

# Development of Iron Oxide Coated Sand (IOCS) Adsorbent for Defluoridation Technology

Esayas Alemayehu, Thamineni Bheema Lingaiah

**Abstract** - Although safe and reliable water supply is badly needed, the installation of advanced defluoridation plants in regions with low economic resources such as Ethiopia is, at present, very scarce mainly due to operational consideration and settlement characteristics of the people. In such cases the development and popularizing of low cost fluoride removal technologies, which does not demand much money and skilled manpower, is important. Therefore, this study focuses on the removal of fluoride from groundwater by using Iron oxide coated sand (IOCS), which could be used as an alternative defluoridation adsorbent. The influence of design parameters such as contact time, adsorbent dose, solution pH, and initial fluoride concentration was investigated. Basic process characteristics were determined under batch conditions. Fluoride adsorption onto IOCS was strongly pH dependent. The maximum adsorption capacity for IOCS was found to be 136 mg kg<sup>-1</sup>. This result was obtained at optimized conditions of solution pH (4.0), contact time (8.0 h), dose (15.0 g L<sup>-1</sup>) and initial fluoride concentration (5.0 mg L<sup>-1</sup>). The uptake of fluoride slightly increased with increasing equilibrium concentration of fluoride ion in solutions. By increasing the initial concentration of fluoride from 3.0 to 10.0 mg L<sup>-1</sup>, the adsorption capacity, increased from 90.73 mg kg<sup>-1</sup> to 252.17 mg kg<sup>-1</sup>. IOCS was found to be promising adsorbent for defluoridation technology.

**Keywords:** Adsorption Technology, Batch Experiments, Defluoridation, IOCS

## I. INTRODUCTION

Iron oxide coated sand (IOCS) is basically a by-product obtained from iron removal groundwater treatment plants i.e. sand used in filters, is coated by iron oxide during filtration process in the plant and time to time it has to be replaced by new sand. Sharma [1] analysed IOCS from twelve different groundwater treatment plants in the Netherlands and found that IOCS had a very high porosity (up to 110 times) and a very large specific surface area (5-200 times) compared to new sand. It was also found that the iron content of the coatings ranged from 27% to 45% as well as the coating developed on a filter grain was not uniform and different regions of the coating on a sand grain could have a different elemental composition and surface characteristics. Additionally, it was observed that iron (II) adsorption capacities of the coated sand from different plants increased with the increase in the time in use and the iron content of the coating.

However, the average annual increase of iron content of the coatings and the iron adsorption capacity were different for the coated sands from different plants, likely due to the difference in water quality, process conditions applied, and time in use. The grain size of the filter sand increased and their density decreased with the development of the coating [2]. The development of the iron oxide coating on the filter media in iron removal plants may be affected by the water quality and the treatment schemes used in the plant i.e. the ground water quality (pH and concentrations of Fe<sup>2+</sup>, Mn<sup>2+</sup>, Ca<sup>2+</sup>, TOC etc.); the process condition applied (filtration rate, depth of supernatant, depth of the filter media, back wash conditions, aeration efficiency); and type and characteristics of the filter media (grain size, specific surface area) [3]. The presence of such coatings as iron (hydro) oxide can remove iron as well as it can adsorb various inorganic and organic compounds [1, 4-5].

It has long been recognized that, if the adsorbent (solid surface) is chosen carefully and the solution chemistry is adjusted appropriately, adsorption-based processes are capable of removing various contaminants over a wider pH range and to much lower levels than processes based on precipitation [6-10]. In addition to offering more reliable and more efficient removal of uncomplexed pollutants, adsorption processes can often remove inorganically and organically- complexed ions that would not be removed by conventional treatment methodology [11-15].

Previous studies mentioned that IOCS could be used as adsorbent in the removal of different heavy metals from water and wastewater [1, 5, 16]. Column packed with the media (IOCS) were found to be successful in removing uncomplexed and ammonia-complexed cationic metals (Cu, Cd, Pb, Ni, Zn), as well as some oxyanionic metals (SeO<sub>3</sub>, AsO<sub>3</sub>) from simulated and actual waste schemes over a wide range of metal concentrations [4]. The ability of IOCS to adsorb iron (II) (a common constituent of ground water), arsenic (one of the black listed contaminates) as well as cadmium, lead, nickel and cooper (some of priority pollutants) from ground water has reported [1, 5, 17]. However, the removal efficiency of this medium to adsorb fluoride (number one groundwater quality problem) has not been studied in detail.

Many countries have regions where the water contains more than 1.5 mg L<sup>-1</sup> of fluoride due to its natural presence in the earth's crust, or discharge by agricultural and industrial activities, such as steel, aluminium, glass, electroplating. For example, in Southern California Lakeland the fluoride concentration in ground water is about 5 mg L<sup>-1</sup>. In Mexico, 5 million people are affected by fluoride in drinking water.

Manuscript published on 28 February 2016.

\* Correspondence Author (s)

Esayas Alemayehu, Assoc. Prof., at School of Civil & Environmental Engineering, Jimma Institute of Technology, Jimma University, Jimma, Ethiopia.

Thamineni Bheema Lingaiah, Asst. Prof., at Jimma Institute of Technology, Jimma University, Jimma, Ethiopia.

