Synthesis and evaluation of Ca-doped ferrihydrite as a novel adsorbent for the efficient removal of fluoride

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Abstract
Ferrihydrate has been extensively applied for the removal of various types of pollutants from wastewater because of its low cost and high efficiency. However, its wide-scale application has been greatly restricted by high-dose and low-adsorption capacity. Therefore, a novel Ca-doped ferrihydrite adsorbent has been synthesized and used for the enhanced removal of fluoride from wastewater in the presence of other co-existing ions. At 5 mg/L initial fluoride concentration and pH 5, the removal efficiency of fluoride approached to 97.5% and remained stable. Similarly, with the increase of dose from 100 to 300 mg/L, the fluoride removal linearly increased to 98% and remained plateau at neutral pH. Also, the presence of co-existing ions such as NO 3 − , SO 4 2 − , Cl − , and natural organic matter has not significantly influenced the removal performance of the adsorbent. Fluoride removal best fit the pseudo-second-order reaction kinetics and Langmuir isotherm model. The prepared adsorbent exhibited a maximum adsorption capacity of 53.21 mg/g for fluoride uptake from water. The SEM-EDX confirmed the doping of Ca onto the ferrihydrite where the elemental peaks of Ca and Fe emerged at the energy value of about 3.6 Kev and 7.1 Kev respectively in EDX analysis. In addition, SEM results of Ca-doped ferrihydrite adsorbent illustrated that a large microplates type of products was acquired after synthesis. The regeneration results confirmed that adsorbent could retain their original adsorption capacity after five regeneration cycles. The current study suggested that Ca-doped ferrihydrite has the application potential for the enhanced adsorption of fluoride from the water phase.

Keywords Ca-doped ferrihydrite · Fluoride · Synthesis · Removal · Adsorption

Introduction
Fluoride is an essential element for the growth of the skeleton and teeth in the human body (Pillai et al. 2020; Tao et al. 2020). However, it can also cause various health problems, if used in excessive amounts. In recent years, the occurrence of fluoride in the aqueous environment has raised serious environmental and public health concerns, due to its toxic adverse effects on the biological and ecological environment (Thompson et al. 2007; Ali et al. 2019). In our geological environment, fluoride is widely distributed (Amini et al. 2008). Globally, around two hundred million people are living...
 Fluoride concentration in water has increased in many countries around the globe as a result of fluorine-containing waste-water discharged from various industries. Such kind of wastewater is generally produced by ceramic and glass manufacturing process (Ponsot et al. 2013), fertilizers industry (Mourad et al. 2009), zinc, and aluminum smelters (Blagojević et al. 2002; Shen et al. 2003), oil refineries (Khatibikamal et al. 2010), coal-fired power stations, uranium enrichment facilities, beryllium extraction plants, steel production, waste incineration plants, semiconductors production (Hu et al. 2005; Warmadewanti and Liu 2009; Bhatnagar et al. 2011), photovoltaic solar cell industry (Drouiche et al. 2013), fluorinated textiles, and through the decomposition of CaF$_2$ in waste sludge (Habuda-Stanić et al. 2014).

Conventional treatment technologies employed for the elimination of fluoride from water include chemical precipitation (Amini et al. 2008), ion exchange (Cai et al. 2015), coagulation and electrocoagulation (Khatibikamal et al. 2010), membrane filtration (Jadhav et al. 2015), electrodialysis (Subba Rao 2003), and adsorption (Abdelgawad et al. 2009). Among the commonly used technologies, adsorption is considered a promising and widely used treatment technology for the enhanced removal of various pollutants from water, due to their process simplicity, high efficiency, and cost-effectiveness (Rafique et al. 2008; Naushad 2014; Ihsanullah et al. 2015, 2016a, 2016b; Aamir et al. 2016; Asmaly et al. 2016; Khalid et al. 2018; Balasubramani et al. 2020; Ihsanullah 2020; Zubair et al. 2020). A variety of adsorbents are being employed for the removal of fluoride including cow and fishbone char (Brunson and Sabatini 2009), goethite (Tang et al. 2010), aluminum hydroxide (Parmar et al. 2006), magnetic cationic hydrogel (Dong and Wang 2016), hydroxyapatite (He et al. 2016), CeO$_2$ (Kang et al. 2017), and HCl-activated red mud (Çengelöğlu et al. 2002). However, several technical drawbacks hindered the widespread use and applications of the synthesized adsorbents for the enhanced removal of fluoride from feedwater. Therefore, the currently used treatment techniques for the uptake of fluoride from water often considered being inefficient because of their high requirements on engineering expertise and supporting infrastructure, thereby precluding their uses and applications around the world.

