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Assesment of De-Fluoridation in Waste Water Using Activated Biochar : Thermodynamic and Kinetic Study

Swapnila Roy*

Department of Chemical Engineering, Jadavpur University, Kolkata, India

***Corresponding author:** Swapnila Roy, Department of Chemical Engineering, Jadavpur University, Kolkata, India. Tel: +913324572696; Email: swapnilaroy@gmail.com

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Abstract

Hydrothermal carbonization of urban food waste is utilized to prepare bio-char, followed by chemical activation to obtain activated bio-char (Bio-char-act) which is used as de-fluoridating agent in contaminated water. The structural property of the synthesized activated bio-char is studied in detail. From batch adsorption study, it is revealed that efficiency of bio-char with lower degree of carbonization has remarkable properties of de-fluoridation. The process parameters such as temperature; contact time and adsorbent dose have strong influence on fluoride uptake process. The adsorption equilibrium data are satisfactorily fitted to the Langmuir isotherm model. Comparatively the data provided by pseudo-second-order kinetic model correlated better experimentally than pseudo-first-ordeetic model. From thermodynamic point of view, it is experimentally proved that de-fluoridation onto activated bio-char is spontaneous and endothermic in nature. Here, a low-cost process is suggested using low-cost starting materials to convert bio-char upon heat treatment at 350˚C and then activated chemically by acid. The prepared adsorbent has higher de-fluoridation efficiency such as 91.24%. So, it may be concluded that activated bio-char is economically and environmentally safe for de-fluoridation in waste water.

Keywords: Activated Bio-char; Desorption Study; De-fluoridation; Kinetic Study; Thermodynamic

Introduction

Fluorine is the most electronegative element and its gaseous form is the strong oxidizing agent. Fluoride ion exists as F- ion. The toxicity of fluoride [1] is mainly observed when it exceeds the threshold limit of 1.5 mg/L [2]. The dental and skeletal fluorosis may occur by excessive consumption of fluoride. So, it is necessary for removal of fluoride [3,4] by using different types of adsorbent such as charcoal, tamarind seed, agricultural waste materials, bermuda grass, ionic resin etc. There is difference between carbonized and chemically treated forms. Only batch process (experimental procedure by varying three process parameters such as contact time, temperature and adsorbent dose) does not give fine optimization of de-fluoridation. So, thermodynamics and kinetics study are used for optimization of the de-fluoridation efficiency. The source of industrial fluoride is Hydrofluoric Acid (HF), Ammonium bi-fluoride (NH_4HF). Fluoride has a very high affinity towards Calcium (Ca) due to high electronegative character in periodic table. As fluoride is negative ion so it is naturally attracted by positive calcium ion. As a result of high fluoride ingestion by children as well as adults, fluorosis [5] is found in mild version and high version. The fluoride removal from contaminated water is done by adding lime followed by precipitation of fluoride in conventional method. There are various other methods used for the de-fluoridation of water such as ion-exchange precipitation, reverse osmosis and electro coagulation. Activated carbon is the most important adsorbents because of excellent adsorptive capacity. There are different types of materials which are used for preparation of activated carbon such as walnut, wheat bran, saw dust, lemon shell etc. Mostly, activated carbons are utilized in waste water treatment, gas and water purification etc.

The present de-fluoridation study was carried out with the objective to prepare chemically activated bio-char [6] prepared from urban food waste. The physical and chemical properties of

the prepared activated bio-char [7-9] were determined and de-fluoridation efficiency is estimated using different experimental procedure by adsorption as a function of contact time, adsorbent dose and temperature.

Materials and Methods

Preparation of Adsorbent

Food waste was collected from local restaurants. The food waste consisted of a variety of cooked food (like rice and chicken gravy), uncooked food (fruit peels, vegetable parts). The collected waste was initially weighed and bones, eggshells, plastic utensils, etc. were separated out. Then food waste was mixed homogeneously using blender and then stored at refrigerator temperature (at 4 0C). All the chemicals used in this experiment were analytical grade reagent.

