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Performance evaluation of alumina cement granules in removing fluoride from natural and synthetic waters

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ABSTRACT

Of late, the ground water sources of many countries remain fragile due to fluoride attack. The intensity and scale of the human stress effects associated with this issue, prompts global research for sustainable solutions. This paper examines and compares the potential of a newly developed adsorbent alumina cement granules (ALC) in removing fluoride from natural ground water, and synthetic water prepared using conditions and concentrations relevant to natural freshwater environments. The batch sorption profiles appeared similar in natural and synthetic systems. The fluoride removal was concentration dependent in synthetic system as the equilibrium adsorption capacity was found to be 4.75 and 3.91 $\mathrm{mg\,g^{-1}}$ corresponding to initial concentrations of 20 and 8.65 $\mathrm{mg\,l^{-1}}$ at optimal conditions. ALC exhibited reduced fluoride adsorption capacity in treating natural water compared to synthetic systems in both batch and column studies. The sorption process is found to be unaffected in the pH range of 3.0–11.5. Though the presence of ions like nitrates, chlorides, sulfates, and bicarbonates did not offer any interference to fluoride sorption, silicates and phosphates at higher concentrations reduced fluoride uptake by ALC. The natural organic matter in ground water appears to play a role in reducing the adsorption capacity of ALC. Thermodynamics of sorption confirms that the process is spontaneous and endothermic in both natural and synthetic systems.

1. Introduction

The presence of fluoride in drinking water has dual significance. At lower concentrations, it guards our teeth against cavities [1], but at higher concentrations imparts ‘fluorosis’ in varying proportions [2,3]. Of late, excess fluoride in drinking water is reported from more than 35 countries around the globe with India and China, being the worst affected [3]. In countries like India, the severe contamination of drinking water with excess fluoride, acquired the dimensions of a socio-economic rather than a public health problem triggering defluoridation research.

Based on the nature of the mechanisms involved, defluoridation techniques can be generally grouped into coagulation, adsorption and/or ion exchange, electrochemical and membrane processes. Among these various processes, adsorption has become an important technique most widely used for excess fluoride removal from aqueous solution in the developing world [3,4]. In this process, a packed bed of adsorbent in fixed columns is continuously used for cyclic sorption and/or desorption of pollutants by effectively utilizing the capacity of an adsorbent bed. From a relatively bulk liquid volume, the pollutant gets concentrated and confined onto a small adsorbent mass which can invariably be regenerated, reused or safely disposed under control [5,6]. As the use of domestic defluoridation units are becoming increasingly popular in the fluoride endemic areas [4,7], the development of novel adsorbents derives attention in defluoridation research.

The success of adsorption process mainly depends on the capacity of adsorbent. In this direction the adsorbent activated alumina has had shown good fluoride scavenging potential in laboratory studies as well as field applications [7,8]. Though laboratory studies on activated alumina suggested adsorption capacities up to 15 $\mathrm{mg\,g^{-1}}$, field experiences demonstrated that it is often about 1 $\mathrm{mg\,g^{-1}}$ only [3,8]. So, it becomes essential that the natural scavenging potential of the adsorbent is to be evaluated, to ensure field application potential. Of late, many adsorbents developed for defluoridation demonstrated reduced adsorption capacities while treating actual ground water [9–11] in comparison to their respective laboratory performance using synthetic water. However, the reasons for the same were not researched into and fully elucidated. The present study stems from this background.

Generally, the important factors influencing adsorption process and capacity of the adsorbent includes pH, interference from other counter-ions in the medium, initial adsorbate concentrations and

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temperature [12–15]. The pH of the system derives significance as it controls the electrostatic interactions within the system, thereby affecting the adsorption capacity and removal rate. Experimental evidence suggest that the sorption profiles of adsorbents like titanium-rich bauxite [11], hydrous alumina [12], alum sludge [13], calcined Zn/Al hydrotalcite-like compounds [14], acivated alumina [16,17], activated bauxite and carbon [16] and manganese-coated alumina [18] are pH dependent. The maximum adsorption capacity of the adsorbent, alum-impregnated activated alumina got reduced by almost 10 times corresponding to an increase in pH from 4.0 to 9.0 [19]. Though the fluoride-rich ground waters are generally alkaline [20–22], an acidic pH range of 5–6 was reported optimal in most of the laboratory studies [12,16]. While it may be easy to adjust the pH for maximum removal at laboratory studies and waterworks, it is necessary to depend on the actual pH of raw water in domestic and small community treatments. So, for design and practical applications, it becomes necessary that the adsorption capacity of the adsorbent has to be investigated under prevailing field conditions apart from confining to studies on synthetic waters.

