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Research Article

Removal of Fluoride from Drinking Water Using Modified Immobilized Activated Alumina

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The study describes the removal of fluoride from drinking water using modified immobilized activated alumina (MIAA) prepared by sol-gel method. The modification was done by adding a specific amount of alum during the sol formation step. The fluoride removal efficiency of MIAA was 1.35 times higher as compared to normal immobilized activated alumina. A batch adsorption study was performed as a function of adsorbent dose, contact time, stirring rate, and initial fluoride concentration. More than 90% removal of fluoride was achieved within 60 minutes of contact time. The adsorption potential of MIAA was compared with activated charcoal which showed that the removal efficiency was about 10% more than the activated charcoal. Both the Langmuir and Freundlich adsorption isotherms fitted well for the fluoride adsorption on MIAA with the regression coefficient R^2 of 0.99 and 0.98, respectively. MIAA can both be regenerated thermally and chemically. Adsorption experiments using MIAA were employed on real drinking water samples from a fluoride affected area. The study showed that modified immobilized activated alumina is an effective adsorbent for fluoride removal.

1. Introduction

Fluoride is present in ground water coming either from natural sources like weathering and volcanic processes or from wastewater of industries like fertilizer, glass, ceramic, brick, iron works, and electroplating [1]. Fluoride has both beneficial and harmful effects on the human health depending upon its level. Among the beneficial effects of fluoride in human body, strengthening of bones and prevention from tooth decay are significant. The permissible limit of fluoride in drinking water is 1.5 mg/L according to the National Standards for Drinking Water Quality of Pakistan [2] and the World Health Organization [3]. Above this limit, fluoride can lead to various diseases such as skeletal and dental fluorosis, brittle bones, cancer, infertility, brain damage, Alzheimer's syndrome, and thyroid disorder [4].

The United Nations Environmental Program (UNEP) estimates that the numbers of individuals affected by fluorosis are in the tens of millions across 25 countries in both developed and developing nations [5]. A number of such cases have been identified in Pakistan where people suffered from harmful diseases due to industrial discharge of fluorides. In July 2000, a tragic situation was reported in Manga Mandi area (near Lahore, Punjab) where level of fluoride reached up to 20 mg/L in drinking water that led to the bone and teeth deformities in local people [6].

The techniques available for defluoridation include coagulation-precipitation, membrane process, ion exchange, and adsorption processes. Although coagulation-precipitation (also known as Nalgonda technique) is an effective and cheap method but its main disadvantage is the generation of harmful waste products. The membrane process is mainly the reverse osmosis technique but it requires high maintenance cost due to fouling, scaling, and degradation of membrane. Similarly, the ion exchange process is very costly [7]. The adsorption method is considered more appropriate for defluoridation due to its simplicity, effectiveness, and economic viability [8].

The important adsorbents that have been tested for the fluoride removal include activated alumina [9], activated

charcoal [10], zeolite [11], biosorbents [12], and nanosorbents [13]. Activated charcoal is considered as a universal adsorbent because of its applications and viability. Tembhurkar and Dongre studied the removal of fluoride using activated charcoal [14]. Activated alumina is also an efficient adsorbent for fluoride removal from drinking water but it has limited regeneration capacity and slow rate of adsorption [15].

Several studies have been conducted to increase the efficiency of activated alumina for defluoridation. In a study, alum impregnated activated alumina was used to remove fluoride from drinking water with the removal efficiency of 99% at pH 6.5 [16]. Similarly, another study reports the adsorption equilibrium and kinetics of fluoride removal using sol-gel-derived activated alumina adsorbent [17]. In this study, calcium oxide and manganese oxide coating were done on sol-gel-derived activated alumina to enhance its fluoride removal efficiency.

The main challenge encountered during the adoption studies is the separation of adsorbent after use from water samples. Generally, filtration is employed for the separation of powdered adsorbents. The aim of the present study was to prepare an immobilized adsorbent in the form of granules that could easily be separated from water without undergoing filtration and centrifugation processes. For this purpose, sol-gel method has been adopted [18] to prepare immobilized activated alumina with uniform surface properties. The immobilized activated alumina has further been modified by adding alum to enhance its adsorption capabilities. The modified immobilized activated alumina (MIAA) was tested for the treatment of water from fluoride affected Manga Mandi area (near Lahore, Pakistan).

