

## DEVELOPMENT OF INORGANIC COMPOSITES FOR WATER DEFLUORIDATION

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(Received 18 October, 2020; accepted 17 November, 2020)

### ABSTRACT

For the removal of fluoride ions from groundwater to make it fit for drinking or industrial use, the main aim of this research was to prepare four types of inorganic composites based on carbon, calcium, silica, and magnesium namely carbon inorganic composite (CIC), calcium inorganic composite (CaIC), silica inorganic composite (SiO<sub>2</sub>IC), and magnesium inorganic composite (MgIC) respectively, and to test the feasibility of their use in defluoridation of water. The sorptive capacity of most effective four ICs (CaIC, MgIC, SiO<sub>2</sub>IC, and CIC), commercial activated alumina (AA), activated carbon (AC), and an anion exchange resin (AER) Ceralite IR 400 (Cl<sup>-</sup> form) were evaluated for fluoride removal under steady-state and transient rate batch processes under different conditions of fluoride concentration, time, sorbent dose, pH and temperature. Sorbents were analyzed and their capacities were compared with AA, AC, and AER. The modified sorbents were better than ordinary sorbents. CaIC showed comparable results to AER. Defluoridation was in the order AER > CaIC > MgIC > AA > SiO<sub>2</sub>IC > CIC > AC over a wide range of initial concentration 1-10 mg/l at sorbent dose range 1-20 g/l, pH 6.0, temperature 25 °C, rpm 150 for 5 hours. Under these conditions from 3.8 mg/l fluoride solution, they could remove 91.7, 90.2, 88.6, 80.4, 75.2, 71.2, and 66.6% fluoride removal. This order of ICs, i.e. CaIC > MgIC > SiO<sub>2</sub>IC > CIC was probably due to several factors such as particle size, ionic potential, pH, surface area, and environmental conditions. The sorption increased with increasing contact time and sorbent dose, but the equilibrium was attained in 2 hours for MgIC and AA, 2.5 hours for AC. The higher uptake at lower initial concentration can be attributed to the availability of more isolated fluoride ions. The sorption rate was very rapid during the initial period of contact. Groundwater samples revealed 3 to 12% lesser removal when correlated to standard sodium fluoride solutions under identical conditions. CaIC was found to be the best of all the fluoride removing ICs studied here. The maximum removal was at pH 6 or slightly lower 5.7 but for others, it was a slightly higher pH than 6. Thus, the weakly acidic medium favored the removal. CaIC showed better sorption than AA and comparable removal to AER.

**KEY WORDS :** Fluoride, Removal, Groundwater, Composites, Carbon, Calcium, Silica, Magnesium

### INTRODUCTION

Excess fluoride, wherever present in groundwater in India, is mainly in the concentration range of 1.5 to 6.5 mg/l against its desirable limit of 1 mg/l and maximum permissible limit of 1.5 mg/l in drinking water (Naika *et al.*, 2020; Hanse *et al.*, 2019; WHO, 2006; CGWB, 1999; Choubisa, 1997; Gupta, 1999; Pathak and Badve, 1999; Reddy, 1998). Potable water should have 0.6 to 1.0 mg/l of fluoride for

substantial protection against the cavity. If fluoride is absent in drinking water, it causes dental caries. Continuous high intake of fluoride results in mottled teeth, skeletal fluorosis, and sometimes severe osteosclerosis (Podgorski *et al.*, 2018; Ali *et al.*, 2016; Bhatnagar *et al.*, 2011; Kang *et al.*, 2011). Agra city and nearby villages have been reported to have very high F content in groundwater, for example up to 22 mg/l, 18.3 mg/l and 8.9 mg/l in Akola Block, Bichpuri Block, and Shamsabad Block, respectively.

