Removal of fluoride using fly ash adsorbent

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Abstract. Fluoride (F\textsuperscript{−}) content in groundwater above 1.5 mg/L is a serious concern all over the world due to adverse health effects beyond that concentration. Hence, apart from its monitoring, an effective and low-cost removal technique is necessary. In this work, the removal of fluoride using fly ash has been studied. Batch adsorption studies, using laboratory shaker, were performed to examine the effect of pH in the range 2-10, adsorbent size (0.225 mm, 0.45 mm, and 0.90 mm), and adsorbent dose, varied from 2-6 g/L, for a contact time of 4 hours in all the experiments. The optimum condition for the F\textsuperscript{−} removal was observed as pH:5, adsorbent size:0.225 mm and adsorbent dose: 5 mg/L, providing 67.20 % F\textsuperscript{−}removal from the solution. Different kinetic models were tested and it was found that adsorption kinetics is of Pseudo second order and Elovich type. The study showed that fly ash can be effectively used for fluoride removal from water.

1. Introduction
Fluoride contaminated groundwater is a serious issue as most Indian populations resort to groundwater for drinking water needs. In rural areas, facilities to remove F\textsuperscript{−} from such water supply are usually not available. Some of the causes of the occurrence of F\textsuperscript{−} in the groundwater are leaching of fluoride bearing rocks, geochemical reactions, and industrial discharges\cite{1}. F\textsuperscript{−} is highly electronegative and has low bond energy which makes it highly reactive, leading to its presence in a combined state such as sodium fluoride, fluorite, etc.\cite{2}. While the presence of F\textsuperscript{−} in amounts 0.5 mg/L to 1.5 mg/L is essential for bones and dental strength in animals and humans\cite{3}, its concentration, more than 1.5 mg/L, as specified by World Health Organization(WHO), causes irreversible demineralization of bones and tooth tissues resulting in skeletal and dental fluorosis, harmful to the brain, kidney liver, skin and death in extreme cases is also possible\cite{2-4}.

The Indian scenario of F\textsuperscript{−} contamination in groundwater is such that 19 of Indian states are severely affected by high F\textsuperscript{−} concentration in groundwater ranging from 2.0 mg/L in Haryana to 38.0 mg/L in Rajasthan. And one of the reasons for such a high concentration of F\textsuperscript{−} in groundwater is attributed to the presence of 12 million out of 85 million of F\textsuperscript{−} deposits on earth surface is present in India only \cite{4}. As the WHO as well as the Bureau of India Standards (BIS) authorizes a safe F\textsuperscript{−} concentration limit in drinking water as 1.5 mg/L, removal of fluoride through a cheap and effective method has become a mandate.

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Adsorption is a favourable technique for water treatment due to a variety of adsorbents available and flexibility of operation. However, a suitable low-cost adsorbent for fluoride removal with high uptake capacity and easy regeneration has always remained a thrust area of research. Available scientific shows the use of red mud [6], high alumina content bauxite [7], waste carbon slurry [8], bone char [9], alun [10], natural materials [11], furnace slag [12], fly ash [10,13]. Bagasse [14], bark of phyllanthus emblica (amla) tree [15] in defluoridation. Fly ash is a solid waste generated mainly from coal fired power plant and bagasse fired plant. It has long been utilized for the defluoridation of water and it is seen as a substitute to activated carbon or zeolites for the purpose [13,16]. Panda and Kar (2018) used coal fired fly ash based zeolite to remove fluoride from contaminated water and observed 90-95% fluoride adsorption efficiency from its initial concentration of 5 mg/L in the solution at pH 6 [17].

According to the 2018-19 report of Central Electricity Authority India, about 196.44 million tons of fly ash was generated from the coal/lignite based power plants. Out of which only 67.13% of fly ash was utilized by different sectors and 32.87% of fly ash remained unutilized, which makes it an attractive adsorbent source for defluoridation of water. Fly ash typically contains 58-77 % SiO2, 1-15 % Al2O3, 1.6-8 % Fe2O3, and 0.5-5 % CaO. Apart from it, MnO, MgO, Na2O, K2O, P2O5 are also present in small amounts [18]. It is a low cost adsorbent and it can be used only after washing and drying, while other biomass adsorbent materials, such as wood and nuts shell, etc. require activation before their use. In this work, a high concentration of fluoride (50 mg/L) in a synthetic fluoride bearing water was considered to examine fly ash’s defluoridation capacity.