© The Authors. Published by Blue Eyes Intelligence Engineering and Sciences Publication (BEIESP). This is an [open access](http://creativecommons.org/licenses/by-nc-nd/4.0/) article under the CC-BY-NC-ND license <http://creativecommons.org/licenses/by-nc-nd/4.0/>

In 1993, fifteen of India's thirty two states were identified as endemic for fluorosis [18-21]. In some regions of Africa the fluoride concentration of ground water reaches 20 mg L<sup>-1</sup> [22-23]. In the Great Rift Valley regions especially in the dry arid and semiarid areas of Ethiopia fluoride concentration is extremely high due to volcanic action. Research conducted in rift valley of Ethiopia revealed that over 40% of deep and shallow wells and springs used for drinking have fluoride levels above the WHO optimal level of 1.5 mg L<sup>-1</sup> for fluoride. Other research conducted in rift valley of Ethiopia also revealed that more than 73.6% of the water samples taken in the rift valley areas had a concentration exceeding the permissible limit (up to 14.8 mg L<sup>-1</sup>) [26]. At present the vast majority of rural population and a considerable number of urban populations are fetching water from unsafe sources like high level fluoride containing groundwater [27–29]. Using the extrapolated 2005 census figures reveal that out of the 10 million population of the Rift Valley Ethiopia almost 8.5 million (i.e. below 40 years of age) would be at risk of developing dental and skeletal fluorosis if they continue to depend on drinking water from deep wells high fluoride

concentrations [24-25]. In this case, groundwater to be used by a community needs some method of eliminating high level of fluoride. Therefore, this study focuses on the removal of fluoride from a modelled groundwater by using IOCS.

## II. MATERIALS AND METHODS

### II.1 Adsorbent – IOCS

IOCS coated in laboratory has been used as an adsorbent in this study. Different authors have used different methods and experimental set-ups to coat the adsorbent (sand) with iron oxide. Table 2.1 presents Iron coating techniques applied by different group of researchers [3, 4, 31, 33-34]. High temperature treatment/precipitation, soaking and using filter column simulating iron removal filter are the main types of coating methods. Temperature, pH and the age of oxide seriously affect the nature and the properties of iron oxide that can be formed on the surface of the adsorbent. In this study Benjamin et al [4] coating method was used to coat sand.

Table 2.1. Iron coating methods used by different researchers

Description	Temp.°C	Method
2.5 M FeCl <sub>3</sub> + sand mixed and heated.	110	Heating [4]
0.01 M FeSO <sub>4</sub> + GAC, soaked for 4 hr. and dried	80 for drying	Soaking [33]
2M Fe(NO <sub>3</sub> ) <sub>3</sub> .9H <sub>2</sub> O + sand, pH 11, mixed and heated	110	Heating [34]
Water containing ferrous filtered at 5 m/h in column filled with sand	Room temperature	Filtration [3]
Iron colloids/precipitate formed, mixed with sand and heated	100	Flocculation and heating [31]

### II.2. Analysis of the iron content of coated media

In order to characterise the adsorbent (IOCS) used in this study, surface extractable iron contents of the coating were analysed. 4 gm of IOCS was added to a solution with 100 ml HNO<sub>3</sub> (65%) and 100 ml demi-water. The mixture was boiled until 50 ml was left in the beaker. Finally it was diluted to 100 ml with demi-water and Fe concentration of samples (2-samples) were analysed with the Phenanthroline Method [35]. The average results are summarised in table 2.2. The method of coating of iron oxides onto sand needs optimization to get an effective coating which gives maximum fluoride adsorption capacity and minimum residual iron in the filtrate.

Table 2.2. Surface extractable iron contents of IOCS

No. of Samples	mg Fe gm <sup>-1</sup> IOCS
Sample I	268.6
Sample II	294.5
Average (mg/g IOCS & %)	281.5 (28.15%)

### II.3. Grain size distribution and sieve analysis

Sieve analysis and related calculations were performed to determine the grain size distribution, the effective size (d<sub>10</sub>) and uniformity coefficient (UC) of IOCS. Wet IOCS was rinsed with water and dried in an oven at 40 °C for 3 hours. One (1) kg of dried IOCS was sieved with sieve equipment (Test Method-ASTM D 422) using ten standard sieves of sizes 0.5, 1.0, 1.2, 1.8, 2.0, 2.5, 3.0, 3.5, 3.8, and 4.0 mm. A

sieving time of 5 minutes, with 5 seconds shaking interval at 1.0 mm amplitude was employed. Figure 2.1 presents grain size distribution curve for IOCS. The d<sub>10</sub> and d<sub>60</sub> were found to be 1.45 and 2.8 mm respectively. The calculated UC was 1.93. The prepared adsorbents were placed in air tight container for further use. These results are in agreement with the findings of previous researches [1].

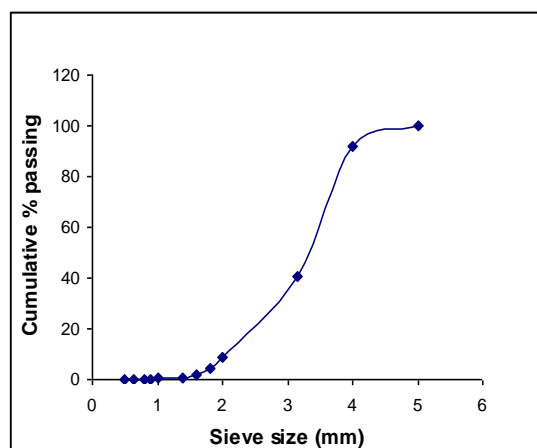


Figure 2.1: Grain size distribution curve for IOCS

#### II.4. Reagents and Apparatus

All the reagents used were analytical reagent grade. Stock solution of fluoride for calibration of the spectrophotometer was prepared by dissolving 0.22 g of sodium fluoride in 1 L of distilled water according to standard methods. Similarly, modeled ground water with various initial concentration of fluoride was prepared as needed. Alizarin red solution was prepared by dissolving 0.75 g of alizarin reds in distilled water. Zirconyl acid reagent was prepared by dissolving 0.354 g zirconyl chloride octahydrate in about 600-800 mL of distilled water and then mixing with 101 mL conc HCl and 33.3 mL conc H<sub>2</sub>SO<sub>4</sub> slowly. The rest of the chemicals and reagents were prepared according to standard procedure [35].

