Fluoride Removal Performance of a Synthesized Adsorbent

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ABSTRACT

Fluoride contamination of water is a major problem in India. World Health Organization (WHO 2004) recommends an upper limit of 1.5 mg/L fluoride in drinking water. Present study reveals performance evaluation studies of Al-Fe-Ac based adsorbent for the fluoride removal from drinking water. The prepared adsorbent was characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM). The material retained amorphous structure and maintained relatively stable fluoride adsorption performance at calcination temperatures around 300 °C. The optimum pH range for fluoride adsorption was 6.0–7.0 and the adsorbent also showed high defluoridation ability around pH 5.5–7.5, which is preferable for actual application. A high fluoride adsorption capacity of 4.5 mg/g was acquired for fluoride concentration of 50 mg/L, adsorbent dose of 1g/L and pH 7.0. Synthetic samples having fluoride concentration 2 to 10 mg/L were treated at optimized dosage and residual fluoride was reduced to 0.1 to 1.4 ppm with different adsorbent dose. Residual aluminium in treated water was well within WHO norms for drinking water.

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1. Introduction

Fluoride is classified as severely harmful contaminant of water for human consumption by World Health Organization (WHO) [1]. In India various states namely Assam, Andhra Pradesh, Bihar, Delhi, Telangana, etc. [2] to have high fluoride concentration in water. The presence of high fluoride content in drinking water makes bones and teeth brittle, harder and dense due to deposition of fluoride as calcium-fluorapatite. The maximum fluoride concentration in drinking water should not exceed 1.0 mg/l.

Fluoride is required in small amount (1.0-3.0 mg/day) on daily basis for prevention of dental problems but taken in large amount can cause dental fluorosis, skeletal fluorosis (Fluorosis is a common symptom of high fluoride ingestion manifested by mottling of teeth in mild cases and embrittlement of bones and neurological damage in severe cases [3], osteoporosis, arthritis, brittle bones, cancer, infertility, brain damage, Alzheimer syndrome, and thyroid disorder, etc. Hence, fluoride can be harmful or beneficial depending upon the amount taken [4]. Human intake of fluoride is mainly from groundwater. Various minerals like fluorite, biotites, and rocks like granite, basalt, etc. are the primary source of fluoride [5]. Industries of glass, ceramic production produces waste containing high fluoride concentration into discharge into water. Different techniques viz. precipitation, adsorption, coagulation, membrane separation have been used previously for de-fluoridation of drinking water [7,8,9].

In the present study we report the synthesis of Al-Fe-Ac based adsorbent by the precipitation method. We optimized the reaction conditions to synthesize adsorbent for better adsorption capacities. The synthesized adsorbent was then used as an adsorbent for removal of fluoride from water.

Table 1
Effects of fluoride in water on human health [6]

Fluoride concentration (mg/L)	Effects
<1.0	Safe limit
1.0–3.0	Dental fluorosis (discoloration, mottling and pitting of teeth)
3.0–4.0	Stiffened and brittle bones and joints
4.0–6.0 and above	Deformities in knee and hip bones and finally paralysis making the person unable to walk or stand in straight posture, crippling fluorosis.

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2. Material and methods

2.1 Preparation of stock solution

All chemical reagents used in the experiments were purchased from Sigma–Aldrich including Aluminium chloride (AlCl_3), ferric chloride (FeCl_3), Activated carbon, Ammonium Hydroxide (NH_4OH), and sodium fluoride (NaF). Mili-Q water was used throughout the synthesis and treatment processes. Standard stock solution (100 mg/L) of fluoride was prepared by dissolving 0.221 g NaF into 1 L Mili-Q water at room temperature. The solutions for different experiments were prepared by appropriate dilution of the stock solution.

