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Enriching trace level adsorption affinity of As^{3+} ion using hydrothermally synthesized iron-doped hydroxyapatite nanorods

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Abstract

Contamination of arsenic in the form of arsenite (As^{3+}) and arsenate (As^{5+}) in potable water causes serious illness in the human body even at a very low concentration ($10 \mu\text{g} / \text{L}$). As^{3+} is comparatively 60 times more toxic than As^{5+} species. Hence, this work is focused on the preparation of adsorbents for efficient removal of As^{3+} with higher adsorption affinity at trace level ($\leq 50 \mu\text{g/L}$). Here, iron-doped hydroxyapatite (Fe-HAp) synthesized by hydrothermal technique is employed as an efficient adsorbent. A very less quantity of Fe^{2+} ion (0.5 wt %) is incorporated in the tetrahedral and octahedral sites of the HAp lattice along the c-axis which lead to drastic reduction in particle size (400%) and enhancing the specific surface area (105%), colloidal

stability, and adsorption affinity. The maximum adsorption capacity of As^{3+} is $139 \pm 2 \mu\text{g/g}$ and $183 \pm 2 \mu\text{g/g}$ for HAp and Fe-HAp, respectively. The adsorption rate of Fe-HAp is very rapid which is 538% higher compared to HAp and also the As^{3+} adsorption affinity or sensitivity ($0.71 \mu\text{g/L}$) significantly improved 83-99% when compared to the adsorbents reported in the previous literature so far. The monolayer adsorption of As^{3+} is purely strong chemisorption as confirmed by the Langmuir and Dubinin–Radushkevich (DKR) isotherm. The structure and morphology of HAp and Fe-HAp remain unchanged after the adsorption of As^{3+} ions and also no secondary toxic products were observed. Hence, the above results reveal Fe-HAp as an efficient and low-cost adsorbent for removal of highly toxic As^{3+} ions at the trace level.

Keywords: Hydrothermal, colloidal stability, surface charge, Surface complexation, As^{3+} adsorption, Adsorption isotherm

1. Introduction

Arsenic (As) is a familiar toxic metal ion that can be found in groundwater as a contaminant. The World Health Organization (WHO) recommended that the limit of arsenic in drinking water is $\leq 10 \mu\text{g/L}$. However, more than 60 million peoples are said to be affected by arsenic contamination, which is exceeding WHO limits [1–5]. Consuming of Arsenic contaminated water causes carcinogenic effects in the skin, urinary bladder, liver, kidney, and lung [6–9]. Generally, Arsenic has four different chemical forms in an aquatic environment based on the oxidation state -3, 0, +3, and +5. The existence of arsenic in 0 and -3 oxidation states in water is extremely rare, while +3 and +5 states are prominently found in the natural water source, which strongly depends on the redox reaction and pH condition [10,11]. In groundwater, As^{3+} is found in neutral species such as $\text{As}(\text{OH})_3$, H_3AsO_3 , $\text{As}(\text{OH})_4^-$, $\text{AsO}_2\text{OH}^{2-}$, and AsO_3^{3-} , whereas As^{5+} is found in anionic forms such as AsO_4^{3-} or H_2AsO_4^- or HAsO_4^{2-} [12,13]. In comparison, the prevalence of As^{3+} contaminated groundwater is approximately 67-99% higher than As^{5+} ions and the toxicity rate of As^{3+} is 60 times greater than the As^{5+} [14]. In addition, As^{3+} shows less adsorption affinity than As^{5+} because As^{3+} is a neutral compound, whereas As^{5+} is an anionic compound. The anionic compound has improved attractive force between the adsorbent and adsorbate ions [7].

Various technologies have been applied to remove the arsenic from contaminated water, such as chemical precipitation, flocculation, ion exchange and reverse osmosis [9,12,13]. But, these

technologies have limitations when implementing them into large-scale processes. The membrane technology, a reverse osmosis process requires high electric power and skilled technicians required to operate. Likewise, the flocculation, ion exchange, and precipitation methods are problematic due to their complexities in the disposal of secondary products [13]. Recently, the adsorption technique has emerged as an effective alternative method, because it is a simple and cost-effective method for the removal of arsenic [15–17]. A variety of adsorbents were employed to removing arsenic from water. They are iron-oxide-coated quartz (IOCQ), biochar, magnetic Fe-hydrotalcite, activated alumina, sulfate-modified iron oxide-coated sand [18–22] etc.,

At the same moment, nano-sized adsorbents were used to remove the metal ions because they have high surface area, adsorption capacity, and affinity. In this work, calcium phosphate (CaP) based adsorbent HAp [$\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$] has been used to remove arsenic from water. Because, HAp is highly biocompatible, porous in nature, relatively inexpensive, easy to modify the structural and morphological characteristics based on synthesis routes, and ensures safe drinking water [23]. Despite, still HAp has a lack of adsorption affinity of arsenic was observed. Hence, the Fe^{2+} ions are introduced into the HAp lattice which is enhanced the adsorption affinity and their capacity. Because it has the capability to control arsenic mobility, and higher adsorption affinity of arsenic ions [24–27].

