Removal of Fluoride using iron (Fe^{3+}) and magnesium (Mg^{2+}) calcinated layered double hydroxide (LDH) coated on silica surface as adsorbent

Tejswini Patil[1], Dr. M. Husain[2], P. R. Punase[3]
[1]PG student, Dept. of Civil Engg., [2]Professor & Head Civil Engineering Department, [3] Assistant Professor
[1,2,3] SSBT College of Engineering & Technology, Bambhori, Jalagaon, MH- India

Abstract:

Fluoride and fluorosis issues are common in a few nations including India. Fluorosis is pandemic in more than 20 states of India. The fluoride comes into ground water by various ways, for example, weathering of rocks, industrial effluents and geochemical reactions. Fluoride in overabundance amount higher than 1.5 mg/l causes dental and skeletal fluorosis other than infertility, kidney harm and affects nervous systems as well. The fluoride removal from drinking water and wastewater has been successful by different techniques, for example, coagulation and precipitation, adsorption, ion-exchange, membrane separation, dialysis, electro-dialysis, electrocoagulation and so on. Adsorption process for defluoridation has favoured for the most part in developing countries as it is techno-economical viable method, environmental friendly and straightforwardness in operation. The present study examines the use of iron (Fe^{3+}) and magnesium (Mg^{2+}) calcinated layered double hydroxide (LDH) coated on silica surface as adsorbent for removal of Fluoride from drinking water. Present work shows that the Fe and Mg compounds can be effectively coated on silica gel to synthesize a granular adsorbent which, can be effectively used for removal of many anions from aqueous phase. Low cost of the chemical, easy synthesis and high recovery of fluoride ions are additional advantages of this method.

1.0. Introduction:

Presence of various hazardous contaminants like fluoride, arsenic, nitrate, sulfate, pesticides, other heavy metals etc. in underground water has been reported from different parts of India. In many cases, the water sources have been rendered unsafe not only for human consumption but also for other activities such as irrigation and industrial needs (Rukah and Alsokhny, 2004). In India, fluoride is the major inorganic pollutant of natural origin found in groundwater.

Fluoride in drinking water and toothpaste attracts public attention nowadays whereas fluoride as a strong oxidant is added to many drinking waters in small quantities to prevent dental caries (Bonnin, 1997). Generally, fluoride is carcinogen a bone seeker and is linked to hip fractures and brittling of bones (Pentchuk *et al.*, 1986). All salts of fluorine are toxic but some of them more or some less.

The treatment methods that are known for removal of fluoride are electrodialysis, adsorption, electrochemical, ion exchange and biological defluoridiation. The adsorption process in general, is considered better among other wastewater treatment technologies because of the low cost, simple design and easy operation.

2.0. Guidelines and limits of fluoride in drinking water

The maximum amount of fluoride consumption by human is 3 mg/day. Fluoride is beneficial to teeth when it is present in the range of 1.0–1.5 mg /L. When fluoride is present in excess of 2 mg/L, it causes dental and/or skeletal fluorosis. Both WHO (World Health Organization) and Indian Standards (IS 10500:1991) for drinking water recommend a desirable limit of 1.0 mg/L and a permissible limit of 1.5 mg/L. In most countries the limit is less than 1 mg/L (WHO, 1984 and 1985).

3.0. Methods for fluoride removal

3.1. Chemical Precipitation

In chemical precipitation process, chemicals are added in aqueous solution to make compounds of less solubility causing settling and removal of contaminants as precipitate. The treated supernatant is then collected and appropriately disposed of or used. The resultant sludge can be dewatered to reduce volume and must be appropriately disposed of. Precipitation is the most common treatment technology for fluoride removal.

3.2. Ion Exchange

Ion exchange is an exchange of ions between two electrolytes or between electrolyte solutions. Typical ion exchangers are ion exchange resins (functionalized porous or gel polymer), zeolites, montmorillonite, clay, and soil humus. Ion exchangers are either cation exchangers that exchange positively charged ions (cations) or anion exchangers that exchange negatively charged ions (anions).
Though ion exchange method can remove fluoride up to 90–95% and retain the taste and color of the water intact, it has got its own limitations like; the efficiency is decreased in presence of other ions like sulfate, carbonate, phosphate etc. Alkalinity also affects the performance of ion exchange process. High cost of ion exchange resins, elaborate pretreatment requirement and regeneration of resin are limitations of ion exchange process (Meenakshi and Maheshwari, 2006).