2. Materials and methods
The removal of F⁻ for groundwater is necessary, therefore, lab scale studies to remove F⁻ from synthetic water was carried out. Batch adsorptive treatment of F⁻ bearing water was carried out in a shaker. 50 ml of Sodium F⁻ solution contaminating 50 mg/L F⁻ was taken in a 100 ml conical flask. To estimate F⁻, at different time intervals about 5 ml samples were taken and its concentration was determined by colorimetry method using a kit provided by Merck, Germany. To estimate F⁻ in the water sample, the F⁻ bearing water was taken in a test tube, in which the reagents were added in the desired amount, as a result, the color was developed. The intensity of color, thus F⁻ concentration in water, was estimated at a wave length of 570 nM using a spectro photometer (model spetroquant prove 300, Merck made) [19]. The effect of influencing parameters like pH, adsorbent dose (g), and contact (shaking) time on F⁻ removal was estimated. The F⁻ removal efficiency after adsorption and the uptake capacity of adsorbent at any time (t) was estimated using Eq 1 and Eq 2, respectively. The fly ash was acquired from Bhoramdev Sugar factory, Kawardha, Chhattisgarh. The fly ash so collected was washed up with tap water and dried at 110°C before utilizing it in further experiments.

\[ R\% = \frac{C_o - C_t}{C_o} \times 100 \]  
\[ q_t = \frac{(C_o - C_t)V}{m} \]  

Where R% is the percentage removal efficiency; C₀ and Cₜ is F⁻ concentration at initial and after time t, respectively, mg/L; qₜ is the amount of F⁻ adsorbed per unit mass of adsorbent, mg/g; V is the volume of solution, L; and m is the mass of adsorbent, g.

3. Results and discussion
The effects of various parameters on fluoride removal are presented and discussed in this section.

3.1. Effect of pH
In the adsorption process, pH was found to be a major factor affecting defluoridation as well as the separations of different ions present in solution. With an increase in pH, the mineral surface becomes more negatively charged, thus it becomes more difficult to adsorb anions compared to cations from the solution [20]. The fly ash was tested for the removal of F⁻ at different pH. The results are presented in
Figure 1. From the figure it may be seen that initial $F^-$ concentration of 50.0 mg/L was reduced to 31.92, 23.28, 17.62, 19.3, 28.4, 36.36 and 37.68 mg/L at pH 2.0, 3.0, 5.0, 6.0, 7.0, 8.0 and 10.0 respectively in a 4 hours of contact time. Maximum $F^-$ removal was observed at pH 5.0. The pH dependence occurs when the $F^-$ ions and hydroxyl ions compete for adsorptions site or when the ions and protons compete for the same active binding sites on the sorbent surface [21], which appears to be a reason for the above trend. At higher pH the presence of hydroxyl ion causes competitive adsorption hence less adsorption of $F^-$ was observed.

![Figure 1](image1.png)

**Figure 1.** Effect of pH on $F^-$ removal using fly ash. $F_i^-$ (initial concentration)= 50 mg/L, Fly Ash=4 g/L, adsorbent size=0.225 mm

3.2. *Effect of adsorbent size*

Experiments with adsorbent size showed that lower adsorbent size gave better $F^-$ removal because smaller particle size provides larger surface area for adsorption per unit mass of adsorbent compared to larger particles. For the particle size of 0.225 mm, the initial concentration of $F^-$ 50 mg/L in the solution decreased to 17.6 mg/L in 4 h of operation, as shown in Figure 2, below. The adsorbent size 0.225 mm was chosen for further studies.