#### II.5. Model water and pH-control

Model water was prepared in volumetric flask by adding enough amounts of demineralised water, HCO<sub>3</sub><sup>-</sup> and the required amount of 2M HCl and 2M NaOH to obtain desired pH. The desired initial concentration of F<sup>-</sup> was prepared from the stock solutions. Experimental test solutions were prepared in a 0.50 L capacity polyethylene bottles by adding 500-ml model water and fixed amount of IOCS. To avoid pH change during experiments due to CO<sub>2</sub> escape, bottles were capped and kept closed during the whole experiments. Moreover 250 mg HCO<sub>3</sub><sup>-</sup> L<sup>-1</sup> were added in the solution in order to maintained almost constant pH. The pH variation during the experiments was within 0.08 – 0.13 units in average.

#### II.6. Batch Experimental set-up

Laboratory scale batch adsorption experiments were conducted to assess applicability of IOCS as adsorbent for the removal of fluoride. Fixed amount of IOCS was put into a 500 ml polyethylene bottles containing model water. The bottles were filled with model water, capped and placed at top of mechanical shaker. Separated capped bottle was placed for each sample. All the experiments were done in duplicate at room temperature 21 ± 2°C. Control experiments had been carried out for each set of experiments.

#### II.7. Shaking Speed

At first, fluoride removal experiments were conducted for IOCS with high shaking speed of 350 rpm. Later on, it was discovered that applied shaking speed could wear off the coat from the sand grains, which may affect adsorption processes onto IOCS. Therefore completed experiments were repeated with constant and optimum shaking speed of 200 rpm using HY-2 (A) Speed Adjusting Multi-purpose Vibrator. It is assumed that this applied shaking speed allows all the surface area to come in contact with fluoride ions over the course of the experiment without wearing off the coat from the grains.

#### II.8. Filtration of sample through 0.45 µm

Preliminary batch experiments were conducted to assess the effect of using 0.45µm pore size cellulose acetate membrane filter on F<sup>-</sup> removal efficiency using IOCS. About 5-mg L<sup>-1</sup> initial concentration of F<sup>-</sup> was added in model water containing 4 g IOCS L<sup>-1</sup>. The pH of 6.8 was adjusted with 2.0 M HCl and NaOH and the contents were shaken (200 rpm). Samples were collected by syringe through the tube after 24 hours of contact time, half of the sample was filtered through the membrane (in order to

separate solid and liquid), and other was unfiltered through the membrane. Both samples (filtered and unfiltered) were analysed for fluoride concentration. The preliminary results indicate that the effect of using 0.45µm pore size cellulose acetate membrane filter on F<sup>-</sup> removal efficiency was negligible (maximum of 0.74 percentage difference between filtered and non-filtered final samples was observed). Thus, for all consecutive experiments 0.45 µm pore size membrane filter had been used to separate solid from liquid by neglecting its effect.

#### II.9. Data analysis and quality management

Standard methods were applied for any procedure of the set of experiments [35]. All the chemical reagents used are of analytical grade and their expiry dates was checked. Instruments were calibrated at each batch of test and their sensitivity was also checked. Average duplicate measurements were reported. Blank and control experiments were run. Data of the results of all tests was honestly and cautiously recorded on a prepared data registration format.

#### II.10. Kinetic studies

IOCS samples (7.5 g) were dispersed in 500 ml of fluoride solutions with a concentration of 5 mg F<sup>-</sup> L<sup>-1</sup> and stirred for 0 - 12 h, with control of solution pH achieved by addition of aqueous solutions of dilute HCl (0.1 M) or NaOH (0.1 M). Aliquots (10 ml) were extracted at selected time intervals, separated by centrifugations, and diluted to 100 mL. The amount of fluoride adsorbed at time t, q<sub>t</sub> and A(%) was calculated from the mass balance equation:

$$q_t = (C_o - C_t) V/M \quad (1)$$

$$A (\%) = \{(C_o - C_t)/C_o\} 100 \quad (2)$$

where: C<sub>o</sub> = initial concentration of fluoride in contact with adsorbents (mg L<sup>-1</sup>), q<sub>t</sub> = The amount of fluoride adsorbed per unit mass of the adsorbent (mg kg<sup>-1</sup>), M = dry mass of IOCS (kg), C<sub>t</sub> = mass concentration of fluoride in aqueous phase, control correction included, at time t (mg L<sup>-1</sup>), V = initial volume of the aqueous phase in contact with IOCS during the adsorption test (L), A(%) = adsorbed amount give as percentage at time t<sub>i</sub> (%).

#### II.11. Equilibrium studies

Separate sets of equilibrium batch experiments were performed to investigate the effect of pH, adsorbent dose and initial F<sup>-</sup> concentration on adsorption. The solution in each set of bottle had different pH values (2 to 10), IOCS dose (5 to 50 g L<sup>-1</sup>) and initial F<sup>-</sup> concentrations (3.0 to 10 mg L<sup>-1</sup>). All other experimental conditions were adjusted as described above. RESULTS AND DISCUSSION

#### III.1. Effect of Contact Time

The influence of contact time was investigated by mixing an initial fluoride concentration of 5 mg L<sup>-1</sup> with 15 g of IOCS per liter. The mixture was shaken on a horizontal shaker for contact times of 0, 2, 4, 8 and 12 h. After a desired contact time the solution was allowed to stand to settle the particles and then 10 ml of the supernatant solution was centrifuged at 2000 rpm. Finally, residual fluoride was analyzed using spectrophotometer at 550 nm applying stannous chloride method. Figure 3.1 and 3.2 and table 3.1 show the effect of contact time on the removal of fluoride using IOCS.