3.3 Reverse Osmosis (RO)

RO is a physical process in which the contaminants are removed by applying pressure on the feed water to direct it through a semi-permeable membrane. The process is the reverse of natural osmosis as a result of the applied pressure to the concentrated side of the membrane, which overcomes the natural osmotic pressure (Mohapatra et al., 2009). RO membrane rejects ions based on size and electrical charge and operates at higher pressures with greater rejection of all dissolved solids (Schneiter and Middlebrooks, 1983; Fu et al., 1995). Reverse osmosis produces water of extremely high purity.

Membranes used in reverse osmosis provide an effective barrier to suspended solids, all inorganic pollutants, organic micropollutants, pesticides and microorganisms, etc. The process permits the treatment and disinfection of water in one step and ensures constant water quality and it also works under wide pH range with no interference by other ions. However, the RO process removes all the ions present in water, though some minerals are beneficial for human; hence remineralization is required after treatment. The water becomes acidic and needs pH correction. The operative cost of this process is very high and large amount of water is wasted as brine, disposal of which is a problem (Meenakshi and Maheshwari, 2006).

3.4 Electrodialysis (ED)

Electrodialysis (ED) is a membrane process in which ions are transported through ion permeable membranes from one solution to another under the influence of an applied electrical potential (Kabay et al., 2002).

3.5 Electro-coagulation (EC)

In electrocoagulation (EC) process, an applied potential generates the coagulant species in situ as the sacrificial metal anode (aluminium or iron) that get dissolved, while hydrogen is simultaneously evolved at the cathode. Coagulant species aggregate the suspended particles or precipitate and adsorb dissolved contaminants. Tiny bubbles of hydrogen and oxygen that are formed during electrolysis of water collide with air bubbles which compel to float the pollutant particles. At the end of the process, treated and decontaminated water is obtained.

3.6 Adsorption

Adsorption is a process that occurs when a gas or liquid solute accumulates on the surface of a solid or a liquid (adsorbent), forming a film of molecules or atoms (the adsorbate). It is different from absorption, in which a substance diffuses into a liquid or solid to form a solution. The term sorption encompasses both processes, while desorption is the reverse process. Adsorption is present in many of the physical, biological, and chemical systems, and is widely used in many of the industrial applications for water and wastewater treatment.

4.0. Objective and scope of the study

The objective of the present study is to synthesize an adsorbent using iron (Fe^{3+}) and magnesium (Mg^{2+}) calcinated layered double hydroxide (LDH) coated on silica surface and to study feasibility of adsorbent for removal of fluoride from aqueous solution. Detailed methodology of the study is developed to fulfill the objective as given below:

(1) Study in batch mode varying the following parameters
  - Reaction pH.
  - Dose of adsorbent
  - Initial concentration of fluoride

(2) Optimize the synthesis of adsorbent with varying amount of Fe and Mg.

(3) Study the competition of other anions on F^- adsorption.

5.0. Materials

5.1 Materials and reagents

Magnesium chloride [$MgCl_2.6H_2O$] was purchased from Qualigens Fine Chemicals. Column chromatographic grade silica gel (60-120 mesh size) and Zirconyl oxychloride [$ZrOCl_2.8H_2O$] were procured from Central Drug House (P) Ltd., Delhi. Ferric chloride [$FeCl_3$] was brought out from SISCO Research Laboratories Pvt. Ltd., Mumbai. SPADNS [2-(p-sulphophenylazo)-1,8-dihydroxynaphthalene-3,6-disulphonic acid trisodium salt] and Sodium fluoride [NaF] were purchased from s.d.fine-chem limited, Mumbai. Distilled water, prepared in the laboratory, was used for all experiments.

5.2 Preparation of adsorbent

The adsorbent preparation was carried out by dissolving 5 g $FeCl_3$ and 10 g $MgCl_2.6H_2O$ in 20 mL of distilled water. pH of this mixture was adjusted to 8 by gradual addition of 4N NaOH. pH of the solution was measured continuously and continuous stirring was employed during this process. Finally a brown colour precipitate was formed. After the formation of precipitate, silica gel (10 g) was added in the mixture. During the process also continuous manual stirring was applied. After proper mixing of silica gel and precipitate, the mixture was oven dried at a temperature of 103-105ºC for 24 hr in drying oven. After the oven drying, the mixture was washed 2 to 3 times with distilled water for removing the impurities. The washed mixture was calcinated in muffle furnace at temperature of 550ºC for 2 hr and stored in desiccator. This calcinated Fe-Mg coated silica gel was used as an adsorbent for removal of fluoride in the present work.