![Figure 2](image2.png)

**Figure 2.** Effect of fly ash size on $F^-$ removal. $F_i^-$ = 50 mg/L, Fly ash 4g/L, $\text{pH}_{i}$=5
3.3. Effect of adsorbent dose
The adsorbent dose is an amount of adsorbent brought into contact with the solute. Adsorption was increased with increase in adsorbent dose, due to the availability of more adsorption sites. The results are given in Figure 3. The final concentrations of F were found to be 22.1, 19.8, 17.6, 16.4, and 16.2 mg/L in the solution for the adsorbent dose of 2, 3, 4, 5, and 6 mg/L, respectively. The reason for increased removal of F with the increase in adsorbent dose can be attributed to the availability of large active surface area for adsorption at higher doses. As there was only a marginal change in the final concentration of F with the increase in adsorbent dose from 5 mg/L to 6 mg/L, the optimum adsorbent dose was fixed at 5 mg/L.

![Figure 3](image.png)

**Figure 3.** Effect of fly ash dose on F removal. F= 50 mg/L, pH = 5, adsorbent size = 0.225 mm

3.4. Effect of Contact Time
The fluoride concentration in the solution was noted from 0 to 4 h at an interval of 0.5 h. The study found that the concentration of fluoride in the solution initially decreased at a higher rate than at a lower rate. This may be due to vacant sites' occupying and reduction in available surface area for adsorption with time. After 3.5 hours, the adsorption rate became very slow, and the concentration of fluoride in the solution was almost steady by 4 hours, indicating an equilibrium condition. Therefore, 4 h was fixed as the optimum contact time for fluoride removal.

3.5. Adsorption Kinetics Study
Kinetics studies were also performed for the adsorption process. The Pseudo-first-order model, Pseudo-second-order model, Elovich Model, and Pore Diffusion Model were tested in the present adsorption process. The Eq. 3, Eq. 4, Eq. 5 and Eq. 6 are used.

Pseudo 1st-Order Model [22]

\[
\log(q_e - q_t) = \log q_e - \frac{K_1 t}{2.303}
\]  

Where, \(q_e\) is the equilibrium uptake capacity of adsorbent in (mg of fluoride/g of adsorbent). The first order constant \(K_1\) gives an idea about the kinetic rate of the process. A larger value of \(K_1\) suggests that the adsorption is not diffusion controlled. The value of constant \(K_1\) is calculated from the graph between the left hand side term of Eq 3 and t.

Pseudo-second-order model [23]
\[
\frac{t}{q_t} = \frac{1}{K_2q_e^2} + \frac{t}{q_e}
\]  \tag{4}

Where, \(K_2\) the pseudo second-order rate constant (g/mg.h). The pseudo second-order model is tested to ascertain the chemisorption behaviour of the adsorption process. The term \(K_2q_e^2\) gives an idea about the initial sorption rate. By plotting the \(t/q_t\) vs \(t\), the value of constant \(K_2\) and \(q_e\) (1/slope) can be calculated, using slope and intercept of the line.

Elovich Model [24]

\[
q_t = \frac{1}{b} \ln(ab) + \frac{1}{b} \ln (t)
\]  \tag{5}

Where a and b are the Elovich constants. The slope of the line between \(q_t\) and \(\ln t\) gives the value 1/b, which indicates available sites for adsorption. The suitability of the model to kinetic data represents the chemisorption mechanism of adsorption.

Pore Diffusion, Intra-Particle Diffusion Model [25]

\[
q_t = K_i t^{0.5} + C
\]  \tag{6}

Where \(K_i\) (mg/g. h^{0.5}) is the intraparticle rate constant. The slope and the intercept of the plot between \(q_t\) and \(t^{0.5}\) give the value of \(K_i\) and \(C\), respectively. The fitness of the model to kinetic data validates the dominance of intraparticle diffusion in the adsorption process.

The respective plots of kinetic models are shown in Fig. 4 to Fig. 7, and the model parameters are presented in Table 1.

Adsorption kinetic study for fluoride removal using fly ash (pH = 5.0; T= 299K; fly ash = 5.0 g/l, adsorbent size =0.225 mm)
Table 1. Kinetic model parameters

| Model                        | Parameter Values          |
|------------------------------|---------------------------|
| Pseudo First Order           | K₁=1.0269, R²=0.941       |
| Pseudo Second Order          | K₂=0.0323, R²=0.979       |
| Elovich Model                | a = 9.5116, b= 0.3945, R²=0.996 |
| Pore diffusion Model         |                           |
|                              | R²= 0.957                |

From the data in Table 1, based on the regression coefficient value (R²) it can be observed that adsorption data fitted well to both the Pseudo Second Order and Elovich model in the present study. Chakraborty and co-workers have also reported similar findings[16].

