HAp/CS4 were found to be 100 ± 0.5 m²g⁻¹, 70 ± 0.2 m²g⁻¹, 77 ± 0.2 m²g⁻¹, 79 ± 0.2 m²g⁻¹, and 82 ± 0.1 m²g⁻¹, respectively. Table 2 shows that the specific surface area of the HAp/CS nanocomposites were reduced by 35% compared to HAp. This might be due to CS that gradually blocks the porous network in HAp matrix, which reduces the specific surface area of HAp/CS nanocomposites. However, higher F⁻ adsorption capacity was observed in HAp/CS1, HAp/CS2, HAp/CS3, and HAp/CS4 than in HAp due to the strong dependency of the adsorption process on the adsorbent’s colloidal stability and surface charge rather than the specific surface area [46]. The outcomes of the present study of HAp/CS nanocomposites were further compared with a few existing reports. The surface volume of the chitosan–hydroxyapatite composite reported by Songlin Fan et al. was 45.63 m²g⁻¹, which was lower (47%) than HAp/CS4 [47]. Sandipan Chatterjee et al. developed chitosan–hydroxyapatite (55.54 m²g⁻¹) composite that had a lower surface area (35%) compared to the present work [48].

Table 2  BET analysis of the adsorbent of average pore size, specific area, and pore volume

| Sample code | Pore size 0 (± 1 nm) | BET surface area (SBET) (± 5 m²/g) | Pore volume (± 0.005 cm³/g) |
|-------------|-------------------|---------------------------------|-----------------------------|
| HAp         | 20                | 100 ± 0.5                       | 0.5683                      |
| HAp/CS1     | 14                | 70 ± 0.2                        | 0.3296                      |
| HAp/CS2     | 13                | 77 ± 0.2                        | 0.3186                      |
| HAp/CS3     | 12                | 79 ± 0.2                        | 0.3698                      |
| HAp/CS4     | 10                | 82 ± 0.3                        | 0.4093                      |

Fig. 6  a BET isotherms of nitrogen adsorption and desorption curve of HAp, HAp/CS1, HAp/CS2, HAp/CS3, and HAp/CS4; b zeta potential in water; and c pH_{zpc} in water
The solution pH is an imperative parameter that affects adsorbent surface characteristics, such as zero-point charge (pHzpc) and colloidal stability, as measured by zeta potential. The effects of pHzpc and colloidal stability were quantified at different pH values of triple-distilled water. In general, the zeta potential mainly depends on the functional groups and surface properties of adsorbents. The zeta potential values of HAp, HAp/CS1, HAp/CS2, HAp/CS3, and HAp/CS4 are 10 mV to −4.5 mV, +12 mV to −10 mV, +16 mV to −13 mV, +18 mV to −16 mV, and +24 mV to −23 mV, respectively. Figure 6b implies that on increasing the concentration of CS, there is an increasing trend of colloidal stability in the positive and negative zeta potential line of HAp/CS nanocomposite adsorbents. The zeta potential value of HAp/CS nanocomposite adsorbents shows higher colloidal stability compared to HAp. These results suggest that HAp/CS nanocomposites contain a large number of functional groups of amine (NH₂) and hydroxyl (OH⁻), which leads to increased colloidal stability that favours F⁻ ion adsorption on the adsorbent surface (Scheme 1). Figure 6c displays the pHzpc of HAp and HAp/CS nanocomposite adsorbents that were measured from distilled water.