Fluoride enters inside the body via different kinds of sources particularly water, air, food, medicines, and cosmetics. The earth crust in India is excessively weighted with fluoride-containing minerals like fluorspar, fluorapatite, phosphatic nodules, topaz, etc. due to which water and food mainly crops are contaminated with fluoride. Fluorspar or calcium fluoride  $\text{CaF}_2$ , cryolite or sodium aluminum fluoride  $\text{Na}_3\text{AlF}_6$ , fluorapatite  $\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2$ , topaz  $\text{Al}_2\text{SiO}_4(\text{F},\text{OH})_2$ , sellaite  $\text{MgF}_2$ , villianmite  $\text{NaF}$ , bastnaesite  $(\text{Ce},\text{La})(\text{CO}_3)\text{F}$ , and fluorine hydrosilicates are the most common fluoride minerals in the earth crust. As a result of the rich mineral content, fluoride leaches out and contaminates the water and earth/soil in general and groundwater especially. Fluoride may be contained 2% in wastewaters from phosphate fertilizer plants. Elevated ranges of fluoride can also be found in discharges from the fluorine industry, glass etching, and in groundwater nearby aluminum smelters. The issue of large fluoride concentration in groundwater resources has developed into a serious health-related Geo Environmental problem in some areas including Agra.

Many investigations have been conducted using different materials and methods for fluoride removal (Bose *et al.*, 2019; Arunachalam *et al.*, 2011; Mandal and Mayadevi, 2011; Jagtap *et al.*, 2011; Kumar *et al.*, 2009; Ayoob and Gupta, 2009; Ayoob and Gupta, 2007; Islam and Patel, 2007; Azhar and Turkman, 2000; Bulusu and Nawlakhe, 1990; Christoffersen *et al.*, 1991; Kabay and Kodama, 2000; Kumar and Gopal, 2000; Mehrotra *et al.*, 1999; Singh *et al.*, 2000; Yang *et al.*, 1999; Seha and Chandran, 2001). The various techniques for defluoridation can be arranged into physical and chemical categories. Numerous chemical methods based on the principle of precipitation, adsorption, ion exchange, electrochemical, and membrane process have been described for fluoride removal. Most of these techniques are cost-intensive and natural defluoridation of drinking water cannot be a great substitute on health grounds. The Nalgonda technique (adding potash alum  $\text{K}_2(\text{SO}_4)$ ,  $\text{Al}_2(\text{SO}_4)_3 \cdot 24\text{H}_2\text{O}$ , calcium oxide  $\text{CaO}$ , and calcium chloro hypochlorite  $\text{Ca}(\text{OCl})\text{Cl}$  accompanied through speedy blending, flocculation, and filtration) is widely used in India. Poly aluminum chloride (PAC) is reported to be a substitute for a commercial alum because it produces less sludge than alum. All available alums increase the sulfate or chloride ion concentration except PAC (Chhabra,

1997).

Although different defluoridation techniques are possible, all of them have various advantages and drawbacks. Fluoride ion ( $\text{F}^-$ ) removal technologies from water suffer from cost and/or efficiency drawbacks (Al-Bedoor *et al.*, 2017). All alums increase sulfate, chloride, and TDS levels. Sludge removal is another problem. Aluminum salts react with fluoride non-stoichiometrically in a narrow pH range. Al (DL = 0.03 mg/l and PL = 0.20 mg/l) can cause neurodegenerative disorders as Alzheimer disease, encephalopathy, dementia, brain damage and anemia (Kawahara, 2005). Processed bones, various formulations of tricalcium phosphate, activated alumina, and AC has a high initial cost, lack of selectivity for fluoride, and poor capacity. The RO, electro dialysis, and resin units are very complex, contamination prone, and expensive. They may be additionally challenging to chemical assaults, clogging, contaminate through particulate matter, and concentrated a huge amount of wastes. The waste volumes in RO are considerably more than in resins. Sometimes, the pre-treatment requirements are extensive. The resins increase the concentration of chloride intreated water which can cause corrosion. The treated water also has a high pH. Bioremediation is slow. Excess chemical methods cause pollution. Adsorption is ecofriendly and cost-effective (Rajkumar *et al.*, 2019; Radha and Pushpa, 2019). The ultimate frequently used adsorbents are activated alumina and activated carbon (Gebrewold *et al.*, 2019; Choong *et al.*, 2020; Zhang *et al.*, 2019). Other adsorbents such as magnesium trisilicate, serpentine, clay minerals like bentonite and kaolinite have been observed to be of academic interest only. The nanoparticles (1 to 100 nm) of  $\text{Al}_2\text{O}_3$ , maghemite ( $\text{Fe}_2\text{O}_3$ ), iron, iron oxide, iron hydroxide, titanium oxide, nickel oxide,  $\text{SiO}_2$ ,  $\text{SnO}_2$ , ZnS, ZnO, zirconia ( $\text{ZrO}_2$ ), anatase ( $\text{TiO}_2$ ), akageneite, cobalt ferrite, copper oxide, etc. are beneficial in water treatment (Idini *et al.*, 2019; Gitari *et al.*, 2020; Gidi *et al.*, 2019; Diaz *et al.*, 2019; Sharma *et al.*, 2017).