4. Conclusion

This study assessed the suitability of fly ash for the removal of F⁻ from potable water. The fly ash showed better removal efficiency of 67.2 % with the adsorbent dose 5 g/L, contact time 4 h, adsorbent size 0.225 mm, and pH 5. The adsorption equilibrium data fitted best with the Freundlich isotherm model (R² = 0.9964). The adsorption data showed the best fit with the Elovich model (R² = 0.996). The study suggests that fly ash could be a suitable adsorbent for reducing the initial higher concentration of fluoride in water sources. Since groundwater contain less fluoride than the initial concentration (50 mg/L) considered in this study, better removal efficiency could be obtained while treating the groundwater with the fly ash.

References

[1] Chaudhary K, Saraswat P K and Khan S 2019 Environ. Saf. 168 164–176
[2] Biswas G, Kumari M, Adhikari K and Dutta S 2017 Current Pollution Reports 3 104–19
[3] Karunanithi M, Agarwal R and Qanungo K 2019 Periodica Polytechnica Chemical Engineering 63 425–37
[4] Yadav K K, Kumar S, Pham Q B, Gupta N, Rezania S, Kamyab H, Yadav S, Vymazal J, Kumar V, Tri D Q, Talaeikhozani A, Prasad S, Reece L M, Singh N, Maurya P K and Cho J 2019. Ecotoxicology and Environmental Safety 182 109362
[5] Dehghani M H, Farhang M, Afsharnia M and Mckay G 2018. Chem.l Eng. Commun. 205 955–65
[6] Cengeloglu Y, Kir E and Ersoz M 2002 Separ. Purif. Technol. 28 81–86
[7] Lavecchia R, Medici, F., Piga, L. and Rinaldi G. Antonio 2012 Chem. Eng. Trans. 26 124-129
[8] Gupta V K, Ali I and Saini V K 2007 Water Res. 41 3307–3316
[9] Rojas M. C K, Bonilla-Petriciolet A, Silvestre-Albero J, Aguayo-Villarreal I A and Mendoza-Castillo D I 2015. Appl. Surf. Sci. 355 748–760
[10] Goswami D and Das A K 2006 J. Sci. Ind. Res. India 65 77–99
[11] Chidambaram S, Ramanathan A L and Vasudevan S 2003 Water SA 29 339–43
[12] Islam M and Patel R 2011 Chem. Eng. J. 169 68–77
[13] Chaturvedi A K, Yadava K P, Pathak K C and Singh V N 1990 Water, Air, Soil Pollut. 49 51-61
[14] Gupta N, Gupta V, Singh A P and Singh R P 2014 Bonfring International Journal of Industrial Engineering and Management Science, 4 DOI 10.9756/bijems.10299
[15] Patil R N, Nagarnaik D P and Agrawal D D 2016 Int. J. Civ. Eng. Technol. 7 11–20
[16] Chakraborty G M, Das S K, Mandal S N 2018 Emerging Trends in Chemical Sciences, 69-87 DOI 10.1007/978-3-319-60408-4_6
[17] Panda L and Kar B B 2018 Asian Journal of Water, Environment and Pollution 15 105–13
[18] Xu Q, Ji T, Gao S, Yang Z and Wa N. 2019 Materials (Basel) 12 39-46
[19] Rice E W, Baird R B, Eaton A D and Clesceri L S 2012 Standard methods for examination of water and wastewater, APHA, AWWA, WEF, 22 Edn, Washington, DC
[20] Singh S P, Ma L Q and Hendry M J 2006 J. Hazard. Mater. 136 654 – 662
[21] Donmez G and Aksu Z 2002 Process Biology and Chemistry 38 751-769
[22] Lagergren S. 1898 Kungliga Svenska Vetenskapsakademiens Handlingar 24 1–39
[23] Ho Y S and McKay G 2000 Adsorp. Sci. Technol. 18 639–650
[24] Chien S H, Clayton W R, 1980 Soil Sci. Soc. Am. J. 44 265–268
[25] Weber W J and Morris J C 1963 J. Sanit Eng. Div. Am. Soc. Civ. Eng. 89 31–60