**Removal of Fluoride using Granular Activated Carbon and Domestic Sewage Sludge**

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**Abstract.** Fluoride is an ionic form of the element fluorine and occurs naturally or used as an additive to municipal water supplies. Presence of fluoride beyond the permissible limit (> 1.5 ppm) in drinking water is harmful and not suitable. Considering the range of health effects associated with high levels of fluoride in water, Granular activated carbon (GAC) and domestic sewage sludge has been employed for its removal. The influence of various operational parameters i.e., effect of adsorbent dose, pH, agitation speed, initial concentration and contact time were studied by a series of batch adsorption experiments at room temperature (25 ± 3°C). The percentage removal was found to increase with adsorbent dose, agitation speed and time for a given initial fluoride concentration (5 ppm) while for increasing fluoride concentration, removal followed a decreasing trend. Although remarkable removal efficiency was observed in acidic range, removal at neutral pH is considered for both adsorbents from drinking water viewpoint. At optimum conditions, the residual fluoride concentration was 1 mg/l in case of GAC and 0.6 mg/l for sludge, which is below the prescribed limit and is thus able to meet the standard. The equilibrium adsorption data are modeled with different isotherm equations applicable to adsorption process. The dewatered sludge fitted better with Freundlich isotherm having correlation coefficients ($R^2$) equal to 0.999 and 0.972 for Langmuir isotherm, respectively. The total pore volume and surface area obtained from BET experiment is 0.3877 cm$^3$ g$^{-1}$ and 884.66 m$^2$ g$^{-1}$ for GAC and 0.00097266 cm$^3$ g$^{-1}$ and 2 m$^2$ g$^{-1}$ for sludge, respectively. FTIR analysis of dewatered sludge showed that major peaks were pertaining to components like amines that usually exist in the sludge.

**Keywords:** Fluoride, Granular activated carbon, Sewage sludge, Adsorption, Adsorption isotherm

1. **Introduction**

Fluoride is one of the chemical element that is found most frequently in groundwater and has become one of the major toxicological environmental hazards globally [1]. The formation of fluoride is based on the interaction of element fluorine with the minerals present in soil and rocks. Even though fluoride is important for mineralization of hard tissues and bones, it can be detrimental to humans when exposed to elevated concentrations. Fluoride is used as an additive to drinking water in an attempt to prevent tooth decay, while this idea has given rise to fear and suspicion. World Health Organization (WHO) and ISO: 10500 recommend that fluoride content in drinking water should be in the range of 1.0 to 1.5 ppm. It is estimated that about 80% of diseases in the world are attributed to poor quality of drinking water, of which fluoride contamination in drinking water is responsible for 65% of endemic fluorosis [2].

One option to prevent fluorosis can be the use of alternate water sources like surface water, rainwater and less fluoride containing groundwater. Yet, periodic monitoring is required to avoid mixing of high fluoride content water from different aquifers and this approach may not be practically feasible. The conventional rural defluoridation techniques like Nalgonda technique and activated alumina generates a large amount of fluoride sludge [3]. Moreover, better and effective removal technologies like reverse osmosis, ion...
exchange, dialysis and electrodialysis, adsorption by commercial carbons, are costly and often just not feasible for that purpose.

Thus, it is important to explore low-cost adsorbents for the adsorption of fluoride from aqueous medium. The removal efficiency of the fluoride by domestic sewage sludge is compared with the commercial activated carbon to assure that low-cost adsorbents can also have good potential to remove fluoride. Effects of various operating parameters that may affect the adsorption process are also assessed.

2. Materials and Methods

2.1. Preparation of synthetic fluoride water

Stock solution of 1000 mg/l was prepared by dissolving 2.21 g of anhydrous sodium fluoride in distilled water. Test solution of 5 mg/l was prepared by serial dilution from fresh stock solution keeping in view that reported concentration of fluoride in groundwater of most of the affected areas is around 5 mg/l.

2.2. Adsorbent collection and preparation

Granular activated carbon (GAC) was chosen as baseline adsorbent and the fluoride removal efficiency of the sewage sludge was compared with activated carbon. Anaerobically digested sludge was collected from wastewater treatment plant near Asian Institute of Technology, Thailand. Collected sludge was washed thoroughly two times with distilled water to remove any coarse impurities and subjected to drying in an oven at 60 °C for 24 h. The dried sludge was grounded by using mortar and pestle to particle size of 150 mesh. The prepared adsorbent was stored in sterilized air tight container for subsequent use as an adsorbent.