Removal percentage (%) as well as  $q_t$  increased rapidly in the first 2 h (60% removal efficiency) and then, slowed down as equilibrium was approached (Fig. 3.1). The increase was not significant after 8 h. Therefore, for all other batch experiments, the contact time was maintained as 8 h. The fast initial uptake rate may be attributed to availability While the superficial sites are occupied within the first few minutes of contact between IOCS and fluoride, sorption

of a large number of bare adsorption sites at the initial stage. As the sites are gradually filled up, adsorption becomes slow and the kinetics becomes more dependent on the rate at which the fluoride ions is transported from the bulk phase to the actual adsorption sites (Fig. 3.2). The observed behavior can also be interpreted in terms of two phase process. inside nano and mesoporous coated sand is diffusion controlled and time dependent [28].

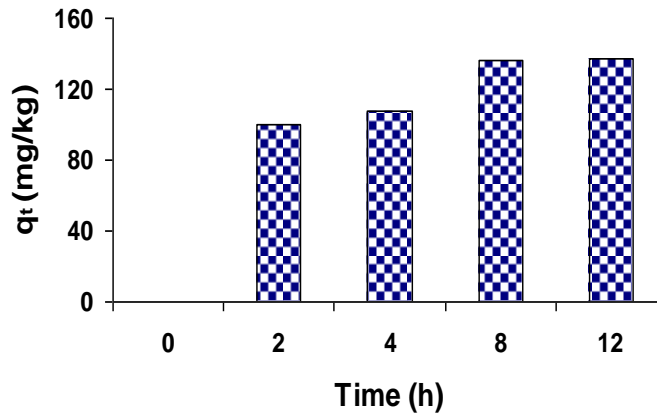


Figure 3.1: Effect of contact time on the amount of adsorbed fluoride per unit mass of the IOCS (major experimental conditions: pH = 4,  $C_o = 5 \text{ mg L}^{-1}$ , Dose  $15 \text{ g L}^{-1}$ , and Time 0 to 12 h)

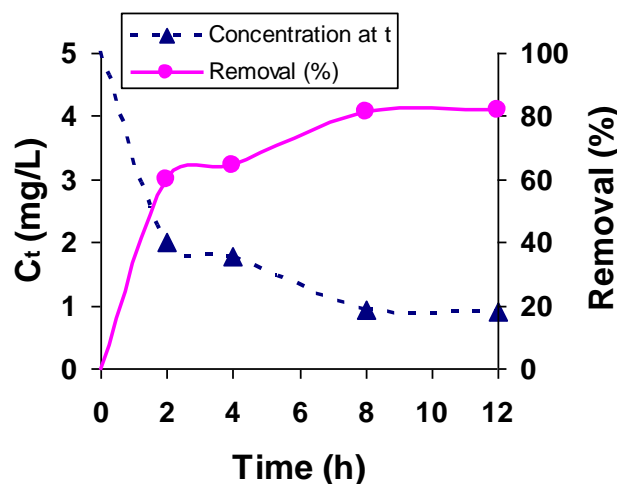


Figure 3.2: Effect of contact time on the removal percentage of fluoride using IOCS (major experimental conditions: pH = 4,  $C_o = 5 \text{ mg L}^{-1}$ , Dose  $15 \text{ g L}^{-1}$ , and Time 0 to 12 h)

Table 3.1: Effect of contact time on the removal of fluoride using IOCS as an adsorbent (major experimental conditions: pH = 4,  $C_o = 5 \text{ mg L}^{-1}$ , Dose  $15 \text{ g L}^{-1}$ , and Time 0 to 12 h)

Time (h)	$C_t$ ( $\text{mg L}^{-1}$ )		$\chi$ ( $\text{mg L}^{-1}$ )	$S_i = (x_i - \chi)^2$	Removal (%)	$q_t$ ( $\text{mg kg}^{-1}$ )
	$C_{t1}$ ( $\text{mg L}^{-1}$ )	$C_{t2}$ ( $\text{mg L}^{-1}$ )				
0	5.00	5.06	5.03	0.0009	-0.60	-1.00
2	1.96	2.04	2.00	0.0016	60.00	100.00
4	1.67	1.89	1.78	0.0121	64.40	107.33
8	0.93	0.91	0.92	0.0001	81.60	136.00
12	0.86	0.93	0.90	0.0012	82.10	136.83
$S$				0.0039		
$SE_x$				0.0028		

Where:  $C_t$  = mass concentration of fluoride in aqueous phase at time  $t$  ( $\text{mg L}^{-1}$ );  $\chi$  = average value of the duplicate experiments ( $\text{mg L}^{-1}$ );  $S_i$  = standard deviation for each experiment;  $S$  = sample standard deviation ( $\sum S_i / N - 1$ );  $SE_x$  = standard error of the mean ( $S / n^{0.5}$ );  $R(\%)$  = adsorbed amount give as percentage at time  $t_i$  (%);  $q_t$  = the amount of fluoride adsorbed per unit mass of the adsorbent ( $\text{mg kg}^{-1}$ )

