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Column defluoridation of groundwater using modified inorganic composites

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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_2IC), and magnesium inorganic composite (MgIC) respectively, and to test the feasibility of their use in defluoridation of water by the column processat different fluoride concentrations, bed heights, pH and flow rates. The sorptive capacity of the most effective four ICs (CaIC, MgIC, SiO_2IC, and CIC), commercial activated alumina (AA), activated carbon (AC), and an anion exchange resin (AER) Ceralite IR 400 (Cl^- form) were evaluated.   CaIC showed comparable results to AER. Defluoridation was in the order AER >CaIC>MgIC> AA > SiO_2IC > CIC > AC over a wide range of initial concentration 1-10 mg/l at BH 30 cm, pH 6.0, temperature 25^{o}C, flow rate 10 mL per minute. Under these conditions from 3.8 mg/l solution, they could remove 19.7, 17.2, 16.6, 15.4, 14.7, 13.2, and 12.6% fluoride removal. This order of ICs i.e., CaIC>MgIC> SiO_2IC > CIC is probably due to several factors such as particle size, ionic potential, pH, surface area, and environmental conditions. The sorption of fluoride ions increased as their concentration decreases from 9.5 to 1.9 mg/l. Leaching increased as the flow rate increased. The solution pH considerably affected the quantity of pollutant elimination. Most of the sorbents showed the maximum fluoride removal percent at pH 6. The sorption increased with increasing BH, but the equilibrium was attained in 2 hours for MgIC and AA, 2.5 hours for AC. Leaching increases considerably as the flow rate increases. It was concluded that CaIC, MgIC, SiO_2IC, and CIC are effective sorbents for F^- ions. CaIC and MgIC are especially effective at a high concentration of fluoride (F^-) ion in water. A mixed solution containing 0.14 mol/l calcium chloride and 0.08 mol/L sodium dihydrogen phosphate with pH adjusted to about 3 can be profitably used to regenerate the spent sorbent. CaIC, MgIC, SiO_2IC, and CIC are ecofriendly sorbents, and their sorption ability is much higher than others. They can be further modified to have enhanced fluoride sorption capacity to be used as a primary remediate of fluoride in wastewater or groundwater like AER.

Key words : *Defluoridation, Groundwater, Composites, Carbon, Calcium, Silica, Magnesium, Column process*

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 DL of 1 mg/l and MPL of 1.5 mg/l in drinking water. 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. 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 (Brajesh and Alam, 2006; Arunachalam and Annadurai, 2011; Bhatnagar *et al.*, 2011; Dwivedi *et al.*, 2011; Hyun *et al.*, 2011; Jadhava *et al.*, 2011; Peter, 2009; Kagne *et al.*, 2008; Islam and Patel, 2007; Apambire *et al.*, 1997; CGWB,1999; Choubisa, 1997; Gupta, 1999; Latha *et al.*, 1999). Fluoride leaches out and contaminates the water and earth/soil in general and groundwater especially (Asare-Donkor and Adimado, 2020; Chen *et al.*, 2017a; Chen *et al.*, 2017b; Elumalai *et al.*, 2019; Nag and Das, 2017; Qian *et al.*, 2019; Rezaei and Hassani, 2018).

Fluoride may be contained 2% in wastewaters from phosphate fertilizer plants. Elevated ranges of fluoride can also be found in effluents from the fluorine industry, glass etching, and in groundwater around 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. Agra city and nearby villages have been reported to have extremely high fluoride in groundwater, for example up to 22 ppm in Akola Block, 18.3 ppm in Bichpuri Block, and 8.9 ppm in Shamsabad Block.