Keeping the above facts in mind the main purpose of this study was to develop efficient, cheaper, reliable, greener, and versatile Al-free inorganic composite materials from indigenous chemicals and minerals for water defluoridation. the main aim of this research was to prepare four types of inorganic composites based on carbon, calcium, silica, and magnesium namely carbon inorganic composite (CIC), calcium inorganic composite

(CaIC), silica inorganic composite (SiO<sub>2</sub>IC), and magnesium inorganic composite (MgIC) respectively, and to test the feasibility of their use in defluoridation of water by the batch process.

## MATERIALS AND METHODS

Coconut shell charcoal was prepared, activated, and modified with Fe(III), Ti(IV), and Zr(IV) salts (Zhang *et al.*, 2019; Brunson and Sabatini, 2016; Tang *et al.*, 2015; Janardhana *et al.*, 2006), cetyl trimethyl ammonium bromide (Sankararamkrishnan *et al.*, 2013), and fly ash from Chula (Soni, 2015). TiO<sub>2</sub> modified-granular activated carbon (GAC-TiO<sub>2</sub>) composites were synthesized by microwave-assisted hydrothermal method (Orhaa *et al.*, 2017). Thinking about smooth availability, low price, and excessive effectively, hydroxyapatite (HAP), and limestone-based procedures can be potential clean selections for fluoride removal if the capacity and sludge disposal are appropriately addressed (Sudasinghe *et al.*, 2020; Sengupta *et al.*, 2020; Nijhawan *et al.*, 2019; Kim *et al.*, 2020; Nath and Dutta, 2015). Hydroxyapatite (HAP), calcium oxide (CaO), calcium hydroxide [Ca(OH)<sub>2</sub>], calcium chloride (CaCl<sub>2</sub>), calcium carbonate (CaCO<sub>3</sub>), calcium phosphate [Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>], calcium nitrate [Ca(NO<sub>3</sub>)<sub>2</sub>], and calcium sulfate (CaSO<sub>4</sub>) were used singly and in different combinations after physicochemical treatment for fluoride removal. The best four calcium ICs were blended with phosphoric acid (PA) (Gogoi and Dutta, 2016), bentonite (Naghizadeh *et al.*, 2017), stannic chloride, TiO<sub>2</sub> (Yan *et al.*, 2017), zeolite (Du *et al.*, 2017), cerium(IV), manganese(II), and iron(III) salts (Alemu *et al.*, 2014). HAP was calcined mixed with starch and water, compacted, and sintered at 1200°C to get macroporous ceramic beads (Nijhawan *et al.*, 2017). Sol-gel and hydrothermal synthesis were used to prepare TiO<sub>2</sub> particles and load them onto SiO<sub>2</sub> particles (Lin *et al.*, 2017; Zeng *et al.*, 2017). Mg/Fe/La hydrotalcite-like compound (Mg/Fe/La HLC) had been synthesized with a easy single-step hydrothermal method (Wu P *et al.*, 2017). Micro-nano hierarchical structured flower-like MgO/MgCO<sub>3</sub> (MHS- MgO/MgCO<sub>3</sub>) was developed for fluoride removal from water (Zhang *et al.*, 2015).