The objective of this paper is to compare the performance of a newly developed adsorbent, alumina cement granules (ALC), in removing fluoride from natural ground waters and synthetic waters. Since a reduction in adsorption capacity was generally reported in treating natural ground waters, the main emphasis is to elucidate the factors responsible for the same.

2. Materials and methods

2.1. Synthesis and characterization of adsorbent

The adsorbent (ALC), selected for the present research, was prepared from a commercially available high alumina cement. The rich presence of alumina and calcium, whose (established) potential for fluoride scavenging was instrumental in the selection of adsorbent. Initially, slurry was prepared by adding distilled water to 1 kg of high alumina cement at a water–cement ratio of ~0.3. The slurry was kept at ambient temperature for 2 days for setting, drying and hardening. This hardened paste was cured in water for 5 days. After curing, it was broken, granulated, sieved to geometric mean size of ~0.212 mm, and kept in airtight containers for use.

The elemental composition of ALC (combined with oxygen) was determined by Energy Dispersive X-ray (EDX) analysis (Oxford ISIS-300 model) by quantitative method in two iterations using ZAF correction, at a system resolution of 65 eV, and results were normalized stoichiometrically. The pH at zero point charge of ALC was determined as per the method suggested by Noh and Schwarz [23]. Different quantities of ALC were placed in 10 ml solutions of 0.1 M NaCl (prepared in pre-boiled water) in various bottles and kept in the thermostat shaker for overnight continuous agitation. The equilibrium pH values of these mixtures were measured and limiting value is reported as pHzpc. The surface area of the adsorbent determined by the BET method at liquid nitrogen temperature using FlowSorb II 2300 (Micrometrics Instruments corporation, USA). The properties of ALC media are presented in Table 1.

Table 1
Properties of ALC media.

Properties	Quantitative value
Geometric mean size (mm)	0.212
Bulk density (g cm^{-3})	2.33
Specific gravity	2.587
Al_2O_3 (%)	78.49
CaO (%)	15.82
SiO_2 (%)	5.39
Fe_2O_3 (%)	0.30
pH of the PZC	11.32
BET surface area (m^2/g)	4.385

2.2. Analyses

All chemicals and reagents used in this study were of reagent-grade and used without further purification. NaF (Merck) was used for the preparation of standard fluoride stock solution in double distilled water. All synthetic samples and fluoride solutions for adsorption and analysis were prepared by appropriate dilution of the stock solution in de-ionized (DI) water. Only plastic wares were used for handling fluoride solutions and is not prepared in or added to glass containers. All plastic wares were washed in dilute HNO_3 acid bath and rinsed thoroughly with DI water prior to use. The natural fluoride-rich drinking water was collected from Baliasingh Patna, a fluoride endemic village (Kurda district, Orissa state) in India, having the characteristics as shown in Table 2. Expandable ionAnalyzer EA 940 with Orion ionplus (96-09) fluoride electrode (Thermo Electron Corporation, USA), using TISAB III buffer was used for fluoride measurement. The pH measurement was done by a Cyber Scan 510 pH meter (Oakton Instruments, USA). A temperature controlled orbital shaker (Remi Instruments Ltd., Mumbai, India) was used for agitation of the samples in batch studies. A high precision electrical balance (Mettler Toledo, Model AG135) was used for weight measurement.