### 3.2 pH effect determination

The effect of pH on the fluoride adsorption by the adsorbents has been examined by varying the pH of the solution (2, 4, 6, 8, and 10). Initial fluoride concentration of  $5 \text{ mg L}^{-1}$  was mixed with 50 g of adsorbents in 500 ml solution and be shaken over a shaker at 200 rpm for the attained equilibrium time,  $t_e$ , to examine this effect. The pH of the solution was adjusted to the required pH using 0.1M HCL and/or 0.1M NaOH. The effects of pH on the removal of fluoride in the aqueous solution are shown in Figure 3.3 and 3.4 and table 3.2. The pH of the aqueous solution is an important variable which controls the adsorption of the ions at the adsorbent interfaces. It is known that its effect on the adsorption capacity of the adsorbents may be attributed to

the combined effect of pH on the nature of the adsorbent surfaces as well as the adsorbed solute species. The fluoride adsorption was found to be varying with respect to initial solution pH. As can be seen in Fig.3.3, the amount removed increases from 22.4% to 82% as the pH decreases from 10 to 2. The variation of removal of fluoride at various pH can be explained on the basis of specific adsorption resulting from surface complexation. This is in agreement with previous results [28-29] which show that amphoteric oxides favour the removal of anions at lower pH while removal of cations increases with increasing pH. Larger fluoride uptake at low pH values indicates that functional oxide groups of the adsorbent are protonated, which favour the removal of anions. Considerable reduction in fluoride removal efficiency was observed at higher pH. The reduction in fluoride removal in the alkaline pH range may be due to the competition from  $\text{OH}^-$  ions present in the aqueous solution with fluoride for the sorption site. The optimal pH for adsorption was found to be between 2 and 4 (Fig.5.4). Thus, we have chosen an initial pH ( $\text{pH}_{\text{int}}$ ) value of 4 for the fluoride adsorption experiments.

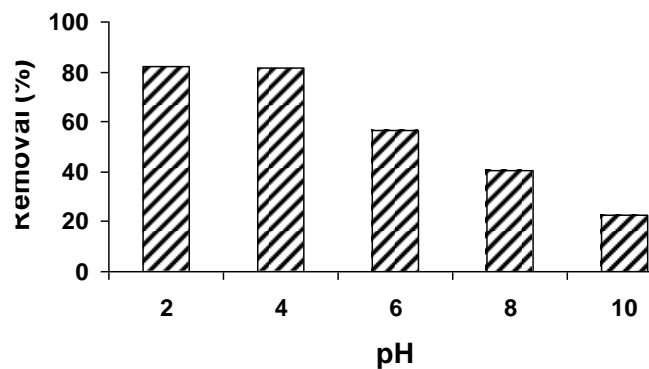


Figure 3.3: Effect of pH on the removal percentage of fluoride using IOCS (major experimental conditions: Time = 8h,  $C_0 = 5 \text{ mg L}^{-1}$ , Dose  $15 \text{ g L}^{-1}$ , and pH 2 to 10)

Table 3.2: Effect of pH on the removal of fluoride using IOCS as an adsorbent (major experimental conditions: Time = 8h,  $C_0 = 5 \text{ mg L}^{-1}$ , Dose  $15 \text{ g L}^{-1}$ , and pH 2 to 10)

pH	$C_t$ ( $\text{mg L}^{-1}$ )		$\chi$ ( $\text{mg L}^{-1}$ )	$S_i = (x_i - \chi)^2$	Removal (%)	$q_t$ ( $\text{mg/ kg}^{-1}$ )
	$C_{t1}$ ( $\text{mg L}^{-1}$ )	$C_{t2}$ ( $\text{mg L}^{-1}$ )				
2	0.900	0.890	0.895	0.000025	82.10	136.83
4	0.930	0.910	0.920	0.000100	81.60	136.00
6	2.140	2.210	2.175	0.001225	56.50	94.17
8	3.060	2.890	2.975	0.007225	40.50	67.50
10	4.120	3.640	3.880	0.057600	22.40	37.33
			$S$	0.016544		
			$SE_x$	0.011698		

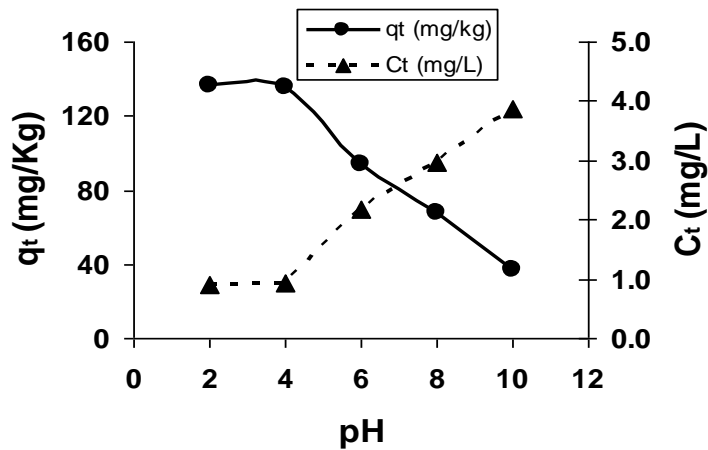


Figure 3.4: Effect of pH on the amount of adsorbed fluoride per unit mass of the IOCS (major experimental conditions: Time = 8h,  $C_o = 5 \text{ mg L}^{-1}$ , Dose  $15 \text{ g L}^{-1}$ , and pH 2 to 10)