2. Materials and Methods

2.1. Materials. Chemicals used in the present study include aluminum tri-sec butoxide (Merck, Germany), activated charcoal (Acros Organics, USA), paraffin oil (MP Biomedicals, LLC Germany), ammonia solution (Burdick and Jackson, Germany), nitric acid (Panreac, Spain), alum, and sodium fluoride NaF (Merck, USA).

2.2. Preparation of Immobilized Adsorbent. For the preparation of adsorbent, sol-gel method of activated alumina [19] was employed with some modifications. The modified boehmite sol was prepared by dissolving drop-wise 100 mL aluminum tri-sec butoxide in 300 mL distilled water at 75°C on a hot plate and adding appropriate amount (10 g) of alum. In order to find out an appropriate alum dose, several boehmite sols were prepared by varying the amount of alum additive from 5 g to 25 g. As 10 g of dose gave maximum fluoride removal efficiency (85%) and considered as appropriate amount of additive. After dissolution, the solution was heated at 90°C for one hour and 15 mL 1 M HNO_3 was added in the slurry. The slurry was refluxed (in a closed vial) in a water bath at 90°C for 10 hours to obtain stable modified boehmite sol. The sol was then heated in a petri dish at 40°C in an electric oven. The gel was dispensed drop-wise with the help of a syringe (without needle) in the ammonia solution that had a top layer of paraffin oil. The droplets were left in the ammonia solution for 45 minutes in order to turn them into solid granules. The granules were washed thoroughly by distilled water and ethyl alcohol, dried, and calcined at 450°C for three hours to obtain modified immobilized activated alumina (MIAA). For each batch adsorption experiment, a fresh adsorbent was prepared as the stated amount is enough for one batch test.

The scanning electron microscope (JEOL JSM-6460, Japan) analysis was performed in order to check the surface of immobilized activated alumina before and after adsorption.

2.3. Adsorption Study. Fluoride adsorption experiments were conducted in order to determine the efficiency of adsorbent and the effect of controlling parameters like dose, contact time, and stirring rate. The stock solution of 5 mg/L of fluoride was prepared by dissolving 0.011 g of reagent grade NaF in 1000 mL distilled water. All adsorption experiments were carried out in a 250 mL conical flask with 100 mL test solution at room temperature (20 ± 1°C) using a mechanical shaker. The adsorption experiments were performed at pH = 7 and at 20 ± 1°C only in order to be as close as possible to natural drinking water conditions for fluoride removal. Fluoride ion concentration was measured using both spectrophotometer (DR 2010, Hach, USA) and ion selective electrode (Ion meter Model 25, Hach, USA).

The effect of adsorbent dose of adsorbent on fluoride removal was studied by varying the dose from 0.5 up to 20 g/L in test solutions containing initial fluoride concentration, 5 mg/L. In order to determine the equilibrium adsorption time, the flasks containing fluoride test solutions (5 mg/L) and optimum adsorbent dose were agitated on the shaker for periods of 5, 15, 30, 45, 60, 75, 90, and 120 minutes. Similarly, for the determination of optimum stirring rate, the flasks containing fluoride test solutions (5 mg/L) and optimum adsorbent dose were agitated on the shaker by changing stirring rate from 50 to 250 rpm. The effect of varying fluoride concentration on adsorption was also studied by changing fluoride concentration from 0.5 to 12 mg/L and employing optimum adsorption conditions. All adsorption tests were run in triplicate to check the precision among the results.

The specified amount of fluoride adsorbed q_e (mg/g) was calculated as follows:

$$q_e = \frac{C_i - C_s}{m}, \tag{1}$$

where C_i is the initial fluoride concentration (mg/L), C_s is the residual fluoride concentration at equilibrium (mg/L), and m is the mass of adsorbent in test solution (g/L).

To compare the efficiency of MIAA, activated charcoal was chosen as standard. All adsorption tests described above were performed again using activated charcoal adsorbent.

2.4. Isotherm Study. The relationship between the amount of substance adsorbed and its concentration in equilibrium solution at constant temperature is called adsorption isotherm. In the present study, the Langmuir and Freundlich isotherms were used to explain the adsorption phenomenon.