Preparation of Biochar by Hydrothermal Carbonization (HTC)

HTC of food waste [10] was conducted in a 500 ml Parr stirred pressure batch reactor (Model 4575, Germany; Heater power: 1000 W). The reactor was run at 623 K with a constant residence time of 30 min. The reactor was sealed and heated to the desired reaction temperature with the help of an electric furnace [11-13]. After the desired residence time, the heater was turned off and the reactor was rapidly cooled to room temperature.

Chemical Activation

In order to obtain the remarkable properties of de-fluoridation in water the bio-char was activated. Firstly, bio-char was washed several times with distilled water to remove surface impurities and then dried at 378 K. Then it was grinded and activated by using phosphoric acid (H3PO4) which was followed by carbonization in muffle furnace. The complete carbonization occurred at 723 K. Then it was cooled to room temperature. After that it was washed with distilled water to make it neutral. Then prepared activated carbon was dried, cooled and stored in an air-tight container for experimental study.

Physicochemical properties of adsorbents

The different physicochemical properties [14,15] of activated bio-char were determined using standard procedures. All the experiments were performed thrice and results are given in (Table 1).

Name of Sample	Bulk Density(g/cm^3)	Porosity (unit less)	Moisture content (%)
Activated Bio-char	0.7	0.58	9.7

Table 1: Physicochemical Analysis:

Determination of Bulk Density: The dry empty 10 ml centrifuge tube was cleaned and weighed ($W1$). Then the centrifuge tube was filled with the prepared bio-char in powder form and then it was weighed ($W2$). The difference in the weight indicates the weight of bio-char in tube. The bulk density was estimated using the following equation:

$$\text{Bulk Density} = \frac{W2 - W1}{volume\ of\ centrifuge\ tube}$$

Porosity Determination

The porosity of bio-char was estimated using the formula:

$$\text{Porosity} = \frac{pore\ volume}{total\ volume}$$

The pore volume of prepared bio-char was achieved using the formula:

$$\text{Pore volume} = \frac{Bulk\ density\ of\ biochar}{density\ of\ water}$$

$$\text{Hence, porosity} = \frac{Bulk\ density\ of\ biochar}{density\ of\ water\ X\ Total\ volume}$$

Determination of Moisture Content

The empty crucible was dried at 383 K and then cooled in a desiccator and weighed ($W1$). Then the prepared bio-char was weighed ($W2$) separately and then dried in an oven at 110 ^{o}C. This weight was taken constantly at 30 minutes interval until the weight became constant. Then sample with crucible was cooled in desiccators and reweighed ($W3$). The weight difference of the sample is used to measure the moisture content (X_o) of prepared bio-char.

$$X_o = \frac{W2 - W3}{W2 - W1} X100$$

Measurement and characterization

The prepared activated bio-char was characterized by Scanning Electron Microscopy (SEM), XRD (X-ray Diffraction) analysis and Fourier Transformed Infrared Spectroscopy (FTIR).

Experimental

Batch Adsorption Procedure

The fluoride solution of desired concentration was prepared by further dilution of the stock solution with suitable volume of distilled water which was used in experimental study.

In this experiment, 100 ml fluoride solutions of concentration 50 mgL^{-1} were taken in 250 mL PTFE (Polytetrafluoroethylene) conical flasks. The particular weighed amount of adsorbent was added to each solution. Then the flasks were agitated at 150 rpm in an incubator shaker at different temperatures. The effects of contact time, adsorbent dose and reaction temperature on the adsorption of fluoride were investigated by using batch studies.

Experimental set up

The batch experiments were carried out in temperature controlled incubator shaker (INNOVA 4430, New Brunswick Scientific, Canada). Temperature fluctuations in the reactor were negligible. After shaking for particular time intervals those samples were collected from the flasks for analysis of fluoride concentration in the solution. The dissolved fluoride in each conical flask was estimated by using ion-meter (Thermo Scientific Orion ion-meter, USA).

The percent removal (%) of fluoride is determined by using the following equation:

$$R(\%)=\frac{C_i - C_0}{C_i} x100 \quad \text{.....(1)}$$

Where C_i is the initial fluoride concentration (mg L^{-1}) and C_0 is the final fluoride concentration in solution (mg L^{-1}).