2.3. Sorption studies

The sorption of fluoride on ALC was carried out in batch system. Polyethylene bottles (Tarson Co. Ltd., India) of 150 ml capacity with 50 ml of fluoride solutions of desired concentration and pH were used. The agitation rate in natural and synthetic waters was optimized by separate studies. ALC was added as per dose requirements and bottles were capped tightly and shaken in the orbital shaking incubator at 230 ± 10 rpm. Synthetic (Syn) samples of the same concentration (8.65 mg l^{-1}) and pH (6.9 ± 0.4) of natural (Nat) water were prepared in DI water for comparison studies. The sorption behavior at a higher fluoride concentration of 20 mg l^{-1} in synthetic sample was also evaluated. The isotherm studies were conducted for ALC dose ranges of 3–12 g l^{-1} in natural and 0.25–3.0 g l^{-1} in synthetic waters for a fixed fluoride concentration of 8.65 mg l^{-1}. All studies for temperature effects (at 290, 300 and 310 K) on equilibrium sorption were conducted with ALC doses of 10 g l^{-1} in natural water and 2.0 g l^{-1} in synthetic waters of fluoride concentrations 8.65 mg l^{-1}. The studies on the effect of pH on synthetic waters of 8.65 and 20 mg l^{-1} were conducted at ALC doses of 1.5 and 3.0 g l^{-1}, respectively. The interference effects of other ions were conducted in synthetic samples of 8.65 mg l^{-1} with an ALC dose of 1.5 g l^{-1}. The

Table 2
Characteristics of natural ground water (collected from Baliasingh Patna, Kurda district, Orissa, India).

Characteristic parameter	Quantitative value (mg l^{-1})
Fluoride	8.65
pH	6.9 ± 0.4
Alkalinity (as $CaCO_3$ equivalents)	260
Chloride	165
Total Hardness (as $CaCO_3$ equivalents)	145
Total organic carbon	59.08
Total phosphorous	0.032
Silicate as SiO_2	39.22
Boron	0.33
Sodium	14.00
Potassium	2.00
Ammonia nitrogen	0.328
Salinity	0.30[a]

[a] Salinity is expressed in PSS (practical salinity scale).

salts $NaNO_3$, KCl, Na_2SO_4, $NaHCO_3$, Na_2SiO_3, $Ca(NO_3)_2$, $Fe(NO_3)_2$, and K_2HPO_4 (Merck) were used for preparing the respective ions for interference studies. Humic acid solutions were prepared from Humic acid, sodium salt (Aldrich chem. USA). For experiments on pH effects, 2 M HCl or NaOH solutions were added as required. The bottles were taken out from the shaker at desired time interval and filtered using Whatman No.-42 filter paper to separate the sorbent and filtrate. From the filtered sample of each batch reactor, 10 ml was taken for analysis and determination of residual fluoride. All batch sorption experiments were duplicated with experimental error limit ±5% and average values reported. In order to check for any adsorption on the walls of the container, blank container adsorption tests were also carried out.

3. Mathematical analysis

The fluoride removal efficiency is calculated through $[(F_i - F_f)/F_i]$, where F_i and F_f are the initial and final fluoride concentrations, respectively. The amount of fluoride adsorbed per unit weight of the adsorbent (q_t, $mg\,g^{-1}$) was calculated as

$$q_t = \frac{C_0 - C_t}{m} V \tag{1}$$

here $C_{0,}$ and C_t are the fluoride concentrations in solution ($mg\,l^{-1}$) initially, and at any time (t), respectively. V is the volume (l) of solution and m is mass of ALC (g). In Eq. (1), when $C_t = C_e$ (fluoride concentrations in solution ($mg\,l^{-1}$) at equilibrium), $q_t = q_e$ (equilibrium adsorption capacity in $mg\,g^{-1}$). The total quantity of fluoride adsorbed (F_{tot}; mg) in the column for a given feed concentration (C_0; $mg\,l^{-1}$) and flow rate (Q; $l\,h^{-1}$) can be found by calculating the area above breakthrough curve by integrating the adsorbed fluoride concentration (Cad; $mg\,l^{-1}$) versus time t (h) plot as

$$F_{tot} = Q \int_{t=0}^{t=et} Cad\,dt \tag{2}$$

similarly, the quantity of fluoride adsorbed up to breakthrough (F_b) as

$$F_b = Q \int_{t=0}^{t=bt} Cad\,dt \tag{3}$$

and

$$Cad = C_0 - C_t \tag{4}$$

where the terms '*bt*' and '*et*' represents the time (h) for breakthrough and exhaust, respectively. The minimum capacity of the adsorbent in the column ($q_{min,col}$) corresponding to the breakthrough point (point at which effluent concentration reaches $1.0\,mg\,l^{-1}$) and the total or maximum capacity of the column (q_{col}) corresponding to the exhaust point (point at which $C_t/C_0 = 0.90$) can be obtained as

$$q_{min,col} = \frac{F_b}{M} \tag{5}$$

$$q_{col} = \frac{F_{tot}}{M} \tag{6}$$

where M represents the mass of ALC in the column.