2.3. Methodology

All the experiments were carried out in 250 ml Erlenmeyer flasks, with 50 ml test solution at room temperature (25±3°C). The adsorption test was carried out in batch mode. This study included the influence of various parameters like adsorbent dose, pH, agitation speed, contact time and initial fluoride concentration. Since, these factors play vital role in the adsorption process, optimization of each parameter is necessary to evaluate the maximum removal, equilibrium time and kinetics, and selection of an isotherm [5]. For optimizing certain parameter, one specific parameter was changed and all other variables are kept constant.

The effect of adsorbent dose was studied by varying the dose of carbon from 2 to 12g/l and 1 to 6g/l for sludge. The mixture was constantly agitated at 150 rpm in the shaker for 2 hours. The removal percentage is obtained as the difference in fluoride concentration before and after the experiment. The effect of pH was studied in the range of 2-10 and pH of test solution was adjusted by adding drops of 0.1N HCl or 0.1N NaOH. The effect of agitation was monitored at low, medium and high agitation speeds (100, 150, 200, 250, 300 rpm) under optimized conditions. In order to determine the contact time required for equilibrium, kinetics of fluoride adsorption was examined as function of time at different intervals (40, 80, 120, 160, 200, 240, 280 and 320 minutes). Lastly, the effect of initial fluoride concentration on the adsorption process was evaluated by varying the fluoride concentration from low to high range (5, 10, 20, 30, 40mg/l).

At the end of experiment, the sample was filtered with Whatman no. 42 filter paper and the filtrate was analyzed for residual fluoride concentration by using ExStik FL700 Fluoride meter. The FL700 allows users to follow the American Society for Testing and Materials (ASTM) and EPA standard methodology using total ionic strength adjustment buffer (TISAB) reagents. The pH values of the solution were measured using the HANNA digital pH meter.

2.4. Adsorption Isotherms

Langmuir and Freundlich isotherm equations were used to describe the equilibrium sorption of GAC and sewage sludge. The isotherm studies were conducted by varying the initial concentration of fluoride from 5 to 40 mg/l at a constant adsorbent dose of 2 g/l.

Langmuir model signifies the homogeneous adsorption in which all adsorption sites have equal affinity for the adsorbate [6]. It is generally given in the form,

\[ q_e = \frac{Q_o b C_e}{1+bC_e} \]  

(1)
where, \( q_e \) is the amount adsorbed per unit weight of adsorbent (mg/g), \( Q_o \) and \( b \) are Langmuir constants related to the measures of monolayer adsorption capacity (in mg/g) and surface energy (L/mg). The linearized form of Langmuir isotherm is given as,

\[
(C_e/q_e) = (1/Q_o b) + (C_e/Q_o) 
\]

(2)

Langmuir constants \( Q_o \) and \( b \) is calculated from intercept and slope of the graph plotted between \( C_e/q_e \) Vs. \( C_e \).

Freundlich adsorption isotherm is based on adsorption on heterogeneous surface for describing the adsorption equilibrium [5]. The non-linear form of this isotherm is generally expressed as,

\[
q_e = K C_e^{1/n} 
\]

(3)

where, \( q_e \) is the amount adsorbed per unit weight of adsorbent (mg/g), \( K \) is the Freundlich adsorption coefficient representing the adsorption capacity and \( n \) represents the intensity of adsorption. This equation is converted to the linear form by using log on both sides, as

\[
\log q_e = \log K + \left(\frac{1}{n}\right) \log C_e 
\]

(4)

The constants \( K \) and \( n \) can be determined from the intercept and the slope of the graph, \( \log q_e \) Vs \( \log C_e \).

3. Results and Discussions

3.1. FTIR and BET surface area analysis

FTIR spectrum of sludge was recorded on Thermo Nicolet 6700 FTIR Spectrometer for the functional group analysis. The surface of the sludge sample was scratched into powder and pressed to make the pellets by mixing the sorbent with KBr [7]. The peak at 2924.9 cm\(^{-1}\) is attributed to the C-H interaction with the surface of sludge and the band at 3448.7 cm\(^{-1}\) is due to the absorption of water molecules as result of an O-H stretching mode of hydroxyl groups and adsorbed water [8]. Amides can be distinguished in the region having two peaks at 1610.1 and 1439.5 cm\(^{-1}\). Moreover, the band at 1500 cm\(^{-1}\) may be attributed to the aromatic carbon–carbon stretching vibration.

The method of Brunauer, Emmet, and Teller (BET) was employed to determine surface area on a model of adsorption which incorporates multilayer coverage. The obtained total pore volume and surface area is 0.3877 cm\(^3\) g\(^{-1}\) and 884.66 m\(^2\) g\(^{-1}\) for GAC and 0.00097266 cm\(^3\) g\(^{-1}\) and 2 m\(^2\) g\(^{-1}\) for sludge, respectively.