Recently, ferrihydrite-based adsorbents have gained considerable attention due to exceptional removal performance toward both anions and cations (Rout et al. 2012; Gomez et al. 2013; Liu et al. 2020; Van Eynde et al. 2020), but the adsorption capacity of ferrihydrite for fluoride is not significant (Kumar et al. 2009; Nur et al. 2014). Calcium-based adsorbents have been emerging as novel contenders for the enhanced uptake of fluoride from source water (Turner et al. 2005; Islam and Patel 2007; Jain and Jayaram 2009). Therefore, it is important to synthesize a novel adsorbent for the enhanced removal of pollutants from feedwater in the presence of other co-existing ions.

The aim of this study was to assess the performance of the novel Ca-doped ferrihydrite for the adsorption of fluoride and to investigate the effect of co-existing ions on the removal process. The proposed research was therefore designed and conducted with five specific objectives: (1) to synthesize Ca-doped ferrihydrite composite adsorbent by co-precipitation method, (2) to determine the characteristics, adsorption behavior, and mechanism of the as-synthesized adsorbent by using extensive characterization methods, (3) to assess the effects of experimental factors affecting the adsorption process, (4) to study the adsorption process by employing the kinetics and isotherm models, and (5) to assess the regeneration ability of Ca-doped ferrihydrite after the removal of fluoride from the water. The findings of the current study provide important insights into the synthesis of the novel adsorbent for the enhanced removal of fluoride from water.

### Experimental materials and chemicals

Ferric nitrate nonahydrate (Fe(NO$_3$)$_3$.9H$_2$O) and calcium chloride (CaCl$_2$) were used for the synthesis of the Ca-doped ferrihydrite. The stock solution for fluoride was prepared by using sodium fluoride (NaF). All the adsorption experiments were performed using ultrapure water, obtained with a Milli-Q system (EPOD, France). The NOM solution was prepared by Suwanee River NOM (SRNOM, batch number 2R101N) and was obtained from the International Humic Substances Society (St. Paul, MN). All other chemicals, including co-existing anions and cations, were bought from Aladdin Industrial Corporation, Shanghai, China.

### Synthesis of Ca-doped ferrihydrite

Ca-doped ferrihydrite was prepared by using a facile co-precipitation approach. Initially, 50 mL mixed solution containing 1 M (Fe (NO$_3$)$_3$.9H$_2$O) and 0.19 M of CaCl$_2$ was prepared. To obtain the desired pH of 7, a dropwise 1 M NaOH was used with constant stirring. The solution was stirred vigorously during the pH maintenance process. A gel-like precipitate was obtained, and the final volume of that slurry was fixed to 200 mL. The obtained suspension was then stored at room temperature for 24 h. After that, the precipitates were washed thoroughly with distilled water by using a G-4 frit crucible. The remaining material was dried in an air oven for 12 h at 100 °C. Finally, the obtained material was grinded by using mortar and pestle and stored for further use. Fig. 1
shows the detailed five-step synthesis process of Ca-doped ferrihydrite used in the study.

**Characterization of the adsorbent**

Several characterization techniques for Ca-doped ferrihydrite adsorbent were carried out. Functional groups of the as-synthesized Ca-doped ferrihydrite adsorbent were analyzed by Fourier transform infrared spectroscopy (FTIR) (Nexus670, Nicolet, USA) before and after the adsorption experiment. The morphology and nanostructure of Ca-doped ferrihydrite were investigated by a scanning electron microscope (SEM) (HITACHI S-4800). Besides, the crystalline structure of the adsorbent was measured using the X-ray diffraction (XRD) analyzer, D8-Advance, Brucker, Germany). To determine the surface charges of the absorbent, the zeta potential of the Ca-doped ferrihydrite was carried out using the laser Doppler velocimetry technique (Nano-Brook 90 Plus-PALS, Brookhaven, US) in liquid suspension at various pH levels. The pore volume and specific surface area of Ca-doped ferrihydrite were determined by the nitrogen adsorption isotherm method on an Autosorb-iQ2-C (Quantachrome Instruments, USA).

