Hydrated cement: A promising adsorbent for the removal of fluoride from aqueous solution

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Abstract

The present study was carried out to investigate the potential of cement hydrated at various time intervals for the removal of excess F^- from aqueous solution by using batch adsorption studies. The influence of different adsorption parameters, viz. effect of adsorbent dose, initial concentration, pH, interfering ions and contact time were studied for their optimization. It was observed that the adsorbent exhibited reasonably significant F^- removal over a wide range of pH. The presence of carbonate and bicarbonate ions in aqueous solution were found to affect the F^- removal indicating that these anions compete with the sorption of F^- on adsorbent. The equilibrium adsorption data were fitted well for both the Freundlich and Langmuir isotherms and the adsorption capacities were calculated. Comparative studies for F^- removal in simulated and field water show relatively higher F^- removal in simulated water. XRD and SEM patterns of the hydrated cement were recorded to get better insight into the mechanism of adsorption process. From the experimental results, it may be concluded that HC was an efficient and economical adsorbent for F^- removal.
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1. Introduction

It is well documented that trace elements are essential and beneficial to human health in minute concentrations, as they play a significant role in many metabolic processes and act as cofactors. However, exceeding their permissible intake is known to be toxic and has adverse effects on general body metabolism. One such trace element, which is ubiquitously distributed in soil, earth and water is fluoride [1]. Fluoride (F^-) in drinking water may be beneficial or detrimental depending on its concentration and total amount ingested [2]. Fluoride is beneficial especially to young children (below 8 years of age) when present within permissible limits of 0.5–1.5 mg/L for the calcinations of dental enamel and bone formation [3]. Concentrations higher than this not only affects teeth and skeleton but also cause several neurological damages in severe cases [4].

Higher concentrations of F^- in groundwater is a global problem, occurring in many continents and affecting millions of people. According to a UNICEF report, fluorosis is endemic in at least 25 countries across the globe. In India alone, excess of F^- in drinking water is prevalent in 150 districts of 17 states of the country [5]. According to the Department of Drinking Water Supply under the Ministry of Rural Development, India, rural supply is, to a large extent dependent on groundwater (85%). Hence, it becomes necessary to reduce the F^- concentration within permissible limit of 1.5 mg/L according to Indian standards. The limit also varies among countries and the age of the people exposed [5].

Various treatment procedures have been reported for the removal of excess F^- from water. These can be broadly classified into three categories namely, precipitation, adsorption and membrane based. Precipitation involves the addition of soluble chemicals to water. Fluoride is removed either by precipitation, co-precipitation or adsorption onto the formed precipitate. Adsorption involves the passage of contaminated water through an adsorbent bed, where F^- is removed by physical, ion-exchange or surface chemical reaction with adsorbent [6]. Other defluoridation methods include membrane processes, nanofiltration, electrodialysis, etc. These processes are effective and can remove F^- to a suitable level but they are expensive and require

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frequent regeneration of beads or membrane and cleaning of the scaling and fouling [7]. Among them adsorption is still widely accepted pollution removal technique because of its ease of operation and cost-effectiveness. Recently, researchers have devoted their study on different types of low-cost but effective materials [7–10].

Portland cement, a low-cost fine-powdered building material usually consists of four main components such as tricalcium silicate, dicalcium silicate, tricalcium aluminate, and a tetracalcium aluminoferrite. Portland cement was mixed with water to get hydrated cement. The main advantage of using hydrated cement for F$^-$ removal over other chemical treatment methods is that it does not produce sludge, abundant availability and low-cost material. So, the main objective of this study was to investigate the F$^-$ removal potential of hydrated cement under different empirical conditions by batch adsorption studies.

## 2. Materials and methods

2.1. Materials

Cement used for this study was obtained from local commercial sources. All other chemicals used in the present study were of analytical grade purchased from E-Merck India Ltd., Mumbai, India. A stock solution of F$^-$ and Ca^{2+} was prepared by dissolving known weight of sodium fluoride and calcium chloride in distilled water and desired working F$^-$ and Ca^{2+} solution was prepared from stock solution by appropriate dilution.