Defects in current defluoridation techniques: Classical procedures of defluoridation involve precipitation, adsorption, ion-exchange, electrochemical and membrane techniques. These methods are cost-intensive (Alhassan *et al.*, 2020; Bose *et al.*, 2019; Singh *et al.*, 2000; Azbar and Turkman, 2000). The most popular and cost-effective is the precipitation of fluoride with lime. However, the resulting calcium fluoride, through sparingly soluble, still poses an environmental concern and must be safely disposed of Methods of the addition of potash alum $K_2(SO_4).Al_2(SO_4)_3.24H_2O$, calcium oxide CaO, and calcium chloro hypochlorite Ca(OCl)Cl accompanied through speedy blending, flocculation, and filtration, called the Nalgonda technique, has been adopted in several Indian States. Poly aluminum chloride (PAC) is reported to be a substitute for commercial alum because it produces less sludge than alum (Chhabra, 1997). All available alums increase the sulfate or chloride ion concentration except PAC. Biological defluoridation of drinking water cannot be a good alternative for health and speed grounds.

Objective and importance: For the removal of fluoride ions from groundwater to make it fit for drinking and industrial use, the main aim of this research was to prepare four types of inorganic composites (ICs) based on carbon, calcium, silica, and magnesium namely carbon inorganic composite (CIC), calcium inorganic composite (CaIC), silica inorganic composite (SiO_2IC) 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 (CIC, CaIC, SiO_2IC, and MgIC), commercial activated alumina (AA), activated carbon (AC), and an anion exchange resin (AER) Ceralite IR 400 (Cl^- form) were evaluated for fluoride removal by the column processat different fluoride concentrations, bed heights, pH and flow rates. It involved modification of CIC, CaIC, SiO_2IC, and MgIC with multivalent metal compounds to develop effective, eco-friendly, and low-cost Al-free sorbents for the removal of fluoride from aqueous solution and groundwater. The main purpose of the research was to develop methods to prepare cheaper and greener sorbents for the defluoridation of water from locally available inorganic and natural materials. The materials discovered through this research can be used to fabricate fluoride filters that can be used even in remote rural fluorosis endemic areas at the household level where piped water supply is not available. In the present work column tests on water samples from St. John's College Chemistry Department, Trans Yamuna, Gokul Pura, and Daresi that contained 2.0, 2.5, 3.5, and 4.2 mg/l of fluoride respectively were conducted using these sorbents. Despite voluminous work done on the use of these materials, no information is available on the effect of a contaminant on the sorption rate and sorption ability of fluoride (Mandal and Mayadevi, 2009). High sorption capacity for some sorbents and low for others has been reported but the extent of sorption is not promising commercial potential as a fluoride remediation product.

Experimental

Column operation: To establish the usefulness of the modified sorbents for in-line removal of fluoride from water, column studies were conducted (Saratale *et al.*, 2011; Vijaya and Krishnaiah, 2010; Yang *et al.*, 1999). Continuous downflow experiments were conducted using a perplex (polymethyl methacrylate) column (100 cm height x 4.5 cm inner diameter) for each contaminant. Five columns were placed in series that can provide different Empty Bed Contact Times (EBCTs of 10, 20, 30, 40, and 50 minutes) and Bed Heights (BHs of 15, 30, 45, 60, and 75 cm). The EBCT (the average residence time) is attained by dividing the bed volume along with voids by the flow rate. The columns were inclined differently to vary flow rates naturally without pumping. All the columns were packed with previously analyzed sorbent on a small plastic wire mesh support. To study the effect of influent concentration 100 ml of each 1.9, 3.8, 5.7, and 9.5 mg/l solutions were passed at the rate of 10 mL per minute through columns each having the BH 30 cm at a pH of 6.0 ± 0.2. The effect of flow rate was investigated using a column of BH 30 cm and varying the flow rate from 1 to 10 mL per minute. The effect of pH was studied by changing the pH of the feed from 4 to 10. To determine exhaustive capacity in all the experiments, the eluant was collected after the breakthrough and analyzed for fluoride (APHA *et al.*, 1998; Sahu *et al.*, 1998; Agrawal *et al.*, 2002). The initial amount of the fluoride in 20 mL feed minus the amount found in the effluent gave the amount of the fluoride retained by the sorbent. The process was continued until the amount of fluoride was the same in 20 ml of the effluent feed and the effluent. The percent amount of effluent fluoride removal was calculated.