**Adsorption experiments**

A 100 ppm stock solution of fluoride was prepared by adding 0.221 mg of sodium fluoride (analytical grade) in distilled water. The desired solution for fluoride was obtained by further diluting the stock solution. The pH of the feed solution was adjusted by adding acid (0.1 N HCl) or base (0.1 M NaOH) solution. All the batch experiments were carried out with 50 mL of water samples at 25 ± 2 °C while shaking at 160 revolutions per minute. The effects of different control parameters were studied by using different amounts of adsorbates and adsorbent. After the adsorption experiments, water samples were then filtered immediately by a 0.45-μm filter to separate adsorbent particles in the samples. To investigate the effects of different parameters, the operation conditions varied over time while others were kept constant.

Besides, salts such as NaNO₃, NaCl, Na₂SO₄, NaHCO₃, Na₃PO₄, CaCl₂, MgCl₂, and Na₂CO₃, were added into the solution to determine the effects of co-existing ions on the adsorption of fluoride from water. The concentration of the co-existing ions in the solution was adjusted between 10 to 200 mg/L. The adsorption experiments were performed at pH 5.75, adsorbent dose 300 mg/L, and shaking at 160 rpm. The initial concentration of fluoride in the solution was adjusted to 5 mg/L. The final concentration of fluoride was measured after equilibrium time. The adsorption experiments were performed at a different initial period to study adsorption isotherms. The time was varied from 30 to 700 min. Ion chromatography (IC) and atomic fluorescence spectrophotometry (AFS) were used to quantify the fluoride in the water samples.

The removal efficiency of the as-synthesized adsorbent was determined using Eq. (1).

\[
\text{Removal} \% = \frac{C_i - C_f}{C_i} \times 100 \quad (1)
\]
where \( C_i \) and \( C_f \) are the initial and final concentrations of fluoride, respectively. All adsorption experiments were performed in replicate runs to avoid experimental errors in the results. The relative errors in the calculated data were below 5% on average.

**Regeneration studies**

For the regeneration, Ca-doped ferrihydrite from the solution was collected and soaked in 0.1 M NaOH solution for a set time. Besides, the effects of time on desorption were investigated, and the concentration fluoride was measured at different time intervals. Desorption efficiency with time was calculated by the total amount of fluoride and the percentage of desorbed fluoride. After the desorption experiment, the adsorbent was collected, activated, and rinsed with ultrapure water and dried. The obtained adsorbent was used again to study the regeneration of adsorbent. The performance of the regenerated adsorbent was evaluated in five adsorption and desorption cycles.

**Results and discussion**

**Characterization of the adsorbent**

The structural morphology and elemental constituents of the as-synthesized Ca-doped ferrihydrite were evaluated by SEM-EDX analysis (Fig. 2a, b). The EDX analysis illustrated that the adsorbent contains Ca and Fe, which confirmed successful doping of calcium onto the ferrihydrite (Fig. 2a). According to the EDX results, the elemental peaks of Ca and Fe emerged at the energy value of about 3.6 KeV and 7.1 KeV respectively. The elemental percentage of Ca was 0.03%, and Fe was 38.63% which represents the presence of Ca and Fe on the surface of Ca-doped ferrihydrite. Besides, the SEM results of Ca-doped ferrihydrite adsorbent illustrated that a large microplate type of products was acquired after synthesis (Fig. 2b). The surface of these large microplates was coarse and connected, which formed a large aggregate.

The XRD analysis of the Ca-doped ferrihydrite was employed to determine the crystalline structure of the as-synthesized adsorbent used in this study. Fig. 3a shows strong diffraction peaks at the angles (2\( \theta \)) of 38°, 44°, and 64°, which are respectively attributed to the planes of (110), (200), and (115) of 6-line ferrihydrite JCPDS (card no: 29-0712). The XRD results further confirmed that the sample is poorly amorphous. The results obtained in this study are in good agreement with the published literature and confirmed that the Ca-doped ferrihydrite was 6 line ferrihydrite (Mohapatra et al. 2012).

In addition, the FTIR spectra of Ca-doped ferrihydrite before and after fluoride adsorption are presented in Fig. 3b. The peak at 3357 cm\(^{-1}\) is corresponding to the stretching of surface OH groups of ferrihydrite, and the peak at 1614 cm\(^{-1}\) is therefore associated with the vibration of the water molecule and ferrihydrite. The absorption band at 1383 cm\(^{-1}\) is attributed to carbonates, which might be owing to the poorly crystalline structure and amorphous capture of CO\(_2\) from the air (Su and Suarez 1997). The band at 1354 and 431 is assigned to hydroxyl bridges of Fe–(OH)\(_2\)–Fe, and Fe–O bonds, respectively.