The crushed IC was pelletized separately by injecting them into a commercial pellet mill. Dry steam was used if the moisture content is low, but no other binders or additives are to be used. The pelletizing process improves the structural and

physical properties of sorbents making them more suitable for use in packed columns. 5 g of IC slurry was put on a silica glass plate or slide. The slip coating was conducted and IC was covered with another silica glass plate with a 0.2-0.3 mm spacing to obtain a uniform film. The plates were tied, sealed, and kept at 80°C for 5 days for the formation of the mesostructured IC film or membrane. After the reaction, the film was washed with distilled water and dried in the air. In case, IC cannot be used in columns because it coagulates among the particles and swells due to its water-absorbing property, it was immobilized on hydrophobic support of cellulose acetate. The selected ICs were refunctionalized or reactivated by treating separately (one by one) with fortifiers or modifiers such as CaO, Ca(OH)<sub>2</sub>, TiO<sub>2</sub>, CeO<sub>2</sub>, bentonite, pyroaurite like compound, and silica gel depending on the previous results. The treatment was expected to introduce additional hydroxo groups on sorbents that could be exchanged with F<sup>-</sup>, and a positive charge to trap F<sup>-</sup> from water. For example, an IC extracted with 0.1N NaOH, washed and dried, and was soaked for 1 hour in 2% modifiers solution. Alum, Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>, Al<sub>2</sub>O<sub>3</sub>, and poly aluminum chloride were also tried as modifiers for comparison. But aluminum salts are to be phased out or limited due to their toxicity. A quaternization agent, N-(3-chloro-2-hydroxypropyl)-trimethylammonium chloride (CHMAC) or cetyltrimethylammonium bromide (CTAB), and a cross-linking agent, epichlorohydrin was also used for a better defluoridation. These activators were tried one by one depending on the previous results to get the best modifier for an IC. A comparative study of the modifying effects of these compounds was conducted. An activated IC was denoted as IC\*.

The sorptive capacity of most effective four ICs (CIC, CaIC, SiO<sub>2</sub>IC, and MgIC), commercial activated alumina (AA), activated carbon (AC) and an anion exchange resin (AER) Ceralite IR-400 (Cl<sup>-</sup> form) was evaluated for toxic removal under steady-state and transient rate batch processes using different conditions of toxic concentration, time, sorbent dose, pH and temperature. The filtrate was analyzed for the F<sup>-</sup> ions with Orion 720 A<sup>+</sup> Benchtop pH/ISE/ORP meter after calibrating the F<sup>-</sup> ISE. The concentration of multivalent metals used to modify sorbents was measured with a Perkin-Elmer AAnalyst 100 AAS. Experiments were triplicated and results averaged. Except as otherwise specified all experiments had been conducted at room

temperature. Attempts were made to desorb fluoride from the loaded sorbents using various molarities of HCl, HNO<sub>3</sub>, NaOH, and other chemicals. The data were analyzed using various isotherms, kinetic and thermodynamic equations (Andersson *et al.*, 2011; Parida *et al.*, 2011; Mustafa *et al.*, 2011; Zhang and Jia, 2016).

CIC, CaIC, SiO<sub>2</sub>IC, MgIC, AA, AC, and AER were analyzed for their physicochemical characteristics (Dayananda *et al.*, 2015; Wu S *et al.*, 2015) namely moisture, ash, carbon, silica, sodium, potassium, calcium, magnesium, phosphorous, iron, pH, conductivity ( $\mu\text{S/m}$ ), specific gravity (g/L), porosity (mL/g) surface area (m<sup>2</sup>/g) and cation exchange capacity (meq/g), X-ray diffraction (XRD) and FTIR studies.