Desorption study: To make the adsorption process more economical, it is necessary to regenerate the spent sorbent. Attempts were made to desorb fluoride from the loaded sorbents using various molarities of NaOH, calcium chloride, sodium dihydrogen phosphate, etc. at adjusted pH. The regeneration cycle was repeated three times. Distilled water was used in washing of the sorbent and dried later, after every cycle.

Results and Discussion

Effect of initial fluoride concentration and nature of sorbent: Defluoridation was in the order of AER >CaIC>MgIC> AA > SiO_2IC > CIC > AC over a wide range of initial concentration 1-10 mg/l at BH 30 cm, pH 6.0, temperature 25 °C, flow rate 10 ml per minute. Under these conditions from 3.8 mg/l solution, they could remove 19.7, 17.2, 16.6, 15.4, 14.7, 13.2, and 12.6% fluoride removal. This order of ICs i.e., CaIC>MgIC> SiO_2IC > CIC 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 and sorbent dose, but the equilibrium was attained in 2 hours for MgIC and AA, 2.5 hours for AC.

Removal decreases with rise in F^- concentration and bed height (BH) but increases with a decrease in flow rate. It is observed in the present case that the sorption of fluoride ions goes on increasing as their concentration decreases from 9.5 to 1.9 mg/l.

The removal was about 30% less than what it was in the batch process. Groundwater samples revealed 3 to 12% lesser removal when correlated to standard sodium fluoride solutions under identical conditions.

Effect of bed depth: The bed depth plays a significant role in the leachability of fluoride. The study was conducted by varying bed depth 15 cm to 75 cm. On increasing bed depth, removal % increases (Table 2).

Effect of pH: The effect of pH was studied by changing the pH of the feed from 4 to 10 with HCl and $Ca(OH)_2$. The solution pH considerably affected the quantity of pollutant elimination. The observed results are shown in Table 3. The results showed a variation of percent removal at various pH values.

Table 1. Removal % of Fluoride at Different Concentrations and BH 30 cm, pH 6.0, Temperature 25 °C, and Flow Rate 10 mL/min by the Column Process.

Water type	F- Concn. mg/L	AER	CaIC	MgIC	AA	SiO_2IC	CIC	AC
B	1.9	19.1	17.6	16.2	15.8	14.6	13.3	12.5
D	3.8	19.7	17.2	16.6	15.4	14.7	13.2	12.6
E	5.7	19.5	16.4	16.9	16.2	15.8	12.2	10.4
E	9.5	19.2	15.8	14.4	13.6	12.3	10.4	9.5
St. John's	2.0	16.8	15.2	14.8	13.4	13.8	12.3	10.1
Trans Yamuna	2.5	15.5	14.3	15.5	14.6	13.9	12.7	10.6
Gokul Pura	3.5	14.0	13.2	14.5	13.8	15.1	12.7	10.9
Dareshi	4.2	13.6	12.1	13.4	12.2	15.4	10.9	9.0

A specific relation of optimum pH was observed. Most of the sorbents showed the maximum fluoride removal percent at pH 6.

With an excess amount (20.0 mmol/l) of calcium ion, fluoride ions are removed from 5.0 to < 0.02 mmol/l in the pH range of 4 to 10. The reaction between fluoride and calcium ions was stoichiometric forming insoluble CaF_2. With an equal molar concentration of calcium ions, both the percentage fluoride removal and the removal rate decrease, especially in acid and alkaline pH ranges. With an excess amount (20.0 mmol/l) of aluminum ions, the fluoride concentration decreases to < 0.02 mmol/l in a narrow pH range of 5.5 to 7.5. Fluoride ions are removed by co-precipitation with aluminum ions (Arnesen, 1998).

Most of the solid trivalent metal compounds are effective in removing fluoride ions down to the concentration of 0.02 mmol/l or lower. The pH values where the lowest fluoride concentration was attained decreases in the order yet to be discovered by the proposed work. The dissolution of the material becomes appreciable around the pH where the lowest fluoride concentration is attained. Of the tetravalent metal compounds, only cerium compounds are effective in removing fluoride ions without a significant dissolution even at a pH of 2. fluoride ions are removed by the ion-exchange with the surface hydroxide group in a neutral pH range but by both ion-exchange and precipitation processes in an alkaline pH range.