The Freundlich equation

$$\log q_e = \frac{1}{n} \log C_S + \log K_f, \quad (2)$$

where q_e (mg/g) = amount of fluoride adsorbed per unit mass of adsorbent, C_s (mg/L) = equilibrium concentration of fluoride, and K_f = adsorption capacity, $1/n$ = adsorption intensity.

The values of K_f and $1/n$ were directly obtained from intercept and slope of the linear plot between $\log q_e$ and $\log C_s$.

The Langmuir isotherm equation

$$\frac{C_S}{q_e} = \frac{C_s}{V_m} + \frac{1}{KV_m}, \quad (3)$$

where q_e (mg/g) = amount of fluoride adsorbed per unit mass of adsorbent, C_s (mg/L) = equilibrium concentration of fluoride, K = adsorption capacity, and V_m = energy of adsorption.

The values of K and V_m were directly obtained from intercept and slope of the linear plot between q_e and C_s.

2.5. Regeneration and Actual Water Sample Treatment. Regeneration of the MIAA was done both thermally and chemically. For thermal treatment, the used adsorbent was heated in a muffle furnace at 450°C for 30 minutes. In case of chemical regeneration, the used MIAA was soaked in 0.1 M NaOH solution for two hours. The adsorbent was then washed with distilled water until the washed water pH became neutral. The regenerated MIAA was tested for the removal of fluoride from test solutions of initial fluoride concentration, 5 mg/L. In this regard, 5 regeneration cycles followed by fluoride removal tests were carried out in succession.

MIAA was also studied for its fluoride removal capabilities from actual water samples. In this regard, five drinking water samples (A–E) were collected from fluoride affected area (Manga Mandi near Lahore) and fluoride removal tests were performed using optimized adsorption conditions.

3. Results and Discussion

The general appearance of MIAA was white hard granules as shown in Figure 1(a). The size of the granules varied from 3 to 6 mm. A number of experiments were conducted in order to find the appropriate conditions like adsorbent dose, concentration of fluoride, contact time, and stirring rate (rpm) for the adsorption of fluoride by MIAA. The SEM images of MIAA before and after adsorption showed that there was a considerable change in the surface after adsorption of fluoride ions which were supposed to adhere on the MIAA surface, refer to Figures 1(b) and 1(c).

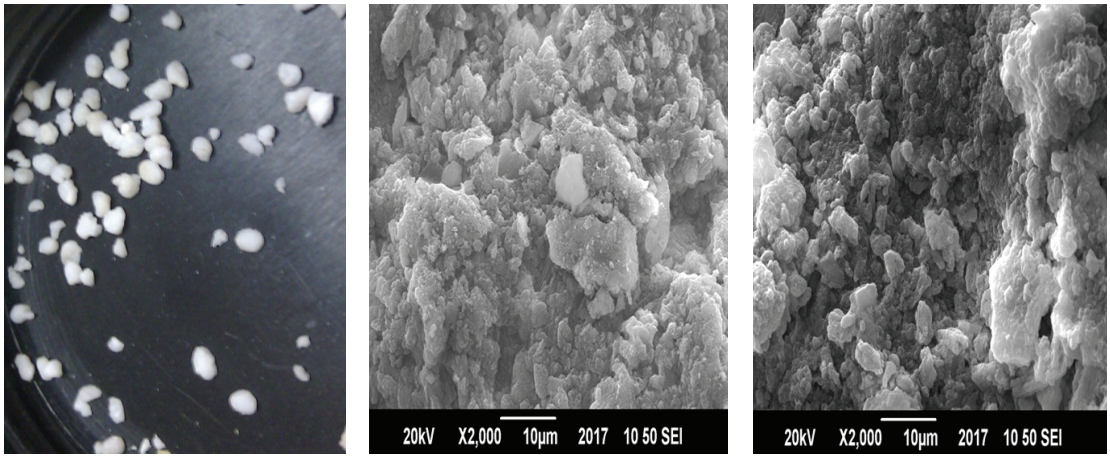
3.1. Effect of Adsorbent Dose. The effect of MIAA and activated charcoal dose on the fluoride adsorption was carried out at 20 ± 1°C. Figure 2 demonstrates that there was an increase in fluoride % removal by increasing dose of the adsorbents. The increase in removal efficiency with increasing dose was due to the increase in surface area and more active sites were available for adsorption of fluoride. But after a specified adsorbent dose, the percentage of removal did not increase considerably and that dose was considered as optimum dose. The optimum dose was 10 g/L for both the adsorbents with the fluoride removal efficiency of 95% and 84% for MIAA and activated charcoal, respectively.