4. Results and discussion

4.1. Sorption performance of ALC

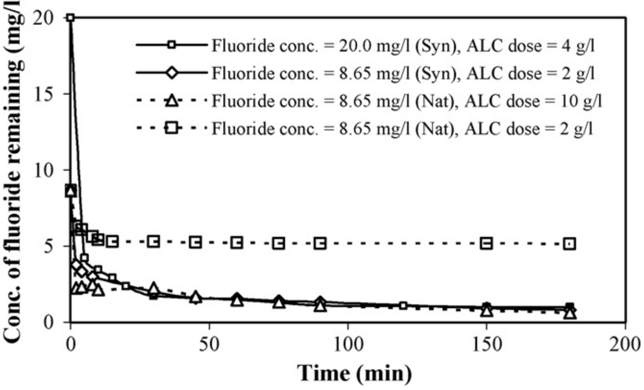

Fig. 1. Sorption profile of fluoride onto ALC in natural and synthetic water in batch study (pH 6.9 ± 0.4, $T = 300\,K$).

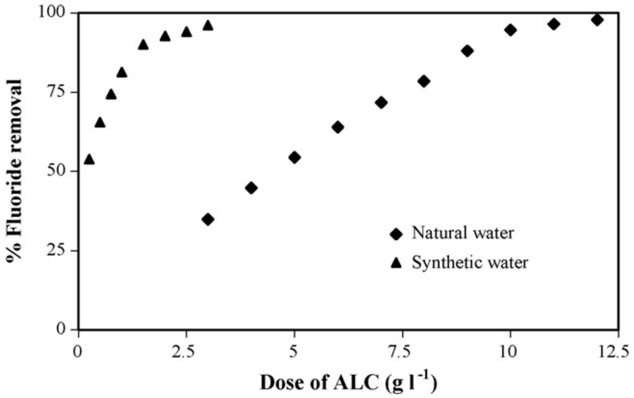

Fig. 2. Effect of dose variations of ALC on fluoride sorption in natural and synthetic water for the same initial concentration of $8.65\,mg\,l^{-1}$ (pH 6.9 ± 0.4, $T = 300\,K$).

The sorption kinetic profiles of ALC for fluoride in natural and synthetic systems are illustrated in Fig. 1. As shown, ALC exhibited similar sorption profiles in natural ground water and synthetic waters of same concentration. The sorption was found to be rapid at the initial few minutes followed by a slow phase with negligible removal after 3 h implying the attainment of equilibrium. The dose requirement in synthetic water was found to be 2 and $4\,g\,l^{-1}$, respectively for bringing initial fluoride concentrations of 8.65 and $20\,mg\,l^{-1}$ to permissible limits of less than $1\,mg\,l^{-1}$. Though an ALC dose of $2\,g\,l^{-1}$ could remove around 93% of initial fluoride in synthetic water, the corresponding removal was only around 40% in natural water. To obtain a removal of around 95%, the ALC dose requirement in natural water was found to be $10\,g\,l^{-1}$, five times higher than that of synthetic water of the same concentration (Fig. 2). The increasing removal efficiency observed with increased ALC dose implies that the process is dependent upon the availability of sorptive binding sites indicating the predominance of surface bound sorption in the removal mechanisms. Since ALC is a composite, its surface may be composed of sites with a wide spectrum of binding energies. It is postulated that at low adsorbent dosages all types of sites are entirely exposed for sorption, and the surface may become saturated faster. Whereas, at higher adsorbent dosages, the availability of higher energy sites may decrease and a larger fraction of lower energy sites may be occupied. This results in an overall decrease in binding energy of the surface, and there may exist a reversible reaction process between fluoride ions attached to low energy sites and those present in bulk solution. This may be a possible reason for the observed increase in fluoride uptake with adsorbent dosage up to a certain stage and remaining nearly constant thereafter. The maximum uptake of ALC at equilibrium was found to be $3.91\,mg\,g^{-1}$ in synthetic water; whereas it was only $0.806\,mg\,g^{-1}$ in natural water. Also, as expected, the maximum