Determination of Optimum Conditions

Determination of Optimum Contact Time

Contact time play a significant role in adsorption study. To study the effect of contact time, 100ml of fluoride solution of 100 mg/Land pH 2.0±0.02, was mixed with 1.0 g activated bio-char, stirred at different contact times (20-100 min) and then filtered. These filtrates were analyzed for residual fluoride concentration using ion-meter.

Determination of Optimum Dosage of Adsorbent

The optimum dosage of activated bio-char is added to the conical flask in different dosage varying from (200-2000mg) which contains 100ml of 50mg/L fluoride solution and pH is maintained as 2.0±0.02. The solution in the PTFE conical flask is subjected to stirring for optimum contact time and then filtered, and finally analyzed. The dosage which gives maximum de-fluoridation efficiency is selected as optimum dosage of adsorbent.

Determination of Optimum Temperature

The effect of temperature on fluoride adsorption was experimented by performing equilibrium adsorption within the range of temperature between 293-363K. The temperature at which maximum fluoride removal happened that is optimum temperature.

Adsorption Isotherm Batch Experiment

- **Langmuir Isotherm**

In this case the following equation [16] is used as follows:

$$\frac{C_e}{Q_e} = \frac{C_e}{q_m} + \frac{1}{K_L q_m} \quad \text{.....(2)}$$

Where Q_e is the amount of fluoride adsorbed at equilibrium (mg/L), C_e is the concentration of fluoride in the aqueous phase at equilibrium (mg/L). K_L and q_m are the Langmuir constants related to energy of adsorption and the adsorption capacity.

- **Freundlich Isotherm**

The Freundlich isotherm [17] constants are estimated using the following equation:

$$\text{Ln } Q_e = \ln K_F + \left(\frac{1}{n}\right) \ln C_e \quad \text{..... (3)}$$

Where Q_e is the amount of fluoride adsorbed at equilibrium and K_F and n are a Freundlich constant indicates adsorption capacity and adsorption intensity respectively

Adsorption Kinetics of Batch Experiment:

The experiments of de-fluoridation were carried out at various temperatures to determine the optimum temperature for maximum adsorption efficiency and to determine the reaction rate constant. 100 ml of fluoride solution of concentration 50 mg/L was taken in PTFE conical flask and 1 g adsorbent is added to it. Then this mixture was agitated at 150 rpm for 1 hour. From this experiment, kinetic rate constant [18] at different temperatures is estimated.

- **Pseudo First Order Kinetics**

The rate constant is estimated using the following equation:

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \quad \text{.....(4)}$$

Where, q_e= fluoride adsorbed at equilibrium/unit weight of adsorbent (mg/g), q_t is the amount of fluoride adsorbed at any instant (mg/g) and k_1 is the rate constant (min^{-1}).

Integrating at these conditions as t=0 and q_t=0 to t=t and q_t=q_t, the final equation is written as given below:

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

- **Pseudo Second Order Kinetics**

The model equation is described as follows:

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

Where k_2 denotes the pseudo-second-order rate constant of adsorption (g mg^{-1} min^{-1}) and q_e and q_t are the amounts of fluoride adsorbed (mg/g) at equilibrium and at time *r*espectively.

- **Activation Energy**

From the obtained the rate constant, activation energy of the adsorption of fluoride is calculated using Arrhenius Equation (7) given as follows:

$$\ln k_2 = \ln A_0 - \frac{E_a}{RT} \quad \ldots\ldots (7)$$

Where E_a=activation energy (kJmol^{-1}); R=gas constant (8.314 J mol^{-1} K^{-1}); and A_0=Arrhenius constant.

Adsorption Thermodynamics

The thermodynamic parameters of de-fluoridation are estimated using the following formulas:

$$K_c = \frac{C_a}{C_e} \quad \ldots\ldots(8)$$

Where, K_c=coefficient of distribution for the adsorption; C_a= fluoride adsorbed per unit mass of the adsorbent (mg L^{-1}); C_e=equilibrium concentration of adsorb ate in aqueous phase (mg L^{-1}).

$$\Delta G^0 = -RT\ln K_c \quad \ldots\ldots (9)$$

Where, ΔG^0 (kJ mol^{-1})=change of Gibb's free energy; R= universal gas constant(8.314 J/mol K); and T=absolute temperature (K); and

$$\Delta G_0 = \Delta H^0 - T\Delta S^0 \quad \ldots\ldots(10)$$

WhereΔH^0 (kJ mol^{-1}) = change of enthalpy; ΔS^0 (J mol^{-1} K^{-1})=change of entropy.