2.2. Preparation of adsorbent

Preliminary studies were carried out by using cement hydrated for various time intervals of 24–120 h, respectively. Among them, cement hydrated for 72 h showed better results and it was used for further study. The detailed procedure for its preparation is as follows. About 1000 g (1 kg) of the commercially available Portland cement was taken in a vessel and the required amount of the distilled water (500 mL) was added to it. The pH of the cement in distilled water was about 9. Then, it was kept for 72 h at room temperature for hydration. After hydration/air-drying, the hydrated cement which is usually obtained in the form of clinkers was broken into small granules of ∼1.4–3 mm size. The entire procedure for preparation of hydrated cement (HC) was shown in Scheme 1.

2.3. Batch adsorption studies

Hundred milliliters of the desired F$^-$ solution was taken into a 250 ml of Tarson conical flask and known weight of the adsorbent was added to it and then shaken (150 rpm) on a horizontal rotary shaker (Model No.CIS-24, Remi Instruments, Mumbai, India) for 24 h in order to attain equilibrium. The conical flasks were removed from the shaker and then allowed to stand for 2 min for settling the adsorbent. All the batch adsorption studies were conducted at room temperature (30 ± 2 °C). Similar procedure was followed to determine the optimum conditions and to study the effect of initial concen-
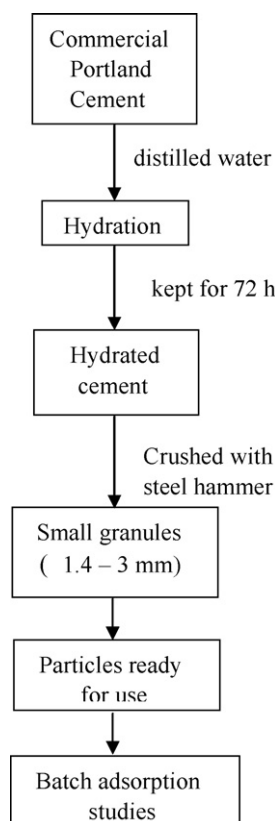
Scheme 1. Schematic diagram for the preparation of hydrated cement as an adsorbent.

tration, pH, adsorbent dose, interfering ions, etc. The specific amount of F$^-$ adsorbed was calculated from the following equation:

$$q_e = \frac{C_0 - C_e}{W} \times V \tag{1}$$

where q_e is the adsorbate loading (mg/g) in the solid (HC) at equilibrium; C_0, C_e are the initial and equilibrium concentrations of F$^-$ (mg/L) respectively; V the volume of the aqueous solution (L) and W is the mass (g) of adsorbent used in the experiments.

The effect of pH on F$^-$ removal was studied by adjusting the pH of solution using 0.1N HCl and NaOH solution. In case of each sample, pH was recorded by using Orion Model 920A$^+$, pH meter (Thermo Electron Corporation, Waltham, MA).

2.4. Methods of analysis

After attaining equilibrium, the experimental samples were filtered through Whatman No. 42 filter paper and filtrate was analyzed for residual F$^-$ concentration by using fluoride ion selective electrode (Orion number 9409 on a Sargent Welch pH/activity meter model PAX 900). Heavy metals if any released from the adsorbent after equilibrium studies were estimated by inductively coupled plasma-atomic emission spectroscopy (ICP-AES, Model OPTIMA-4100DV) method. Similar procedure was used for experiments on effect of anions, initial concentration, pH, etc.

2.5. Physical characterization

The HC before (untreated) and after (treated) batch adsorption experiments was characterized using XRD and SEM. A representative experiment was carried out under the given conditions: 30 °C, initial F$^-$ concentration = 50 mg/L, shaking speed = 150 rpm and contact time = 6 h respectively, for the preparation of XRD and SEM samples. The X-ray diffraction patterns were recorded using X-ray diffractometer, Model (Phillips, 'X' Pert). The sample was scanned for 2θ range from 10° to 60°. The SEM analysis was carried out using Jeol, JXA-840 A, Electron probe microanalyser, Japan, with different magnifications. The results were obtained in the form of micrograph on a 35 mm B/W film. In order to know the chemical composition, chemical analysis of hydrated cement was also carried out by weight percentage, which is expressed in terms of oxides.

