



Comparative assessment of Commercial activated carbon and fish scale derived activated carbon for adsorptive removal of fluoride from drinking water

Disha A. Khandare,^{a*} and Somnath Mukherjee^b

^a Research Scholar, Civil Engg. Dept., Jadavpur University, Kolkata, India

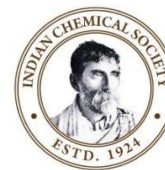
^b Professor, Civil Engg. Dept., Jadavpur University, Kolkata, India

*E-mail: dishakhandare@gmail.com

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Abstract: Excessive fluoride concentration above WHO (2011) standard (> 1.5 mg/L) is observed worldwide in groundwater. Considering its serious concern a laboratory based investigation was undertaken to find the fluoride elimination potential by the Commercial Activated Carbon (CAC) and indigenously developed Fish Scale Activated Carbon (FSAC) from water solution. Batch sorption studies were carried out to observe some important process parameters such as adsorbent dose, contact time, pH etc on removal kinetics. At pH -2, CAC could remove upto 75 % of fluoride whereas FSAC could remove up to 92.68 % of fluoride at pH -6. The percent removal of fluoride enhanced with the increase in sorbent mass. The equilibration state was found to be achieved within 2 and 3 hours for CAC and FSAC respectively. Both CAC and FSAC exhibit reasonably well fluoride uptake capacity for initial fluoride level of 7 and 5 mg/L respectively. The equilibrium data fitted well into Freundlich as well as Langmuir isotherms models. The experimental investigations suggest that both Commercially Available Activated Carbon (CAC) and Fish Scale Derived Activated Carbon (FSAC) can be adopted as adsorbent for defluoridation purpose in the treatment of drinking water. Fish scale derived activated carbon (FSAC) showed more fluoride uptake capacity than commercially available activated carbon (CAC).

Keywords: adsorption, fluoride, commercial and fish scale carbon, removal kinetics



1. Introduction

Water is elixir of all forms of life. Presence of undesirable element in excess in water makes the water unfit for consumptive use. Fluoride is one such kind of pollutant of concern. Excessive fluoride concentration above WHO standard (i.e. > 1.5 mg/L) is observed in groundwater throughout the globe. Prolonged consumption of water with excess fluoride (> 1.5 mg/L) is responsible for fluorosis in human beings. Prolonged exposure of fluoride through drinking water is being contributed to a serious health hazard of dental and skeletal fluorosis. The fluorine-containing rocks are main natural geological sources of elevated fluoride levels in groundwater. Besides this, anthropogenic sources like discharges from aluminium smelters, ceramic production units, and coal fired power stations, electroplating processes, fertilizer manufacturing industries, glass manufacturing and processing industries, and semiconductor manufacturing industries are contributing to fluoride contamination of water environment.¹ Numerous endeavours are attempted earlier to establish a sustainable engineering method of fluoride removal under different constraints in developing countries. A surge of conventional engineering methods are used and practiced for defluoridation of water with various physico-chemical unit operation.² Membrane filtration techniques are broadly comprised of electro-dialysis, nano-filtration and reverse osmosis.³ The challenges in adopting most of these methods are their limited fluoride removal capacities, high operational and maintenance cost, post-treatment alterations of water quality, generation of toxic sludge and its disposal into the environment.⁴

Among these techniques of defluorination, adsorption method is most favoured method due to its ease of operation, greater accessibility to variety of adsorbents, lower cost of treatment. In water purification and industrial wastewater

treatment, activated carbons are widely used an important and efficient commercial adsorbents.⁵ In recent years, many defluoridation studies have focused on preparation and use of carbons derived from naturally available materials. The CAC is very costly and in developing countries like India the cost of treatment limits its at large scale application.⁶ Therefore the researchers are prompted to develop indigenous low-cost adsorbents for defluoridation of water.

Plenty of carbons derived from naturally available materials such as rice husk^{7,8}, coffee husk^{9,10}, bone char^{12,13}, coconut shell carbon¹⁴, sweet lime waste activated carbon¹⁵ have been prepared to use for defluoridation purposes. The present study provides comparative assessment of fluoride removal capacities of Commercial Available Activated Carbon (CAC) and a natural biomaterial-Fish Scale Derived Activated carbon (FSAC) under batch adsorption mode.