Fig. 4a displays the pore size distribution and the N\(_2\) adsorption-desorption isotherms of the as-synthesized Ca-doped ferrihydrite. The BET surface area of the Ca-doped ferrihydrite was determined to be 82.44 m\(^2\)/g. The pore volume (0.088 cm\(^3\)/g) and the average pore size (3.515 nm) of the Ca-doped ferrihydrite were calculated by the BJH method. The increased surface area, as well as pore

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**Fig. 2** SEM and EDX analysis of Ca-doped ferrihydrite before adsorption. (a) EDX before adsorption, (b) SEM before adsorption

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volume and decrease pore size, was observed due to the
doping of ferrihydrite with calcium. The high surface area
provided more adsorption sites and played a significant
role in the adoption of fluoride from the aqueous phase.

Zeta potential measurement was employed to deter-
mine the surface charge on the Ca-doped ferrihydrite.
The negative zeta potential of adsorbent increased with
increasing the pH level of the Ca-doped ferrihydrite sus-
pension (Fig. 4b). The point of zero charge (pHzc) of the
adsorbent was found to be 6.14, which means that below
this pH level, the surface of the as-synthesized adsorbent
was positively charged. Likewise, at pH 6.14 and higher,
the surface of the synthesized adsorbent was negatively
charged.

**Adsorption experiment**

**Effect of initial pH**

The effect of pH on the removal of fluoride is presented in Fig.
5a. The solution pH was varied from 3 to 11. The pH of the
point of zero charge (pHzc) for the Ca-doped ferrihydrite ad-
sorbent was 6.14. At pH 3, the removal of Ca-doped ferrihy-
drite for fluoride was 90.6%, while increasing the pH to 6.14,
the removal of fluoride increased to 97.79%. However, in-
creasing pH from 6.14 to 11, the removal of fluoride gradually
reduced to 89%. This means that there are abundant positive
charges on the surface of Ca-doped ferrihydrite adsorbent
when the pH is less than 6.14, which is favorable for the
electrostatic attraction of negative fluoride ions. However, the (pHzc) of the Ca-doped ferrihydrite has decreased from 11 to 6.14 after fluoride adsorption, suggesting that the negative fluoride ions neutralized some positive charges on the Ca-doped ferrihydrite surface (Zhang et al. 2012; Tang and Zhang 2016). In an acidic environment, the H+ species predominates, which is weakly bonded to the adsorption sites. Increasing the pH from acidic to alkaline environment leads to the predominance of OH\(^-\) ions which can be adsorbed onto the adsorbent. The effect of pH on the removal of fluoride is presented in Fig. 5a. The solution pH was varied from 3 to 11. At pH 3, the removal of Ca-doped ferrihydrite for fluoride was 90.6%, while increasing the pH to 5, the removal of fluoride increased to 97.79%. However, increasing pH from 5 to 11, the removal of fluoride gradually reduced to 89% (Fig. 5a). This behavior can be explained on the basis of surface charge of the adsorbent and ionic chemistry of the solution. The value of point of zero charge of Ca-doped ferrihydrite in this study was reported about 6.14. The maximum adsorption of fluoride in this study is reported at pH 5 that might be attributed to the strong electrostatic interaction between the fluoride ions and positively charged adsorbent surface. The comparative less removal of fluoride at lower pH 3 is because of less availability of free fluoride ions due to HF formation. The decrease in the fluoride removal percentage at higher pH (≥ 7) is attributed to the competition between hydroxyl ions and fluoride to cover the limited adsorption sites on the surface of Ca-doped ferrihydrite adsorbent (Mohapatra et al. 2012).

Hence, these results suggest that electrostatic attraction is not the main reason for the removal of fluoride from water. The removal of fluoride occurs through surface coordination of Fe–OH groups. Hence, adsorption of fluoride in Ca-doped ferrihydrite happened due to ion exchange. Finally, in an alkaline environment (pH=11 in this work), OH\(^-\) ions predominate and compete with other ions in solution to bond onto the surface of the adsorbent (Zarrabi et al. 2014). The reduction in fluoride adsorption is possibly attributed to the following statements:

a) Due to electrostatic repulsion, the negatively charged Ca-doped ferrihydrite failed to adsorb fluoride ions on the surface.

b) Abundant hydroxide ions led to a competition of fluoride ions for adsorption sites.