## RESULTS AND DISCUSSION

The results of sorbent analysis for their physicochemical characteristics are depicted in Table 1. Many variables affect the ability of sorbents to bind to the sorbates. Even the orientation of sorbate molecules on the surface could lead to a lower adsorption capacity. The zero-point charges of SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, and CaO are 2.2, 8.3, and 11.0 respectively. Thus, the negatively charged silica surface sites of adsorbents get neutralized by cations such as metal or H<sup>+</sup> ions, thereby reducing hindrance to diffusion of anions present in the aqueous phase. Along with other favorable properties, CaIC has the highest surface area, and hence it gave the highest fluoride removal.

Defluoridation was in the order of AER > CaIC >

MgIC > AA > SiO<sub>2</sub>IC > CIC > AC over a wide range of initial concentration 1-10 mg/l at sorbent dose range 1-20 g/l, pH 6.0, temperature 25 °C, rpm 150 for 5 hours (Table 3). Under these conditions from 3.8 mg/l solution, they could remove 91.7, 90.2, 88.6, 80.4, 75.2, 71.2, and 66.6% fluoride removal. This order is probably due to several factors such as particle size, ionic potential, pH, surface area, and environmental conditions. The sorption increased with increasing contact time (Table 4) and sorbent dose, but the equilibrium was attained in 2 hours for MgIC and AA, 2.5 hours for AC. The higher uptake at minor initial concentration can be ascribed to the availability of additional isolated fluoride ions. The sorption rate is very rapid during the initial period of contact. Groundwater samples revealed 3 to 12% lesser removal when correlated to standard sodium fluoride solutions under identical conditions. Adsorption decreased with rising in F<sup>-</sup> concentration but increases with an increase in adsorbent dose and contact time.

The effect of adsorbent dose on the adsorption of fluoride using different adsorbent at pH 6 and temperature 25 °C is depicted in Table 5. It indicates that the percent F<sup>-</sup> removal increases with an increase in adsorbent dose.

100 ml solution of 3.8 mg/l F<sup>-</sup> concentration was adjusted to pH 4 to 10 with HCl/Ca(OH)<sub>2</sub> and treated with 0.5 g of the sorbent at rpm 150 for 5 hours. The influence of the pH of a solution on the extent of adsorption of F<sup>-</sup> is depicted in Table 6. The F<sup>-</sup> removal is highly dependent on the pH of the medium which affects the surface charge of the adsorbent and degree of ionization. The maximum

**Table 1.** Characteristics of adsorbents

Characteristics	CIC	SiO <sub>2</sub> IC	MgIC	CaIC
Density (g/cc)	0.90	0.90	2.09	0.70
Moisture (%)	14.31	14.31	15	10.31
Bulk density (g/ml)	0.60	0.60	1.20	0.50
Ash (%)	6.65	6.65	15.32	9.65
Volatile matter (%)	6.74	6.74	6.08	5.74
Loss of ignition (%)	3.02	3.02	5.96	6.02
SiO <sub>2</sub> (%)	18.35	18.35	3.92	17.92
Al <sub>2</sub> O <sub>3</sub> (%)	1.83	1.83	2.44	1.44
CaO (%)	1.35	1.35	45	49.15
Fe <sub>2</sub> O <sub>3</sub> (%)	2.51	2.51	2.26	2.56
MgO (%)	1.04	1.04	2.36	1.73
Surface area (m <sup>2</sup> /g)	198	198	478	558

The results of groundwater analysis for fluoride are listed in Table 2. The samples were categorized as A, B, C, D, and E with fluoride concentration ranges 0-1, 1-2, 2-3, 3-4, and > 4 mg/L respectively. Four groundwater samples (C, D, and E types) had been taken for fluoride removal.

removal was at pH 6 or slightly lower 5.7 for bony materials but for others, it was a slightly higher pH than 6. Thus, the weakly acidic medium favored the removal.

Most of these sorbents consist of oxides of silicon, aluminum, iron, calcium, magnesium, etc. Many researchers have found that anion adsorption sites on such minerals like alumina and clay are aqua groups ( $-M-OH_2-$ ) and hydroxo groups ( $-M-OH$ ). The surface chemistry of oxide in contact with an aqueous solution is determined to large extent by deprotonation or a hydroxyl ion association reaction. The presence of oxides of alumina, calcium, and silicon of the adsorbent develop charge in contact with water according to the pH of the solution.