3.2. Effect of Contact Time. The effect of contact time on fluoride adsorption is shown in Figure 3. As the contact time increased, the adsorption capacity of both adsorbents also increased. The increase in the adsorption capacity in the first 40 minutes was very rapid. This might be due to the diffusion of fluoride ions into the surface pores of the adsorbents. After 40 minutes, the increase was less rapid probably due to the migration of fluoride ions from upper adsorbent surface to inner pores. MIAA removed most of the fluoride ions around 60 minutes and then attained equilibrium, whereas activated charcoal adsorption reached equilibrium after 90 minutes.

3.3. Effect of Stirring Rate. The influence of varying stirring rate on fluoride removal efficiency of MIAA and activated charcoal is depicted in Figure 4. It was observed that at lower rpm, the removal capacity was low but as the rpm increased, the fluoride removal also increased. This might be due to the better contact between adsorbent and adsorbate at higher rpm. The optimum stirring rates for activated charcoal and MIAA were 125 rpm and 150 rpm, respectively.

3.4. Effect of Initial Fluoride Concentration. The effect of increasing fluoride concentration on adsorption capacity of MIAA and activated charcoal is shown in Figure 5. For both adsorbents, the adsorption capacity increased to a specified level then attained equilibrium. The maximum adsorption capacity of MIAA and activated charcoal were 0.76 mg/g and 0.47 mg/g, respectively, when the initial fluoride concentration (C_i) was 12 mg/L.

3.5. Isotherm Study. The adsorption isotherm is useful in investigating the feasibility of an adsorbent for an adsorbate. The Freundlich and Langmuir isotherms provided deep insight into the adsorption of fluoride on MIAA and activated charcoal, refer to Figures 6 and 7. The values of the adsorption constants K_f, n, K, and V_m are given in Table 1. The Freundlich model fitted well for both adsorbents with the regression coefficient R^2 of 0.98 and 0.97 for MIAA and activated charcoal, respectively. K_f is the Freundlich constant representing the relative adsorption affinity of the adsorbent toward the adsorbate molecules, and n represents the heterogeneity of the adsorbent. K_f value in case of MIAA is almost three times higher as compared to the value for activated charcoal. The value of n for both adsorbents was greater than unity indicating that the amount adsorbed increased less rapidly than the concentration [19]. The nonlinearity of the adsorption isotherms is evident because $n > 1$ as shown in Figures 6 and 7.



(a) (b) (c)

Figure 1: (a) MIAA, (b) SEM image of pure MIAA, and (c) SEM image of MIAA after adsorption.

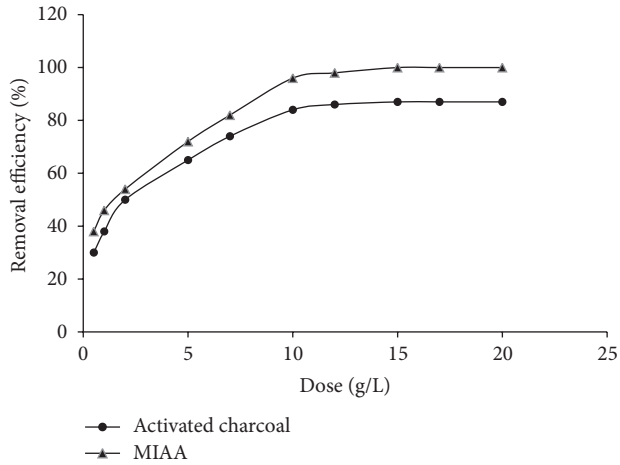


Figure 2: Effect of an adsorbent dose on the removal of fluoride at 20 ± 1°C.