5.3 Characterization of the adsorbent

5.3.1 Determination of pH_{zpc}

A procedure outlined by Huang and Ostovic (1978) was used to determine the pH of the zero point of charge (pH_{zpc}) of calcinated Fe-Mg coated silica gel, where the net surface charge on the adsorbent is zero. Sodium chloride (0.1N and 0.01N) was used as the background electrolyte. Adsorbent samples were titrated with 0.1N HCl and 0.1N NaOH. The net titration curves met at a point that is defined as pH_{zpc} (Huang and Ostovic, 1978; Jha et al., 1988).

5.4 Experimental design

Experimental work was carried out in batch mode with synthetic fluoride bearing wastewater using calcinated Fe-Mg coated silica gel as the adsorbent. Batch adsorption studies were carried out with following variable parameters: reaction pH, initial fluoride concentration, adsorbent dose. Kinetics of fluoride removal was also investigated. All studies were carried out at room temperature without temperature control.

5.4.1 Initial pH

Studies with reaction pH, as variable parameter, were conducted in 250 mL of conical flask with 100 mL of fluoride (F^-) containing aqueous solution. Reaction pH was varied from 2 to 10. Adsorbent dose was made constant at 5 g/L. Initial solution pH was adjusted using dilute (0.1N) hydrochloric acid (HCl) or dilute (0.1N) sodium hydroxide (NaOH). The reaction started upon addition of the adsorbent. Fluoride and the adsorbent containing conical flasks were kept in a horizontal shaker for three hours at 120±5 rpm. After three hours time, mixing was stopped and adsorbent was allowed to settle and thus it was kept in an undisturbed condition for half an hour, allowing the particle to coalesce. Supernatant was collected from conical flasks and used for final pH and fluoride estimation. This study was conducted for an initial fluoride concentration of 10 mg/L.

5.4.2 Controlled solution pH

Studies were also conducted at controlled solution pH (2 - 10). One liter of fluoride solution was taken in a glass beaker (initial F^- 10 mg/L). Initial pH was adjusted at 2 using 0.1 N HCl. Adsorbent dose of 3 g/L was added in the beaker. Adsorbent and liquid were mixed using a paddle stirrer at 120±5 rpm. One pH electrode was immersed in the beaker during the reaction. Reaction was continued for 3 hr at constant pH of 2. Then mixing was stopped and solid was allowed to settle for 30 min. The supernatant was collected from and used for residual fluoride analysis. Similarly the study was conducted at controlled pH of 3, 4, 5, 6, 7, 8, 9 and 10.

5.4.3 Initial fluoride concentration

Initial F^- concentration was varied at six levels: 3, 5, 10, 15, 20 and 21 mg/L. This study was conducted in plastic beaker in a similar way like pH kinetics. Mixing was achieved by a paddle stirrer at 120±5 rpm and samples were withdrawn at regular time intervals. Study was conducted at a constant reaction pH of 3 and adsorbent dose of 5 g/L. All studies were conducted for 3 hr.

5.4.4 Kinetics of fluoride removal at varying initial fluoride concentration

Kinetics of fluoride removal at varying initial fluoride concentration was conducted in a 2 L glass beaker with 1 L of fluoride containing aqueous solution. Adsorbent dose and reaction pH were maintained constant at 5 g/L and 3 respectively. Initial fluoride concentration was varied from 3 – 21 mg/L (3, 5, 10, 15, 20 and 21 mg/L). Initial solution pH was adjusted using dilute (0.1 N) hydrochloric acid (HCl) or dilute (0.1 N) sodium hydroxide (NaOH) as before. The reaction started upon addition of the adsorbent. Mixing of adsorbent in solution was achieved by a paddle stirrer at a constant speed of

120±5 rpm. Effluent was collected through a pipette from the top of the beaker at regular time intervals and stored in the specimen tube for subsequent F^-analysis. This study was carried out for 3 hr.

5.4.5 Adsorbent dose

Studies with adsorbent dose as variable parameter were conducted in 1 L plastic beaker with 500 mL of initial fluoride solution. Adsorbent dose was varied at eight levels: 0.5, 1.0, 2.0, 3.0, 4.0, 5.0, 6.0 and 8.0 g/L. With each dose of adsorbent, studies were conducted with constant initial concentrations of F^- ions of 6 and 16 mg/L. The reaction mixture was vortexed using a paddle stirrer at a constant speed of 120±5 rpm. The initial solution pH was adjusted to 2, 3 and 4 with 0.1 N HCL and 0.1 N NaOH. All studies with adsorbent dose were conducted for 3 hr. Samples were extracted through a pipette from top of the beaker at regular intervals and stored in specimen tubes. The supernatant was analyzed for remaining fluoride concentration with visible spectrophotometer using SPADNS–$ZrOCl_2$ reagent. The adsorption capacity at any time, t (q_t, mg/g) was calculated using the following relation:

$$q_t = \frac{V\,(C_i - C_t)}{m} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots.. \quad \text{(Eq. 1)}$$

Where, C_i = initial fluoride concentration (mg/L) in solution when time, t=0; C_t = concentration of fluoride solution (mg/L) at a time (t, min); m = mass of solid (adsorbent) added (g) and V is the solution volume (L).