Effect of flow rate: The effect of flow rate was investigated using a column of BH 30 cm and varying the flow rate from 1 to 10 ml/min (Table 4). Leaching increases considerably as the flow rate increases.

Encouraged by the results of studies on the effect of flow rate the following experiment was done: A slurry prepared from 10 g of aluminum treated sorbent and 100 ml of water had a pH of 8.5. All chemicals were of analytical reagent grade, and distilled water was used throughout. Sorption experiments were conducted at 20 °C in a column packed with 450 g of sorbent. The concentrations of fluoride in water feed on the column were 1, 5, 10, 20, 50, and 100 mg/l. The procedure was as follows (Singh *et al.*, 2003): 250 ml of a fluoride solution was first poured onto the column to moisten the sorbent. Then a 250 mL portion of the solution was placed in

Table 2. Removal % of Fluoride at Different Bed Heights and Initial Concentration 3.8 mg/l, pH 6.0, Flow Rate 10 ml/min, and Temperature 25 °C by the Column Process.

Bed Depth (cm)	AER	CaIC	MgIC	AA	SiO_2IC	CIC	AC
15	10.2	9.9	9.1	8.7	8.3	7.2	6.1
30	19.7	17.2	16.6	15.4	14.7	13.2	12.6
45	38.9	32.5	29.8	25.6	23.7	19.8	17.8
60	42.7	37.6	34.7	30.6	27.4	25.5	23.8
75	50.7	47.8	41.2	36.4	34.7	32.8	28.1

Table 3. Removal % of Fluoride at Different pH Values and F^- Concentration 3.8 mg/L, BH 30 cm, Flow Rate 10 ml/min and Temperature 25 °C by Column Process.

pH	AER	CaIC	MgIC	AA	SiO_2IC	CIC	AC
4	15.2	15.4	13.5	13.1	12.9	10.3	9.4
6	19.7	17.2	16.6	15.4	14.7	13.2	12.6
8	17.0	16.4	16.2	15.1	14.5	12.6	12.3
10	9.4	8.8	8.2	7.8	7.4	5.7	4.9

Table 4. Removal % of Fluoride at Different Flow Rates and Initial Concentration 3.8 mg/l, BH 30 cm, Temperature 25 °C, and pH 6 by Column Process.

Flow Rate (mL/min)	AER	CaIC	MgIC	AA	SiO_2IC	CIC	AC
1	60.7	57.8	49.5	44.6	43.2	40.2	35.6
3	50.7	47.8	41.2	36.4	34.7	32.8	28.1
7	42.7	37.6	34.7	30.6	27.4	25.5	23.8
10	19.7	17.2	16.6	15.4	14.7	13.2	12.6

the top reservoir and the draining rate was adjusted to ≤ 2.0 ml/hour, i.e., 40 drops per 60 minutes. The fluoride level in the effluent was determined every 24- or 48-hours by using a fluoride ion-selective electrode of Orion 720 A^+. Each experiment with the solution of a given concentration was run in duplicate with a fresh portion of the sorbent. At the minimal Fluoride concentration (1 mg/l), the Fluoride stage within the effluent first of all increased (maybe due to F^- of the sorbent) after which progressively decreased down to 0 mg/l after 60 hours. With higher Fluoride concentrations within the feed solutions, the Fluoride concentration within the effluent regularly decreased reaching 0 mg/l after 60 - 100 hours.