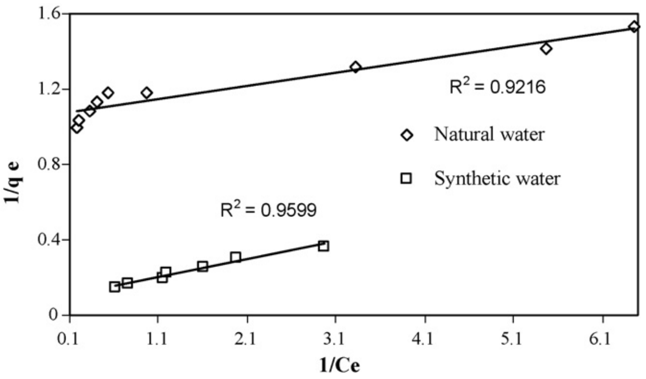

Fig. 3. Langmuir isotherm fitting of fluoride sorption onto ALC in natural and synthetic water (pH 6.9 ± 0.4, T = 300 K).

equilibrium uptake was found to be higher (4.75 mg g^{-1}) at higher initial fluoride concentrations (20 mg l^{-1}) in synthetic water. This may be due to high intra-molecular competitiveness to occupy the unsaturated lower energetic surface sites [14] at higher adsorbate concentrations.

The equilibrium sorption data on natural and synthetic waters (of same initial fluoride concentration and pH) were modeled using Langmuir isotherm represented by Eq. (7) [4,24] to obtain the maximum monolayer adsorption capacity ($q_{\max}$), indicative of the scavenging potential of the adsorbent (Fig. 3).

$$\frac{1}{q_e} = \frac{1}{bq_{\max}C_e} + \frac{1}{q_{\max}} \tag{7}$$

The term q_e in Langmuir equation represents the amount of fluoride adsorbed at equilibrium per unit weight of ALC (mg g^{-1}), C_e is the equilibrium fluoride concentration (mg l^{-1}), b is a constant related to binding energy. The $q_{\max}$ values of the model are presented in Table 3. The maximum saturated monolayer adsorption capacity of ALC is found to be almost 4.25–10 times higher than that of the popular adsorbent, activated alumina reported recently [17,18].

To evaluate and compare the field application potential of ALC, column studies were performed for the same initial fluoride concentrations of 8.65 mg l^{-1} both in natural and synthetic water. The respective breakthrough profiles are illustrated in Fig. 4. The time for breakthrough and exhaust in synthetic water were found to be 17 and 139 h; whereas the corresponding values in natural water got reduced to 3 and 14 h. The adsorptive capacities of ALC at breakthrough and exhaust in both systems are shown in Table 3. These sorptive responses of ALC clearly suggest a reduction in scavenging potential in treating natural water compared to synthetic systems in both batch and column studies. The reported limited attempts of batch studies in defluoridation research also support these findings [9–11].

Table 3
A comparative evaluation of the adsorbent performance in synthetic and natural systems.

S. no.	Systems of study	Nature of the medium	
		Synthetic water	Natural ground water
1	Dose requirement of ALC in batch study (for an initial fluoride concentration of 8.65 mg l^{-1}, pH of 6.9 ± 0.4 at 300 K)	2 g l^{-1}	10 g l^{-1}
2	Langmuir saturated monolayer adsorption capacity ($q_{\max}$)	10.214 mg g^{-1}	0.935 mg g^{-1}
3	Minimum adsorption capacity of ALC by column study ($q_{\min,\mathrm{col}}$)	1.847 mg g^{-1}	0.317 mg g^{-1}
4	Maximum adsorption capacity of ALC by column study (q_{col})	6.965 mg g^{-1}	0.75 mg g^{-1}

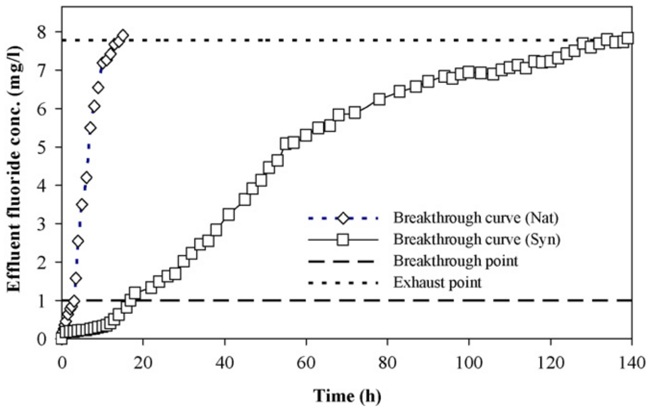

Fig. 4. Breakthrough curves of fluoride sorption onto ALC in natural and synthetic water (Co = 8.65 mg l^{-1}, pH 6.9 ± 0.4, T = 300 K, flow rate = 8 ml min^{-1}).