Results and Discussion

Characterization of Adsorbent

- **SEM (Scanning Electron Microscopy)**

From (Figure 1) it is revealed that the structure of bio-char contain major characteristics of the physical structure of the original feedstock. It is shown in the SEM images [JEOL-JSM-7600F] of the bio-chars that there is a remarkable difference in porosity (approximately 1m diameter) of structure and the amount of organic and inorganic matter coated to the surface.

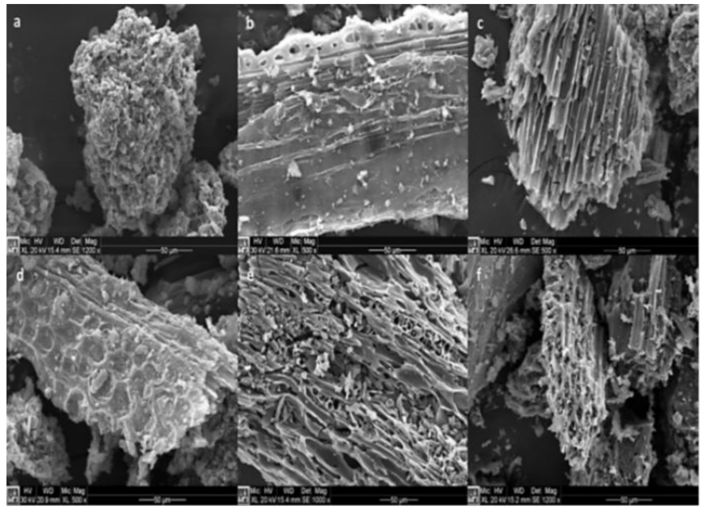

Figure 1: SEM of Activated Bio-char at different temperature

- **FTIR (Fourier Transformed Infrared Spectroscopy)**

FT-IR spectra of the bio-char samples are given in the (Figure 2). Clear distinctions can be made between the different feedstock and pyrolysis process intensity. Comparing the FT-IR spectra of the bio-chars derived at different temperatures (400, 550, and 700◦C), a reduction of the peak intensity of 1070 cm^{-1} (characteristic of C O stretching of carbohydrate-like substances) and 1470 cm^{-1}(attributed to C O of phenolic, carboxylic, and alcohol groups)can be observed.

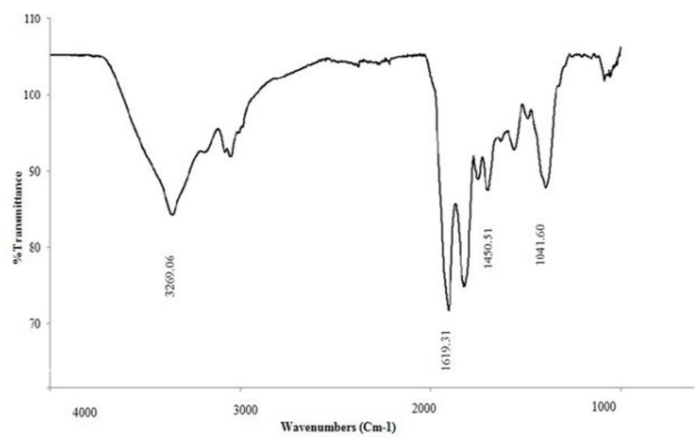

Figure 2: FTIR of Activated Bio-char.