### 3.3 Effect of adsorbent dose

The influence of the amount of adsorbents on the adsorption of fluoride by the adsorbents was evaluated varying the dose (5, 15, 30, and  $50 \text{ g L}^{-1}$ ). The initial fluoride concentration of  $5 \text{ mg L}^{-1}$  was mixed with the adsorbents and the mixture was shaken horizontally on a horizontal shaker at 200 rpm at room temperature for  $t_e$ . Figure 3.5 and 3.6 and table 3.3 show the effect of adsorbent dose on the removal of fluoride using IOCS. Adsorbent dosage is an important design parameter because it quantifies the capacity of an adsorbent for a given initial

concentration of adsorbate. Thus, the effects of IOCS dose on adsorption of fluoride ions were also investigated. By changing the dose ratio from 5 to  $50 \text{ g L}^{-1}$ , the removal of fluoride ions significantly increases from 67.6 to 81.4%. This observation can be attributed to the increase of the availability of free adsorption sites. However, an adsorbent dosage more than  $15 \text{ g L}^{-1}$  does not exhibit an enhanced removal. Therefore the maximum removal is exhibited at ( $15 \text{ g L}^{-1}$ ) dosage. So, this amount of dose was used for further study.

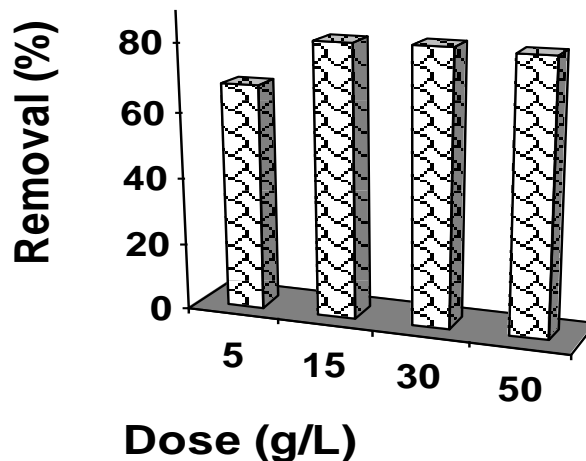


Figure 3.5: Effect of dose on the removal percentage of fluoride using IOCS (major experimental conditions: Time = 8h,  $C_o = 5 \text{ mg L}^{-1}$ , pH = 4 and Dose 5 to  $50 \text{ g L}^{-1}$ )

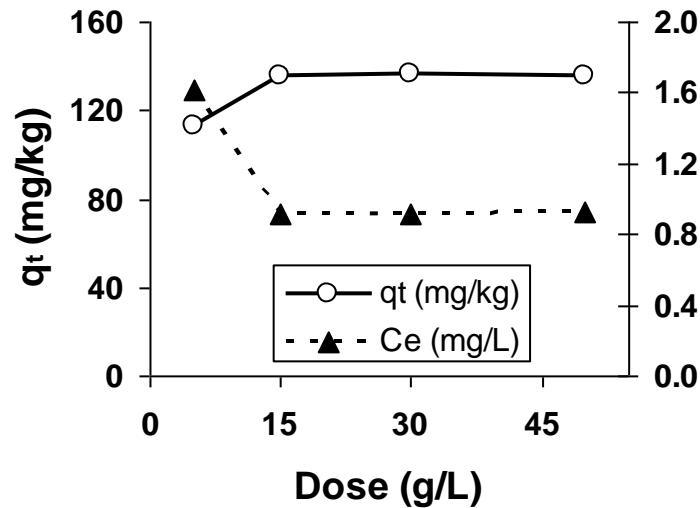


Figure 3.6: Effect of dose on the amount of adsorbed fluoride per unit mass of the IOCS (major experimental conditions: Time = 8h,  $C_0 = 5 \text{ mg L}^{-1}$ , pH 4, and dose 5 to 50  $\text{g L}^{-1}$ )

Table 3.3: Effect of dose on the removal of fluoride using IOCS as an adsorbent (major experimental conditions: Time = 8h,  $C_0 = 5 \text{ mg L}^{-1}$ , pH = 5, and dose 5 to 50  $\text{g L}^{-1}$ )

Dose ( $\text{g L}^{-1}$ )	$C_t$ ( $\text{mg L}^{-1}$ )		$\chi$ ( $\text{mg L}^{-1}$ )	$S_i = (x_i - \chi)^2$	Removal (%)	$q_t$ ( $\text{mg/kg}$ )
	$C_{t1}$ ( $\text{mg L}^{-1}$ )	$C_{t2}$ ( $\text{mg L}^{-1}$ )				
5	1.560	1.680	1.620	0.0036	67.60	112.67
15	0.930	0.910	0.920	0.0001	81.60	136.00
30	0.890	0.930	0.910	0.0004	81.80	136.33
50	0.980	0.880	0.930	0.0025	81.40	135.67
			$S$	0.002200		
			$SE_x$	0.001556		

### 3.4 Effect of initial concentration

Initial fluoride concentration was varied (3, 4, 6, 8, and 10  $\text{mg L}^{-1}$ ) to examine its influence on the adsorption of properties of IOCS. The optimum dose of the adsorbents was mixed in 500 ml solution of the fluoride and shaken on the horizontal shaker at 200 rpm for  $t_e$  at room temperature.

The fluoride adsorption efficiencies and calculated adsorption densities depending on the initial concentration are shown in Fig 3.7 and table 3.4 as expected, fluoride

adsorption percentage decreased by increasing initial concentration. While the fluoride adsorption yield was found as 90.7% for 3  $\text{mg L}^{-1}$  of initial concentration, this value was 75.6% for that of 10  $\text{mg/L}$ . however, amount of fluoride adsorbed per unit mass of the adsorbent increased gradually with more and more fluoride ions in the solution. With changing the concentration from 3 to 10  $\text{mg L}^{-1}$ , the uptake increases from 90.73 to 252.17  $\text{mg}$  fluoride per kilogram of IOCS (table 3.4).