The isotherm experiment was also conducted as above with agitation of mixture for 3 h for the equilibrium. The fluoride solution (pH 2, 3 and 4) of concentrations (mg/L) 6 and 16 was used for the equilibrium test. The residual fluoride concentration (C_e, mg/L) was analyzed in equilibrated solution and, equilibrium capacity (q_e, mg/g) was calculated using above equation [Equation (1)] putting C_e in place of C_t.

5.4.6 Effect of $FeCl_3$ and $MgCl_2$ variation during adsorption synthesis

Seven types of adsorbents were prepared with different molar ratios of Fe and Mg, by varying the proportions of $FeCl_3$ and $MgCl_2.6H_2O$ (ratios of Fe and Mg). Amount of silica gel was maintained constant at 10 g. Experiments were conducted in 250 mL conical flask and the mixing was achieved in a horizontal shaker at 120±5 rpm for 3 h. After 3 h, fluoride was analyzed in supernatant solution. In all experiments initial fluoride concentration was taken as 10 mg/L, with adsorbent dose of 5 g/L and the experiments were conducted for two different pH of 2 and 3. pH was maintained constant during the reaction.

5.4.7 Effect of other co-existing anion

The interference effect of different anions usually present in ground water sample on fluoride sorption by calcinated Fe-Mg coated silica gel was also studied. Equimolar concentrations of all anions, including Cl^- , NO_3^- , SO_4^{2-} , PO_4^{3-} and F^-, were taken in 1 L volumetric flask and dissolved by using distilled water. Adsorption studies were carried out as described earlier in section 3.4.4, with an adsorbent dose of 5 g/L and at constant pH of 2 and 4 for 3 hr. The liquid samples were withdrawn after 3 hr, filtered and analyzed for residual fluoride concentrations and concentration of other anions.

5.5 Analytical methods

The pH of the solution was measured by pH meter and the concentration of fluoride in the aqueous solution was measured by SPADNS colorimetric method (Clesceri et al., 1998; Bellack and Schouboe, 1958). In a 50 mL of fluoride solution, 5 mL each of SPADNS solution and zirconyl-acid reagent were added and concentration of fluoride was measured using spectrophotometer at a wave length of 570 nm.

The unknown fluoride concentration in solution was measured from the calibration curve prepared with known concentrations of fluoride.

6.0 Results.

6.1 Effect of initial solution pH

Initial solution pH was adjusted at nine levels: 2, 3, 4, 5, 6, 7, 8, 9 and 10 and fluoride removal was estimated at various uncontrolled pH condition. Initial fluoride concentration of the aqueous solution was 10 mg/L. Fluoride removal and uptake (mg/g) were calculated using Equation 4.1 and 4.2 respectively.

$$Fluoride\ Removal\ (\%) = \frac{C_o - C_e}{C_o}\ x\ 100 \text{……………………………………….(Eq. 2)}$$

$$Fluoride\ uptake\ \left(\frac{mg}{g}\right) = \frac{[C_o - C_e]\ (mg/L)\ \ x\ Sample\ Volume\ (L)}{Adsorbent\ Added\ (g)} \text{…………… (Eq. 3)}$$

Where; C_0 = Initial concentration of F^- ions in solution (mg/L)
C_e = Equilibrium concentration of F^- ions in solution (mg/L).

Result of initial pH on fluoride removal and final pH after adsorption are shown in Figures 6.1 and 6.2 respectively. Figure 6.1 shows that the maximum fluoride removal from the aqueous solution was achieved at strong acidic pH of 2 (around 60%). This value decreased to 41%, when the initial pH was increased to 3 and decreased further with increase in initial pH. It can be inferred from the figure that the initial solution pH 2 was increased to 2.30 during the adsorption process. However, solution pH increased significantly to 8.2, when initial pH of the solution was adjusted to 3. When initial pH was higher than 3, final pH of the solution was always constant at 8.5-8.9. Fluoride uptake (mg/g) with varying reaction pH is shown in Table 6.1. A maximum uptake of fluoride was observed at pH 2 with a value of about 1.29 mg/g (Equation 3), for an initial F^- concentration of 10 mg/L and at pH 3, this decreased to 0.82 mg/g. In the alkaline pH range, there is sharp drop in adsorption, which may be due the competition of the hydroxyl ions with the fluoride ions for adsorption on to the calcinated Fe-Mg coated silica gel. Thus the fluoride uptake decreased with an increase in initial solution pH.