Scheme 1  Schematic representation for F⁻ ion adsorption

**Zeta potential and zero-point charge**

The solution pH is an imperative parameter that affects adsorbent surface characteristics, such as zero-point charge (pHzpc) and colloidal stability, as measured by zeta potential. The effects of pHzpc and colloidal stability were quantified at different pH values of triple-distilled water. In general, the zeta potential mainly depends on the functional groups and surface properties of adsorbents. The zeta potential values of HAp, HAp/CS1, HAp/CS2, HAp/CS3, and HAp/CS4 are 10 mV to −4.5 mV, +12 mV to −10 mV, +16 mV to −13 mV, +18 mV to −16 mV, and +24 mV to −23 mV, respectively. Figure 6b implies that on increasing the concentration of CS, there is an increasing trend of colloidal stability in the positive and negative zeta potential line of HAp/CS nanocomposite adsorbents. The zeta potential value of HAp/CS nanocomposite adsorbents shows higher colloidal stability compared to HAp. These results suggest that HAp/CS nanocomposites contain a large number of functional groups of amine (NH₂) and hydroxyl (OH⁻), which leads to increased colloidal stability that favours F⁻ ion adsorption on the adsorbent surface (Scheme 1). Figure 6c displays the pHzpc of HAp and HAp/CS nanocomposite adsorbents that were measured from distilled water.
water. The pHzpc values of all adsorbents (HAp, HAp/CS1, HAp/CS2, HAp/CS3, and HAp/CS4) were $7.0 \pm 0.1$. If the solution pH is lower than pHzpc, the protonation action of $H^+$ ions increases at the adsorbent surface, which induces more electrostatic interaction with the $F^-$ ion adsorption. If the solution pH is higher than pHzpc, the adsorbent surface is deprotonated with $OH^-$ ions, causing repulsion between the $F^-$ ions and the adsorbent surface [33].

**Adsorption**

**Effect of contact time**

The influence of contact time was examined at different time intervals (0–120 min) to find the equilibrium time. According to Fig. 7a, $F^-$ adsorption comprises two parts. In the first part, it can be noticed that adsorbents promptly adsorb the $F^-$ ions in 10 min due to the numerous active sites on the adsorbent surface. Subsequently, in the second part, the $F^-$ ion adsorption was linearly adsorbed with increasing time and reached the equilibrium adsorption capacity at 50 min for HAp and 30 min for HAp/CS1, HAp/CS2, HAp/CS3, and HAp/CS4 nanocomposites. Sairam et al. also reported a similar equilibrium time for chitosan–HAp biocomposites [25]. On comparing these results, HAp/CS nanocomposites exhibited an adsorption rate that was 1.3 times greater than the HAp due to the reactive functional groups of CS (such as amine and hydroxyl) that strongly interact with $F^-$ ions through the mechanisms of electrostatic attraction and ion exchange process. Hence, the equilibrium $F^-$ adsorption time of all adsorbents was fixed at 30 min for the subsequent $F^-$ adsorption batch studies.

**Effect of initial concentration**

The maximum adsorption capacity of adsorbents was determined by changing the initial concentration of $F^-$ ions (50–500 mg/L), as shown in Fig. 7b. A 20 mg of adsorbent was immersed in varying initial $F^-$ ions concentration. The residual adsorption parameters were fixed (temperature = 303 K, pH = 9, time = 30 min, and shaking speed = 200 rpm). The $F^-$ equilibrium adsorption capacity of adsorbents ($q_e$) escalated with increasing initial $F^-$ ions concentration. The higher concentration of $F^-$ ion solution reduced the mass transfer resistance and improved the driving force between the surface of the adsorbent and $F^-$ ions, thus enhancing the adsorption capacity of $F^-$ ions. According to this, the maximum $F^-$ ion adsorption capacity of HAp HAp/CS1, HAp/CS2, HAp/CS3, and HAp/CS4 was found to be 10 mg/g, 51 mg/g, 57 mg/g, 61 mg/g, and 70 mg/g, respectively, which is significantly (60%–98%) higher than the existing reports. HAp/CS4 displayed the maximum $F^-$ adsorption capacity compared to the existing reports, as shown in Table 3. Gao et al. developed hierarchical hollow hydroxyapatite microspheres by a hydrothermal technique with a lower adsorption rate (48 times) and adsorption capacity (70%) than the HAp/CS4 nanocomposite [49]. J. He et al. found HAp nanowire displaying
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A lower adsorption rate (6 times) and 60% lower adsorption capacity compared to HAp/CS4 [44]. The maximum adsorption capacity (1.5 mg/g) using calcinated HAp (400 °C) reported by Sundaram et al., was 98% lower than HAp/CS4 [50]. Muthu et al. synthesized the surface-coated HAp (CTAB, HDPC, and DTAB) nanocomposites which exhibited 90% lower adsorption capacity [51]. The calcinated HAp/chitosan nanocomposites had shown 98% lower adsorption capacity than HAp/CS4 [25]. Likewise, Agatha et al. reported the maximum F⁻ ion adsorption capacity (1.90 mg/g), of the crustacean-derived chitosan–hydroxyapatite, which is 52 times lower than HAp/CS4 [52]. The La (III)-incorporated carboxylated chitosan beads exhibited lower F⁻ adsorption capacity (95%) [53]. Muthu et al. developed Ce-loaded silica gel/chitosan biocomposites which had a 95% lower removal capacity.