3.2. Effect of adsorbent dose

The response of adsorbent dose on fluoride removal is shown in Fig. 1. The removal of fluoride increased from 60 to 74% for 2 to 10 g/l dosage of GAC and 72 to 86% for 1 to 6 g/l dose of sludge, respectively. At higher dosage, there is a high possibility of sorbent-sorbate interaction due to the increase in number of sorption sites, but at lower dose, the number of fluoride ions is relatively higher compared to the availability of adsorption sites [9]. However, after dose of 4g/l in case of GAC and 3g/l for sludge, there was no significant change in removal. In this study, 2 g/l is chosen as optimum dose for further experiments.

3.3. Effect of pH

The adsorption process is highly influenced by the pH of medium. The effective removal is observed in acidic and near neutral range as shown in Fig. 2. At lower pH, the concentration of positive charge increases due to the protonation of functional groups, which causes the strong interaction of fluoride with the adsorbents. But as the pH of the solution increased above 8, the number of OH groups are increased resulting in the decrease of positively charged sites [10]. From the drinking water viewpoint, neutral pH is desirable for both adsorbents at which removal of 70% for GAC and 82% for sludge were observed.

Fig. 1: Effect of adsorbent dose on adsorption of fluoride by GAC and dewatered sludge

Fig. 2: Effect of pH on adsorption of fluoride by GAC and dewatered sludge
3.4. Effect of agitation speed

The removal increased for both adsorbents on increasing the agitation speed. This is because the degree of agitation reduces boundary layer resistance and increase the mobility of the fluoride in the system[11]. At lower speed, the adsorbents accumulated in the flask instead of spreading in sample. From Fig. 3, it can be seen that the maximum removal of 86% and 76% occurred at the speed of 250 rpm for sludge and activated carbon, respectively. No significant uptake was noticed for the further increment of rotational speed.

3.5. Effect of contact time

The effect of contact time is presented graphically in Fig. 4 as percentage removal at different contact of times. It can be observed that as contact time increases, percent removal also increases and gradually attains equilibrium in nearly 180 minutes, then become constant thereafter. The removal at this time is 80% in case of activated carbon and 88% for sludge, respectively. The increase in removal may be due to involvement of active sites on adsorbent surface. Similar result is obtained by Vardhan [12] using rice husk as an adsorbent.

3.6. Effect of initial fluoride concentration

The removal percentage decreased with the increase in initial concentration of the fluoride ions as shown in Fig. 5. This is because of the less available active sites on the adsorbent surface due to saturation. However, 82% removal was observed for 10 mg/l concentration when sewage sludge was used as an adsorbent. So, the fixed number of active sites can adsorb only the fixed amount of fluoride. Similar type of pattern was observed on using Neem charcoal and other bio-adsorbents [9, 13].

3.7. Adsorption Isotherms

As shown in Fig. 6, a plot of $C_e/(q_e)$ against $C_e$, yielded a straight line for both the adsorbents, which indicates the applicability of Langmuir adsorption isotherm for the adsorption of fluoride. The value of $Q_o$ and $b$ are 15.87 and 0.12 for GAC, and 7.75 and 0.20 for sludge, respectively. Comparing Fig. 6 and 7, it can be seen that both the adsorbents fitted Freundlich isotherm better than the Langmuir with high correlation coefficient. From the Freundlich equation, the value of $K$ and $1/n$ are 1.83 and 0.65 for GAC, and 1.46 and 0.528 for sludge, respectively. Since the value of the adsorption intensity ($1/n$) is less than one, it indicates favorable adsorption for both GAC and sludge. High values of $K$ indicate that fluoride removal rate is high.

4. Conclusions
The defluoridation studies of the Granular activated Carbon (GAC) and domestic sewage sludge has been carried out in batch mode. Experimental data at optimum conditions reveal that the sludge showed maximum fluoride removal of 88 % followed by 78% for GAC at 5 mg/l F concentration. The operational parameters such as pH, initial fluoride concentration, adsorbent dose and contact time were found to have an effect on the adsorption efficiency of both the adsorbents. Values of correlation coefficient for Freundlich isotherms are 0.997 and 0.999, where as for Langmuir the values are 0.986 and 0.972, for activated carbon and sludge, respectively. Sludge as well as highly porous GAC with surface area of 884.66m$^{2}$g$^{-1}$ followed the Freundlich isotherm better than Langmuir. The results clearly suggest that easily available and low-cost materials like domestic sewage sludge is effective in removing fluoride from water to acceptable levels.

5. Acknowledgements

Authors are thankful to Sirindhorn International Institute of Technology, Thammasat University for supporting the budget and laboratory for this research.

6. References