Herein, the removal of highly toxic As^{3+} ion at trace level using hydrothermally synthesized nano-sized Fe-HAp was employed as an adsorbent to overcome the above mentioned problem. The incorporation of the Fe^{2+} ion improves adsorbent characteristic features. That results show the narrow mesoporous structure, reduction of particle size, higher surface area, and higher colloidal stability as shown in **Fig. 1**. Also, this work elucidates the importance of colloidal stability and zero point charge of the adsorbent. The maximum adsorption capacity was found by the batch adsorption process. The nature of the adsorption process was discussed using Langmuir, Freundlich, and DKR isotherm. Ultimately the aim of this work is to enhance trace level adsorption affinity, As^{3+} adsorption capacity, and maintain the water quality.

2. Experimental section

2.1. Materials and methods

Calcium nitrate tetrahydrate ($\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$), diammonium hydrogen orthophosphate ($(\text{NH}_4)_2\text{HPO}_4$), Iron (II) chloride (FeCl_2), Hydrochloric acid (HCl), Ammonia solution (NH_4OH), and Sodium arsenite (NaAsO_2). All the chemicals were purchased from Merck analytical grade. Triple distilled water was used to prepare adsorbent and adsorbate ion.

2.2. Synthesis of HAp and Fe-HAp

1M of calcium nitrate tetrahydrate and 0.6 M of di-ammonium hydrogen orthophosphate were dissolved in 100 mL of triple distilled water in separate beakers. 1M of calcium nitrate tetrahydrate was added drop-wise into 0.6 M of diammonium hydrogen orthophosphate by maintaining the pH of the product solution at 10 using ammonia to synthesize HAp. The obtained precipitated solution was continuously stirred for 2h and transferred into a 100 mL Teflon-lined stainless-steel autoclave and kept in an oven at 150°C for 36 h. Subsequently, the autoclave was allowed to reach room temperature and the solution was centrifuged with triple distilled water to remove the unreacted ammonia from the precipitated HAp. Finally, the collected precipitates were dried in a vacuum oven at 80°C for 24 h. The Fe-HAp was synthesized by mixing 0.1M of ferric chloride with 1M of calcium nitrate tetrahydrate. The rest of the synthesis procedure is the same as the preparation of HAp described above.

2.3. Characterizations

Powder X-ray diffraction (XRD) of the synthesized adsorbent was recorded by Rigaku Ultima IV X-ray diffractometer equipped with $\text{Cu K}\alpha$ radiation ($\lambda = 0.154 \text{ nm}$) in the 2θ range of 10° to 70° with scanning step size of 0.02°. The functional group of the adsorbent was analyzed by Fourier transform infrared spectrometer (FT-IR-JASCO-6300) using the KBr pellet technique. The adsorbent morphology was obtained using transmission electron microscopy (TEM-PHILIPS-CM 200) and Scanning electron microscopy (SEM-Carl Zeiss-EVO 180). The specific surface area, pore size, and pore volume of the adsorbent material were measured by Brunauer-Emmett-Teller (BET) isotherm model by using surface area analyzer-TPD/TPR (Model: Quanta chrome). The adsorbent zeta potential was measured by Dynamic Light Scattering (DLS-Malvern Zetasizer Nano-ZS). The removal capacity of As^{3+} was evaluated using an Atomic Absorbance spectrometer (AAS-iCE 33-00 from Thermo fisher) equipped with a hydrate generator. The pH of the solution was measured using a Eutech pH meter with a sensitivity of 0.01.

24. Batch adsorption study

1000 µg/L of As³⁺ stock solution was prepared from sodium arsenite as a precursor material. The required concentrations were obtained by the dilution of stock solution using triple distilled water. Initially, 100 mg of adsorbents were added to 20 ml of 1000 µg/L of As³⁺ solution that was used to investigate the effect of contact time (0 to 50 min). The rest of the parameters pH (7), rpm (180), and temperature (25 ± 1 °C) were kept constant. After that, the evaluated contact time (10 min) was fixed to subsequent studies on the concentration effect of As³⁺ (100 µg/L to 1000 µg/L), and the rest of the adsorption parameters were kept constant. The maximum removal capacity of As³⁺ is measured from **Eq. (1)**. All the experiments were conducted in triplicate with an error percentage of ± 1%. After adsorption of As³⁺, HAp and Fe-HAp were named as HAp-As and Fe-HAp-As.

$$\text{Adsorption capacity}(Q_e) = (C_o - C_f) \times \left(\frac{V}{M}\right) \quad (1)$$

Where Q_e is the equilibrium adsorption capacity (µg/g). C_o and C_f are the initial and final concentration of adsorbate solution (µg/L). V and M are the volume of the solution (mL) and mass of the adsorbent dosage (mg), respectively [28–31].

