

## EFFICIENCY OF GRANULAR FERRIC HYDROXIDE (GFH) FOR REMOVAL OF FLUORIDE FROM WATER

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**SUMMARY:** Granular ferric hydroxide (GFH), a combination of poorly crystallized FeOOH, was investigated for removal of fluoride (F) from water. Adsorption was studied in batch experiments at room temperature together with the effect of contact time, pH, initial F concentration, and  $\text{SO}_4^{2-}$  and  $\text{Cl}^-$  as interfering anions. Lower pH with higher initial F concentration and longer contact time increased the F removal efficiency. In the absence of interfering anions, maximum removal of F approaching 88 percent was achieved at pH 6 after 30 min from water containing 7 mg F/L. Considering economic and feasibility aspects, adsorption of F with GFH is recommended as a successful method of F removal from water and wastewater treatment plants.

Keywords: Fluoride removal; Granular ferric hydroxide (GFH); Water treatment.

### INTRODUCTION

Dental and skeletal fluorosis commonly result from elevated fluoride (F) intake, especially from drinking water.<sup>1</sup> Many investigations have reported the F content of air,<sup>2</sup> groundwater,<sup>3-5</sup> drinking water,<sup>6</sup> bottled water,<sup>7</sup> and some forms of black tea.<sup>8</sup> Removal of F by coagulation and precipitation processes is often effective when sufficiently insoluble sediments are present. Adsorption is another popular technique for F removal in which various adsorbents such as bone char,<sup>9</sup> activated alumina,<sup>10</sup> activated carbon,<sup>11</sup> super phosphate,<sup>12</sup> synthetic zeolite<sup>13</sup> are widely used. Today, reverse osmosis, nano-filtration, ultra filtration, Dannon dialysis, and electro dialysis have gained in popularity.<sup>14-15</sup> In this study we investigated the efficiency of F removal from synthetic water samples using a form of commercially available granular ferric hydroxide (GFH).

### MATERIALS AND METHODS

GFH, a poorly crystallized form of FeOOH, consists mainly of akaganeite.<sup>16</sup> Having a high porosity and suitable sites smaller than 4.5 microns, GFH is an excellent adsorbent for arsenic and other impurities in water.<sup>17-18</sup> In the present study for F removal, GFH was obtained from MERCK with properties noted in the table.

For activation, the GFH was heated at 103–105°C for 30 min and cooled in a desiccator before use. A stock F solution was prepared by dissolving 0.221 mg of NaF in 1000 mL of distilled water. GFH (1.25 g) was added to 250 mL of synthetic F solution samples, and the mixture shaken in a HEIDOLPH mixer at 300 rpm. Samples were then filtered using 0.45-micron Whatman filter paper, and the concentration of the F remaining was measured using by the SPADNS method

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with a DR 5000 spectrophotometer. The concentration of iron released into the samples from the GFH during adsorption was measured using a DR 2000 spectrophotometer.

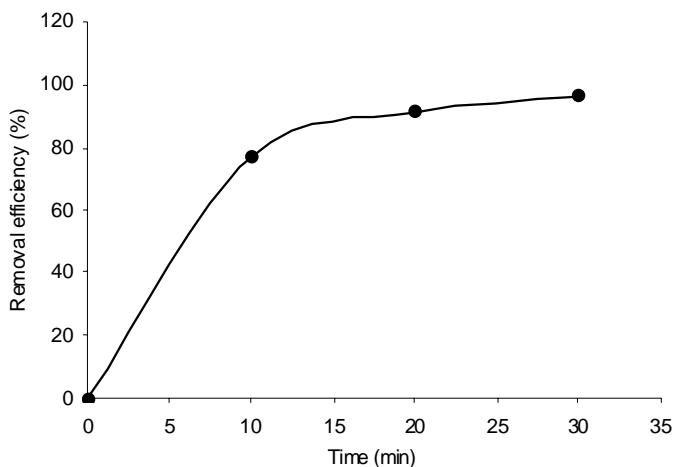
**Table.** GFH properties used in experiments

Property	Unit	
Saturation	percent	43-48
Porosity	percent	72-77
pH	na	7.5-8.2
Specific surface	m <sup>2</sup> /m <sup>3</sup>	280
Effective size	mm	0.32-1
Uniformity coefficient	na	About 3