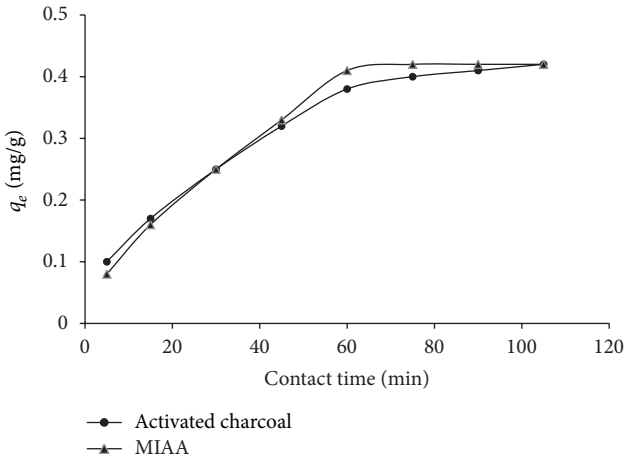


Figure 3: Effect of contact time on adsorption capacity of MIAA and activated charcoal at (20 ± 1°C).

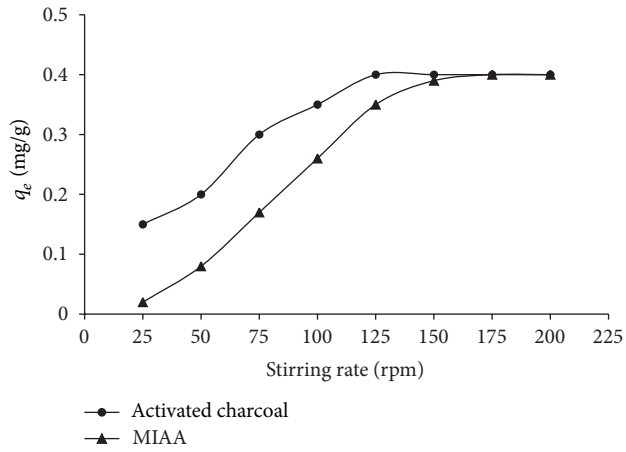


Figure 4: Effect of stirring rate on adsorption capacity of MIAA and activated charcoal at (20 ± 1°C).

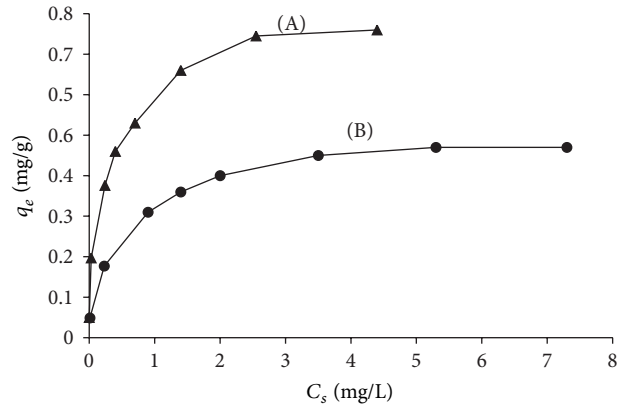


Figure 5: Effect of initial concentration of fluoride on adsorption capacity of (a) MIAA and (b) activated charcoal at 20 ± 1°C.