2.5. Quantification of Fe²⁺ ion

The presence of doping iron in HAp was estimated by dissolving 10 mg of Fe-HAp in 20 ml of HCl (0.1M) solution. Furthermore, the concentration of Fe²⁺ ion released in triple distilled water and As³⁺ contaminated water was calculated by the following procedure. 100 mg of Fe-HAp was soaked in 20 mL of triple distilled water and As³⁺ contaminated water (pH = 7; shaking speed=180 rpm) at room temperature. After the equilibrium time (10 min), the supernatant solution was tested in AAS.

3. Result and discussion

3.1. X-ray diffraction analysis

The XRD patterns of the synthesized and As³⁺ ion adsorbed HAp and Fe-HAp nanoparticles are shown in **Fig. 2a**. The diffraction pattern of both adsorbents exhibited crystalline nature and matched well with the characteristic peaks of HAp phase in accordance with JCPDS card No. 09-

0432 [32,33]. The absence of any significant shift in diffraction peak towards the lower angle confirms that the Ca^{2+} ion was not substituted by the Fe^{2+} ions [34]. In HAp, the a -axis is positively charged due to the presence of Ca^{2+} ions, whereas the c -axis is negatively charged due to the influence of phosphate and hydroxide ions, which enables the incorporation of cationic Fe^{2+} ion as shown in schematic representation of **Fig. 2b** [35,36]. Hence, the doped Fe^{2+} ions were expected to be incorporated in the interstitial position either at the tetrahedral or octahedral vacancy of hexagonal geometry in [0001] direction along the c -axis. The crystallite size, crystallinity, dislocation density, and microstrain of HAp and Fe-HAp could be calculated using the **Eqs. (2-5)** [3,37–39].

$$\text{Crystallite-Size}(D_c) = \frac{K_B \lambda}{\beta \cos \theta} \quad (2)$$

$$\text{Crystallinity}(X_c) = \left(\frac{K_c}{\beta}\right)^3 \quad (3)$$

$$\text{Dislocation-density}(\delta) = \frac{1}{(D_c)^2} \quad (4)$$

$$\text{Microstrain}(\varepsilon) = \left(\frac{\beta}{4 \tan \theta}\right) \quad (5)$$

Where K_B is the broadening constant 0.9, λ is the wavelength of X-ray ($\lambda=1.5414$ nm), β is full width half maximum (FWHM), K_c is constant 0.24. The incorporated Fe^{2+} ion increases microstrain (190%) and dislocation density (360%) in the crystalline plane, and peak broadening were observed causes to decrease in crystallinity and crystallite size (**Fig. S1a-d**) [28]. The crystallite size was calculated using the scherrer formula from the characteristic peaks of HAp and Fe-HAp which were found to be 11 ± 1 nm and 6 ± 1 nm respectively. After the adsorption of As^{3+} ions, the phase purity of HAp-As and Fe-HAp-As was analyzed by XRD. The phase purity of the adsorbent is not affected but the full-width half maximum (FWHM) of HAp-As and Fe-HAp-As reduced compared to before adsorption. Hence, this result indicates the crystallite size has been increased and it was found to be 27 ± 1 nm for HAp-As and 18 ± 1 nm for Fe-HAp-As (**Fig. S1e**). In addition, the average crystallinity of HAp and Fe-HAp was increased by adsorption of As^{3+} ion as shown in **Fig. S1f**. Accordingly, a drastic reduction were observed in microstrain (61% for HAp-As and 69% for Fe-HAp-As) and dislocation density of the crystalline lattice (84% for HAp-As and 90% for Fe-HAp-As) as shown in **Fig. S1g-h**.

3.2. Fourier transform infrared spectroscopy

The functional groups of HAp and Fe-HAp are shown in **Fig. 2c**. The broad absorbance band at 3458 cm^{-1} and the narrow band at 3792 cm^{-1} is observed due to the stretching vibration of O-H. The C-O stretching vibrations are observed at 1382 cm^{-1} and 1460 cm^{-1} due to the absorption CO_3^{2-} from the atmosphere [34]. The presence of OH^- in the HAp lattice was confirmed from the OH⁻ vibrational band were observed at 1625 cm^{-1} and 634 cm^{-1} , which are the characteristic vibrations of HAp. The presence of bending vibration of PO_4^{3-} groups are confirmed at 464 cm^{-1} and 534 cm^{-1} . Symmetric and asymmetric stretching vibration of PO_4^{3-} occurred at 957 cm^{-1} and 1135 cm^{-1} , respectively [40]. The characteristic vibrations of PO_4^{3-} intensities decreased at 534 cm^{-1} and 634 cm^{-1} , due to the incorporation of Fe^{2+} ion in HAp (**Fig. 2b**). Since $400 - 600\text{ cm}^{-1}$ is the fingerprint region of the Fe-HAp structure [41–43]. The incorporation of Fe^{2+} ions into vacant sites of HAp lattice affects the vibrational symmetry leading to the reduction in the intensity of the PO_4^{3-} group [44]. Accordingly, the FTIR spectra of HAp-As and Fe-HAp-As show the intensity reduction of hydroxyl and carbonate groups as seen in **Fig. 2c**. Likewise the stretching and bending vibrational mode of PO_4^{3-} band intensity were increased distinctly after the adsorption of As^{3+} ions due to charge neutralization with PO_4^{3-} site. This neutralization affects the chemical environment of the phosphate ions consequently improving the vibrational symmetry.