**Effect of adsorbent dose**

The removal of fluoride was significantly increased up to 85% by increasing the adsorbent dose to 200 mg/L (as presented in Fig. 5b). Further increase of the adsorbent dose from 200 to 300 mg/L improved the removal of fluoride by 98% Fig. 5b. These results showed that there was an immediate and remarkable increase in the percentage removal of fluoride when the dose range increased from 100 to 300 mg/L. The enhanced removal of fluoride is owing to the increased number of active surface sites available on adsorbent for the adsorption of fluoride ions (Bhaumik et al. 2011). Also, the removal percent of fluoride remained the same when the dose range was increased to 400, 600, 800, and 1000 mg/L. This is most probably due to saturation of the active adsorption sites on the surface of the adsorbent. Therefore, no further increase in the removal of fluoride was reported (Swain et al. 2012; Srivastav et al. 2013).

**Effect of co-existing ions**

The effects of co-existing ions on the removal of fluoride for the same adsorption sites were investigated. Co-existing ions such as phosphate (PO\(_4^{2-}\)), sulfate (SO\(_4^{2-}\)), nitrate (NO\(_3^-\)), chloride (Cl\(^-\)), carbonate ions (CO\(_3^{2-}\)), and bicarbonate (HCO\(_3^-\)), and cations such as calcium (Ca\(^{2+}\)) and magnesium...
(Mg$^{2+}$) were added to the feed solution before the adsorption experiment. Besides, the concentration of co-existing ions was varied in the range from 10 to 200 mg/L. The presence of SO$_4^{2-}$, NO$_3^-$, and Cl$^-$ exhibited no detrimental effects on the removal of fluoride from water; however, the removal of fluoride slightly reduced when the concentration of SO$_4^{2-}$, NO$_3^-$, and Cl$^-$ ions reaches up to 200 mg/L (Fig. 6a). It may be due to the reasons that some anions would enhance cumbic forces while others would compete with fluoride for active sites. Multivalent anions, on the other hand, are said to be absorbed more quickly than monovalent anions (Onyango et al. 2004; Mondal et al. 2015). The same results were also reported by authors in the past for different adsorbents (Zhu et al. 2015; Zhang et al. 2016). Higher concentrations of PO$_4^{3-}$, HCO$_3^-$, and CO$_3^{2-}$ have significant effects on the adsorption rate of fluoride. At lower concentrations, these ions have no considerable effects on the fluoride removal by Ca-doped ferrihydride. The results suggest that the low or almost none removal of fluoride at high concentration of PO$_4^{3-}$, HCO$_3^-$, and CO$_3^{2-}$ is because of the competitions of these ions with fluoride on the same adsorption sites by Ca-doped ferrihydrite, which forms complexes with the hydroxyl group of the adsorbent and prevents any possible interaction of fluoride ions with the as-synthesized adsorbent.

Increased removal of fluoride was obtained when the feed solution contained cations such as Mg$^{2+}$ and Ca$^{2+}$ ions (as observed in Fig. 6b). The enhanced removal is accredited to the formation of insoluble CaF$_2$ and MgF$_2$ (Chen et al. 2010). Similar effects of these cations on the removal fluoride through the adsorption process are also reported in previous studies (Kagne et al. 2008; Maliyekkal et al. 2010).

**Effect of NOM**

The presence of NOM in water influences the removal efficiency of fluoride during adsorption. Therefore, the influence of NOM on the removal of fluoride is indeed important for large-scale applications of the as-synthesized Ca-doped ferrihydrite for water treatment. The presence of NOM in all the studied concentrations ranged from 5 to 25 mg/L. It can be seen in Fig. 7a, the Ca-doped ferrihydride removed about 95% of fluoride from the aqueous solution in the presence of 5 mg/L of NOM. A gradual decline (i.e., about 5%) in the removal of fluoride was seen by increasing the NOM concentration to 25 mg/L (Fig. 7a). In addition, the influence of contact time of NOM on the removal of fluoride was investigated from 1 to 12 h. The removal of fluoride in the first 1 h was about 90%, while after 2 h of contact time the removal of fluoride by Ca-doped ferrihydride suddenly increased to 94% (Fig. 7b). After 2 h, the removal percentage of fluoride by Ca-doped ferrihydrite was remained constant at about 95% until 12 h (Fig. 7b). Overall, the results demonstrate that the contact time has no substantial effects on the removal of fluoride in the presence of NOM by Ca-doped ferrihydrite. A Ca-doped ferrihydride is a form of iron base adsorbents, and the removal efficiency of Ca-doped ferrihydrite is not significantly affected by the presence of organic matter (Tang et al. 2014). Therefore, the results suggest that NOM did not compete with fluoride during the adsorption process by the Ca-doped ferrihydrite, and the novel adsorbent has the application potential in real water treatment. Moreover, the effects of NOM on the as-synthesized adsorbent are not fully explored in the literature and warrant future studies. However, the effects of NOM on adsorption efficiency of MWCNTs are determined by two different effects such as spatial distribution of adsorption sites and blockage of the adsorbent pores by NOM respectively (Abedi et al. 2019).