2.2 Synthesis of adsorbent

The composite material in this paper was synthesized by traditional co-precipitation method. In a typical synthesis process, 0.6M FeCl_3 and 0.6M AlCl_3 were mix to prepare solution A. 100 g of activated carbon was dissolved in 500 mL of water which was considered as solution B and 3 M of NH_4OH solution was considered as solution C. Solution C was added drop wise into mixer of solution A and B to maintain pH between 6.5-7.0 under constant stirring condition at 200 rpm. In order to obtain uniform mixture, the mixed solution was stirred for 30 min after the addition. After filtration, the precipitates were washed sequentially with mili Q water and ethanol until chlorine was washed ($<0.02\%$), and then the filtrate was dried in oven at 110°C for overnight. Furthermore, the obtained materials were calcined at 200°C for 3 h. The materials were allowed to cool to room temperature and then used for subsequent adsorption experiments.

2.3 Characterization of adsorbent

The structure of the adsorbent was characterized using an X-ray diffraction analyser (XRD) (Pananalytical model-xpert pro) equipped with Cu $K\alpha$ radiation at a scanning speed of 5° per min from 10° to 90° . The XRD data were matched with standard JCPDS data. The morphologies of adsorbents were determined by Nova Nano 450 scanning electron microscopy (SEM) operating at 15 kV. The pH of the systems was adjusted from 4.0 to 10.0 with 0.05 M H_2SO_4 or 0.05 M NaOH. Equilibration of samples was performed by shaking at 25°C for 24 h, and the final pH was measured using pH meter (Model HI5522, HANNA).

2.4 Adsorption studies in batch mode

The batch adsorption experiments were performed to determine the efficiency of adsorbent and the optimum operating conditions required for effective removal of fluoride from the drinking water. The adsorption experiments were carried out by taking 100 ml of F solution with varying initial concentration (3 mg/L to 10mg/L). Then varying amount of adsorbent was added in each conical flask and was kept in a water shaker bath (120 rpm) for 1 to 5 hours. Supernatant was separated by filtration using whatman filter paper and analyzed for remaining F content by using Thermo Scientific Orion 2109XP Fluoride Analyzer. The amount of fluoride adsorbed by adsorbent at equilibrium q_e (mg/g of adsorbent) was then estimated by Eq. 1

$$q_e = \frac{C_o - C_e}{m} V \quad (1)$$

Where, C_o and C_e are the initial and final equilibrium concentrations (mg/L) of fluoride, respectively, V is the volume of the adsorbate solution (L) and m is the mass of adsorbent added (g)[11]. Adsorption experiments were executed at different pH (3 to 10), dosage (1 – 5 g/l), and contact time (1 to 5 hours). Initial pH of the solution was adjusted to the desired value with the help of NaOH and H_2SO_4 solution. The percentage removal (% R) of fluoride by adsorbent was calculated by Eq. 2

$$\% R = \frac{C_o - C_e}{C_o} \times 100 \quad (2)$$

Where, C_o and C_e have the same meaning as explained earlier.

3. Results and Discussion

3.1 X-ray diffraction analyzer (XRD)

The amorphous structure of the adsorbent was characterized using an X-ray diffraction analyzer (XRD) (PANanalytical X'pert powder X-ray diffractometer) equipped with Cu $K\alpha$ radiation at a scanning speed of 2° per min from 10° to 90° , operated at 40 kV and 40 mA. The XRD data were matched with standard JCPDS data.

Fig 2 XRD image of the synthesized Fe-Al-Ac Adsorbent

3.2 Scanning electron microscopy (SEM)

The morphologies of adsorbents were determined by Nova Nano SEM 450 (FEI, Netherland) scanning electron microscopy (SEM) operating at 15 kV. The surface morphology of adsorbent is shown in fig.2, showed an irregular surface morphology