- **XRD (X-ray Diffraction) Analysis**

X-ray diffraction was carried out on bio-char and activated bio-char using a Diffractometer (Bruker, D8 Advance). Two different types of char were granulated for powder diffraction using Cu Kα radiation (40 kV, 40 mA) from 5° to 65° (2θ) with 0.1 step size and 2 second measurement interval. The resulting peaks (Figure 3) were observed for two different samples

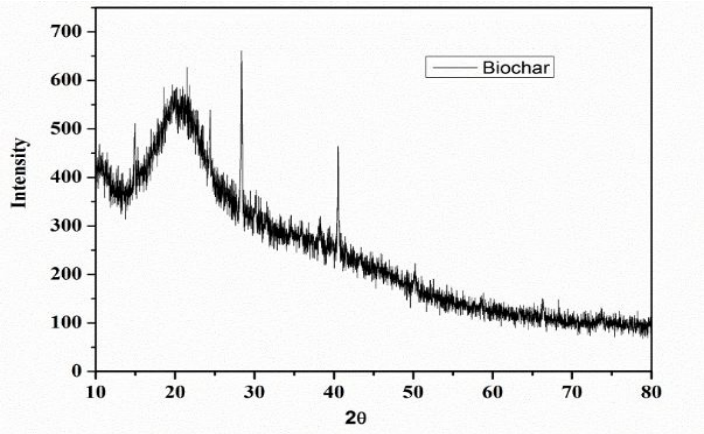

Figure 3: XRD of Activated Bio-char.

Interaction Effect

Effect of Adsorbent Dose

Within the experimental range of adsorbent dose in between 0.2 g-2.0 g/l, percent removal of fluoride firstly increases (upto1.0g/l), then decreases slowly. The adsorbent dose in the range of 0.2-1.0g/l de-fluoridation efficiency increases due to the number of ions increases on the adsorbent surface as the attractive force between adsorb ate ions and adsorbent. While increasing dosage of adsorbent higher than 1.0 g /l, it shows decrease in de-fluoridation on the adsorbent surface because surface of adsorbent is saturated by adsorbate ions, and in that case the repulsive force between fluoride ions and adsorbent surface occurs. From (Figure 4), it was observed that the removal efficiency of fluoride increases with increasing dosage of adsorbent (up to1.0 g /l), then decreases slowly. So, it can be inferred that activated bio-char can be used as effective adsorbent for de-fluoridation in water.

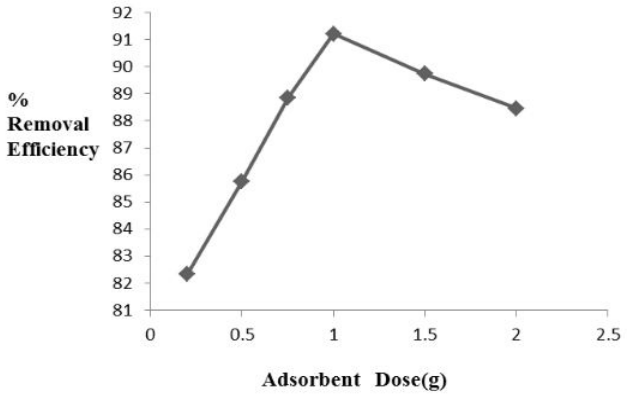

Figure 4: Effect of adsorbent dose on de-fluoridation by activated bio-char (experimental conditions:C0 = 50 mg L^{-1}, agitation speed = 150 rpm, T = 333 K, adsorbent dose = 1.0 g/100 ml).

Effect of Contact Time

It is observed from (Figure 5) the experimental results that on increasing the contact time at pH 2 and optimum dosage of adsorbent, de-fluoridation efficiency increases. As the contact time increases, higher the number of fluoride ions attached on the adsorbent surface. Chemically it is explained that the accumulation of fluoride ions on adsorbent surface increases due to attractive force between adsorb ate and adsorbent which results in increasing the de-fluoridation in solution. Within the experimental limit of contact time (20-100 min), after certain point (80 min), de-fluoridation efficiency decreases. The reason behind these phenomena is that maximum number of the fluoride ions attached on adsorbent surface when reaction time was 80 minutes. Beyond 80 min removal efficiency decreases. From Figure 5, it was observed that the removal efficiency of fluoride increased firstly and then decreases slowly, which was reflected in the plot.