Fig. 7 Fluoride adsorption effect: a contact time [pH = 7; concentration = 50 mg/L; dosage = 20 mg; V = 20 ml; rpm = 200; and temperature = 303 K], b Initial concentration of F⁻ ion [pH = 7; time = 30 min; dosage = 20 mg; V = 20 ml; rpm = 200; and temperature = 303 K], c pH [time = 30 min; concentration = 500 mg/L; dosage = 20 mg; V = 20 ml; rpm = 200; and temperature = 303 K], d pH value of before and after F⁻ ion adsorption.
than HAp/CS4 [54]. The zirconium–chitosan/graphene oxide membrane for F⁻ ion adsorption displayed a 70% lower adsorption capacity than HAp/CS4 [55]. These results confirm that the HAp/CS4 nanocomposite is a sustainable and efficient adsorbent to remove F⁻ ions from water compared to the reported absorbents.

Effect of pH

The pH plays a significant role in the adsorption process, mainly influenced by the surface interaction and the colloidal stability of the adsorbents. The experiment was performed with different pH values (3 to 11) using 1 M of HCl and 1 M of NaOH solution. The rest of the optimized adsorption parameters were set constant (temperature = 303 K, M = 20 mg, V = 20 ml, shaking speed = 200 rpm, time = 30 min, and Ce = 500 mg/L). The higher F⁻ ion adsorption capacity on HAp and HAp/CS nanocomposite adsorbent was observed at lower pH. This can be attributed to surface protonation, as it leads to higher adsorption of F⁻ ion through the electrostatic attraction between F⁻ ions and the adsorbent surface. The maximum F⁻ ion adsorption capacity of HAp, HAp/CS1, HAp/CS2, HAp/CS3, and HAp/CS4 was 70 mg/g, 120 mg/g, 170 mg/g, 185 mg/g, and 210 mg/g, respectively. Further, by increasing the solution pH (5–7), the adsorbent surface slightly moved towards the negative, and the respective adsorption capacity was 60 mg/g, 80 mg/g, 82 mg/g, and 100 mg/g for HAp/CS1, HAp/CS2, HAp/CS3, and HAp/CS4. At pH (9–11), the adsorbent surface (NH₂ and OH⁻) was deprotonated, reducing the adsorption through electrostatic repulsion. The maximum F⁻ ion adsorption capacity was 20 mg/g, 50 mg/g, 57 mg/g, 55 mg/g, and 70 mg/g for HAp, HAp/CS1, HAp/CS2, HAp/CS3, and HAp/CS4, respectively (Fig. 7c). From this, we observe that the lower surface area of HAp/CS nanocomposite shows increasing adsorption capacity compared to HAp. This might be due to the colloidal stability of the adsorbent influencing the ion exchange process with F⁻ ion and the surface functional group, which were evident from zeta potential analysis.