4.2. The interference effects

4.2.1. Effect of pH

The observed reduction in adsorption potential could not be ascribed to the effect of pH as the sorption studies on synthetic water was carried out at the same pH of natural water (6.9 ± 0.4). However, the sorptive responses of ALC were investigated at different pHs to understand the mechanism and ascertain its field use. As demonstrated in Fig. 5, the percentage removal of fluoride was almost consistent in the pH range of 3–11.5 and reduces thereafter in both concentration ranges. This could be readily explained as, when $pH < pH_{ZPC}$, the net surface charge on solid surface of ALC is positive due to adsorption of excess H^+, which favors adsorption due to coulombic attraction; whereas at $pH > pH_{ZPC}$, the net surface charge is negative due to desorption of H^+ and adsorption must compete with coulombic repulsion as

$$MOH + H^+ = MOH_2{}^+ \tag{8}$$

$$MOH = MO^- + H^+ \tag{9}$$

where M represents the metal (Al, Si, Fe, etc.) and $MOH_2{}^+$, MOH and MO^- are positive, neutral and negative surface hydroxo and oxo groups, respectively. As suggested by Hao and Huang [12], the fluoride removal is expected to take place (pH > 7) through a ligand

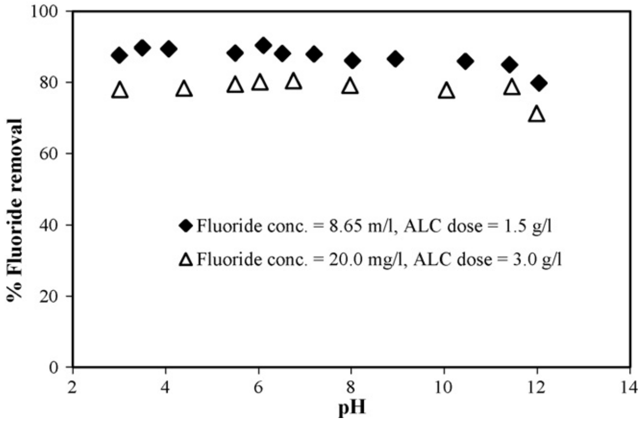

Fig. 5. Effect of pH on fluoride sorption onto ALC in synthetic water at different initial fluoride concentrations at 300 K.

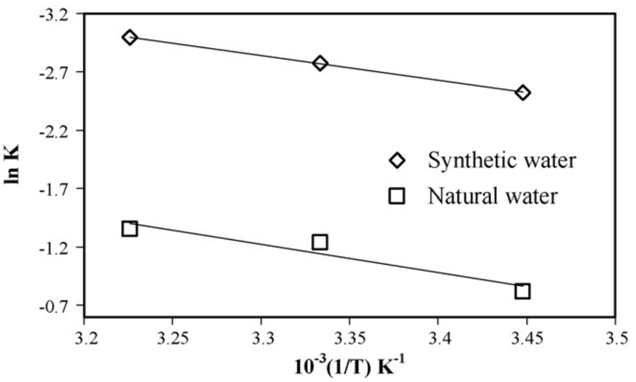

Fig. 6. Effects of temperature on fluoride sorption onto ALC in synthetic and natural water at pH 6.9 ± 0.4.

exchange process as

$$MOH + F^- = MF + OH^- \quad (10)$$

when pH exceeds 11.5, the hydroxo groups (MOH) will gradually disappear forming an increasingly negatively charged surface. In addition, OH^- ions may compete with F^- ions for remaining available sites on the surface, resulting reduced fluoride removal.