Above and below pH, the extent of adsorption was considerably low (Table 6). Except for silica, all other oxides (the major constituent of fly ash being alumina) possess a positive charge for a pH range of interest. As the pH decreases below 4.5,  $Al_2O_3$  is dissolved as  $Al^{3+}$  and subsequently, the surface of  $Al_2O_3$  becomes further positively charged with a

decrease in pH. As pH increase, the hydroxo group ( $-M-OH$ ) goes on disappearing and forming an increasingly negatively charged surface. Also,  $OH^-$  competes for the available sites left on the surface.

The effect of temperature on  $F^-$  adsorption on sorbents was studied by conducting the batch adsorption at different temperatures of 15, 20, 25, and 35 °C (Table 7). With an increase in temperature, the adsorption came down rapidly indicating the adsorption process to be exothermic. The values of the thermodynamic parameters were computed from the following relations:

$$\log K_d = \Delta S/2.303R = \Delta H/2.303RT \quad .. (1)$$

$$\Delta G = \Delta H - T\Delta S \quad .. (2)$$

where  $K_d$  is the distribution coefficient for the adsorbate and is equal to the ratio of the amount adsorbed per unit mass (g) (i.e.  $x/m$ ) to the adsorbate concentration in unit volume ( $cm^3$ ) of the solution. The plots of  $\log K_d$  vs  $1/T$  in combination with equation (2) gave the value of  $\Delta H$ ,  $\Delta G$  and  $\Delta S$ . The mean values of the standard enthalpy change  $\Delta H$  remained in the range  $-27.74$  to  $61.80$  kJ/mol

**Table 2.** The concentration of fluoride in groundwater of Agra City

Sr. No.	Area	No. of samples analyzed	Mean conc. of F <sup>-</sup> (mg/l)	Standard deviation	Type*
1	Agra Fort	3	3.3	0	D
2	Balkeshwar	7	1.5	0.4	B
3	Belanganj	4	0.9	0.1	A
4	Bagh Muzaffer Khan	8	2.3	0.2	C
5	Dareshi	6	4.2	0.2	E
6	Dayalbagh	3	2.6	0.4	C
7	Gokul Pura	3	3.0	0	C
8	Kamla Nagar	5	2.0	0	B
9	Khandari	3	1.9	0.2	B
10	Nai Ki Mandi	5	3.5	0.3	D
11	Nehru Nagar	3	2.2	0	C
12	New Agra	4	2.9	0.1	C
13	Peepal Mandi	4	2.5	0.1	C
14	Raja Ki Mandi	9	2.0	0	B
15	Ram Bagh	10	1.6	1.2	B
16	Sanjay Place	4	1.8	0.2	B
17	Shah Ganj	3	1.7	0.2	B
18	Shahjahan Park	2	4.1	0.1	E
19	Surya Nagar	2	2.1	0	C
20	Taj Ganj	8	2.9	0.1	C
21	Transport Nagar	7	2.8	0.3	C
22	Trans Yamuna	7	2.6	1.2	C
23	Waterworks	7	1.7	0.4	B
24	Wazir Pura	9	3.8	0.3	D

\*Type indicates type of groundwater samples with fluoride concentration ranges A = 0-1, B = 1-2, C = 2-3, D = 3-4, and E = > 4 mg/L.

conforming to the adsorption process to be exothermic. The considerable high values of  $\Delta H$  indicated a very strong interaction between organic matter and the sorbents. This also explained the rapid decrease in adsorption with increasing temperature.

The mean values of the standard Gibbs energy change,  $\Delta G$  were in the range  $-4.92$  to  $-9.92$  kJ mol<sup>-1</sup>. Thus, the adsorption resulted in a significant decrease in Gibbs energy pointing to a spontaneous and energetically favorable process. The average value of standard entropy change,  $\Delta S$  values (range  $0.13$  to  $-0.22$  kJ mol<sup>-1</sup>) were also negative showing that the adsorption of fluoride on sorbents was accompanied by a decrease in entropy. The immobilization of the fluoride ions on specific sites of the sorbent surface might have led to the restoration of order (in comparison to the solution phase) resulting in a decrease of entropy. The evaluation of the thermodynamic parameters shows that F<sup>-</sup> ions bind very strongly to the sorbent surface by a chemisorptive process and is accompanied by a

decrease in enthalpy, entropy, and Gibbs free energy. Thus, the adsorption process is exothermic and spontaneous as well as thermodynamically favorable.