Table 3 Comparison of F⁻ ion adsorption using existing reports of hydroxyapatite- and chitosan-based adsorbent

| Adsorbent                                      | Time (min) | pH | Capacity (mg/g) | References     |
|------------------------------------------------|------------|----|-----------------|----------------|
| Hydroxyapatite                                 | 1440       | 4  | 29.82           | [49]           |
| Hydroxyapatite nanowires                       | 180        | 7  | 40.65           | [44]           |
| Nanohydroxyapatite                             | 30         | 7  | 1.38            | [50]           |
| Surface-coated hydroxyapatite powders          | 30         | 3  | 9.39            | [51]           |
| Chitosan–hydroxyapatite                        | 720        | 7  | 1.90            | [52]           |
| n-HAp/chitosan                                 | 30         | 7  | 1.560           | [25]           |
| La(III)-incorporated carboxylated chitosan beads| –          | 7  | 4.711           | [53]           |
| Ce-loaded silica gel/chitosan biocomposite     | 30         | 7  | 4.821           | [54]           |
| Zirconium–chitosan/graphene oxide membrane     | 45         | 7  | 29.06           | [55]           |
| HAp/CS4                                        | 30 (7)     | 3  | 240             | Present work   |
|                                                | 7          |    | 100             |                |
|                                                | 9          |    | 70              |                |
In addition, after adsorption of $F^-$ ion the final solution pH was measured (Fig. 7d). At lower pH, the adsorption capacity of $F^-$ ion significantly increased while the acidic pH maintained the same level (3.4±0.2). This result demonstrates that, at lower pH, the adsorbents have higher colloidal stability and hold a positive charge on the surface that can enhance the adsorption capacity through the surface complexation/electrostatic interaction between fluoride and surface functional groups of adsorbent. At the same time, increase in the solution pH of 5 and 7, the final pH values exhibits neutral pH around 6.9–7.1, which indicates that the surface-active sites of hydroxyl ions (OH$^-$) was replaced by fluoride ions (F$^-$) through the ion exchange process, leading to the formation of the fluorapatite. These results suggest that HAp and HAp/CS nanocomposite adsorbents could be used for $F^-$ adsorption in wastewater treatment.

**Adsorption isotherm**

**Kinetic isotherm**

Kinetic isotherms explain the adsorption mechanism and adsorption rate on the surface of adsorbents. The experimental kinetic data are fitted into two different kinetic models such as pseudo-first-order [56] and pseudo-second-order kinetics [57]. Their expression is given in Eqs. (2) and (3).

$$\log(Q_e - Q_t) = \log(Q_e) - (\frac{k_1}{2.303})t$$  \hspace{1cm} (2)

$$\frac{t}{Q_t} = \frac{1}{(K_2 \times Q_e^2)} + \left(\frac{1}{Q_e}\right)t$$  \hspace{1cm} (3)

where $Q_e$ is the equilibrium $F^-$ ion adsorption capacity (mg/g), $Q_t$ is the adsorption capacity of $F^-$ ions at a given time, and $t$ is the adsorption time (min). $k_1$ and $k_2$ are equilibrium rate constants of pseudo-first- and pseudo-second-order kinetics, respectively. In pseudo-first-order kinetics, $k_1$ and $Q_t$ are derived from the slope and intercept of the linear fit plot of log($q_e$-$q_t$), and $t$ (min) shown in Fig. 8a. In pseudo-second-order kinetics, the values of $k_2$ and $Q_t$ are derived from the intercept and slope of the linear fit plot of $t/q_t$ vs $t$ (min), as shown in Fig. 8b. The parameters of the first- and second-order kinetics are presented in Table 4. $R^2$ value and the theoretical $F^-$ adsorption capacity of HAp, HAp/CS1, HAp/CS2, HAp/CS3, and HAp/CS4 are well matched with second-order kinetics compared to first-order kinetics, indicating the adsorption of $F^-$ ions on the surface of adsorbents through chemisorption.