na: not applicable

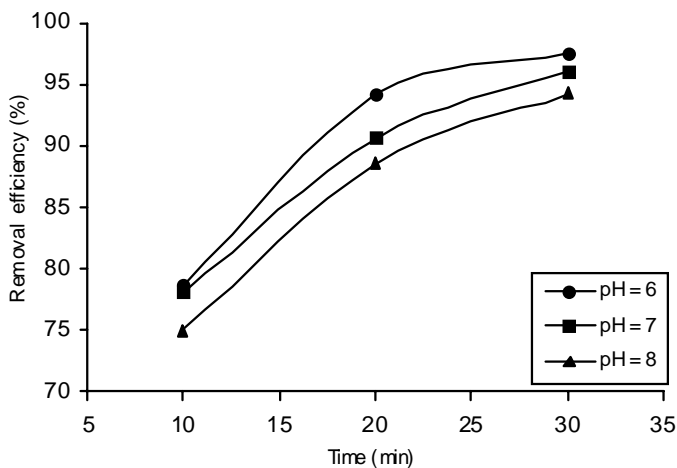
### RESULTS AND DISCUSSION

To examine the effect of contact time on F removal efficiency, experiments were conducted over periods of 10, 20, and 30 min. Figure 1 shows the increasing of overall removal of F with contact time. The early steep portion of the removal curve indicated that the rate of removal is faster in the first minutes of adsorption. In the absence of interfering anions the overall removal efficiency was about 88 percent from a solution containing 7 mg F/L.

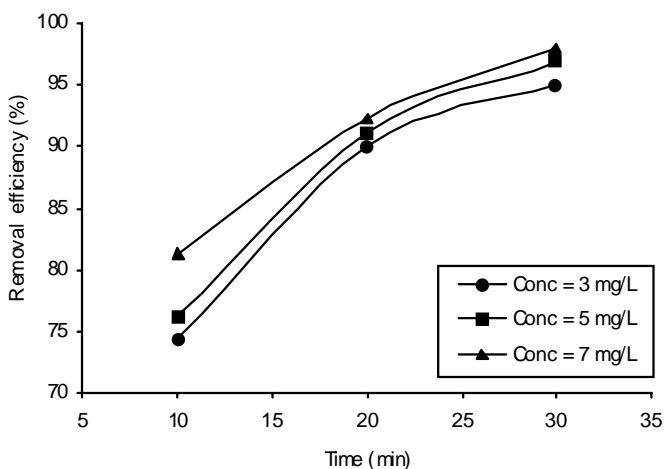


**Figure 1.** Contact time effect on F removal efficiency by GFH.

The influence of pH on removal efficiency was investigated at pH 6 to 8 with the best results at pH 6 as shown in Figure 2. The effect of initial F concentration on adsorption efficiency was investigated using 3, 5, and 7 mg F/L in the sample solutions. As seen in Figure 3, adsorption efficiency improved with increasing F concentration.



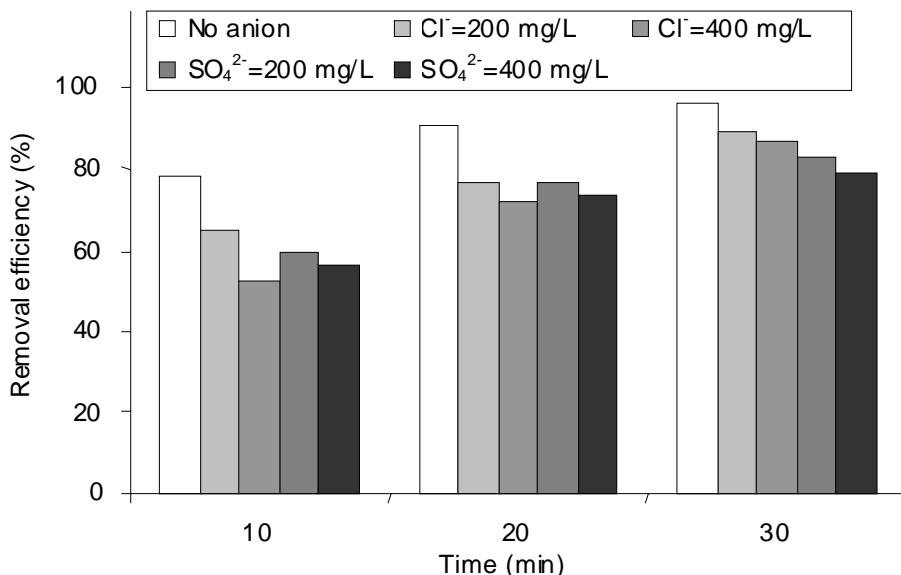
**Figure 2.** Effect of pH on F removal efficiency by GFH with 3 mg F/L in sample.