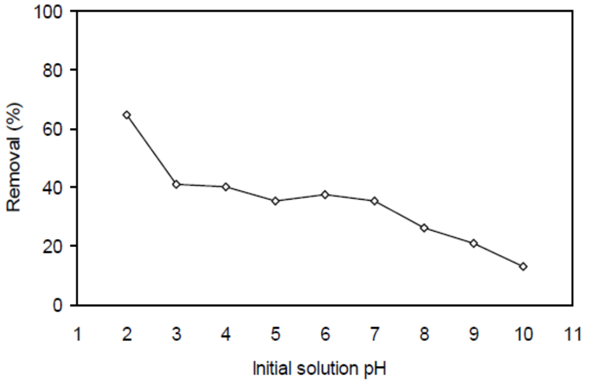

Figure 6.1: Effect of initial solution pH on removal of fluoride (Initial Fluoride concentration 10 mg/L, adsorbent dose 5 g/L, reaction time 3 hr)

Table 6.1: Uptake of fluoride ion at varying initial solution pH

Initial solution pH	Fluoride uptake (mg/g)
2	1.29
3	0.82
4	0.80
5	0.71
6	0.75
7	0.71
8	0.52
9	0.42
10	0.26

Initial F^- 10 mg/L and adsorbent dose 5 g/L

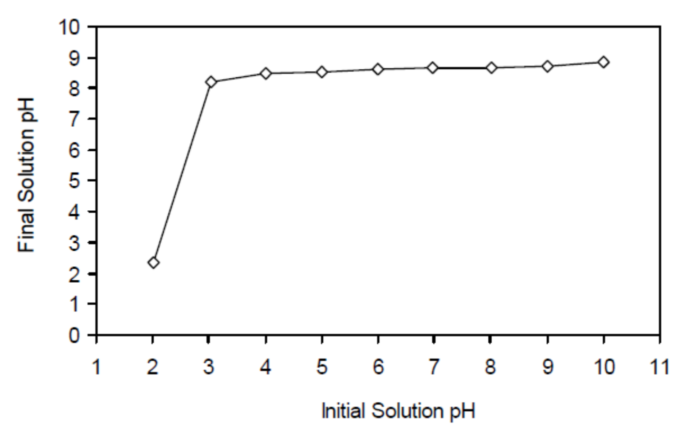

Figure 6.2: Final solution pH after fluoride adsorption (Initial fluoride concentration 10 mg/L, reaction time 3 hr)

6.2 Effect of controlled solution pH

The addition of adsorbent into the aqueous solution changed its pH during the experiment. Hence effort was made to determine fluoride removal at controlled pH. That is after the addition of adsorbent into the aqueous solution containing 10 mg/L as the initial fluoride concentration, the initial solution pH was maintained at 2 using (0.1N) dilute HCL. The results of the pH controlled experiment are shown in Table 6.2 and Figure 6.3.

From Table 6.3 it can be seen that the removal efficiency of fluoride at pH 2 is comparatively greater than the removal efficiency at all other pH. The results have showed (Figure 6.3) that the fluoride adsorption capacity (mg/g) declines sharply with increasing pH from 2 to 4, and remains nearly constant up to pH 7 and that declines again with increasing initial pH from 7 to 10.

Table 6.2: Removal of fluoride under controlled pH environment

pH	Adsorption Capacity (mg/g)	Removal (%)
2	1.77	53.0
3	0.86	25.8
4	0.79	23.8
5	0.64	19.2
6	0.59	17.6
7	0.69	20.6
8	0.51	15.3
9	0.46	13.9
10	0.38	11.4

(Initial F^- concentration = 10mg/L, Adsorbent dose = 3 g/L, Reaction time = 3h)