**Effect of temperature**

The effects of temperature on the removal of fluoride by Ca-doped ferrihydrite were investigated. The adsorption experiments were out at different pre-defined temperatures such as 20, 25, 30, 40, and 45 °C, as depicted in Fig. 8a. A small
increase in temperature from 20 to 25 °C has resulted in an increase in the removal of fluoride from 90 to 94%. However, a slight increase from 94 to 98% in the removal of fluoride was observed while increasing the temperature from 25 to 45 °C. The increase in the removal efficiency of fluoride by Ca-doped ferrihydrite with temperature is accredited to the increase in the kinetic energy of the fluoride molecules. The similar nature of fluoride adsorption was also reported for iron-mixed oxides particles (Biswas et al. 2009). The findings from this study suggest that the adsorption process of fluoride by Ca-doped ferrihydrite was endothermic.

Adsorption isotherms and kinetics studies

The adsorption kinetics of fluoride onto the as-synthesized adsorbent is of great interest for its application in water treatment. The adsorption of fluoride was carried out at a range of contact time from 30 min to 12 h (Fig. 8b). In addition, the adsorption of fluoride in the first 30 min was 85% and then dramatically increased to about 98% after 2 h of contact time of the adsorbent. However, the removal of fluoride remained at 98% for the rest of the contact time (as shown in Fig. 8b).

The following Eqs. (2)–(3) represent the Langmuir and Freundlich isotherm, and Eqs. (4)–(5) represent the pseudo-first-order (McKay and McConvey 1981; Ho and McKay 1998) and second-order (Ho and McKay 1999) kinetic models, respectively.

\[
\frac{1}{q_e} = \frac{1}{q_{\text{max}}} + \left( \frac{1}{q_{\text{max}} K_L} \right) \frac{1}{C_e}
\]  

(2)

\[q_e = K_f C_e^{1/n} \]  

(3)

\[\ln(q_e - q_t) = \ln q_e - k_1 t \]  

(4)

\[\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \]  

(5)

where \(q_e\) and \(q_{\text{max}}\) are the equilibrium and maximum adsorption capacity of the Ca-doped ferrihydrite (mg/g), respectively, while \(C_e\) denotes the concentration of fluoride in the solution (mg/L) at equilibrium, and \(K_L\) is constant. Furthermore, \(K_f\) denotes the Freundlich isotherm model.
constant that is an indication of the extent of adsorption and $1/n$ shows the intensity of adsorption. Furthermore, $q_e$ (mg/g) and $q_t$ (mg/g) are the adsorption capacity of Ca-doped ferrihydrite at equilibrium and time $t$ (min), respectively, and $k_2$ (g/mg/min) is a rate constant of the pseudo-second order.

The underlying mechanism of the as-synthesized adsorbent and the rate of fluoride adsorption on the surface of the Ca-doped ferrihydrite was studied using the pseudo-second-order kinetic model. The pseudo-second kinetic model assumes that the adsorption mechanism for contaminants is chemisorption and involves the exchange of electrons between the adsorbent and fluoride ions (Ali et al. 2018; Mohammed et al. 2019).

### Adsorption isotherms

Modeling the adsorption data is essential for the optimization of adsorbent utilization and explaining the interactive nature, adsorption mechanisms, and performance of the adsorbent. The most frequently used isotherm models are the Langmuir and Freundlich isotherms (Mohammed et al. 2019). Langmuir model (1918) has characterized the homogeneous, monolayer, and identical energies over a specific number of adsorption sites. In this study, two of the isotherms, Freundlich and Langmuir, have been employed.