**Intraparticle diffusion**

Intraparticle diffusion explains rate-controlling mechanisms and adsorbate ion diffusion on an adsorbent surface [58]. The linear expression of intraparticle diffusion is given in Eq. (4).
where $K_i$ is the intraparticle diffusion rate constant and $C_i$ is the thickness of the boundary layer; the calculated values of these parameters are listed in Table 4. The

$$Q_t = K_i \sqrt{t} + C_i$$  \hspace{1cm} (4)
values of $K_i$ and $C_i$ are derived from the slope and intercept from a linear fit model between $q_t$ and $t^{1/2}$, as shown in Fig. 8c. The correlation coefficient of $R^2$ value is comparatively close to pseudo-second-order kinetics. The theoretical value of $F^-$ adsorption capacity using this model concurs with pseudo-second-order kinetics compared to pseudo-first-order kinetics. These results imply the chemisorption of $F^-$ ions on the surface of HAp and HAp/CS nanocomposite adsorbents. Furthermore, this graph shows the two stages of $F^-$ ion adsorption in HAp. The first stage of the linear plot refers to the rapid $F^-$ adsorption due to the presence of abundant active sites on the surface (external). The second stage refers to the adsorbed $F^-$ ions reaching the equilibrium state due to a decrease in the number of active sites. On the other hand, nanocomposites (HAp/CS1, HAp/CS2, HAp/CS3, and HAp/CS4) comprise a three-stage adsorption of $F^-$ ions: (1) external surface diffusion, (2) pore diffusion, and (3) equilibrium adsorption process. However, the linear plots of $q_t$ versus $t^{0.5}$ did not pass through the origin for all the four adsorbents that implied the intraparticle diffusion (IPD) was not rate-controlling step and the $F^-$ ion adsorption process on the adsorbents surface was governed by complex mechanisms [59].

**Langmuir and Freundlich isotherms**

The adsorption equilibrium mechanism is explained by Langmuir and Freundlich isotherms. Langmuir isotherm is a homogeneous surface with identical active sites [60]. The Freundlich isotherm represents the multilayer adsorption process on the heterogeneous adsorbent surface by van der Waals forces [61]. Langmuir and Freundlich isotherms are expressed in the linear Eqs. (5) and (6)

\[
\frac{C_e}{Q_e} = \frac{1}{Q_m K_L} + \frac{C_e}{Q_m} \\
\log Q_e = \log K_F + \left(\frac{1}{n}\right) \log C_e
\]

(5)

where $Q_m$ is the maximum adsorption capacity (mg/g), $C_e$ is the equilibrium adsorption concentration (mg/L), $1/n$ is the adsorption intensity, and $K_L$ and $K_F$ are Langmuir and Freundlich constants, respectively. The values of $K_F$ and $1/n$ are derived from the slope and intercept of the linear fit of $\log C_e$ vs. $\log q_e$, as shown in Fig. 8d. $Q_m$ and $K_L$ are derived from the slope and intercept of the linear fit of $1/C_e$ vs. $1/q_e$, as depicted in Fig. 8e. The correlation coefficients of $R^2$ values of HAp, HAp/CS1, HAp/CS2, HAp/CS3, and HAp/CS4 are better while correlating with Langmuir than the Freundlich isotherm. Similarly, the theoretical and experimental values of $F^-$ ion adsorption capacity are well matched with the Langmuir isotherm. Moreover, the value of $n$ suggests that the adsorption of $F^-$ ions is unfavourable for Freundlich isotherm, as denoted in Table 5. Hence, the adsorption of $F^-$ ions on the surface of the HAp, HAp/CS1, HAp/CS2, HAp/CS3, and HAp/CS4 is a monolayer. The maximum monolayer adsorption capacity of HAp, HAp/CS1, HAp/CS2, HAp/CS3, and HAp/CS4 is 10 mg/g, 50 mg/g, 57 mg/g, and 70 mg/g, respectively.
Dubinin–Kaganer–Radushkevich (DKR) isotherms

DKR isotherm distinguished for the adsorption process is carried out by physisorption or chemisorption. The linear form of DKR isotherms is given in Eq. (7).

\[
\ln Q_e = \ln Q_m - \beta \varepsilon^2
\]  

(7)

\[
\varepsilon = RT \ln(1 + \frac{1}{C_e})
\]  

(8)

\[
E = \frac{1}{\sqrt{-2\beta}}
\]  