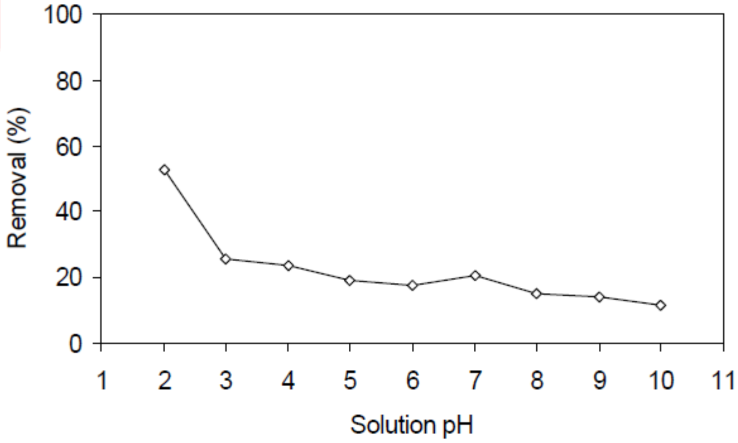

Figure 6.3: Effect of controlled solution pH on removal of fluoride
(Initial fluoride concentration 10 mg/L, adsorbent dose 3 g/L, reaction time 3 hr)

The mechanism of fluoride removal by calcinated Fe-Mg coated silica gel adsorbent was presumably due to the electrostatic attraction of fluoride by the surface positive charge or ligand/anion-exchange reaction of fluoride with surface hydroxyl group of the solid adsorbent as shown in [Equations 4.3(a) and 4.3 (b)].

$$[Mg_{1-x}Fe_x(OH)_2](Cl)_{x/2(s)} \rightarrow [Mg_{1-x}Fe_xO_{1+x}]^+ + (x/2)Cl^- + H_2O \qquad (4.3a)$$

$$[Mg_{1-x}Fe_xO_{1+x/2}] + (x)F^- + (1+(x/2)+y)H_2O \rightarrow [Mg_{1-x}Fe_x(OH)_2](F)_x + xOH^- \qquad (4.3b)$$

where, $[Mg_{1-x}Fe_x(OH)_2](Cl)_{x/2(s)}$ stands for the adsorbent.

At acidic solution pH, the solid adsorbent is more protonated thus favouring higher fluoride adsorption. With increase in solution pH, the adsorbent surface was deprotonated and fluoride adsorption decreased. Equation 6.3 (b) shows that due to fluoride adsorption, OH^- ion is released causing increase in pH. During experiment at uncontrolled pH, it was observed that solution pH increased significantly [Figure 6.3].

6.3 Effect on initial fluoride concentration

To study the effect of the initial fluoride concentration on the removal and the uptake of the F^-ions by calcinated Fe-Mg silica gel coated adsorbent, batch experiments were performed varying the initial F^- concentrations (3 to 21 mg/L) with 5 g/L of adsorbent. Initial solution pH was adjusted to 3 in all experiments. Residual F^- concentrations with time at various initial F^-concentrations are shown in Figure 6.4.

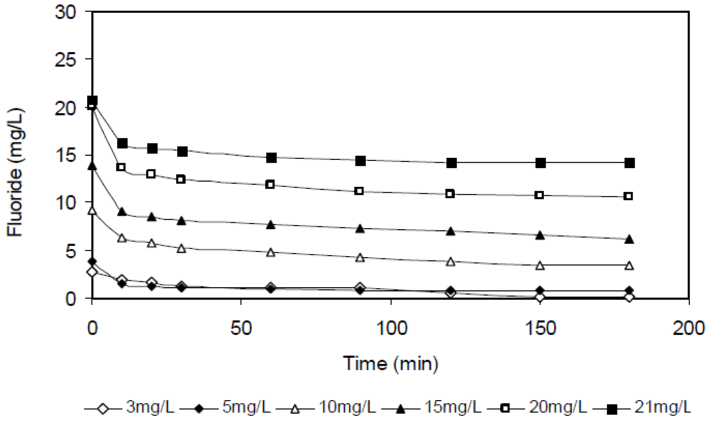

Figure 6.4: Effect of initial F^- concentration on removal of F^- ions by calcinated Fe-Mg coated silica gel (pH 3, adsorbent dose 5 g/L)

The equilibrium time was 90 min at initial F^- concentration of 5 mg/L. Equilibrium time increased to 180 min with increase in initial concentration of F^- to 21 mg/L. The time curves in Figure 6.4 are smooth and continuous thus suggesting the possibility of formation of a monolayer on adsorbent surface.

Fluoride removal and uptake at varying initial fluoride concentrations are shown in Table 6.4. F^-removal was 95% at initial concentration of 3 mg/L. When initial F^- was increased to 5 mg/L, removal of fluoride decreased to 80%. With further increase in initial fluoride concentration, removal decreased steadily and at initial fluoride concentration of 21 mg/L, removal was only 30%.