3. Results and discussion

3.1. Adsorbent characterization

The XRD and SEM patterns of the HC before (untreated) and after treatment (treated) with F$^-$ ions are shown in Figs. 1 and 2 and the XRD data are given in Table 1. It is evident from the XRD studies (Fig. 1a and b) that the crystal structure of the HC showed significant changes after the adsorption of F$^-$ ions. This also suggests that the uptake of F$^-$ ions by HC was due to

Table 1
X-ray diffraction data for the HC before and after treatment with fluoride ions

d-Spacing (Å)	Relative intensity (%)	Angle, 2θ (°)	Peak height (counts)
Before adsorption			
2.6233	100.00	34.18	425
4.8949	94.64	18.12	402
3.0299	87.21	29.48	371
2.7700	52.17	32.32	222
1.9244	40.03	47.23	170
3.1034	28.62	28.77	122
1.7946	23.39	50.88	99
3.3364	16.68	26.72	71
2.2847	15.54	39.44	66
2.8768	14.49	31.09	62
After adsorption			
3.0195	100.00	29.58	1001
4.8649	18.58	18.24	186
2.2760	16.48	39.60	165
1.8713	16.07	48.66	161
1.9073	14.42	47.68	144
2.0885	14.20	43.32	142
2.7632	11.83	32.40	118
2.6358	10.75	34.01	108
2.6173	10.69	34.26	107
2.4842	10.20	36.16	102

chemisorption and precipitation, in the form of calcium and aluminum salts (F$^-$), with the alteration in the crystal structure of HC [7,11]. The possibility of calcium fluoride formation by reaction of fluoride with soluble or exchangeable calcium present in soil at near neutral pH has also been reported [12].

In order to see the surface of HC before and after adsorption, scanning electron microscope (SEM) images for the untreated and treated samples were recorded. It is evident from Fig. 2a that the SEM micrographs of the HC before treatment of F$^-$ shows irregularly shaped particles with surface agglomerates of small size particles adhered on bigger particles while the SEM micrographs (Fig. 2b) of the HC after treatment of F$^-$ shows nearly octahedral and stretched cubic structures which may be formed by the precipitation of aluminum and calcium salts (F$^-$) [13–15]. In order to know the chemical composition, chemical analysis of HC was carried out by weight percentage which is expressed in terms of oxides as Al_2O_3 (3.70%), Fe_2O_3 (3.65%), SiO_2 (17.44%), CaO (51.21%), and MgO (0.73%).

3.2. Effect of adsorbent dose

The effect of adsorbent dose on F$^-$ removal at a fixed initial F$^-$ concentration of 5.9 mg/L, pH 6.7, shaking speed = 150 rpm and contact time = 24 h is shown in Fig. 3. It was observed that percentage removal of F$^-$ increased from 47.46% to 92.37% with increase in adsorbent dose of 2–20 g/L of HC. However, after a dosage of 10 g/L, there was no significant change in the percentage removal of F$^-$ and also it was required to bring down the F$^-$ level to 1 mg/L which is also the maximum permissible limit for F$^-$ in drinking water [16]. It may be due to the overlapping of active sites at higher dosage as well as the decrease in the effective surface area resulting in the conglomeration of exchanger particles [17]. So, 10 g/L was used for further study.
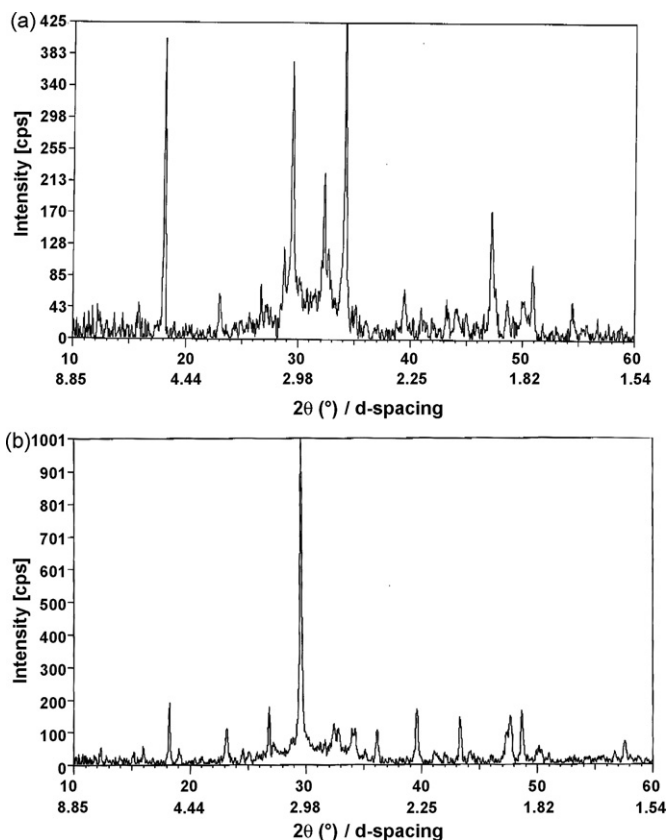