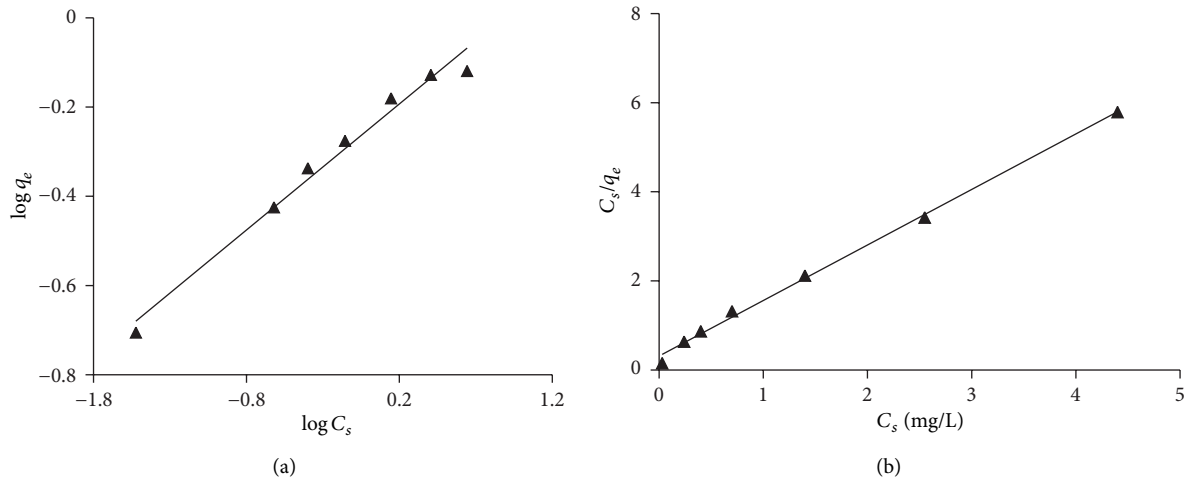


Figure 6: The Freundlich and Langmuir isotherms for fluoride adsorption using MIAA at (20 ± 1°C).

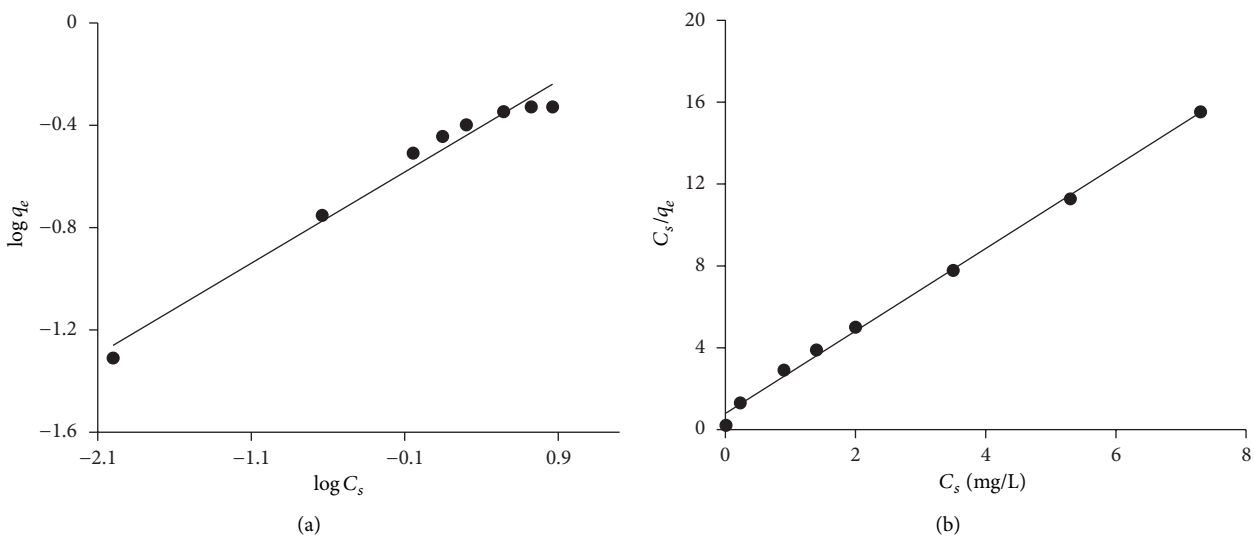


Figure 7: The Freundlich and Langmuir isotherms for fluoride adsorption using activated charcoal at (20 ± 1°C).

The Langmuir adsorption isotherm fitted very well for the fluoride adsorption on both adsorbents with the regression coefficient R^2 of 0.99 as shown in Figures 6 and 7. The values of the adsorption coefficient K and the monolayer capacity V_m calculated from the Langmuir equation are given in Table 1. The values of K and V_m are higher for MIAA as compared to values for activated charcoal that indicates that adsorption of fluoride on MIAA is more favorable.

The Langmuir constant K can be used to predict whether an adsorption system is favorable or unfavorable [20]. For this purpose, a dimensionless separation factor R_L is generally employed:

$$R_L = \frac{1}{1 + KC_i}, \tag{4}$$

where R_L = dimensionless separation factor, C_i = initial fluoride concentration (mg/L), and K = Langmuir constant.

Table 1: Values of Freundlich and Langmuir isotherms constants.