3.3. BET analysis

The N_2 adsorption desorption of HAp and Fe-HAp is shown in **Fig. 2d**. According to IUPAC classification, the adsorption desorption curve of HAp and Fe-HAp indicates the type IV isotherm [45]. The pore size distribution shows the well-developed cylindrical shape mesoporous structure and the pore size is $15 \pm 0.5\text{ nm}$ and $9 \pm 0.5\text{ nm}$ which corresponds to HAp and Fe-HAp. The specific surface area of HAp and Fe-HAp is $39 \pm 1\text{ m}^2/\text{g}$ and $80 \pm 1\text{ m}^2/\text{g}$ respectively is shown in **Table S1**. The specific surface area of Fe-HAp has increased 105% due to narrow pores distribution and partial reduction of particle size. Consequently, an increment of specific surface area leads to enhanced As^{3+} ion adsorption capacity and their affinity [46].

3.4. TEM and SEM analysis

The TEM micrograph of synthesized HAp and Fe-HAp adsorbents shows uniform distributions of rod-like morphology as seen in **Fig. 3a-b**. The dimension of HAp is 220 ± 5 nm in length and 45 ± 5 nm in width, whereas Fe-HAp is 55 ± 3 nm in length and 20 ± 3 nm in width. It was observed that the incorporation of Fe^{2+} ions in HAp lattice significantly reduces the particle size, which increases the number of active sites and adsorption capacity of As^{3+} . The SEM images of HAp and Fe-HAp nanoparticles are shown in **Fig. 3c-d**. In the micrograph, uniformly distributed rod-like particles are revealed, the length of HAp was found to be 230 ± 5 nm and 52 ± 5 nm in width; the length of Fe-HAp was 63 ± 5 nm and width was 24 ± 5 nm, which matched well with the TEM measurements. Similarly, HAp-As and Fe-HAp-As exhibit a uniform distribution of rod-like morphology as shown in **Fig. 3e-f**. After adsorption, average size of the particles are increased; HAp-As with a length of 250 ± 3 nm and width of 58 ± 3 nm; also the length of Fe-HAp is 70 ± 3 nm and width is 30 ± 3 nm. Elemental analysis of pure and As^{3+} ion adsorbed HAp and Fe-HAp is shown in **Fig. S2a-d**. The energy dispersive X-ray (EDX) spectra of HAp shows the presence of Ca, P, O and C elements. In addition, Fe-HAp confirms the presence of Fe^{2+} ion. Also, the occurrence of the adsorbed As^{3+} was confirmed in HAp-As and Fe-HAp-As. The Ca/P ratio of HAp and Fe-HAp was 1.65 and 1.64 respectively, whereas the Ca/P ratio of HAp-As is 1.52 and Fe-HAp-As is 1.53. Furthermore, the elemental mapping of As^{3+} ion adsorbed in different pH values of HAp and Fe-HAp is shown in **Fig. S3**. From **Fig. S3a** shows the uniform distribution of Ca, P, C, and O for HAp and Fe-HAp. In addition, Fe-HAp were shows the uniform distribution of Fe^{2+} ion also. In pH 3, distribution of As^{3+} ions is significantly less due to the lower colloidal stability. Whereas, the distribution of As^{3+} sufficiently improved in the alkaline pH (**Fig. S3b-c**). However, the pH values higher than 9.2 revealed an improper distribution of the As^{3+} ion by electrostatic repulsion between adsorbent and As^{3+} .

3.5. pH effects on zeta potential and isoelectric point

The pH of the solution plays a crucial role in the adsorption process because it influences the dissociation of adsorbate ion, colloidal stability, and isoelectric point charge (pH_{pzc}) [9,47]. Quantification of colloidal stability and pH_{pzc} in different pH values of triple distilled water and As^{3+} contaminated water are shown in **Fig. 4a-b**. Generally, Colloidal stability has a significant impact on the adsorption process and it was measured from zeta potential (ζ). The smaller value of the zeta potential (ζ is either positive or negative) indicates the lower colloidal stability whereas