Fig. 1. (a) XRD of untreated HC and (b) XRD of treated HC.
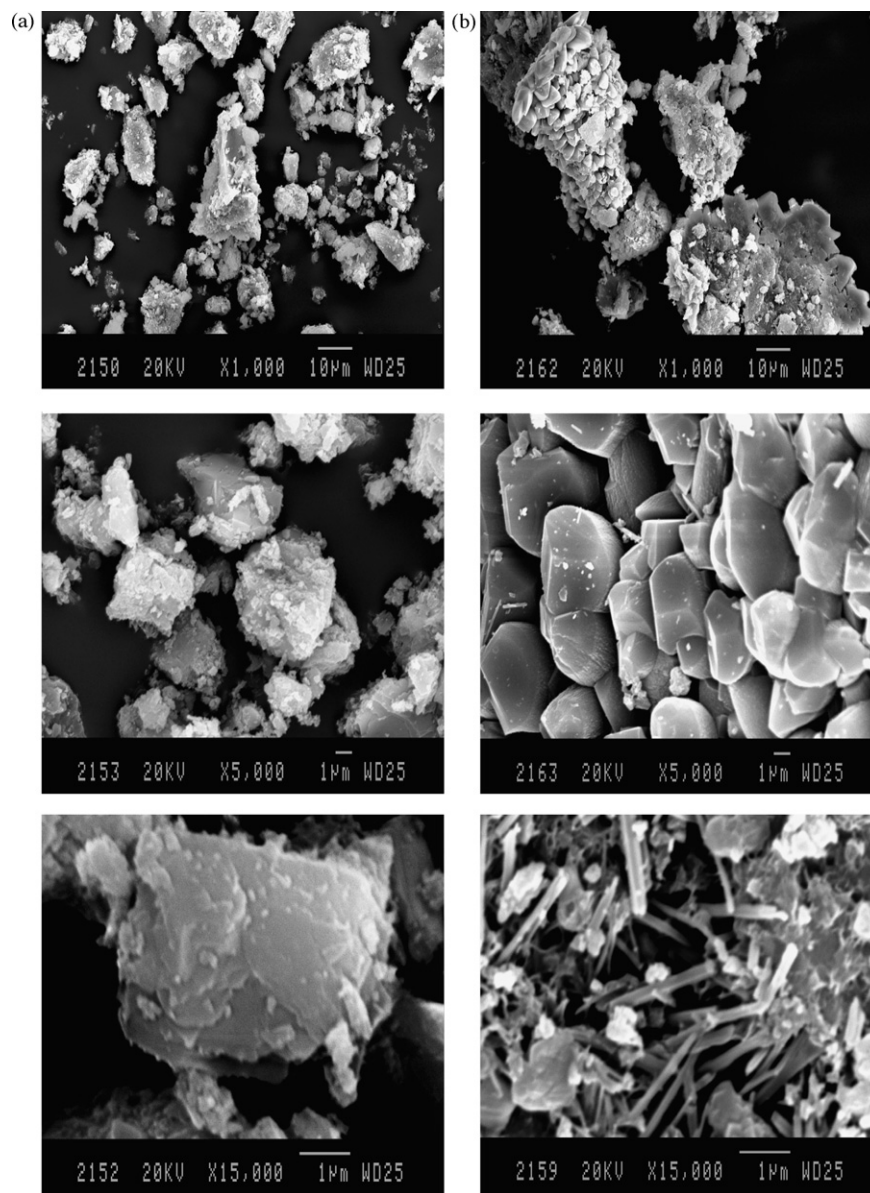
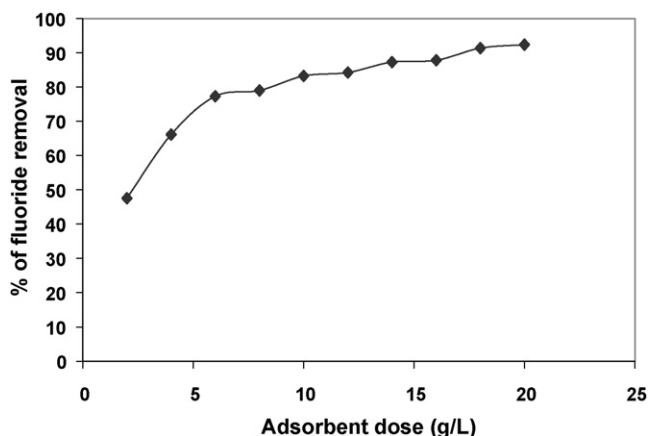Fig. 2. SEM of (a) untreated HC and (b) treated HC.