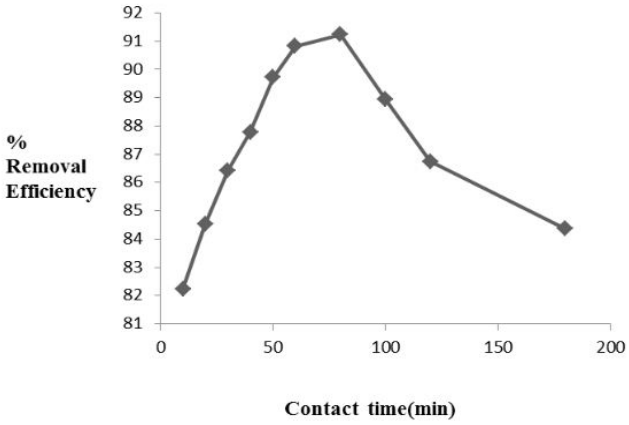

Figure 5: Effect of contact time on de-fluoridation by Activated Bio-char (experimental conditions: C0 = 50 mg L^{-1}, agitation speed = 150 rpm, T = 333K, contact time: 80 min).

Effect of Temperature

In the above experiment, it is represented that with increasing temperature, the removal efficiency of fluoride increases sharply at 333K then it decreases. Following the adsorption process, 333 K is the feasible condition for batch de-fluoridation (Figure 6). Above 333K the de-fluoridation efficiency decreases. With increasing temperature, the attractive force between adsorbent and fluoride ions increases, resulting adsorption capacity of activated bio-char increases. So, the residual amount of fluoride ions decreases in the solution. Above 333 K, the amount of residual fluoride increases slowly. In (Figure 6) this phenomenon is reflected properly.

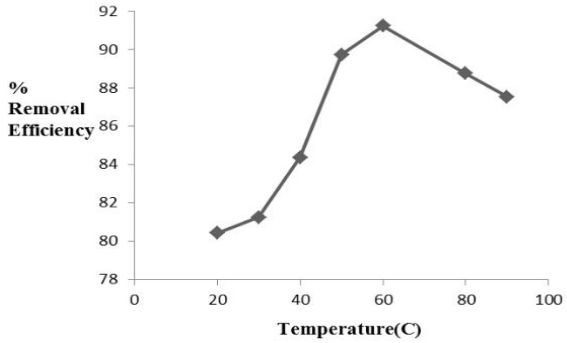

Figure 6: Effect of temperature on de-fluoridation by Activated Bio-char (experimental conditions: C0 = 50 mg L−1, agitation speed = 150 rpm, adsorbent dose=1.5 g/100ml, contact time: 80 min).

Adsorption Isotherm Study

From (Table 2) it is summarized the corresponding constants for all the isotherms. R2 value of Langmuir isotherm model (0.999) was higher than that of Freundlich (0.9863). It implies that Langmuir model (Figure 7) showed good agreement on de-fluoridation onto activated bio-char than Freundlich (Figure 8) in present work. This is also indicated that the surface of adsorbent is homogeneous for de-fluoridation. With increasing temperature adsorption capacity increased which implies that the process is endothermic in nature. In comparative study, it is shown that activated bio-char has potentiality for de-fluoridation.

Langmuir Isotherm	Estimated Value	Freundlich Isotherm	Estimated Value
qm(mg/g)	21.562	*KF*(mg/gm)	20.521
KL(L/mg)	0.0273	*1/n*(L/mg)$^{1/n}$	0.141
R^2	0.9991	R^2	0.9863

Table 2: Parameter of Langmuir and Freundlich isotherm models for de-fluoridation by Activated Bio-char (condition: weight of adsorbent =1.0 mg/100ml, stirring = 150 rpm, temperature = 333 K, contact time = 80 min).

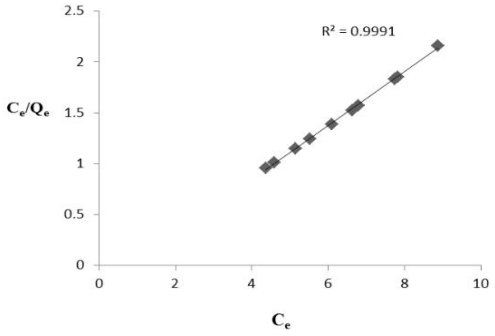

Figure 7: Langmuir Adsorption Isotherm plots of de-fluoridation onto Activated Bio-char.