### Table 1 Adsorption isotherm parameters

| Langmuir | Freundlich |
|----------|------------|
| $q_m$ (mg/g) | 53.21 | $1/n$ | 0.503 |
| $K_L$ (L/mol) | 0.045 | $K_f$ (mg g$^{-1}$) (L mg$^{-1}$)$^{1/n}$ | 6.87 |
| $R^2$ | 0.993 | $R^2$ | 0.975 |

### Figures

**Fig. 9** Adsorption isotherm models for fluoride adsorption. (a) Freundlich isotherm (b) and the Langmuir isotherm

**Fig. 10** Kinetic models. (a) The pseudo-first-order kinetic plot (b) and the pseudo-second-order kinetic plot
to the adsorption input to inspect its reliability. Factors for the Langmuir model are estimated from the plot for $C_e/q_e$ versus $C_e$, and the Freundlich model is calculated from the plot log of $q_e$ versus log $C_e$ (as shown in Fig. 9a, b). Based on the correlation coefficient values, experimental data for the adsorption of fluoride best fitted to the Langmuir model ($R^2 = 0.99$) compared to the Freundlich isotherm model ($R^2 = 0.97$). The relative parameters corresponding to the fitting results of Langmuir isotherm and Freundlich isotherm models are shown in Table 1. Langmuir model shows single layer adsorption having an $R^2$ value of 0.99 while comparing the Freundlich isotherm with a deprived $R^2$ value of 0.97 follows multilayer adsorption. From these results, we can conclude that the reaction was chemisorption and suited better to the Langmuir model. Therefore, the possible mechanism was the exchange of ions on the active surface sites of the as-synthesized adsorbent.

### Adsorption kinetics

To better understand the adsorption process and the underlying mechanisms, kinetic models such as the pseudo-first and pseudo-second order were applied to illustrate the kinetics of the adsorption of fluoride. In addition, the correlation coefficients and kinetic parameters were determined from the linear log plots such as $(q_e - q_t)$ versus $t$ and $t/q_t$ versus $t$, for the pseudo-first and pseudo-second-order kinetics (Fig. 10a, b). The pseudo-second-order model well fitted with the adsorption results based on $R^2$ values of 0.99, indicating that the chemisorption of fluoride on the active surface sites of the as-synthesized adsorbent occurred due to the exchange of ions. The calculated $q_e$ values estimated from the pseudo-second order were very close to the value obtained from the adsorption experiments (Table 2). Thus, the pseudo-second-order kinetic model is an appropriate model to describe the adsorption of fluoride pollutants onto Ca-doped ferrihydrite. This also confirms that the removal of fluoride best fitted the Langmuir isotherm model assumptions of the monolayer adsorption by the novel Ca-doped ferrihydrite. This clearly shows that chemisorption is the dominant mechanism for the removal of fluoride by the Ca-doped ferrihydrite (Habuda-Stanić et al. 2014; Chaudhary et al. 2016).

### Adsorption mechanism

The proposed adsorption mechanism of fluoride by the Ca-doped ferrihydrite is depicted in Fig. 11. The major mechanisms involved in the adsorption of fluoride onto the surface

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**Table 2** Kinetic model parameters

| Kinetic model parameters | $C_0$ (mg/L) | $q_{e,\exp}$ (mg/g) | $k_1$ (min$^{-1}$) | $R^2$ |
|--------------------------|-------------|---------------------|------------------|------|
| Pseudo-first-order kinetic model | 7 | 12.34 | 6.909$\times10^{-3}$ | 0.7547 |
| Pseudo-second-order kinetic model | $q_{e,\text{cal}}$ (mg/g) | $R^2$ | $q_{e,\exp}$ (mg/g) | $C_0$ (mg/L) | $k_2$ (g mg$^{-1}$ min$^{-1}$) |
| 15.62 | 0.999 | 15.15 | 7 | 0.021 |

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**Fig. 11** Proposed mechanism of fluoride adsorption onto Ca-doped ferrihydrite
of Ca-doped ferrihydrite are electrostatic interaction, physical adsorption, and π-π interactions. Electrostatic interactions are dominant at pH below pH_{zc} (6.14) due to attraction of F\(^{-}\) ions toward the positively charged Ca-doped ferrihydrite surface.

**Regeneration of Ca-doped ferrihydrite**

To determine the stability and reusability of adsorbent, fast and effective regeneration after adsorption is necessary, which makes the adsorption process more convenient, sustainable, and cost-effective (Biswas et al. 2009). Therefore, the adsorption and desorption studies of fluoride for five consecutive cycles were conducted to determine the regeneration capability of Ca-doped ferrihydrite (Fig. 12). We used a 0.1 M NaOH solution for the desorption of fluoride from the surface of Ca-doped ferrihydrite. *Many other reports suggest that NaOH can be used for regeneration of various sorbents* (Biswas et al. 2009; Bhaumik et al. 2011; Mohapatra et al. 2012; Shah et al. 2015; Zhu et al. 2015).