higher value indicates the higher colloidal stability. At lower colloidal stability, the adsorbent is more prone to change crystal structure and morphology, and increasing aggregation. Whereas, at high colloidal stability, less aggregation takes place, which increases the number of active sites on the adsorbent surface. In triple distilled water at pH 3, HAp exhibited more aggregation or lower colloidal stability, due to lower zeta potential of HAp ($\zeta = -2$ mV); whereas Fe-HAp showed the incipient stability since the zeta potential value is higher ($\zeta = -15$ mV). Hence, enhanced colloidal stability of Fe-HAp was observed in a wide range of pH at 3 to 11 due to the presence of interstitial Fe^{2+} ion in the HAp lattice. When the solution pH was increased towards alkaline, the colloidal stability of both the adsorbents significantly improved as seen in **Fig. 4a**. This improvement leads to the enhanced adsorption affinity and capacity by increasing surface activity. Moreover, the isoelectric point charge (pH_{pzc}) plays an essential role of adsorption by influencing the electrostatic interaction. To analyze the adsorption mechanism, the pH_{pzc} was calculated from the pH drift method[48]. The pH_{pzc} of adsorbents HAp and Fe-HAp was measured in triple-distilled water is found to be 7.1 and 7.3, respectively, as shown in **Fig. 4b**. Adsorbent surface charge was positive at pH value below pH_{pzc} (7 ± 0.2) due to the complexation of H^+ ions and the dissolution of phosphate ion from the adsorbent surface. Whereas, the surface charge was negative when the pH value was higher than the pH_{pzc} due to complexation with OH^- ions [49].

The colloidal stability and pH_{pzc} of the adsorbents were determined from arsenic contaminated water. The colloidal stability of HAp and Fe-HAp improved significantly with an increase in pH value 3 to 11 and also, the isoelectric point charge of the adsorbents increased from 7.1 to 8.6 for HAp and 7.3 to 9.3 for Fe-HAp. Consequently, this enhancement indicates the As^{3+} ion complexation on HAp and Fe-HAp adsorbent surface. The As^{3+} was dissociated in to non-ionic state [H_3AsO_3 , $\text{As}(\text{OH})_3$] at pH value below 9.2, therefore the adsorption of As^{3+} on HAp and Fe-HAp was enhanced by the surface complexation process. When the pH value was above 9.2; As^{3+} dissociated into anionic states of $\text{As}(\text{OH})^{4-}$, $\text{AsO}_2\text{OH}^{2-}$, and the anionic states were highly repulsed by the negatively charged adsorbent as shown in the schematic representation of **Fig. 4c** [6,14,29,49–51].

4. Adsorption

4.1. Effect of contact time

The determination of equilibrium contact time is essential for the adsorption process. Initially, 20 mL of 1000 $\mu\text{g/L}$ As^{3+} solution in pH 7 was mixed with 100 mg of HAp and Fe-HAp in different sterilized containers. The mixture of the solution was stirred (180 rpm) at room temperature ($25\pm 1^\circ\text{C}$) for different time intervals. The adsorption capacity of As^{3+} in the various time intervals is calculated and it is shown in **Fig. 4d**. The whole adsorption process can be divided into two stages as linear and equilibrium of As^{3+} adsorption. The adsorption capacity was found to increase with contact time and the maximum capacity was achieved at 10 min. After that the adsorption turned sluggish and reached equilibrium. Hence, an equilibrium adsorption time of 10 min was fixed for the subsequent study of As^{3+} adsorption. Kinetic isotherm was used to understand the adsorption rate and adsorption mechanism of As^{3+} on the surface of HAp and Fe-HAp.

4.2. Effect of the initial concentration of As^{3+}

The maximum adsorption capacity of HAp and Fe-HAp obtained by varying the initial concentration of As^{3+} ion (100 $\mu\text{g/L}$ - 1000 $\mu\text{g/L}$) is shown in **Fig. 4e**. 100 mg of HAp and Fe-HAp were taken into different sterilized containers with various initial concentrations of As^{3+} solution (pH 7), at room temperature ($25\pm 1^\circ\text{C}$). The contact time was fixed at the equilibrium time (10 min), and the shaking speed was set to be 180 rpm. The removal capacity of both adsorbents improved with the increasing initial concentration of As^{3+} . This indicates that the higher initial concentration of As^{3+} enhanced adsorbate mobility, driving force and reduced mass transfer resistance between adsorbate and adsorbent [52]. The adsorption of As^{3+} were increased up to a concentration of 500 $\mu\text{g/L}$ thereafter, adsorption was attain equilibrium. The equilibrium adsorption capacity of As^{3+} on HAp and Fe-HAp was found to be 139 $\mu\text{g/g}$ and 183 $\mu\text{g/g}$, respectively.

4.3. Adsorption isotherm

4.3.1. Kinetic isotherm

The experimental kinetic data was fitted to two different isotherms, such as Lagergren pseudo-first and Lagergren pseudo-second-order kinetics [53]. The first and second-order kinetics reveal the physisorption and chemisorption, respectively. The linear fit expression of first and second-order kinetics is given in **Eqs. (6-7)**.

$$\text{Log}(Q_e - Q_t) = \text{Log}(Q_e) - \left(\frac{K_1}{2.303}\right)t \quad (6)$$

$$\frac{t}{Q_t} = \frac{1}{(K_2 \times Q_e^2)} + \left(\frac{1}{Q_e}\right)t \quad (7)$$

Where Q_t and Q_e represent the given time and equilibrium adsorption capacity ($\mu\text{g/g}$), respectively. K_1 is the first-order rate constant (min^{-1}). The values of Q_e and K_1 were determined from intercept and slope in the linear fit of $\log(Q_e - Q_t)$ as a function of time t , as shown in **Fig. 5a**. K_2 is the second-order rate constant ($\text{g}/\mu\text{g min}^{-1}$). The values of K_2 and Q_e were calculated from the intercept and slope in a linear plot of $1/Q_t$ as a function of time t , as shown in **Fig. 5b** [54,55].