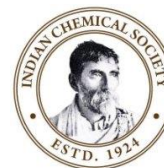
2. Materials and methods

2.1 Fluoride sample solution

All reagents used in the present study were of Analytical grade. The stock fluoride sample was prepared dissolving 1.10 gm Sodium fluoride in 500 mL deionized water. Fluoride solutions of different strength have been made by diluting stock solution with predetermined dilution factor.

2.2 Apparatus and Instruments

Various apparatus and equipments such as Digital weighing balance, Muffle furnace, ceramic crucibles, grinding materials (mortar and pestle), filter paper (Whatman number 42), Tarson plastic beakers and bottles (different capacity), Thermo Scientific Orion Fluoride Ion Selective Electrode (Orion Star™ A214 pH/ISE Bench top Meter). One reciprocating type mechanical shaker were employed for conducting the batch adsorption study. To evade possible chemical reaction between fluoride and borosilicate plastic



beakers and bottles were used for all laboratory works.

2.3. Adsorbent preparation

Commercially available activated carbon (CAC) (GR grade, E Merck) was used in powdered form without any modification. The fish scale derived carbon was prepared following the procedure as mentioned in Khandare and Mukherjee (2019)¹⁵. Both the adsorbents were stored in an air-tight container.

2.4. Batch experiments

Batch adsorption study was conducted with a view to explore the capacity of fluoride adsorption by both CAC and FSAC. Effect of Adsorbent dose, Agitation Speed, Contact Time, Initial Fluoride Concentration and pH was observed with 50 ml of test solution in 100 ml plastic bottles at room temperature. A reciprocating type mechanical shaker was used for this purpose. Standard pH buffer solution was used to maintain constant desired pH level. For optimizing the process parameter, one specific influencing parameter was varied keeping other variables constant. The plastic bottles containing synthetic fluoride sample were agitated with mechanical shaker at constant speed of 150 rpm. At regular interval of time the samples were collected till the equilibrium was achieved. The collected samples were analyzed to measure residual fluoride concentration. The percent removal of fluoride was calculated using equation (1).

$$\% \text{ Removal} = \frac{(C_i - C_e)}{C_i} \times 100 \quad \dots\dots\dots (1)$$

where, C_i and C_e are initial and equilibrium fluoride concentration of sample in mg/L.

2.5 Adsorption Isotherms

An adsorption isotherm reveals insight into the interaction between pollutant and adsorbent. The batch experimental data obtained have been tested by fitting in both Freundlich and Langmuir isotherms. These widely applied isotherms are empirical models in which former

one postulates on adsorption takes place on heterogenous surface whereas Langmuir isotherm model is based on a monolayer adsorption on homogeneous surface (Ibrahim M., et al, 2019). The linearised form of Freundlich and Langmuir isotherms are shown in Eq. (2) and (3) respectively.

Equation (2)

$$\log q_e = \log k_f + \frac{1}{n} \log C_e \quad \dots\dots\dots (2)$$

Equation (3)

$$\frac{C_e}{q_e} = \frac{1}{q_m} C_e + \frac{1}{K_1 q_m} \quad \dots\dots\dots (3)$$

In the above expression, C_e is the concentration of solute at equilibration time, k_f, n are Freundlich constants related to the adsorption capacity and effectiveness, q_e is the amount of fluoride adsorbed per unit mass of adsorbent (mg/g), q_m and k_1 are the Langmuir constants related to maximum adsorption capacity (mg/g) and energy of adsorption (g/L), respectively.