Table 6.3 shows that F^- uptake increased with increase in initial fluoride concentration. The fluoride uptake was 0.62 mg/g when initial fluoride concentration was 5 mg/L and increased to 1.9 mg/g when the initial fluoride concentration was 20 mg/L. Since the uptake is dependent on the initial concentration of fluoride in solution, the higher uptake at higher concentration can be
explained as: at higher initial concentration the ratio of initial number of moles of fluoride to the available surface area is high; hence fractional adsorption becomes dependent on initial concentration. For a given adsorbent dose the total number of available adsorption sites is fixed thereby adsorbing almost the same amount of adsorbate, thus, resulting in a decrease in the percentage removal of the adsorbate corresponding to an increase in initial adsorbate concentration (Das et al., 2007).

Table 6.3: Removal of fluoride ions by coated silica gel at varying initial fluoride concentrations

Initial F^- (mg/L)	**Removal (%)**	**Fluoride uptake (mg/g)**
3	95.69	0.52
5	79.45	0.62
10	63.32	1.17
15	55.73	1.55
20	46.50	1.90
21	32.26	1.35

pH 3, adsorbent dose 5 g/L

6.4 Effect of adsorbent dose

Effect of dose was studied at varying calcinated Fe-Mg coated silica gel dose of 0.5, 1.0, 2.0, 3.0, 4.0, 5.0, 6.0 and 8.0 g/L. Experiments were conducted at initial F^- concentration of 6 and 16 mg/L and results are shown in Figures 4.5 and 4.6 and Tables 4.4 and 4.5 respectively. For initial fluoride concentration 6 mg/L at pH 2 and adsorbent dose of 0.5 g/L, the removal was about 16%. This increased to 66% at dose of 4 g/L. When the dose was further increased to 6 g/L, removal increased to 80% and with the further increase in the adsorbent dosage to 8 g/L, the fluoride removal efficiency increased to 86%. Similar results were inferred from initial fluoride concentrations of 6 and 16mg/L and for different pH (2, 3 and 4) and are presented in the Table 6.5 and 6.6.

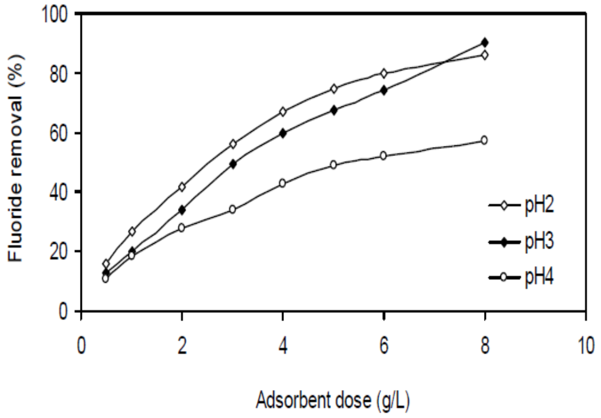

Figure 6.5: Effect of the calcinated Fe-Mg coated silica gel dose on F^- removal (%) at various solution pH 2, 3 and 4 (Initial fluoride concentration 6mg/L, reaction time 3 hr)

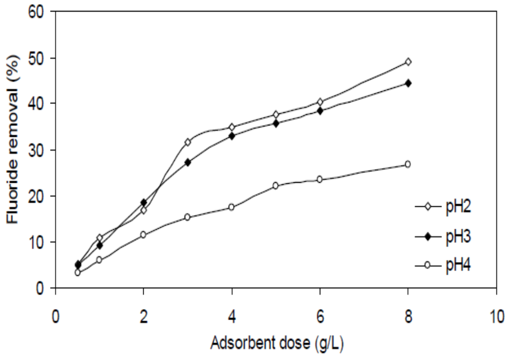

Figure 6.6: : Effect of the calcinated Fe-Mg coated silica gel dose on F^- removal (%) at various solution pH 2, 3 and 4 (Initial fluoride concentration 16mg/L, reaction time 3 hr)

Table 6.4: Removal of fluoride ions by coated silica gel at varying adsorbent dose (Initial concentration 6 mg/L)

Adsorbent Dose (g/L)	**pH 2**		**pH 3**		**pH 4**	
	Removal (%)	Fluoride uptake (mg/g)	Removal (%)	Fluoride uptake (mg/g)	Removal (%)	Fluoride uptake (mg/g)
0.5	16.02	1.59	12.99	1.55	10.63	1.27
1	26.89	1.34	19.93	1.19	18.36	1.09
2	42.01	1.05	33.77	1.01	27.79	0.83
3	56.16	0.93	49.35	0.98	34.15	0.69
4	66.81	0.83	59.75	0.89	42.93	0.64
5	74.85	0.75	67.38	0.81	48.73	0.58
6	80.08	0.61	74.46	0.74	52.18	0.52
8	86.32	0.34	90.04	0.67	57.35	0.43