4.2.2. Effect of temperature

Since sorption studies on both systems were conducted at the same temperatures of 300 K, the reduction in adsorption potential in natural water could not be ascribed to the effect of temperature. However, temperature effects of sorption was evaluated in both systems within the range from 290 to 310 K to delineate the nature of sorption mechanisms in terms of the thermodynamic parameters like, Gibb's free energy (ΔG°), standard enthalpy (ΔH°), and standard entropy changes (ΔS°). These values are calculated using Eqs. (11) and (12):

$$\Delta G^\circ = -RT \ln K \quad (11)$$

$$\ln K = \frac{\Delta S^\circ}{R} - \left(\frac{\Delta H^\circ}{R}\right)\left(\frac{1}{T}\right) \quad (12)$$

where K is the equilibrium constant (ratio of the solid phase concentration of fluoride at equilibrium (mg l^{-1}) to the equilibrium concentration in solution (mg l^{-1})), R is the gas constant (J mol^{-1} K^{-1}) and T is the absolute temperature (K). The ln K versus (1/T) plot is shown in Fig. 6. The respective parameter values are illustrated in Table 4. The increase in fluoride sorption with temperature in both systems reflects the surface heterogeneity of ALC and its increased activity, which is resulting in enhanced diffusion of fluoride ions into its pores. It would be expected that higher temperatures stimulate the surface reactivity of the bound oxides/hydroxides, which may increase the sorption capacity of the system. The negative values of ΔG° confirm the spontaneity of sorption in both systems within the conditions applied. Also, the higher negative value at elevated temperatures, assures more energetically favorable adsorptions. Further, the decrease in its magnitude with increasing temperature indicates more efficient sorption at elevated temperatures. The endothermic nature of the sorption process in both systems is confirmed by the negative enthalpy values (ΔH°). The positive value of entropy change (ΔS°) reflects the affinity of ALC towards fluoride, which may also indicate some structural changes within the adsorbent [15,25]. Generally, the enhanced adsorption at elevated temperatures indicates the significant role of a chemisorptive sorption process. Recently, the defluoridation of drinking water by many adsorbents like calcined Mg/Al hydrotalcite-like compounds (HTCs), calcined Mg–Al-CO_3 layered double hydroxides, algal biosorbents, bone char, carbonized biomass, and granular calcite also showed identical response to temperature variations [26–31].

Table 4
Thermodynamic parameters of adsorption of fluoride onto ALC in natural and synthetic water.

System	ΔH° (kJ mol^{-1})	ΔS° (kJ mol^{-1} K^{-1})	ΔG° (kJ mol^{-1})		
			290 K	300 K	310 K
Synthetic Water	36.569	0.144	−5.191	−6.631	−8.071
Natural Water	83.810	0.301	−3.480	−6.490	−9.50

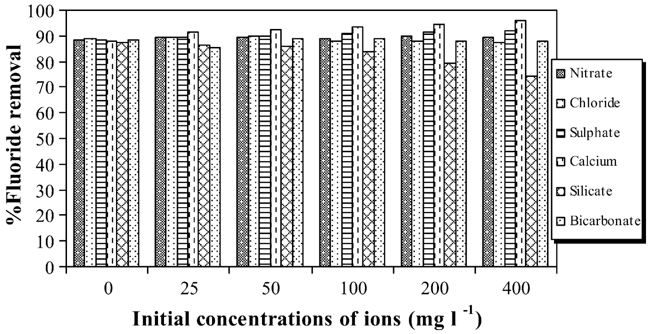

Fig. 7. Interference effects of various ions on the sorption of fluoride by ALC in synthetic water (Co = 8.65 mg l^{-1}, ALC dose = 1.5 g l^{-1}, T = 300 K).

4.2.3. Effect of other ions and NOM

The possible interferences from other ions in natural water are also investigated to ensure its field use. As illustrated in Fig. 7, nitrates, chlorides, sulfates, and bicarbonates did not significantly affect the sorption process. The effect of silicate is insignificant up to 25 mg l^{-1}, thereafter it slightly reduces the fluoride removal and at 400 mg l^{-1} the reduction was about 13%. The presence of calcium gradually enhanced the removal and at 400 mg l^{-1} by around 7%. The presence of iron also did not affect the removal up to 10 mg l^{-1}; whereas, the interference of phosphate was considerable. At a concentration of 4 mg l^{-1}, it reduces the removal by around 6% and at 8 mg l^{-1} by more than 10%.