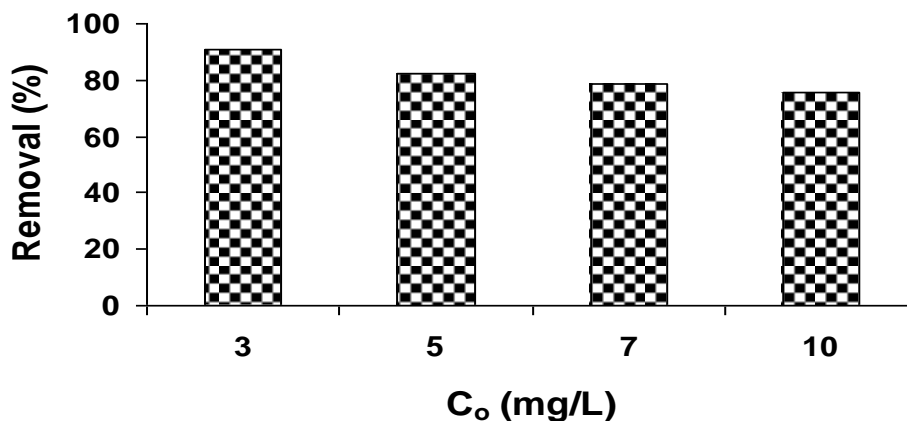


Figure 3.7: Effect of initial concentrations of fluoride on the removal percentage using IOCS (major experimental conditions: Time = 8h, pH = 4, Dose = 15  $\text{g L}^{-1}$ , and  $C_0 = 3$  to 10  $\text{mg L}^{-1}$ )

**Table 3.4: Effect of initial concentrations of fluoride on the removal percentage using IOCS (major experimental conditions: Time = 8h, pH = 4, Dose = 15 g L<sup>-1</sup>, and C<sub>0</sub> = 3 to 10 mg L<sup>-1</sup>)**

Co (mg L <sup>-1</sup> )	C <sub>t</sub> (mg L <sup>-1</sup> )		$\chi$ (mg L <sup>-1</sup> )	$S_i = (x_i - \chi)^2$	Removal (%)	$q_t$ (mg kg <sup>-1</sup> )
	C <sub>t1</sub> (mg L <sup>-1</sup> )	C <sub>t2</sub> (mg L <sup>-1</sup> )				
3	0.310	0.246	0.278	0.001024	90.73	90.73
5	0.879	0.910	0.895	0.000240	82.11	136.85
7	1.510	1.490	1.500	0.000100	78.57	183.33
10	2.410	2.460	2.435	0.000625	75.65	252.17
			$S$	0.000663		
			$SE_x$	0.000469		

### III. CONCLUSION

This study provides valuable information about the adsorption behaviour of IOCS in aqueous solutions, and its efficiency to reduce fluoride mobility and availability. It is very interesting to note that IOCS is able to reduce the fluoride concentration beyond the safe limit established by the World Health Organization of 1.5 mg L<sup>-1</sup>. Although the study parameters such as the contact times, adsorbent doses, and initial fluoride concentrations of the solution significantly affect the removal efficiency, F<sup>-</sup> uptake is primarily a function of pH. The amount F<sup>-</sup> removed increases as the pH decreases. Defluoridation technology using IOCS, which is low cost and high surface area, could be technically feasible, especially in regions with low economic resources such as Ethiopia.