Adsorbent	Freundlich constants			Langmuir constants		
	K_f	n	R^2	K	V_m	R^2
MIAA	0.60	3.57	0.98	4.0	0.80	0.99
Activated charcoal	0.26	2.81	0.97	2.63	0.49	0.99

The parameter R_L indicates the isotherm shape accordingly.

In this work, the values of R_L were in the range 0.02–0.11 against the initial fluoride concentration, C_i = 2–12 mg/L as given in Table 2. The values of R_L suggest that the adsorption of fluoride on MIAA is favorable at 20 ± 1°C.

3.6. Regeneration and Actual Water Sample Treatment. Figure 8 describes results of the MIAA regeneration study. In case of thermal regeneration, the removal efficiency of MIAA is up

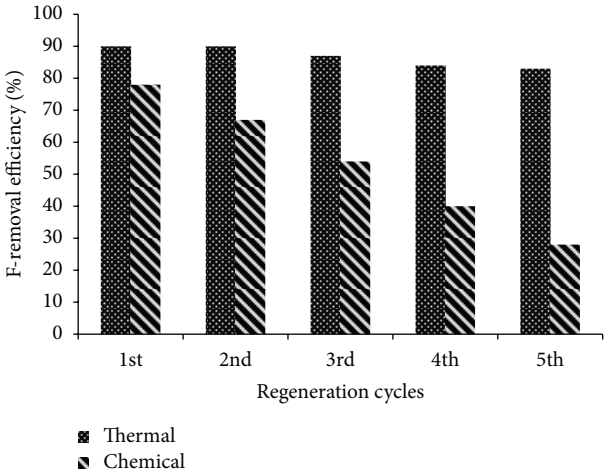


Figure 8: Regeneration of MIAA by thermal and chemical processes.

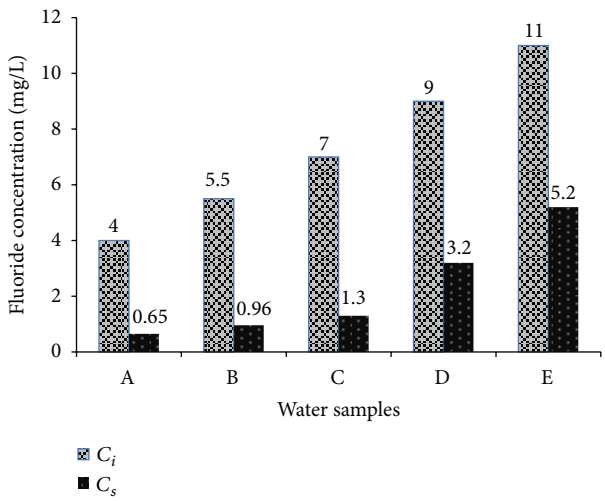


Figure 9: Real water samples with initial fluoride concentration (C_i) and final concentration (C_s).

Table 2: The value of R_L factor and type of isotherm.

R_L	Type of isotherm
Greater than 1	Unfavorable
1	Linear
Between 0 and 1	Favorable
0	Irreversible

to 85% even after 5th regeneration cycle, whereas in case of chemical regeneration, the efficiency considerably decreased after every cycle. It may be due to vigorous washing of MIAA after soaking in NaOH in order to neutralize the pH.

Figure 9 demonstrates removal of fluoride from five drinking water samples (A–E) taken from fluoride affected area Manga Mandi using MIAA under optimized adsorption conditions. The matrix of actual samples is complex and there may be several competing ions present in the samples, but still the removal efficiency ranged from 53% (sample E) to 84% (sample A). This indicates effectiveness of the MIAA for the removal of fluoride from drinking water.

4. Conclusion

Modified immobilized activated alumina (MIAA) has efficiently been utilized for the removal of fluoride from drinking water with the removal efficiency up to 95% at 20 ± 1°C. The adsorption capacity of MIAA was much higher (0.76 mg/g) as compared to the adsorption capacity of activated charcoal (0.47 mg/g) for the same concentration fluoride samples. Both the Langmuir and Freundlich adsorption isotherms fitted well for the fluoride adsorption on MIAA with the regression coefficient R^2 of 0.99 and 0.98, respectively. MIAA can both be regenerated thermally and chemically. MIAA proved effective for the treatment of fluoride contaminated actual drinking water samples.

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