Fig. 3. Effect of adsorbent dose for fluoride removal (pH 6.7, initial concentration = 5.9 mg/L, shaking speed = 150 rpm, contact time = 24 h).

3.3. Effect of initial concentration

The effect of initial F^- concentration on the percentage removal of F^- was studied at different initial F^- concentrations by keeping all other parameters constant such as adsorbent dose = 10 g/L, pH 6.7, shaking speed = 150 rpm and contact time = 24 h. The effect of initial F^- concentration on F^- removal is shown in Fig. 4. It was noticed that with increase in initial F^- concentration, the percentage removal of F^- decreases. It may be because at higher adsorbate concentration, the binding capacity of the adsorbent approaches saturation, resulting in a decrease in overall percent removal.

3.4. Effect of pH

The pH of the medium is one of the important parameters that significantly affect the extent of F^- adsorption. Fluoride removal
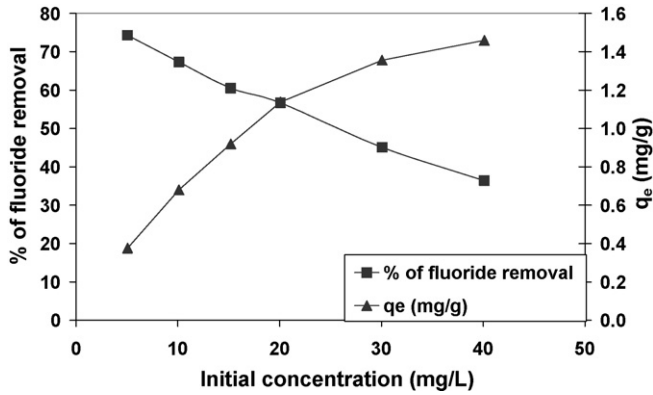
Fig. 4. Effect of initial F^- concentration for fluoride removal (pH 6.7, q_e = equilibrium adsorption capacity, dose = 10 g/L, shaking speed = 150 rpm and contact time = 24 h).

by the adsorbent was studied over the pH range of 3–12 with an adsorbent dose = 10 g/L, initial concentration = 5.37 mg/L, shaking speed = 150 rpm and contact time = 24 h as shown in Fig. 5. It was evident from the results that the adsorbent exhibited reasonably significant fluoride removal over a wide range of pH. Even, the defluoridation capacity of the adsorbent was appreciable in acidic range which may be due to the presence of alumina. However, at highly alkaline pH, the defluoridation capacity drops sharply. It may be because of the competition between hydroxide and F^- ions in this pH range [11].

3.5. Effect of co-ions

Originally, fluoride contaminated water contains several other ions which can equally compete in the adsorption process. In order to investigate the effect of interfering ions on F^- removal, adsorption studies were carried out in the presence of 0.01 M salt solutions of chloride, sulfate, nitrate, carbonate, and bicarbonate independently at an initial concentration = 5.9 mg/L, adsorbent dose = 10 g/L, shaking speed = 150 rpm and contact time = 24 h, respectively. The effect of these co-existing ions on F^- removal are shown in Fig. 6.
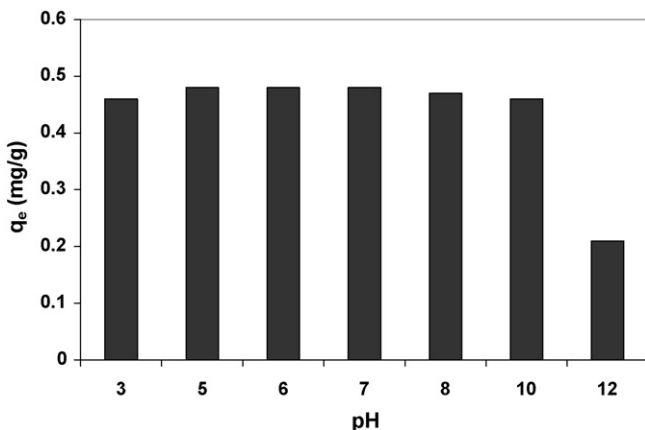