Fig 2 SEM image of the synthesized Fe-Al-Ac Adsorbent

3.3 Adsorption studies in batchmode

3.3.1 Effect of adsorbent dose

The effect of adsorbent dose was studied by varying the adsorbent quantity from 1g to 10 g with initial fluoride concentration 7 mg/L, contact time of 2 hour, pH 7 and temperature $27 \pm 2^\circ\text{C}$. The removal of fluoride increases with increasing the adsorbent dose due to increased number of adsorption sites [11]. A significant increase in percentage fluoride removal was observed when the adsorbent dosage was increased from 1 g/L to 7 g/L; beyond which there was no significant change in fluoride removal (Fig. 3). This might be due to the fact that the equilibrium between the fluoride and the adsorption sites was achieved at this dose. The trend shown in Figure 3 depicts that fluoride removal from 68.42% to 97.4% occurs as adsorbent dose increased from 1g/L to 10 g/L. To bring fluoride concentration under permissible limit, 5 g/L of adsorbent dose has been set as optimum dose.

Fig. 3 Effect of adsorbent dosage on % fluoride removal

3.3.2 Effect of initial concentration

The extent to which the initial fluoride concentration will affect the fluoride removal depends on the immediate relation between concentration of fluoride and available adsorption sites on the surface of adsorbent particles. In order to interpret the effect of the fluoride concentration on the rate of adsorption, the adsorption experiments were conducted at different fluoride concentrations (2-10 mg/L) at pH 7, adsorbent dosage of 5 g/L, temperature 27°C and agitation speed at 180 rpm and contact time to 2 hour. It is also evident that as the initial fluoride concentration increases from 2 to 10 mg/L, the percentage removal reduced from 94.5% to 85.9% (Fig. 4). This might be due to the saturation of adsorption sites; hence at higher fluoride concentrations more fluoride molecules are left un-adsorbed [12].

Fig. 4 Effect of initial fluoride concentration on % dye removal

3.3.3 Effect of contact time

All the batch experiments were performed at room temperature with initial fluoride concentration of 7 mg/L using adsorbent dose 5 g/L at pH 7 with agitation speed of 180 rpm in water bath shaker. Figure 5

shows the effect of varying contact time from 30 minutes to 180 minutes on fluoride removal. It was observed initially that in 120 minutes percent removal of fluoride increases from (70.2 % to 87.56%) then after it becomes constant as all the adsorption sites were occupied and no further adsorption was possible. Thus 120 minutes was considered as the optimum time for maximum fluoride removal at 5 g/L of adsorbent dose.

Fig. 5 Effect of contact time on % fluoride removal

3.3.4 Effect of pH

The efficiency of fluoride removal by adsorption largely depends on pH of solution, as its variation leads to the alteration in the degree of ionization of adsorptive molecules and the surface properties of the adsorbent [13]. The impact of solution pH was observed for adsorption of fluoride on adsorbent at temperature 27°C , initial concentration of fluoride 10 mg/L and adsorbent dosage of 5g/L. Removal of fluoride was studied in 3-10 pH range to study the removal behavior in both acidic and basic nature. It was observed that maximum fluoride removal around 92.18% was obtained at pH 7 (Fig. 6).

Fig. 6 Effect of pH value on % dye removal

4. Regeneration of synthesized adsorbent

The regeneration studies were carried out to investigate the possibilities of reusability of used adsorbent. Amongst different desorbing agents like HCl, NaOH, and $\text{Al}_2(\text{OH})_3\text{Cl}_3$ desorption was maximum for 0.5M HCl. The adsorption capacity was remained constant up to 4 cycles. Table 2 show the percent removal of fluoride up to 4 cycles with little difference in their removal efficiencies.

Table 2 Regeneration of adsorbent

Cycle	Percentage Adsorption
1	98.29
2	94.45
3	91.20
4	86.99

5. Conclusion

In this study, Fe–Al–Ac based adsorbent was developed having amorphous structure for fluoride adsorption. The optimum pH range for fluoride removal was 6.0–7.0 and the adsorbent was also effective at pH 5.5–7.5. A high adsorption capacity of 4.5 mg /g was acquired at pH 7.0. In all experiments, residual aluminium was found to be within WHO prescribed limits thus making it a safer de-fluoridating agent.

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