The removal efficiency of Ca-doped ferrihydrite for fluoride was slightly declined with the regeneration of the adsorbent, as shown in Fig. 12. After the first cycle of regeneration, the removal efficiency of Ca-doped ferrihydrite toward fluoride was 91%. After the fifth cycle, the removal percentage gradually declined to 80% Fig. 12, which is still promising for the removal of fluoride from the feed water. Therefore, these results suggest that Ca-doped ferrihydrite can be used for the long-term adsorption of fluoride from drinking water without any decrease in adsorption efficiency.

**Comparison of adsorption capacity with other adsorbents**

Table 3 provides a comparative analysis of the various adsorbents for the adsorption of fluoride. As evident from the table, the as-synthesized Ca-doped ferrihydrite adsorbent exhibited a higher adsorption capacity for fluoride as compared to most of the adsorbents reported in the literature. This confirms that the novel Ca-doped ferrihydrite has a promising potential to be employed for the decontamination of fluoride-containing water.

**Conclusion**

A novel Ca-doped ferrihydrite adsorbent was successfully synthesized and used as a simple, green, and cost-effective way to remove fluoride in an aqueous solution under controlled environmental conditions. The prepared synthesized exhibited tremendous adsorption potential for the uptake of fluoride from water. The effects of interfering anions and

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**Table 3** Comparison of adsorption capacities of various iron-based adsorbents for fluoride

| Adsorbents                                      | Adsorption capacity (mg/g) | Reference                      |
|------------------------------------------------|----------------------------|--------------------------------|
| Ferric hydroxide                               | 7.0                        | (Kumar et al. 2009)            |
| Boehmite                                       | 2.06                       | (Jiménez-Becerril et al. 2012) |
| Neodymium-modified chitosan                    | 22.38                      | (Yao et al. 2009)              |
| Activated quart                                | 1.16                       | (Fan et al. 2003)              |
| Hydrous ferric oxide                           | 16.5                       | (Dey et al. 2004)              |
| PPy/Fe\(_2\)O\(_4\)                            | 22.3                       | (Biswas et al. 2010)           |
| 2-Line ferrihydrite                            | 23.89                      | (Mohammed et al. 2019)         |
| Calcite                                        | 0.39                       | (Mohammed et al. 2019)         |
| Iron(III)–tin(IV) mixed oxide                  | 10.47                      | (Biswas et al. 2009)           |
| CTAB-assisted mixed iron oxide                 | 40.4                       | (Mohapatra et al. 2011)        |
| Hydrated Fe(III)–Al(III)–Cr(III) ternary mixed oxide | 31.9            | (Biswas et al. 2010)           |
| Ca-doped ferrihydrite                          | 53.21                      | This study                     |
natural organic matter were negligible at low concentrations, while the presence of cations enhanced the removal of fluoride. The optimum conditions of the reaction parameters were found as fluoride conc. = 5 mg/L, pH = 5.75, time = 120 min, rpm = 160, adsorbent dosage = 300 mg L\(^{-1}\), and operating temperature = 25 ± 2 °C. The best fit to the isotherm models, i.e., Langmuir and Freundlich, was determined. It is concluded that fluoride removal follows the pseudo-second-order reaction kinetics and Langmuir isotherm model. The adsorption isotherm models (Langmuir and Freundlich) were plotted, demonstrating the data obtained from the fluoride adsorption mechanism following the Langmuir isotherm model. The adsorption kinetic behavior followed pseudo-second-order kinetics with a very good correlation coefficient, which shows that the basic phenomenon involved was chemisorption. The results obtained in this study confirmed that the adsorption of fluoride by Ca-doped ferrihydrite was endothermic. The prepared adsorbent can be regenerated easily and reused in multiple cycles to uptake fluoride from water. The novel Ca-doped ferrihydrite adsorbent holds a tremendous practical application potential in wastewater treatment.

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Data Availability The datasets used in this study are available from the master study research.

Declarations

Consent to participate We confirm that the manuscript has been read and approved by all named authors and that there are no other persons who satisfied the criteria for authorship but are not listed. We further confirm that the order of authors listed in the manuscript has been approved by all of us.

Consent for publication The authors agree to publish this article in the Environmental Science and Pollution Research.

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