The experimental data were analyzed using four sorption kinetic models: the pseudo-first-order, the Ritchie second order, the modified second order, and the Elowich equations. The values of specific reaction rate or velocity coefficient  $k$  were calculated for all the sorbents, and they were found constant when calculated using the first-order equation:

$$k = 2.303/t \log a/(a-x)$$

where  $a$  mol/L is the initial fluoride concentration from which  $x$  mol/L has been removed after  $t$  seconds.

The data were also analyzed using Langmuir and Freundlich equations:

$$\log a = \log k_f + 1/n \log c \quad \text{Freundlich equation}$$

$$c/a = 1/Q_b + c/Q \quad \text{Langmuir equation}$$

Where  $a$  (mg/g) is the fluoride sorbed per unit mass of sorbent ( $a = x/m$  where  $x$  mg of fluoride is sorbed on  $m$  grams of sorbent),  $k_f$  (mg/kg), and  $n$

**Table 3.** Removal % of fluoride at different concentrations and sorbent dose 10 g/l, rpm 150, pH 6.0, at 25 °C for 5 hours

Water Type	F <sup>-</sup> Conc'n mg/l	AER	CaIC	MgIC	AA	SiO <sub>2</sub> IC	CIC	AC
B	1.9	93.1	85.6	80.2	75.8	71.6	68.3	62.5
D	3.8	91.7	90.2	88.6	80.4	75.7	71.2	66.6
E	5.7	92.5	87.4	84.9	81.2	78.8	62.2	53.4
E	9.5	92.2	84.8	81.4	70.6	63.3	57.4	47.5
St. John's	2.0	89.8	82.2	82.8	72.4	70.8	62.3	55.1
Trans Yamuna	2.5	91.5	88.3	84.5	81.6	79.9	62.7	54.6
Gokul Pura	3.5	94.0	89.2	85.5	80.8	76.1	65.7	50.9
Dareshi	4.2	85.6	83.1	80.4	78.2	74.4	57.9	47.0

**Table 4.** Removal % of fluoride at different contact times and fluoride concentration 3.8 mg/l, adsorbent dose 10 g/l, rpm 150, pH 6.0, at 25 °C

Contact Time (hours)	AER	CaIC	MgIC	AA	SiO <sub>2</sub> IC	CIC	AC
1.0	56.8	52.8	50.5	46.5	43.6	31.9	27.4
2.0	87.8	85.9	71.6	69.4	65.4	56.4	42.3
3.0	90.4	88.5	86.2	78.5	68.9	65.7	57.9
4.0	91.4	89.8	87.9	79.2	74.1	67.3	58.8
5.0	91.7	90.2	88.6	80.4	75.7	71.2	66.6

**Table 5.** Removal % of fluoride at different sorbent doses and fluoride concentration 3.8 mg/l, rpm 150, pH 6.0, at 25°C for 5 hours

Sorbent Dose (g/l)	AER	CaIC	MgIC	AA	SiO <sub>2</sub> IC	CIC	AC
1	48.4	42.8	40.2	36.8	32.4	25.7	21.9
5	78.2	75.4	71.5	69.1	67.9	51.3	44.4
10	91.7	90.2	88.6	80.4	75.7	71.2	66.6
20	92.2	91.6	90.4	81.8	76.8	72.3	68.8