Table 6.5: Removal of fluoride ions by coated silica gel at varying adsorbent dose (Initial concentration 16 mg/L)

Adsorbent Dose (g/L)	**pH 2**	**pH 3**	**pH 4**

	Removal (%)	Fluoride uptake (mg/g)	Removal (%)	Fluoride uptake (mg/g)	Removal (%)	Fluoride uptake (mg/g)
0.5	5.18	1.65	5.03	0.78	3.34	0.41
1	11.00	1.55	9.38	0.73	6.08	0.47
2	16.83	1.39	18.44	0.72	11.38	0.44
3	31.71	1.24	27.28	0.71	15.40	0.40
4	34.95	1.16	33.08	0.64	17.40	0.34
5	37.54	1.12	35.65	0.56	22.08	0.34
6	40.43	1.05	38.51	0.50	23.42	0.30
8	49.09	0.95	44.42	0.43	26.76	0.26

Tables 6.4 and 6.5 show that with increase in adsorbent dose, though fluoride removal increased, the adsorption capacity (q_e, mg/g) decreased at a constant fluoride concentration. This agrees well with the increase of solid dose for a fixed solute load, and surface sites heterogeneity of the adsorbent. According to surface site heterogeneity model, the surface is composed of sites with a spectrum of binding energies.

6.5 Comparison with other adsorbents

It can be deemed from Table 6.6 that fluoride adsorption capacity by various adsorbents varied in a wide range from 0.42-69.5 mg/g. In the present work, fluoride removal capacity of the calcinated Fe-Mg coated silica gel was within literature values. Further study is required to improve fluoride adsorption capacity of this adsorbent.

Table 6.6: Comparison of fluoride adsorption among various adsorbents

Adsorbent	**pH**	**Maximum Fluoride uptake (mg/g)**	**Efficiency (%)**	**Contact Time**	**Reference**
Schwertmannite	3 -11	64	85	1day	Eskandarpour et. Al. (2008)
Granular Red Mud	4.7	0.851	50	6 hrs.	Tor Et al (2009)
Alum Impregnated activated alumina	6.5	40.3	99	3 Hrs.	Tripathy et al. (2006)
Mixed rare earth oxides	6.5	12	90	1 Hrs	Raichur & Basu (2001)
Hydrous Manganese oxide coated alumina	4 - 6	7.09	92.5	4 Hrs.	Teng Et. Al (2009)

Adsorbent	**pH**	**Maximum Fluoride uptake (mg/g)**	**Efficiency (%)**	**Contact Time**	**Reference**
China Clay	6.5	0.42	93	2 Hrs.	Chaturvedi et al. (1988)
Calcined Mg-Al-CO3-LDH	6	213.2	98	6 Hrs.	Lv et. Al. (2006)
Calcinated Fe-Mg Hydroxide coated on silica gel	2	1.598	75	3 Hrs.	Present work

7.0. Conclusions

The laboratory scale investigation was conducted on synthesis of the adsorbent (calcinated Mg-Fe hydroxide coated on silica gel) and the study feasibility of adsorbent for the removal of fluoride from aqueous solution. Experimental observations can be summarized as follows:

1. Reaction pH was the most critical parameter, which controlled fluoride (F^-) ion removal by calcinated Fe-Mg coated silica gel. Removal of fluoride ion decreased with increase in solution pH due to less competition with OH^- ion. It was found that maximum removal of fluoride from aqueous solution occurred at pH 2 in 3 hr with an initial fluoride concentration of 10 mg/L, and that the retention of fluoride ions by the calcinated layered double hydroxide material was almost 50%.

2. Removal of fluoride decreased with increase in initial concentration of fluoride in aqueous solution (95% and 32% at F^- concentrations of 3 mg/L to 25 mg/L). The uptake of fluoride ion increased with increase in initial concentration of fluoride.
3. Equilibrium time increased from 60 min for initial F^- concentration of 3 mg/L to 120 min for initial F^- concentration of 25 mg/L.

4. With increase in adsorbent dose from 0.5 g/L to 8.0 g/L, fluoride removal increased from 16% to 86% at initial F^- concentration 10 mg/L and at pH 2.0.

5. The adsorption capacity (q_e) decreased from 1.65 mg/g to 0.95 mg/g with increase in the dose of calcinated Fe-Mg coated silica gel from 0.5 g/L to 8.0 g/L for initial fluoride concentration of 16 mg/L and pH 2.0

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