4.3.2. Intra-particle diffusion

The intra-particle diffusion isotherm was used to find the rate-controlling mechanism of As^{3+} diffusion on HAp and Fe-HAp during the adsorption [5]. The linear expression of the intra-particle diffusion is given in **Eq. (8)**.

$$Q_t = K_i \sqrt{t} + C_i \quad (8)$$

Where K_i is the intra-particle diffusion rate constant ($\mu\text{g/g min}^{-1/2}$) and C_i is the boundary layer thickness of As^{3+} adsorption. Further, K_i and C_i can be calculated from the slope and intercept of intra-particle diffusion linear fit of Q_t as a function of $\sqrt{t}$ is shown in **Fig. 5c** [56].

The linear regression of R^2 is well matched in second-order kinetics compared to first-order kinetics. Also, the adsorption capacities of theoretical and experimental values are in good agreement with second-order kinetics. Hence, it confirms the chemisorption of As^{3+} on HAp and Fe-HAp. The second-order rate constant (K_2) indicates that the adsorption rate (1 min) and their capacity ($Q_e=538\%$) are higher for Fe-HAp when compared to HAp nanoparticles (**Table 1**). The As^{3+} adsorption on HAp and Fe-HAp shows the two-stage adsorption process. Initially, the linear portion revealed the adsorption of As^{3+} as a combination of surface and pore diffusion process. The last linear part represents the equilibrium adsorption as shown in **Fig. 5c**.

4.3.3. Langmuir, Freundlich, and DKR isotherm

The equilibrium adsorption of As^{3+} is either monolayer or multilayer distribution, which is determined from Langmuir and Freundlich isotherm, respectively. In monolayer adsorption, active sites on the adsorbent surface are distinct and identical to each other [57,58]. The linear expression of Langmuir isotherm is given by **Eq. (9)**.

$$\frac{C_e}{Q_e} = \frac{1}{Q_m K_L} + \frac{C_e}{Q_m} \quad (9)$$

Where C_e represents the equilibrium concentration ($\mu\text{g/L}$), K_L is Langmuir isotherm constant ($\text{L}/\mu\text{g}$), suggesting the adsorption affinity (or) sensitivity, and Q_m is theoretical monolayer adsorption capacity ($\mu\text{g/g}$). The values of Q_m and K_L are calculated from the intercept and slope in a linear fit of $1/C_e$ vs. $1/Q_e$ as shown in **Fig. 5d**. The essential feature of Langmuir is a dimensionless constant called the separation factor (R_L), which is given as **Eq. (10)**. The value of the R_L indicates the various types of adsorption, such as linear ($R_L = 1$), unfavorable ($R_L > 1$), favorable ($0 < R_L < 1$) and irreversible ($R_L = 0$) [59]. Freundlich isotherm explains multilayer adsorption on heterogeneous surfaces and it gives the empirical relationship between the adsorbate and adsorbent, the linear expression of Freundlich isotherm is given by **Eq. (11)** [47,60].

$$R_L = \frac{1}{(1 + K_L C_o)} \quad (10)$$

$$\text{Log} Q_e = \text{log } K_F + \left(\frac{1}{n} \right) \text{log } C_e \quad (11)$$

Where K_F is the adsorption capacity ($\mu\text{g/g}$) of Freundlich isotherm and $1/n$ is the Freundlich exponent. The values of K_F and $1/n$ are determined from the intercept and slope of the linear fit of $\text{log } C_e$ vs. $\text{log } Q_e$ as shown in **Fig. 5e**. The value of $1/n$ indicate the adsorption behavior as it is linear [$(1/n) = 1$] or unfavorable [$(1/n) > 1$] or favorable [$0.1 < (1/n) < 1$] or irreversible [$(1/n) = 0$].

The Dubinin–Radushkevich isotherm is generally applied to distinguish between physisorption and chemisorption based on the Gaussian energy distribution. The physisorption process occurs when the atom/molecule is adsorbed by Van der Waals force of the material, whereas chemisorption occurs either by valance electron sharing or ion exchange between adsorbate and adsorbent [61–63]. The linear expression of Dubinin–Radushkevich isotherm is given in **Eq. (12)**.