(9)

where \( R \) is the universal constant, \( T \) is the temperature, \( E \) is the mean free energy, and \( \varepsilon \) is the Polanyi’s potential, as summarized in Table 5. The values of \( Q_m \) and \( \beta \) are derived from the slope and intercept of a linear fit model of \( \varepsilon^2 \) vs. \( \ln Q_e \), as depicted in Fig. 8f. The calculated value of \( F^- \) equilibrium adsorption capacity by this model is a better fit with the Langmuir isotherm model compared to Freundlich model. Hence, these results signify monolayered \( F^- \) adsorption. The value of \( E \) reveals the nature of the adsorption process, i.e. \( E < 8 \) kJ/mol specifies the physisorption, \( 8 \leq E \leq 16 \) kJ/mol indicates a chemical ion exchange occurrence, or \( E > 16 \) kJ/mol represents stronger chemisorption than the ion exchange process [62].

The calculated \( E \) values of HAp, HAp/CS1, HAp/CS2, HAp/CS3, and HAp/CS4 are 17 kJ/mol, 7 kJ/mol, 7 kJ/mol, 13 kJ/mol, and 10 kJ/mol, respectively. Hence, these results imply that HAp, HAp/CS1, and HAp/CS2 follow the chemical ion exchange process, whereas HAp/CS4 indicates stronger chemisorption rather than an ion exchange process.

### Table 5 Langmuir and Freundlich isotherm constant and correlation coefficients

| Isotherm | Parameters | Adsorbent | \( Q_{exp} \) (mg/g) | \( Q_m \) (mg/g) | \( K_L \) (mg/L) | \( R^2 \) | \( K_F \) (mg/g) | \( 1/n \) | \( R^2 \) | \( Q_m \) (mg/g) | \( \beta \) (mol/J)^2 | \( E \) (kJ/mol) | \( R^2 \) |
|----------|------------|-----------|-----------------|-----------------|----------------|----------|----------------|-------|----------|----------------|-----------------|--------------|--------|
| Langmuir | \( Q_m \) (mg/g) | HAp | 10±2 | 50±3 | 53±3 | 61±3 | 70±2 | HAp/CS1 | 56±1 | 58±5 | 65±2 | 72±5 |
|          | \( K_L \) (mg/L) | HAp/CS1 | 0.04123 | 0.01521 | 0.04117 | 0.01936 | 0.06950 |
|          | \( R^2 \) | HAp/CS2 | 0.99137 | 0.99585 | 0.99264 | 0.99027 | 0.99442 |
| Freundlich | \( K_F \) (mg/g) | HAp/CS3 | 5.31141 | 10.0463 | 0.22739 | 17.23733 | 37.6755 |
|          | \( 1/n \) | HAp/CS4 | 9.26612 | 3.68459 | 1.07543 | 0.20456 | 9.40910 |
|          | \( R^2 \) | HAp | 0.92857 | 0.92558 | 0.76228 | 0.95011 | 0.93073 |
| DKR | \( Q_m \) (mg/g) | HAp | 12 | 55 | 59 | 58 | 74 | HAp/CS1 | 1.9991E-9 | 1.36459E-8 | 9.84963E-9 | 2.92231E-9 | 5.48745E-9 |
|          | \( \beta \) (mol/J)^2 | HAp/CS2 | −1.9991E-9 | −1.36459E-8 | −9.84963E-9 | −2.92231E-9 | −5.48745E-9 |
|          | \( E \) (kJ/mol) | HAp/CS3 | 17 | 7 | 7 | 13 | 10 |
|          | \( R^2 \) | HAp/CS4 | 0.9559 | 0.9834 | 0.9760 | 0.97 | 0.9806 |
Effect of Co-anions