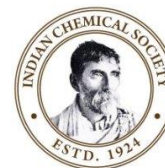
R_L is a separation factor associated with significance of adsorption attributing type of isotherm which defined in equation (4),

$$R_L = \frac{1}{1 + k_1 C_e} \quad \dots\dots\dots (4)$$

where, C_e (mg/L) is the initial sorbate concentration and k_1 is Langmuir constants in (g/L)

2.7 Adsorption Kinetics

Rate kinetics study and evaluating order of reaction plays an important role for explaining the mechanism and efficacy of fluoride sorption on adsorbents.¹⁶ The pseudo first and second order models have been tested to examine the adsorption kinetics of fluoride onto the surface of CAC and FSAC. The above models as proposed by Lagergren later given by order in following



form by Ho and McKay (1988)¹⁷ as Eqs. (5) and (6) respectively.

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \quad \dots\dots (5)$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} \quad \dots\dots (6)$$

where, q_e and q_t represents the amounts of fluoride adsorbed (mg/L) on surface of adsorbent at equilibrium and at any time t (min), respectively. The k_1 , k_2 are constants related to pseudo first and second order rate kinetics respectively

3. Results and Discussions

3.1 Influence of adsorbent mass

The effect of adsorbent amount on fluoride removal efficiency was explored with variable amount of adsorbent dose in the range of 2-12 gm/L. During batch experiments, it was observed that as the amount of adsorbent is increased, percentage removal enhanced and ceases as it reached towards state of equilibrium. At higher dose availability of sorption sites are more.^{18, 19, 20} **Fig.3.1** exhibits the influence of adsorbent dose versus percentage of fluoride removal. Maximum removal was found to be 83 % at 14 gm/L and 91.4 % at 10gm/L for CAC and FSAC respectively.

3.2 Influence of contact time

Fig.3.2, demonstrates adsorption of fluoride on CAC and FSAC increases with contact time and gradually reaches to equilibrium after 120 minutes for CAC and 180 min for FSAC. Maximum removal achieved was about 84.3 % at 120 min for CAC and 92.80 % at 180 min for FSAC with adsorbent dose of 10 gm/L for an initial fluoride concentration 5mg/L. Similar trend of results are reported in publication of Alkurdi S.(2020)¹² and Araga R.(2019)¹³.

3.3. Influence of pH

Fig.3.3 shows efficiency of percentage removal of fluoride found to be descended with

elevated level of initial pH. This is occurred due to the fact that at higher pH, the anions are absorbed less than at a low pH due presence of H^+ ions. At higher pH, the fluoride adsorption decreases because of competition with OH^- ions.^{21, 22} In the present study, maximum removal was obtained as at 84.2 at 2 pH and 90.4 % at 6 pH for CAC and FSAC respectively.

3.4. Influence of initial fluoride concentration

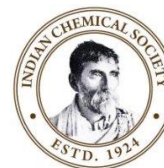
The effect of initial concentration on fluoride removal has been studied with varied, fluoride ion concentration from 2 – 15 mg/L. Experimental data were plotted in **Fig. 3.4**, where it is evident that the percent removal of fluoride decreases with increase in initial fluoride ion concentration of water. The maximum fluoride removal was observed to be 82 and 92.6 % for CAC and FSAC at corresponding to initial concentration of 7 mg/L and 5 mg/L respectively.

3.5. Influence of agitation speed

The speed of agitation in the mixture greatly influences the efficiency of fluoride removal by the said adsorbents as evidenced during the study. Mixing provides more chances and contact with the increase in the speed of agitation, which facilitates more entrapment of solute within the adsorbent surfaces.^{19, 23, 24} **Fig. 3.5** shows the plots of experimental data regarding the effect of agitation speed on fluoride removal percentage. In present experimental investigation it is found that the maximum fluoride removal was achieved at 120 and 150 rpm speed of stirring for CAC and FSAC respectively.

3.6. Isotherms Study

Isotherm data were plotted in both models as stated in section 2.5, to examine the type of sorption process and its validity. The **Fig. 3.6 (a)** and **(b)** shows the plot of Freundlich isotherm whereas **Fig. 3.7 (a)** and **(b)** shows plot of Langmuir isotherm for CAC and FSAC. The experimental data with different adsorbent dosages was utilized to determine isotherm



constants. The **Table 3.1** summarises the isotherm parameters studied for CAC and FSAC. It is observed that the adsorption of fluoride CAC and FSAC follows the Freundlich isotherm model with the R^2 values of 0.979 and 0.994 respectively. For CAC and FSAC, the adsorption intensity $1/n$ was found to be < 1 indicating favourable adsorption of fluoride.