**Figure 3.** Effect of initial F concentration on GFH removal efficiency.

The effect of two important natural anions was studied using 200 and 400 mg/L of chloride ( $\text{Cl}^-$ ) and sulfate ( $\text{SO}_4^{2-}$ ) at pH 7 with 3, 5, and 7 mg/L as the initial F concentration. Mean Fe removal efficiencies in the presence and absence of interfering anions are shown in Figure 4 in which  $\text{SO}_4^{2-}$  is seen to have a greater effect on F removal performance than  $\text{Cl}^-$ . At 200 and 400 mg/L,  $\text{Cl}^-$  and  $\text{SO}_4^{2-}$  decreased the efficiency about 11.5 and 18.3, and 15.4 and 18.6 percent, respectively. Since more than 70 percent of adsorption took place in the first minute of contact time, use of GFH as an adsorbent in a batch or a continuous mode of operation in water and wastewater treatment plants could significantly reduce capital and operational costs. Although F removal efficiency increases with decreasing pH, in normal pH of natural waters (6–8.5), good removal can be achieved. In a related study by Kumar et al.,<sup>19</sup> F adsorption by GFH was

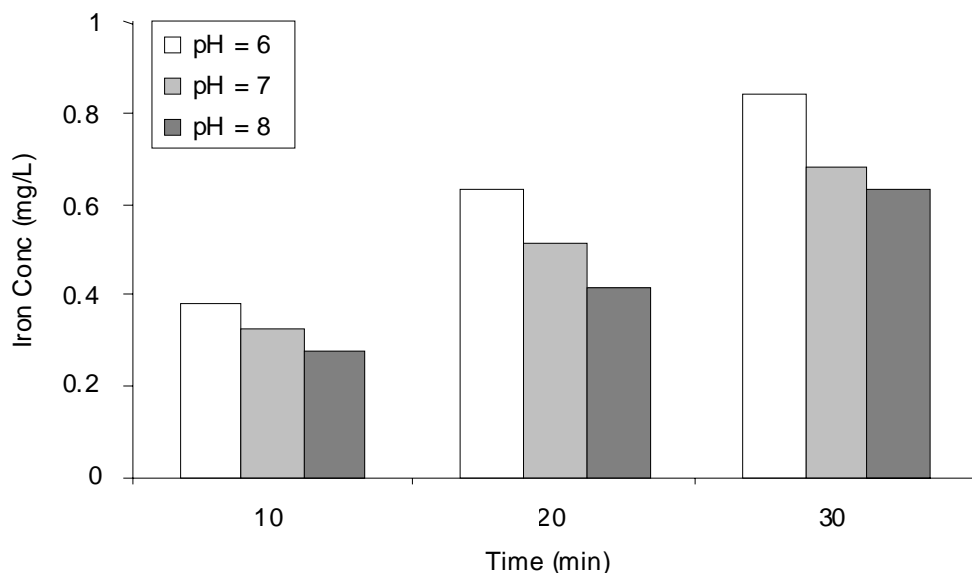
maximized at a lower pH. Their work also showed that by increasing pH above 8, adsorption of F diminished dramatically due to increased negative charges on the GFH surfaces. Decreasing removal efficiency as increasing pH can be explained by competition of anions, particularly hydroxide ion vs. F replacement in active sites of GFH.



**Figure 4.** Influence of interfering anions on F removal efficiency by GFH with 3 mg F/L in the sample.

GFH has been successfully used to remove different pollutants such as arsenic,<sup>18</sup> bromate,<sup>20</sup> phosphate,<sup>21</sup> natural organic matter NOM,<sup>16</sup> and other contaminants from water and wastewater. Other iron compounds, including hydrous ferric oxide (HFO),<sup>22</sup> polymers,<sup>23</sup> iron-coated materials,<sup>24</sup> zero valent-iron,<sup>25</sup> and other types of iron-containing coagulating agents have been used in water and wastewater purification systems. Hybrid sorbent resins<sup>26</sup> have also been successfully investigated.

As seen in Figure 3, Cl<sup>-</sup> and SO<sub>4</sub><sup>2-</sup> at concentrations found in groundwater have a negative effect on adsorption performance. As shown in Figure 5, the concentration of iron released into the solution increases with contact time and decreases with increasing pH. Without considering the initial F concentration, the minimum Fe concentration added to the samples was 0.28 mg/L after 10 min at pH 8 and can even reach over 0.6 mg/L after 30 min time at pH 8. Initial fluoride concentration does not have a significant effect on released Fe concentration in samples. Considering economic and feasibility aspects, GFH as an adsorbent is recommended for partial removal of F from water and in wastewater treatment plants.



**Figure 5.** Mean iron concentration added to solution by GFH as a function of contact time and pH, regardless of initial F concentration.