Generally, nitrate, hydroxyl, chloride, carbonate, sulphate, and fluoride anions are present in natural water. This study has focused on the effects of other competing anions ($\text{NO}_3^-$, $\text{OH}^-$, $\text{Cl}^-$, $\text{CO}_3^{2-}$, and $\text{SO}_4^{2-}$) on the $\text{F}^-$ ion adsorption capacity. Accordingly, the experiment was performed by mixing 20 mg of adsorbent in 20 mL of 500 mg/L of $\text{F}^-$ ion solution with the 50 mg/L of other competing ions under the following adsorption parameters: time = 30 min, shaken period = 200 rpm, and temperature = 303 K. The presence of $\text{NO}_3^-$, $\text{SO}_4^{2-}$, and $\text{Cl}^-$ ions did not have any significantly impact the $\text{F}^-$ adsorption capacity of HAp, HAp/CS1, HAp/CS2, HAp/CS3, and HAp/CS4. The presence of $\text{CO}_3^{2-}$ and $\text{OH}^-$ significantly affected the $\text{F}^-$ adsorption capacity due to the high alkaline pH, which led to the electrostatic repulsion and reduced surface-active binding sites for $\text{F}^-$ ion adsorption (Fig. 9a). The interference of co-anions on $\text{F}^-$ ion adsorption was as follows: $\text{NO}_3^- < \text{SO}_4^{2-} < \text{Cl}^- < \text{CO}_3^{2-} < \text{OH}^-$. In addition, pH values were measured before and after $\text{F}^-$ ion adsorption process for these co-anions (Table 6). Furthermore, the final pH values of $\text{F}^-$ adsorbed solution for the interfering of co-anions was found to be about 7 ± 0.5, which resulted in the prepared adsorbents (HAp, HAp/CS1, HAp/CS2, HAp/CS3, and HAp/CS4) acting as a buffer capacity. This may be due to the fact that the adsorbents contain a functional group of protonated amines ($\text{NH}_2^+$) and a large number of hydroxyl groups (OH$^-$). These functional groups release or adsorb the protons depending on the pH values, which assist in maintaining the pH values in the range of 7 ± 0.5 (Fig. 9b). Similarly, Sapna et al. investigated cerium impregnated pectin/silica–gel composite and implied that after the adsorption of anions, the final solution pH was maintained between 5 and 7 [63].

Regeneration

Regeneration is a significant aspect of the adsorption process for determining the cost and stability of adsorbent. To investigate the reusability of $\text{F}^-$ ion adsorption on HAp, HAp/CS1, HAp/CS2, HAp/CS3, and HAp/CS4, seven consecutive cycles of adsorption–desorption were performed. In the first cycle, the regeneration efficiency of HAp, HAp/CS1, HAp/CS2, HAp/CS3, and HAp/CS4 was found to be 100%. Subsequently, each cycle of $\text{F}^-$ adsorbed samples was regenerated with 1 M of NaOH solution. The defluoridation efficiency of each cycle gradually decreased due to the hydroxyl ion (OH$^-$) of NaOH being replaced by the $\text{F}^-$ ions through the ion exchange mechanism, as shown in Eqs. (10–11). After 7th cycle, HAp, HAp/CS1, HAp/CS2, and HAp/CS3 showed a decreased recycling efficiency of 32%, 60%, 80%, and 82%, respectively (Fig. 9c). However, HAp/CS4 exhibited excellent recycling efficiency and maintained an enhanced sustainable regeneration process up to the 7th cycle, with a defluoridation efficiency of 90%, which is 2.5 times over HAp. Further, Abri et al. reported the magnetic chitosan-based nanocomposite adsorbent with a recycling efficiency of 74.64% up to 5 cycles of regeneration [64]. HAp/CS4 showed excellent sustainable recycling efficiency of 90% was achieved up to the 7th
Fig. 9  a Competing ion effect of F⁻ ion on HAp, HAp/CS1, HAp/CS2, HAp/CS3, and HAp/CS4 [pH = 7; time = 30 min; concentration = 50 mg/L; dosage = 20 mg; V = 20 ml; rpm = 200; and temperature = 303 K], b pH value before and after co-anion adsorption, and c Regeneration of F⁻ ion on HAp, HAp/CS1, HAp/CS2, HAp/CS3, and HAp/CS4 [pH = 7; time = 30 min; concentration = 500 mg/L; dosage = 20 mg; V = 20 ml; rpm = 200; and temperature = 303 K]
cycle, as it possessed more active functional groups. This result indicates that the HAp/CS4 nanocomposite could be used as sustainable adsorbent adsorption of F\(^-\) ions. Furthermore, the desorbed F\(^-\) ion solution, which on treatment with Ca(OH)\(_2\) solution, yields CaF\(_2\) precipitate. The precipitate is recovered by filtration, and the filtrate containing NaOH is recycled for the regeneration of the adsorbent [65–67]. The residue of Ca(OH)\(_2\) is of commercial value because it is one of the ingredients of toothpaste (Eq. 12).