Fig. 5. Effect of pH for fluoride removal (initial fluoride concentration = 5.37 mg/L, dose = 10 g/L, shaking speed = 150 rpm and contact time = 24 h).
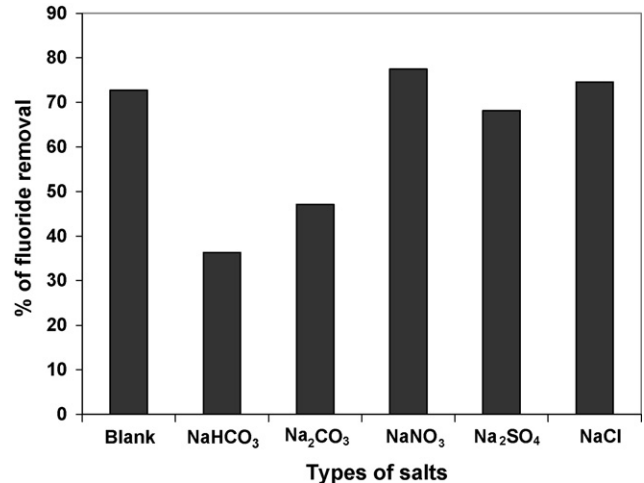

Fig. 6. Effect of interfering ions for fluoride removal (initial concentration = 5.9 mg/L, dose = 10 g/L, shaking speed = 150 rpm and contact time = 24 h).

From the results, it was observed that carbonate and bicarbonate showed negative effect while chloride, nitrate, and sulfate really did not affect the F^- removal. This may be due to the change in pH as well as competing effect of these co-ions for the active sites of the adsorbent. The pH of the F^- solutions were 7.9, 7.0, 6.97, 8.26, and 10.9, respectively, for Cl^-, SO_4^{2-}, NO_3^-, HCO_3^-, and CO_3^{2-} while the pH of the F^- solution was 6.7 without addition of salt/anions. It was also confirmed from our experiments on the effect of pH (Section 3.4) that the F^- removal decreases in highly alkaline pH as also explained. Even, the effect of calcium ion on F^- removal was studied by varying its concentration from 100 to 800 mg/L, respectively. It was observed that the F^- removal increased with increasing Ca^{2+} concentration till 400 mg/L and thereafter remained constant.

3.6. Adsorption modeling

The distribution of F^- between the liquid and solid phase is a measure of the position of equilibrium in the adsorption process and can be expressed by the Freundlich and Langmuir equations. The Freundlich isotherm, which is an indicative of surface heterogeneity of the adsorbent, is given below

$$q_e = K_F C_e^{1/n} \qquad (2)$$

The linearized Freundlich isotherm is given below

$$\log q_e = \log K_F + \frac{1}{n} \log C_e \qquad (3)$$

where K_F and $1/n$ are Freundlich constants, related to adsorption capacity and adsorption intensity (heterogeneity factor), respectively. The values of K_F and $1/n$ were obtained from the slope and intercept of the linear Freundlich plot of $\log q_e$ versus $\log C_e$ and were found to be 0.07419 mg/g and 0.8986 respectively, with regression coefficient (R^2) of 0.97. Since the value of adsorption intensity (heterogeneity factor) is less than unity, it indicates that system shows favorable adsorption [18].

The Langmuir equation, which is valid for monolayer sorption onto a surface is given below

$$q_e = \frac{q_0 b C_e}{1 + b C_e} \tag{4}$$

or

$$\frac{1}{q_e} = \frac{1}{q_0 b} \times \frac{1}{C_e} + \frac{1}{q_0} \tag{5}$$

where q_0 is the maximum amount of the F^- ion per unit weight of HC and b is the equilibrium constant of HC at equilibrium which indicates the affinity of the F^- towards the HC. q_e and C_e are the equilibrium adsorption capacity and equilibrium concentration of F^- in solution.

The values of Langmuir parameters, q_0 and b were calculated from the slope and intercept of the linear plots of $1/q_e$ versus $1/C_e$ and were found to be 2.6788 mg/g and 0.6013 l/mg respectively, with regression coefficient (R^2) of 0.95.

In order to predict the adsorption efficiency of the process, the dimensionless quantity (r) was calculated by using the following equation [8]:

$$r = \frac{1}{1 + b C_0} \tag{6}$$

where C_0 and b are the initial concentration of F^- and Langmuir isotherm constant.