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#### REFERENCES

- 1 Rao, Nagendra CR. Fluoride and environment: a review. In: Martin J, Bunch V, Suresh VM, Kumaran TV, editors. Proceedings of the 3rd International Conference on Environment and Health; 2003 Dec 15-17; Chennai, India. Chennai: Department of Geography, University of Madras and Faculty of Environmental Studies; York University. p. 386-99.
- 2 Dobaradaran S, Fazelinia F, Mahvi AH, Hosseini S. Particulate airborne fluoride from an aluminium production plant in Arak, Iran. *Fluoride* 2009;42: 228-32.
- 3 Dobaradaran S, Mahvi AH, Dehdashti S, Abadi DRV. Drinking water Fluoride and child dental caries in Dashtestan, Iran. *Fluoride* 2008; 41:220-6.
- 4 Dobaradaran S, Mahvi AH, Dehdashti S, Dobaradaran S, Shoara L. Correlation of fluoride with some inorganic constituent in groundwater of Dashtestan, Iran. *Fluoride* 2009;42:50-3.
- 5 Nouri J, Mahvi AH, Babaei AA, Ahmadvpour E. Regional pattern distribution of groundwater fluoride in the Shush Aquifer of Khuzestan County, Iran. *Fluoride* 2006;39:321-5.
- 6 Mahvi AH, Zazoli MA, Younecian M, Nicpour B, Babapour A. Survey of fluoride concentration in drinking water sources and prevalence of DMFT in 12 year old students in Behshahr City. *Journal of Medical Sciences* 2006;6:658-61.
- 7 Dobaradaran S, Mahvi AH, Dehdashti S. Fluoride content of bottled drinking water available in Iran. *Fluoride* 2008;41:93-4.
- 8 Mahvi AH, Zazoli MA, Younecian M, Esfandiari Y. Fluoride content of Iranian black tea and tea liquor. *Fluoride* 2006;39:266-8.
- 9 Bhargava DS, Killedar DJ. Fluoride adsorption on fishbone charcoal through a moving media adsorber. *Water Res* 1992;26:781-8.
- 10 Ku Y, Chiou HM. The adsorption of fluoride ion from aqueous solution by activated alumina. *Water Air Soil Poll* 2002;133:349-60.

- 11 Daifullah AAM, Yakout SM, Elreefy SA. Adsorption of fluoride in aqueous solutions using KMnO<sub>4</sub>-modified activated carbon derived from steam pyrolysis of rice straw. *J Hazard Mater* 2007;147:633-43.
- 12 Fan X, Parker DJ, Smith MD. Adsorption kinetics of fluoride on low cost materials. *Water Res* 2003;37:4929-37.
- 13 Exchange Resin. *Chemical Abstracts* 1951;45:5033 and 7725.
- 14 Cotton FA, Wilkinson G. *Advanced Inorganic Chemistry*. New York: John Wiley and Sons; 1988. p. 546.
- 15 Pathak BD. Occurrence of fluorides in ground waters in Uttar Pradesh. *Proceedings of the Symposium on Fluorosis*; 1974; Hyderabad. p. 237.
- 16 Genz A, Baumgarten B, Goernitz M, Jekel M. NOM removal by adsorption onto granular ferric hydroxide: equilibrium, kinetics, filter and regeneration studies. *Water Res* 2008;42:238-48.
- 17 Runaska W, Kawane M, Kajima T. Removal of fluoride ion by anion. Driehaus W. Arsenic removal: experience with the GEH® process in Germany. *Water Supply* 2002;2:275-80.
- 18 Saha B, Bains R, Greenwood F. Physicochemical characterization of granular ferric hydroxide (GFH) for arsenic (V) sorption from water. *Separ Sci Technol* 2005;40:2909–32.
- 19 Kumar E, Bhatnagar A, Ji M, Jung WS, Lee SH, Kim SJ, et al. Defluoridation from aqueous solutions by granular ferric hydroxide (GFH). *Water research* 2008;43(2):1-9.
- 20 Bhatnagar A, Choi YH, Yoon YJ, Shin Y, Jeon BH, Kang JW. Bromate removal from water by granular ferric hydroxide (GFH). *J Hazard Mater* 2009; 170:134-40.
- 21 Grzmil B, Wronkowski J. Removal of phosphates and fluorides from industrial wastewater. *Desalination* 2006;189:261-8.
- 22 Dey S, Goswami S, Ghosh UC. Hydrous Ferric Oxide (HFO): a scavenger for fluoride from contaminated water. *Water Air Soil Poll* 2004;158:311-26.
- 23 Karthikeyan M, Kumar KKS, Elango KP. Conducting polymer/alumina composites as viable adsorbents for the removal of fluoride ions from aqueous solution. *Journal of Fluorine Chemistry* 2009;130(10):894-901.
- 24 Katsoyiannis IA, Zouboulis AI. Removal of arsenic from contaminated water sources by sorption onto iron-oxide-coated polymeric materials. *Water Res* 2002;36:5141-55.
- 25 Rangsviek R, Jekel MR. Removal of dissolved metals by zero-valent iron (ZVI): kinetics, equilibria, processes and implications for storm water runoff treatment. *Water Res* 2005;39:4153-63.
- 26 Rahmani BM, Mahvi AH, Dobaradaran S, Hosseini SS. Evaluating the effectiveness of a hybrid sorbent resin in removing fluoride from water. *Int J of Environ Sci Tech* 2009;6:629-32.