3.7 Adsorption Kinetics

The kinetic reaction order model described by Ho and McKay(1988)¹⁷ were applied in the present study to examine the rate kinetics for fluoride removal by CAC and FSAC.. The batch experimental data was tested for fitting different model equation to determine order of reaction.. The pseudo first order showed reasonably fitted R^2 value 0.936, 0.964 for CAC and FSAC respectively. The results are shown in tabular form in **Table 3.2**. It is observed that the correlation coefficient (R^2) of pseudo first-order kinetic model was better than pseudo-second order kinetic model indicating the removal of fluoride with of CAC and FSAC is favoured by physisorption.

4. Comparative results on fluoride removal capacity of CAC and FSAC with Low-cost-adsorbents

The commercial usages and application for removal of fluoride from water environment largely depends on the uptake capacity and economic aspect of the adsorbent preparation. Uptake capacities of few efficient low cost adsorbents prepared by different scientists earlier for fluoride from water are listed below along with FSAC and CAC (**Table 4.1**) FSAC has been found better fluoride removal capacity as compared to CAC and previously used adsorbents given in the table below.

5. Conclusion

The experimental data obtained in this study clearly suggest that both CAC and FSAC have potential to remove fluoride from water environment. The fluoride removal is largely dependent on pH, adsorbent dose, initial

concentration of fluoride and contact time. The adsorption capacity of FSAC was found to be higher (1.93mg/g) as compared to CAC(1.02 mg/g). The Equilibrium isothermal models Langmuir and Freundlich were established and the regression coefficient R^2 showed that experimental data fits well into the Freundlich isotherm model. The sorption kinetic data suggest that fluoride removal is mainly due to physisorption taking place onto the surface of adsorbents. The use of CAC and commercially adsorbents for fluoride removal can be replaced by effective low cost adsorbents like FSAC.

Conflict of interest

There are no conflicts to declare.

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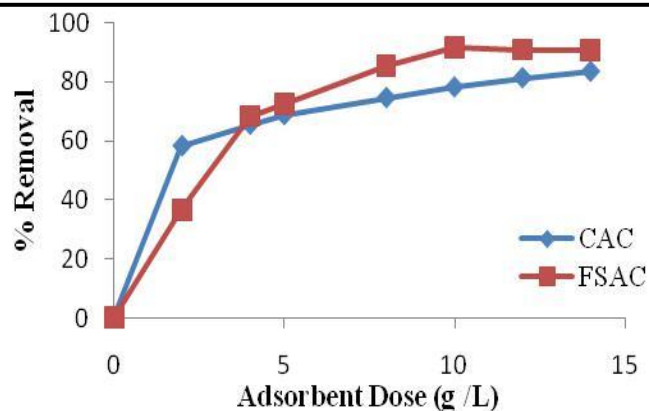
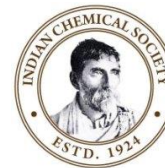