The interference analyses suggest that high levels of salinity and hardness in water did not affect fluoride removal efficiency of ALC. Since fluoride-rich ground waters are generally associated with high bicarbonate ions in alkaline environments [20,21] its applications turns important. The interference of phosphate [13,14,26] and silicate [13] associated with fluoride sorption was already reported. The reduction of fluoride sorption in the presence of high silicates may be due its scavenging of aluminium ions forming aluminosilicate solute species, especially in alkaline environment [32]. Also silicic acid is known to inhibit the formation of aluminum hydroxide precipitates by replacing hydroxylated aluminium(III) ions. High silica concentrations may also result in its polymerization resulting in an increase in negative surface charge [33]. The reduction in fluoride removal efficiency in the presence of phosphates, may be due to the strong affinity of aluminum(III) for phosphate. The absence or negligible competitive effect from most of the ions is indicating that fluoride is strongly adsorbed [34] onto ALC. The interference pattern indicates that the presence of ions chlorides, nitrates, bicarbonates may form outer-sphere but sulfates and silicates forms partial inner-sphere complexes with ALC.

The TOC of natural water sample (Table 2) deserves mention. It typically quantifies the amount of natural organic matter (NOM) concentrations in the natural water sources [35] present as a result of adsorption onto aquifer solids or depositional history [36]. Aqueous NOM represents a wide range of structurally complex compounds derived from the chemical and biological degradation of plants and animals, which composed mainly of humic substances (humic and fulvic acids), and are hydrophobic [37]. Humic substances are complex mixtures containing both aromatic and aliphatic components with mainly carboxylic and phenolic functional groups [36] and were found to interfere with anionic adsorption [9,38,39] through stable metal complex formations [40,41]. In the present study, additions of 5, 10, 20 and 40 mg l^{-1} of humic acid to fluoride samples (Co = 8.65 mg l^{-1}) reduced the percentage removal by 5.5, 11.54, 14.65 and 18.03%, respectively. A high reduction of 50% in fluoride removal was reported by the addition of 10 mg l^{-1} humic acid in the case of manganese-oxide-coated alumina [18].

As the structurally complex product of biomass decomposition, NOM molecules possess unique combinations of functional groups, including carboxylic, esteric, phenolic, quinone, amino, nitroso, sulfhydryl, hydroxyl, and other moieties, the majority of which are negatively charged at neutral pH. As a result of the predominant anionic character coupled with its high reactivity towards both metals and surfaces, NOM can compete with fluoride for its sorption onto ALC. In sorptions involving natural ground water, the adsorption capacity may be depending on the accessibility of the organic molecules to the inner surface of the adsorbent. The small molecules can access micropores and NOM can access mesopores of the adsorbent [42]. This pre-sorbed NOM may reduce or destruct the sorption sites of the adsorbent. It was suggested that NOM readily forms both aqueous and surface inner-sphere complexes with cationic metals and metal oxides [41]. Aqueous NOM–metal complexes may, in turn, associate strongly with dissolved anions like fluoride, presumably by metal-bridging mechanisms, diminishing the tendencies of fluoride ions to form surface complexes. This metal bridging appears to be a potential mechanism for reduced fluoride uptake in natural water. However, further experiments on ground water samples from different locations and chemistry are needed to properly elucidate this mechanism.

Though silicates and phosphates are posing interferences to fluoride sorption in synthetic systems, since their respective concentrations in natural water is less, may not be responsible for the reduced fluoride intake. It is plausible that the presence of NOM represented by the high TOC value may be playing a role in the reduced capacity of the adsorbent in natural water. However, further studies are warranted to precisely elucidate the reduced uptake in natural waters, including the synergetic effects of various ions, which remains as a fertile area for future research.

5. Conclusions

The adsorbent ALC exhibited similar sorption profiles of fluoride uptake in natural and synthetic systems in batch studies. The sorption was observed endothermic with identical thermodynamic behavior in both systems. Both batch and column experiments demonstrated a reduction in adsorption potential in treating natural ground water compared to synthetic waters of same fluoride concentrations. The presence of silicates and phosphates poses interferences to fluoride uptake; whereas the natural organic matter present in ground water appears to play a role in the reduced performance in natural systems. However, detailed studies on ground waters of different geological locations and chemistry are warranted to precisely elucidate the reduced uptake from natural systems.

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