$$\ln Q_e = \ln Q_m - \beta \varepsilon^2 \quad (12)$$

$$\varepsilon = RT \ln \left(1 + \frac{1}{C_e} \right) \quad (13)$$

Where β is DKR constant; it gives adsorption mean energy (mol/J)². ε is Polanyi potential expressed in **Eq. (13)**; Q_m is maximum adsorption capacity ($\mu\text{g/g}$), R is the universal gas constant 8.314 (J/mol K), and T is the absolute temperature (K). The β and Q_m can be calculated from the slope and intercept of the $\ln Q_e$ vs. ε^2 linear fit, as shown in **Fig. 5f**. The adsorption is divided into three types based on the value of Gaussian energy (E) distribution as given in **Eq. (14)**. They are physisorption ($E < 8 \text{ kJ / mol}$), chemical ion exchange ($8 \text{ kJ / mole} \leq E \leq 16 \text{ kJ / mole}$), and strong chemisorption than ion exchange ($E > 16 \text{ kJ / mol}$) [64]. The adsorption of As^{3+} will follow any one of the above-mentioned adsorption processes.

$$E = \frac{1}{\sqrt{-2\beta}} \quad (14)$$

The linear fit of Langmuir, Freundlich and DKR isotherms is shown in **Fig. 5d-f**. The linear regression R^2 values are well-matched with the Langmuir isotherm when compared to the Freundlich and DKR isotherms. Also, the experimental and theoretical values of the As^{3+} adsorption capacity are better suited for Langmuir and DKR isotherm than the Freundlich isotherm. Moreover, separation factor RL indicates that the adsorption favored Langmuir isotherm, hence the adsorption of As^{3+} is monolayer was confirmed. The maximum adsorption capacity of As^{3+} on HAp and Fe-HAp is $139 \mu\text{g/g}$ and $183 \mu\text{g/g}$, respectively. The As^{3+} adsorption affinity or sensitivity found to be $3.85 \mu\text{g/L}$ for HAp and $0.71 \mu\text{g/L}$ for Fe-HAp (shown in **Table 1**). The adsorption affinity of Fe-HAp was enhanced at the trace level ($\leq 50 \mu\text{g/L}$), which is 83-99.9% higher than the previous reports as so far shown in **Table 2**. The Gaussian energy distribution on HAp and Fe-HAp is 18.6 kJ/mol and 21.3 kJ/mol , respectively and these results suggest stronger chemical adsorption than ion-exchange process.

5. Quantification of Fe^{2+} ion release test

Fig. S4. shows the quantification of Fe^{2+} ion in HAp nanoparticle (Sample C) and also Fe^{2+} leached from As^{3+} contaminated water (Sample B), and triple distilled water (Sample A). The concentration of Fe^{2+} ion on Fe-HAp was estimated to be $5.06 \pm 0.05 \text{ mg/g}$. The concentration of

Fe²⁺ ion released in triple-distilled water and As³⁺ contaminated water was found to be 0.005 ± 0.001 mg/L and 0.019 ± 0.001 µg/L respectively, which is 600 times below the acceptable level of iron in drinking water (1-3 mg/L) [65]. In a very low quantity of iron incorporation, it leads to highly efficient adsorption of As³⁺ and also confirms the insignificant release of iron during the adsorption process.

6. Conclusion

The HAp and Fe-HAp nanorods were synthesized via a simple and cost-effective hydrothermal method for the removal of As³⁺ ion. Merely 0.5 wt % of Fe²⁺ ion is incorporated in the HAp which results in enhanced physiochemical properties of the adsorbent and improves adsorption of As³⁺. Remarkably, the Fe²⁺ ion improves the HAp colloidal stability, particle size (Drastic reduction of 400% in length and 225% in width), and specific surface area (105% higher than the HAp). As a result, more active sites are formed in Fe-HAp than HAp which leads to obtaining a maximum adsorption capacity of As³⁺. It was found to be a maximum adsorption capacity of As³⁺ is 183 µg/g with a higher adsorption rate (538%) at trace level contamination (≤ 50µg/L). In addition, the dopant Fe²⁺ ion ensures the higher adsorption affinity (83-99.9%) compared to previously reported literature so far. The adsorption of As³⁺ ion, could not change the hydroxyapatite phase and morphology of adsorbent. From isotherm theoretical evaluation, the adsorption of the As³⁺ ion confirmed to be monolayer chemisorption rather than the ion-exchange process. Furthermore, quantification of iron studies showed a very lower concentration (0.005 to 0.019 mg/L) of Fe²⁺ ion was leaked during the adsorption process which was 600 times lower than the WHO toxic limits of iron in water. Hence, the Fe-HAp is a cost-effective, potential adsorbent, and promising for removal of highly toxic As³⁺ even at trace level (≤ 50µg/L) and maintaining water quality.