If the value of $r < 1$ represent favorable adsorption and greater than 1.0 represent unfavorable adsorption. The value of r for an initial F^- concentration of 5.9 mg/L was found to be 0.22. It indicates that our system is favorable for adsorption.

3.7. Adsorption kinetics

The adsorption kinetics was studied to explain the F^- removal mechanism in the HC. It was noticed that the F^- removal increased with the lapse of time. However, sorption of F^- onto HC was rapid in the first 6 h after which the rate slowed down as the equilibrium approached. The results obtained from the experiments were used to study the rate-limiting step. Kinetic models are used to examine the rate of the adsorption process and potential rate-controlling step. The capability of the pseudo-first-order kinetic model was examined in this study. The pseudo-first-order equation of Lagergren is generally expressed as follows [19]:

$$\frac{dq}{dt} = k_1(q_e - q) \tag{7}$$

where k_1 is the rate constant of pseudo-first-order sorption (min^{-1}). Integrating this equation for boundary conditions $t = 0$–t and $q = 0$–q_e gives

$$\log (q_e - q) = \log q_e - \frac{K_{ad} t}{2.303} \tag{8}$$

where q_e and q (both in mg/g) are the amount of F^- adsorbed per unit mass of adsorbent at equilibrium and time "t", respectively and K_{ad} is the rate constant (min^{-1}).

The adsorption rate constant (K_{ad}) for F^- sorption was calculated from the slope of the linear plot $\log(q_e - q)$ versus time
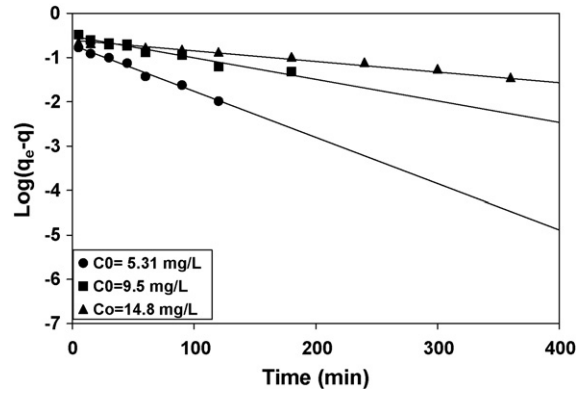

Fig. 7. Lagergren plot for fluoride removal (pH 6.7).

(t) as shown in Fig. 7. The values of adsorption rate constants (K_{ad}) were found to be 0.0323, 0.0113, and 0.0055 min^{-1} for initial F^- concentrations of 5.31, 9.5, and 14.8 mg/L, respectively. However, in case of strict surface adsorption, a variation of adsorption rate should be proportional to the first power of concentration. But when pore diffusion limits the adsorption process, the relationship between initial solute concentration and the rate of adsorption is no longer linear. So, the possibility was studied in terms of a graphical relationship between the amount of F^- adsorbed and square root of time as shown in Fig. 8.

In order to test the contribution of intraparticle diffusion on the adsorption process, the rate constant for intraparticle diffusion was obtained by using following equation:

$$q = K_p t^{1/2} \tag{9}$$

For calculating the intraparticle diffusion rate constant K_p ($mg\,g^{-1}\,min^{-1/2}$) the amount of F^- adsorbed per unit mass of adsorbent, q at any time t, was plotted as a function of square of time, $t^{1/2}$. The K_p values were obtained from the slope of the linear portions of the curves and were found to be 0.0149, 0.0049, and 0.0121 $mg\,g^{-1}\,min^{-1/2}$ for the initial F^- concentration of 5.31, 9.5, and 14.8 mg/L, respectively. It was also observed from Fig. 8 that all the plots have common general features (initial curved and subsequent linear portion). The initial curved portion reflects film or boundary layer diffusion effect while the
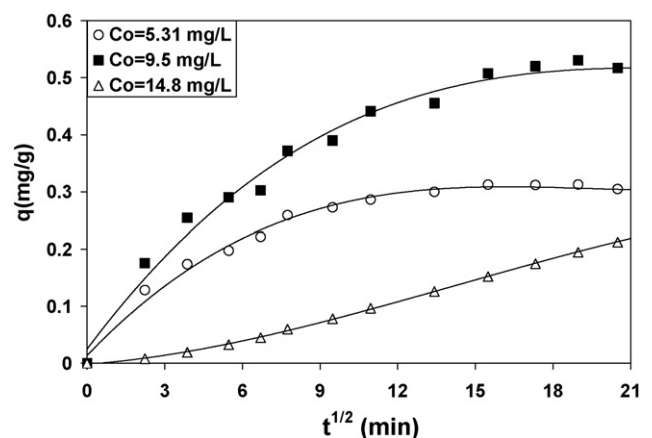

Fig. 8. Intraparticle mass transfer curves for fluoride removal (pH 6.7).