Fig.3.1 Percent removal versus adsorbent dose

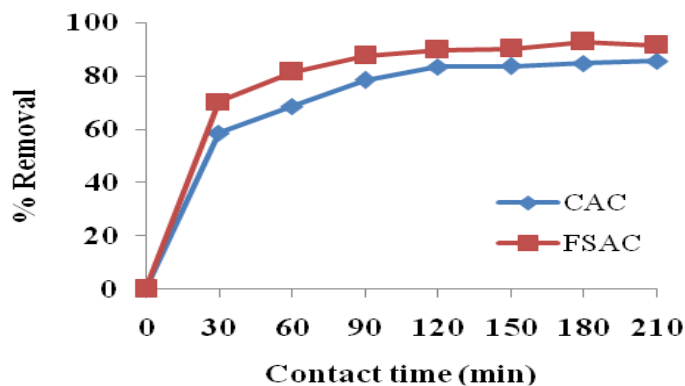


Fig.3.2 Percent removal versus contact time

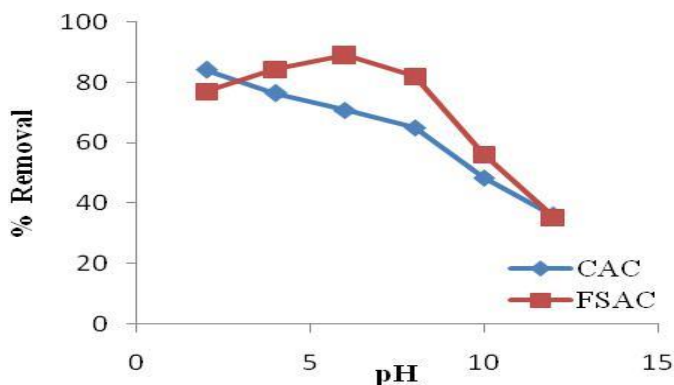


Fig.3.3 Influence of pH on removal efficiency

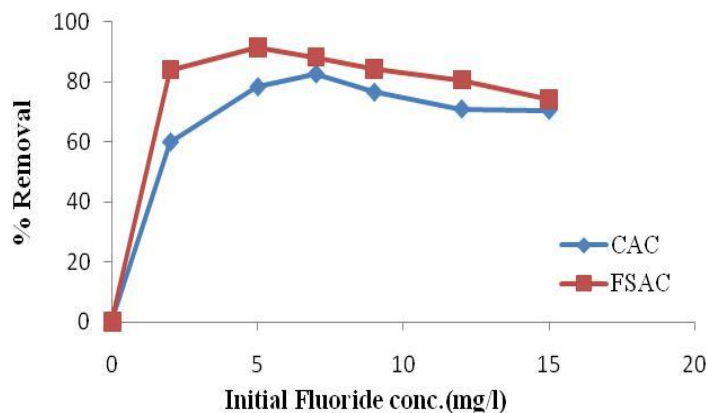


Fig.3.4 Plot of initial fluoride concentration versus removal efficiency

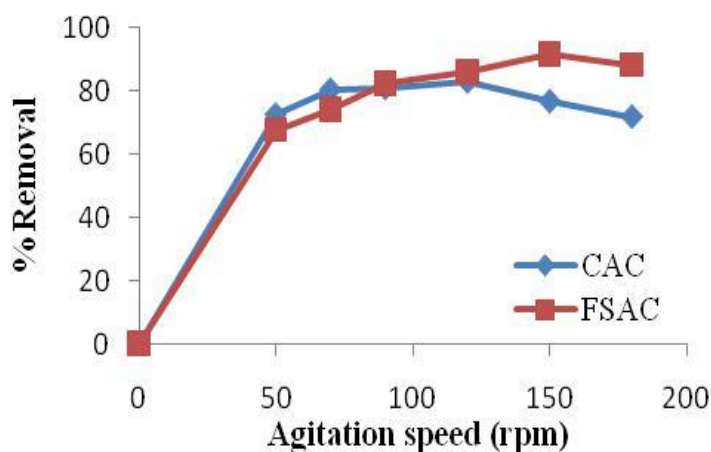


Fig.3.5 Effect of agitation speed

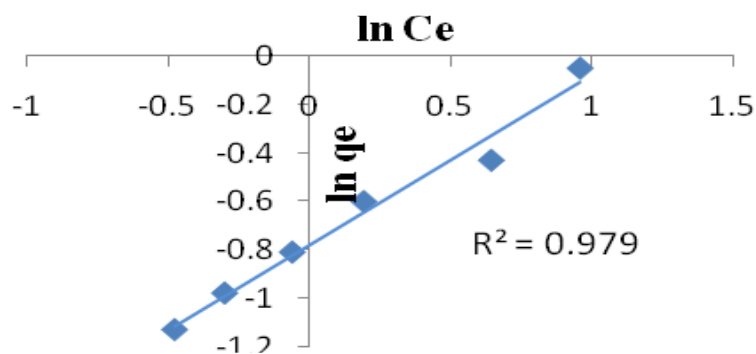


Fig.3.6(a) Freundlich Isotherm CAC

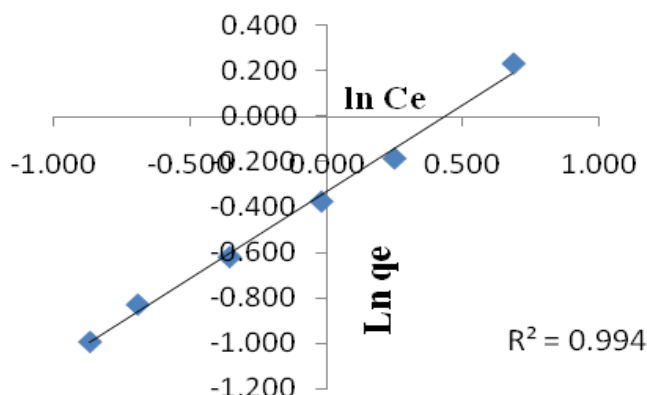


Fig.3.6(b) Freundlich Isotherm FSAC

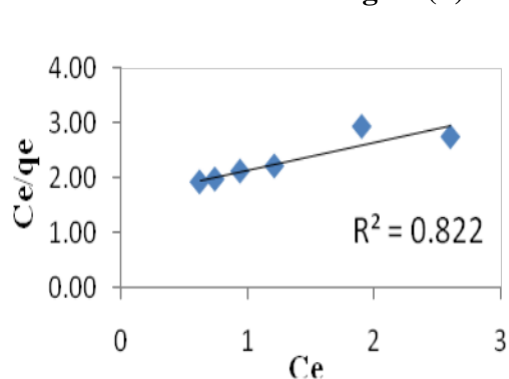


Fig.3.7 (b) Langmuir Isotherm CAC

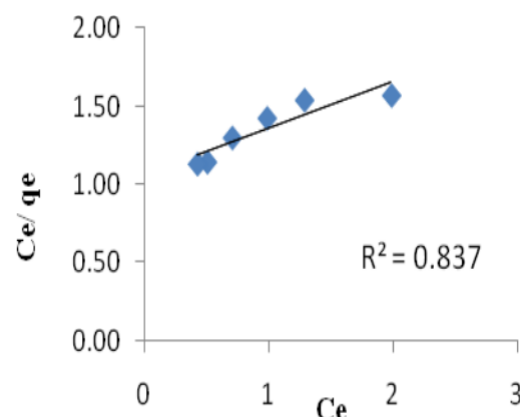


Fig.3.7 (b) Langmuir Isotherm FSAC

Table 3.1 Adsorption Isotherm parameters CAC and FSAC

Isotherm model	Constants	CAC	FSAC
Freundlich model	R^2	0.979	0.994
	$1/n$	0.743	0.763
	K_f	1.46	1.87
Langmuir model	R^2	0.822	0.837
	q_{max}	1.26	0.68
	K_1	3.35	3.57
	R_L	0.23	0.324



Table 3.2 Kinetic parameters of CAC and FSAC for fluoride adsorption.

Adsorbent	Pseudo-first-order model			Pseudo-second-order model		
	Calculated q_e (mg/g)	K_1 (1/min)	R^2	Calculated q_e (mg/g)	K_2 (g/mg min)	R^2
CAC	0.98	0.099	0.936	1.16	0.0027	0.896
FSAC	2.01	0.021	0.964	1.53	0.0041	0.771

Table 4.1 Fluoride removal capacity of various adsorbents

Adsorbent	q_{max} (mg/g)	Reference
Activated carbon from Dolichos lab lab	0.233	[6]
Used tea leaves	0.253	[25]
Eggshell	1.09	[24]
Activated alumina (GradeOA-25)	1.45	[26]
Hydrous bismuth oxides	0.196	[27]
Zirconium impregnated ground nut shell (ZIGNSC) carbon	1.26	[28]
Moringa indica based activated carbon	0.23	[29]
Commercial available activated carbon	1.02	Present study
Fish scale derived activated carbon	1.93	Present study