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Credit authorship contribution statement

Sandeep Eswaran Panchu: Conceptualization, Methodology, Writing - Original Draft. **Saranya Sekar:** Validation, Investigation. **Vani Rajaram:** Writing - Review & Editing. **Elayaraja Kolanthai:** Writing - Review & Editing. **Sarojini Jeeva Panchu:** Formal analysis, Writing - Review & Editing. **Hendrik C.Swart:** Writing - Review & Editing. **Narayana Kalkura Subbaraya:** Writing - Review & Editing, Supervision, Investigation, Project administration

Declaration of competing interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper. This article is original and new, has been written by the stated authors who are all aware of its content and approve its submission, has not been published previously, it is not under consideration for publication elsewhere, no conflict of interest exists. The article will not be published elsewhere in the same form, in any language, without the written consent of the publisher

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Graphical abstract

Fig. 1 Schematic representation of tailoring ability of incorporated Fe^{2+} ion and enhances physicochemical properties of the adsorbent

Fig. 2 (a) XRD pattern of synthesized and As^{3+} ion adsorbed HAp and Fe-HAp, (b) Schematic representation of growth of HAp nano-rod and Fe^{2+} ion affect the negative charge of PO_4^{3-} sites in $\langle 0001 \rangle$ direction of c-axis, (c) FT-IR Spectra of before and after As^{3+} ion adsorbed HAp and Fe-HAp, and (d) N_2 adsorption-desorption plot of HAp and Fe-HAp

Fig. 3 (a-b) TEM micrograph of synthesized HAp and Fe-HAp, (c-d) SEM micrograph of HAp and Fe-HAp, and (e-f) SEM micrograph of As^{3+} ion adsorbed HAp (HAp-As) and Fe-HAp (Fe-HAp-As)

Fig. 4 Effect of pH on HAp and Fe-HAp in deionized water and As³⁺ ion contaminated water: (a) Zeta potential, (b) Point zero charge (c) Schematic representation of pH affect the zero point charge of before and after adsorption of As³⁺ ion, (d) Effect of contact time [pH=7; concentration = 1000μg/L; Dosage=100 mg; rpm=180 and temperature= 298 K], and (e) Effect of initial concentration of As³⁺ [pH=7; Time = 10 min; Dosage=100 mg; rpm=180 and temperature= 298 K]

Fig. 5 As^{3+} ion adsorption isotherms of HAp and Fe-HAp: (a) Pseudo 1st order kinetics, (b) Pseudo 2nd order kinetics, (c) Intra particle diffusion (d) Langmuir, (e) Freundlich, and (f) DKR

Table 1. Adsorption isotherm of As³⁺ ion adsorption using HAp and Fe-HAp

	Adsorbent		
		HAp	Fe-HAp
	Q_{exp} ($\mu\text{g/g}$)	132 ± 5	184 ± 5
pseudo-first-order kinetics	Q_m ($\mu\text{g/g}$)	83 ± 3	37 ± 3
	K_1 (min^{-1})	0.036	0.047
	R^2	0.9971	0.9360
pseudo-second-order	Q_m ($\mu\text{g/g}$)	144 ± 3	188 ± 3
	K_2 ($\mu\text{g/g} \cdot \text{min}^{-1}$)	28.9 ± 1	185 ± 1
	R^2	0.9999	0.9999
Intra-particle diffusion	K_i ($\mu\text{g/g} \cdot \text{min}^{1/2}$)	8.85 ± 0.1	3.20 ± 0.1
	C_i ($\mu\text{g/g}$)	71.94 ± 1	161.84 ± 1
	R^2	0.9035	0.8314
Langmuir isotherm	Q_m ($\mu\text{g/g}$)	139 ± 3	183 ± 3
	K_L ($\mu\text{g/L}$)	3.85	0.71
	R_L	$3.8e^{-3}$	$7.11e^{-4}$
	R^2	0.9966	0.9989
Freundlich isotherm	K_F ($\mu\text{g/g}$)	7.31 ± 2	2.77 ± 2
	$1/n$	1.18	1.43
	R^2	0.9932	0.9900
DKR	Q_m ($\mu\text{g/g}$)	127 ± 2	181 ± 2
	β (mol/J^2)	$-1.439e^{-9}$	$-1.096e^{-9}$
	E (kJ/mol)	18.6 ± 0.1	21.3 ± 0.1
	R^2	0.9907	0.9970

* Q_{exp} is experimental adsorption capacity ($\mu\text{g/g}$)

Table 2. Comparison of Literature review of Arsenic adsorption capacity and affinity

Adsorbent	Time (min)	pH	Capacity (mg/g)	Arsenic	Affinity (mg/L)	Ref
Iron-oxide-coated quartz (IOCQ)	1440	6	0.097	As ⁵⁺	--	[18]
Biochar	1440	7	0.422	As ⁵⁺	41.49	[19]
Magnetic Fe-hydroxalcite	15	9	0.121	As ³⁺	0.004	[20]
Activated alumina	360	7.6	0.180	As ³⁺	0.117	[21]
Sulfate-modified iron oxide-coated sand	480	7.2	0.096	As ³⁺	0.326	[22]
Fe-HAp (Iron-Hydroxyapatite)	1	7	0.183	As ³⁺	7.11e ⁻⁴	This work

Highlights

1. Enhanced colloidal stability and surface area due to Fe²⁺ doped in HAp lattice
2. Dopant Fe²⁺ drastically reduced the particle size of HAp (L=400% and W=225%)
3. Rapid removal of highly toxic As³⁺ ion at trace level (1 min)
4. As³⁺ adsorption affinity higher (83-99.9%) than previous reports
5. No secondary toxic sludge were observed during adsorption

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