**Table 6.** Removal % of F<sup>-</sup> at different pH values and initial concentration 3.8 mg/l, sorbent dose 10 g/l, contact time 5 hours, temperature 25 °C and rpm 150

pH	AER	CaIC	MgIC	AA	SiO <sub>2</sub> IC	CIC	AC
4	78.2	75.4	71.5	69.1	67.9	51.3	44.4
6	91.7	90.2	88.6	80.4	75.7	71.2	66.6
8	86.0	85.4	85.7	78.6	74.5	68.6	61.9
10	48.4	42.8	40.2	36.8	32.4	25.7	21.9

**Table 7.** Removal % of F<sup>-</sup> at different temperatures and initial concentration 3.8 mg/l, sorbent dose 10 g/l, pH 6.0, contact time 5 hours, and rpm 150

Temperature °C	AER	CaIC	MgIC	AA	SiO <sub>2</sub> IC	CIC	AC
15	97.1	89.6	84.2	79.8	75.6	72.3	66.5
20	92.2	91.6	90.4	81.8	76.8	72.3	68.8
25	91.7	90.2	88.6	80.4	75.7	71.2	66.6
35	87.5	82.4	79.9	77.2	73.8	57.2	48.4

**Table 8.** Analysis of data using kinetic and isotherm models

Sorbent	First-order rate constant K (1/min)	Langmuir constants and R <sup>2</sup>			Freundlich constants and R <sup>2</sup>		
		Q, mg/g	B, 1/g	R <sup>2</sup>	K <sub>f</sub> , mg/g	1/n	R <sup>2</sup>
AER	0.0099	10.9032	0.0925	0.9633	7.9245	0.0945	0.9935
CaIC	0.0089	9.0526	0.0854	0.9578	6.0235	0.0745	0.8523
MgIC	0.0078	8.9035	0.0772	0.9635	5.9245	0.0645	0.7934
AA	0.0070	7.7222	0.0602	0.9223	4.7045	0.0512	0.7112
SiO <sub>2</sub> IC	0.0045	5.2256	0.0517	0.9785	3.2246	0.0313	0.8312
CIC	0.0035	4.9323	0.0408	0.9677	2.2345	0.0245	0.6612
AC	0.0030	4.1567	0.0345	0.9897	2.1236	0.0201	0.5343

are Freundlich constants related to adsorption capacity and adsorption intensity respectively, and Q (mg/g) and b (kg/g) are Langmuir constants related to the adsorption capacity of sorbent and adsorption maximum (energy of adsorption) respectively. Freundlich and Langmuir's constants were calculated at four initial concentrations under optimal conditions. The sorption data fitted very well to the Langmuir isotherm as well as the Freundlich equation. The values of Q and k<sub>f</sub> in Table 8 indicate the sorptive capacities of different sorbents.

ICs contain many functional groups. Fluoride adsorption on such materials is due to the presence of aqua groups (—M—OH<sub>2</sub>—) and hydroxo groups (—M—OH), high surface area, and charge on their tiny particles. The surface chemistry of oxide in contact with an aqueous solution is determined to a large extent by deprotonation or a hydroxyl ion association reaction (Mehrotra *et al.*, 1999). However, some evidence suggests that an anion like F<sup>-</sup> can be adsorbed by the ion-exchange mechanism even though the surface is neutral.



## CONCLUSION

It can be concluded from the results that the defluoridation order of ICs i.e. CaIC > MgIC > SiO<sub>2</sub>IC > CIC is probably due to several factors such as particle size, ionic potential, pH, surface area, and environmental conditions. The sorption increases with increasing contact time and sorbent dose, but the equilibrium is attained in 2 hours for MgIC and AA, 2.5 hours for AC. The higher uptake at minor initial concentration can be ascribed to the availability of additional isolated fluoride ions. The sorption rate is very rapid during the initial period of contact. Groundwater samples reveal 3 to 12% lesser removal when correlated to standard sodium fluoride solutions under identical conditions. CaIC is the best of all the fluoride removing ICs studied here. The maximum removal at pH 6 shows that a weakly acidic medium favors the removal. CaIC has better sorption than AA and is comparable removal to AER. Kinetics indicates it to be the first-order

sorption. Thermodynamics shows the process to be exothermic and spontaneous as well as thermodynamically favorable.

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