### REFERENCES

- Sharma S. K. (2001) Adsorptive Iron Removal from Groundwater. Swets and Zeitlinger B. V., Lisse.
- Sharma, S. K. (1997) Iron Removal in Water Treatment by Sorption of Iron (II) onto Filter Media. M. Sc. Thesis, IHE, Delft.
- Sharma, S.K., Ijpelaar, G.F., Schippers, J.C. (2000) Iron oxide Coating Development on Filter Media, Transactions of the Filtration society, 1 (3), 68-72
- Benjamin, M.M., Sletten, R.S., Bailey, R.P., Bennett, T. (1996) Sorption and Filtration of Metals Using Iron-Oxide-Coated Sand, *Water Research*, 30 (11). 2609-2620
- Petrusevski, B, Boere, J., Shahidullah, S.M., Sharma, S.K., Schippers, J.C. (2000) Adsorbent Based Point Of Use System For Arsenic Removal In Rural Areas, Proceeding Of Conference On Innovation In Conventional And Advanced Water Treatment Processes, Amsterdam
- Dugger, D. L. et al, (1964) The Exchange Of Twenty Metal Ions At The Weakly Acidic Silanol Group Of Silica Gel. *J. Phys. Chem.* 68, 757.
- James, R. O. and Healy T. W. (1972) Adsorption of Hydrolyzable Metal Ions at the Oxide Water Interface. II. Charge Reversal Of SiO<sub>2</sub> And TiO<sub>2</sub> Colloids By Adsorbed Co (II), La (III), And Th (IV) As Model Systems. *J. Colloid Interface Sci.* 40, 53 – 64.
- Kinniburgh, D. G., Jackson M. L. and Syers J. K. (1976) Adsorption Of Alkaline Earth, Transition, And Heavy Metal Cations By Hydrous Oxide Gels Of Iron And Aluminum. *Soil Sci. Soc. Am. J.* 40, 796 – 799.
- Schindler, P. W., Furst, B., Dick, B. and Wolf, P. U. (1976) Ligand Properties of Surface Silanol Groups. I. Surface Complex Formation with Fe<sup>3+</sup>, Cu<sup>2+</sup>, Cd<sup>2+</sup>, And Pb<sup>2+</sup>. *J. Colloid Interface Sci.* 55, 469 – 475.
- Benjamin M. M. (1983) Adsorption and Surface Precipitation of Metals on Amorphous Iron Oxyhydroxide, *Environ. Sci. Technol.* 17, 686 – 692.
- Davis J. A. and Leckie J. O. (1978) Effect Of Adsorbed Complexing Ligands On Trace Metal Uptake By Hydrous Oxides. *Environ. Sci. Technol.* 12, 1309 - 1315.
- Bourg A. and Schindler P. W. (1978) Ternary Surface Complexes. I. Complex Formation In The System Silica- Cu (II) – Ethylenediamine. *Chimia* 32, 166 – 168.
- Elliott, H. A. and Huang C. P. (1980) Adsorption Of Some Copper (II)- Amino Acid Complexes At The Solid Solution Interface. Effect Of Ligand and Surface Hydrophobicity. *Environ. Sci. Technol.* 14, 87 – 93.
- Benjamin M. M., Hayes K. F. and Leckie J.O. (1982) Removal Of Toxic Metals From Power – Generation Waste Streams By Adsorption And Coprecipitation. *Journal WPCF*, 54(11) 1472-1481.
- Dillard, J. G. and Schenick C. V. (1986) Interaction of Co (II) And Co (III) Complexes on Synthetic Birnessite: Surface Characterization. In *Geochemical Processes at Mineral Interfaces* (Edited by Davis J. A. and Hayes K. F.). *ACS Symposium Ser. No. 323*, American Chemical Society, Washington, D.C.
- Edwards, M. and Benjamin, M.M. (1989) Adsorptive Filtration Using Coated Sand A New Approach for the Treatment of Metal Bearing Wastes. *Journal of WPCF*, 61 (9), 1523 – 1533.
- Alemayehu, E. (2003) Removal of heavy metals from groundwater using iron oxide coated sand: M. Sc. Thesis, UNESCO-IHE Institute for Water Education, the Netherlands. <http://www.unesco-ihe.org/>
- Lounici H, Addour L, Belhocine D, Grib H, Nicolas S, Bariou B. (1997) Study of a new technique for fluoride removal from water. *Desalination* 114:241–51.
- Srimurali M, Pragathi A, Karthikeyan J. (1998) A study on removal of fluorides from drinking water by adsorption onto low-cost materials. *Environ Pollut* 99:285–9.
- Alemayehu, E. (2008) IOCS and natural iron enriched adsorbents as an alternative low-cost defluoridation technique in rift valley of Ethiopia. Sustainable Management of Water Resource in the East-African Rift System (MAWARI – Fluoride project report), unpublished. <http://www.mawari.net>
- Hichour M, Persin F, Sandeaux J, Gavach C. (2000) Fluoride removal from waters by Donnan dialysis. *Sep Purif Technol* 18:1–11.
- Amor Z, Malki S, Taky M, Bariou B, Mameri N, Elmidaoui A. (1998) Optimization of fluoride removal from brackish water by electro dialysis. *Desalination* 120:263–71.
- Hasany SM, Chaudhary MH. (1996) Sorption potential of Haro River quartz for the removal of antimony from acidic aqueous solution. *Appl Radioactive Isot* 47(4): 467–71.
- Cohen D, Conrad HM. (1998) 65000 GPD fluoride removal membrane system in Lakeland California USA. *Desalination* 117:19–35.
- Tklehaimanot R. (2005) Study of fluoride and fluorosis in Ethiopia with recommendations on appropriate defluoridation technologies: A UNICEF sponsored consultancy. Addis Ababa, Ethiopia. May 5, 2005 report (unpublished).
- Datta, M. M. (1995) Excess Fluoride in drinking water in Ethiopia. *Maji* . 9, 14 – 23
- Devi, R., Alemayehu, E., Singh, V., Kumar, A., Mengiste, E. (2008) Removal of fluoride, arsenic and coliform bacteria by modified homemade filter media from drinking water. *Bioresource Technology*. 99, 2269-2274.
- Fufa, F., Alemayehu, E., Lennartz, B. (2013) Defluoridation of groundwater using termite mound. *Water, Air, & Soil Pollution. An International Journal of Environmental Pollution*. 224, 1-15
- Fufa, F., Alemayehu, E., Deboch, B. (2014) Defluoridation of Groundwater Using Gypsiferous Limestone. *Journal of Environmental and Occupational Science*. 3 (2):-doi: 10.5455/jeos.20140314041743
- Sharma et al (2002) Effect of groundwater quality on adsorptive iron removal. *Journal of water supply: Research and Technology. -AQUA*, 51(4), 199-208.
- Shang-Lien, Lo. et al, (1997) Characteristics And Adsorption Properties Of Iron Coated Sand, *Jornal of Wat. Sci. Tech.*, 35 (7), 63-70.



32. Dzombak, D. A. and Morel, F. M. M. (1990) Surface Complexation Modelling – Hydrous Ferric Oxides: John Wiley and Sons.
33. Huang, C. P., and Vane, L. M. (1989) Enhancing As (V) removal by Fe(II) – Treated Activated Carbon. *Journal of WPCF*, 61 (9), 1596 – 1603.
34. Joshi, A. and Chaudhurri, M. (1996) Removal of Arsenic from Ground water by Iron Oxide-Coated Sand, *Journal of Environmental Engineering*, 122 (8), 769-772.
35. Eaton AD, Lenore SC & Arnold EG (1995) Standard Methods for the Examination of Water and Wastewater, 19<sup>th</sup> ed. *American Public Health Association, American Water Work association & Water Environment Federation*: United Book Press, Inc., Baltimore, Maryland, USA.