Regeneration or desorption study: Attempts were made to desorb arsenate from the loaded sorbents using various molarities of HCl, HNO_3, NaOH, and other chemicals. The regeneration cycle was repeated three times. After each cycle, the sorbent was washed with distilled water and dried 0.41 liter of the regenerating solution containing 0.14 mol/l calcium chloride and 0.08 mol/l sodium dihydrogen phosphate with pH adjusted to about 3 worked very profitably to regenerate the spent sorbent. The regenerating solution was also produced by dissolving the waste part of the sorbent in dil. HCl. During regeneration, the maximal of the pre-adsorbed fluoride is retained by using the sorbent (particularly CaIC) and the precipitating stage is apatitic. The "regeneration" is in this way a surface coating procedure (Christoffersen *et al.*, 1991). Regeneration of the saturated Al_2O_3 is performed by exposing the medium to 4% NaOH, in batch and/or in the column, producing in a few breakthrough volumes (BV) of caustic wastewater contaminated with fluoride (Bulusa and Nawlakhe, 1990). Residual caustic soda is then washed out and the medium is neutralized with a 2% sulfuric acid rinse. During this process, about 5-10% of the alumina is lost, and the capacity of the remaining medium is significantly reduced by 30-40%. After only 3-4 regenerations the medium must be replaced. Alternatively, to avoid on-site regeneration, the saturated alumina can be recycled to a dealer, who can adjust the capacity of the activated alumina to the desired value by using an appropriate mixture of fresh and regenerated media. In development water supply projects where the process is operated at the domestic level, the regeneration cannot be left to the users. Instead, a central chemical store is set up in each village, where the users can get the regeneration done along with motivation and encouragement to continue the fluorosis prevention. It must be mentioned that the regeneration may result in the presence of aluminum at a concentration greater than 0.2 mg/l if the pH is not fully readjusted to normal.

Conclusion

In the column process also the order of fluoride removal capacities for the sorbents was found to be AER >CaIC>MgIC> AA > SiO_2IC > CIC > AC over a wide range of initial concentration 1-10 mg/l at BH 30 cm, pH 6.0, temperature 25 °C, flow rate 10 ml per minute. Under these conditions from 3.8 mg/l solution, they could remove 19.7, 17.2, 16.6, 15.4, 14.7, 13.2, and 12.6% fluoride removal. This order of ICs, i.e., CaIC>MgIC> SiO_2IC > CIC is probably due to several factors such as particle size, ionic potential, pH, surface area, and environmental conditions. The leaching order should be the reverse of the sorption order. The sorption of fluoride ions goes on increasing as their concentration decreases from 9.5 to 1.9 mg/l. Leaching increases as the flow rate increases. The solution pH considerably affected the quantity of pollutant elimination. The results showed a variation of percent removal at various pH values. A specific relation of optimum pH was observed. Most of the sorbents showed the maximum fluoride removal percent at pH 6. The sorption increased with increasing BH, but the equilibrium was attained in 2 hours for MgIC and AA, 2.5 hours for AC. Leaching increases considerably as the flow rate increases. At the minimal Fluoride concentration (1 mg/l), the Fluoride stage within the effluent first of all increased (maybe due to F^- of the sorbent) after which progressively decreased down to 0 mg/l after 60 hours. With higher Fluoride concentrations within the feed solutions, the Fluoride concentration within the effluent regularly decreased reaching 0 mg/l after 60 - 100 hours. It was concluded that CaIC, MgIC, SiO_2IC, and CIC are effective sorbents for F^- ions. CaIC and MgIC are especially effective at a high concentration of fluoride (F^-) ion in water. Removal decreases with rising in F^- concentration and bed height (BH) but increases with a decrease in flow rate. It is observed in the present case that the sorption of fluoride ions goes on increasing as their concentration decreases from 9.5 to 1.9 mg/l. The removal was about 30% less than what it was in the batch process. Groundwater samples revealed 3 to 12% lesser removal when correlated to standard sodium fluoride solutions under identical conditions. A mixed solution containing 0.14 mol/l calcium chloride and 0.08 mol/l sodium dihydrogen phosphate with pH adjusted to about 3 can be profitably used to regenerate the spent sorbent. CaIC, MgIC, SiO_2IC, and CIC are ecofriendly sorbents, and their sorption ability is much higher than others. They can be further modified to have enhanced fluoride sorption capacity to be used as a primary remedy for fluoride pollution in wastewater or groundwater like AER.

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