Table 2
Detailed characteristics of the field water before and after treatment with HC

Parameters	Values of field water before treatment of HC	Values of field water after treatment with HC
Turbidity (NTU)	0.60	3.0
Total hardness as $CaCO_3$ (mg/L)	56.00	152
Chloride as Cl (mg/L)	140.00	160
Fluoride as F (mg/L)	13.2	1.95
Sulfate as SO_4 (mg/L)	56.96	130
Alkalinity as $CaCO_3$ (mg/L)	44.00	120
Total dissolved solids (mg/L)	510.00	724
pH	7.78	10.38
Cadmium (mg/L)	<0.01	<0.01
Chromium (mg/L)	<0.05	<0.05
Lead (mg/L)	<0.01	<0.01
Manganese (mg/L)	<0.1	<0.1
Zinc (mg/L)	0.06	0.07
Iron	0.11	<0.3
Arsenic (mg/L)	<0.01	<0.01
Aluminum (mg/L)	<0.03	<0.03

linear portion attributes for the intraparticle diffusion effect. It is also evident from Fig. 8 that the linear portion of the curve does not pass through origin, which indicates that mechanism of F^- removal by HC is complex and both surface adsorption and intraparticle diffusion contribute to the rate-determining step [20].

3.8. Comparison of fluoride removal in simulated and field water

The applicability of the adsorbent was tested by treating ground water sample (field water) collected from F^- affected areas of Dhar, Madhya Pradesh, Central India. The detailed composition of the field water before and after treatment of HC is given in Table 2. It was found that the percentage removal of F^- in simulated water (prepared by dissolving NaF in distilled water) was higher than that of the field water as shown in Fig. 9. This could be due to two reasons: (i) higher pH of the field water and (ii) due to the presence of different types of cations and anions in the field water. It was also confirmed that
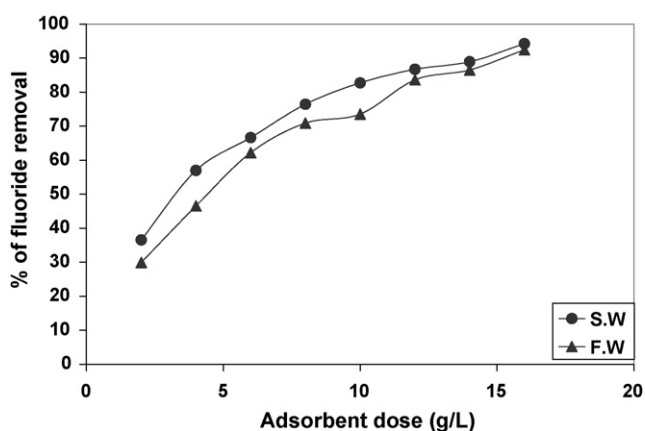

Fig. 9. Comparison of fluoride removal in simulated (SW) and field water (FW) (initial concentration = 13.2 mg/L, shaking speed = 150 rpm and contact time = 24 h).

no heavy metals were released from the adsorbent into the filtrate after the equilibrium studies by estimating it with the ICP-AES method.

4. Conclusion

Hydrated cement (HC) a low-cost building material, has considerable potential for the removal of excess F^- from aqueous solution. One of the major advantages of using HC for F^- removal over other chemical treatment methods is that it does not produce any chemical sludge. It was found that the HC shows significant F^- removal over a wide range of pH (3–10). The experimental data generated from batch adsorption experiments fitted well into the linearly transformed Freundlich and Langmuir isotherms. The value of equilibrium parameter, "*r*" suggests that F^- removal by HC system is favorable. XRD and SEM studies suggest that F^- uptake by HC is due to chemisorption and precipitation. The fluoride removal by the adsorbent from simulated water was relatively higher than field water, it may be because of the presence of different types of ions and also higher pH of the field water. No significant leaching of the heavy metals was observed from the adsorbent into the filtrate after the equilibrium studies.

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