\[
\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2 + 2\text{NaF} \rightarrow \text{Ca}_{10}(\text{PO}_4)_6F_2 + 2\text{NaOH} \text{(Adsorption)} \tag{10}
\]

\[
\text{Ca}_{10}(\text{PO}_4)_6F_2 + 2\text{NaOH} \rightarrow \text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2 + 2\text{NaF} \text{(Regeneration)} \tag{11}
\]

\[
2\text{NaF} + \text{Ca(OH)}_2 \rightarrow \text{CaF}_2 + 2\text{NaOH} \tag{12}
\]

### Conclusion

The nanorods of HAp and HAp/CS\(_x\) (\(x = 1, x = 2, x = 3, \) and \(x = 4\)) nanocomposites were successfully synthesized by a facile technique of co-precipitation followed by lyophilization. These cross-linker-free lyophilized mesoporous HAp/chitosan nanocomposites were effectively utilized for the adsorption of F\(^-\) ions. Furthermore, the chitosan (CS)-incorporated HAp matrix leads to an improved colloidal stability and spreads positive charges on the surface. These characteristics enrich the F\(^-\) ion adsorption through the ion exchange process and electrostatic interaction, as well as maintain the sustained regeneration efficiency. The maximum F\(^-\) adsorption capacity was found to be 56 mg/g, 80 mg/g, 82 mg/g, and 100 mg/g for HAp/CS1, HAp/CS2, HAp/CS3, and HAp/CS4, respectively, at pH 7. The adsorption of F\(^-\) ions on adsorbent surfaces indicates monolayer chemisorption rather than the ion exchange process, as confirmed by the Langmuir and DKR isotherms, respectively. Moreover, HAp/CS4 (4 wt. % of CS) had a sustained F\(^-\) ions regeneration efficiency (90% in 30 min) up to the 7th cycle compared to HAp (2.5 times). The morphology of F\(^-\) ion

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**Table 6** Before and after solution pH of F\(^-\) ion adsorption for coexisting anions

| Anions | pH Before adsorption | pH After adsorption |
|--------|----------------------|---------------------|
|        | Initial pH of solution | HAp | HAp/CS1 | HAp/CS2 | HAp/CS3 | HAp/CS4 |
| NO\(_3\)\(^-\) | 8.9 | 7.2 | 6.9 | 6.9 | 6.8 | 6.9 |
| OH\(^-\) | 11.1 | 10.2 | 8.8 | 8.6 | 8.5 | 8.1 |
| CO\(_3\)\(^2-\) | 9.1 | 7.5 | 7.4 | 7.4 | 7.1 | 7 |
| Cl\(^-\) | 8.5 | 7.1 | 7 | 7 | 7 | 7 |
| SO\(_4\)\(^2-\) | 8.8 | 7.3 | 7 | 7 | 7.1 | 7.1 |
adsorbed material surface was transformed from rod to sphere. XRD, FTIR, and XPS results confirmed the formation of fluorapatite through ion exchange process and electrostatic interaction. The solutions in the initial pH range of 5–7 were stabilized at pH 7 after the fluoride adsorption, rendering them potable. Overall, these results imply that HAp/CS4 nanocomposite adsorbent has the potential to function as an efficient adsorbent for F− ions removal from water.

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Author contributions SS was responsible for conceptualization, methodology, and investigation; SS and SEP wrote and prepared the original draft; SEP was involved in software and formal analysis; EK and NKS participated in writing—reviewing and editing; NKS carried out investigation, supervision, and project administration. All authors have read and agreed to the published version of the manuscript.

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Declarations

Conflict of interest The authors declare that they have no known competing interests in this paper.

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