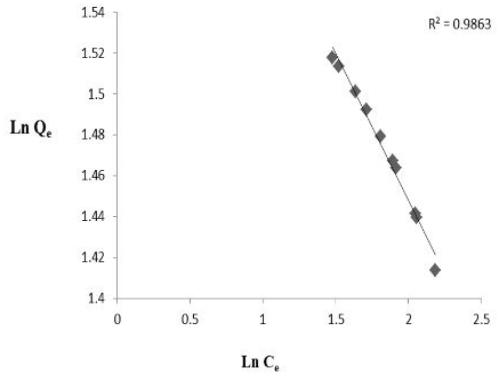

Figure 8: Freundlich Adsorption Isotherm plots of de-fluoridation onto Activated Bio-char.

Adsorption Kinetics

The present adsorption kinetics studies were carried out for de-fluoridation using activated bio-char prepared from food waste. The parameters of kinetic studies are discussed in this description**.** From this study, it is observed that pseudo second order kinetics study is well fitted than pseudo first order reaction. From the pseudo second order kinetic reaction it is indicated that adsorption capacity of activated bio-char is dependent on available binding site. The plot of t/q_t Vs t (Figure9) and ln K_c vs 1/T (Figure not shown) are represented. The value of k_2 and q_e were calculated from the intercept and slope of plot of t/q_t against t. Each kinetic model was analyzed by comparing the expected and calculated values of q_e and correlation coefficient (R^2). The value of R^2 (Table 3) was 0.9968 and the corresponding k_2 value was 0.0438, while the calculated q_e (mg/g) was 24.17. The value of R^2 for pseudo-second-order was greater than pseudo-first-order process. From these experimental values, it is suggested that de-fluoridation onto activated bio-char followed pseudo second order kinetics.

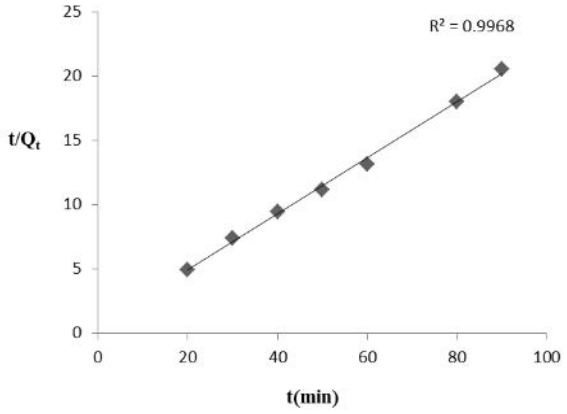

Figure 9: Pseudo second order kinetic model for adsorption of fluoride by Activated Bio-char.

Adsorbents	Pseudo second order kinetics		
	k_2(g mg^{-1})	qe (mg g^{-1})	R^2
Activated Bio-char	0.0438	24.17	0.9968

Table 3: Pseudo second order rate constants for Activated Bio-char at optimized conditions.

Thermodynamic Study

In order to determine the feasibility of reaction, the thermodynamic parameters such as Gibbs free energy change (ΔG°), enthalpy (ΔH°) and entropy (ΔS°) had to be estimated from equation which are shown in (Table 4). The thermodynamic parameters are estimated using the equations (**8-10**). ΔH° and ΔS° were estimated by slope and intercept from the plot of in K_c vs. 1/T. The values of ΔG° were negative at all temperatures, implies that the adsorption process is feasible and spontaneous nature of de-fluoridation onto activated bio-char. The decrease in the value of ΔG° with increasing temperature represents that affinity of fluoride on activated bio-char was higher at high temperature. The positive value of ΔH° (25.2215 kJ mol^{-1}) indicated that the adsorption process was endothermic. If the value of ΔH° lies in between 80 and 200 kJ, then the adsorption process is chemisorption in nature, but here it is obtained as 25.2215kJ, denoting that de-fluoridation onto adsorbent followed physicochemical process. The positive value of ΔS° (92.24 J mol^{-1} K^{-1}) indicated the affinity of fluoride towards activated bio-char and at solid-liquid interface increased during adsorption.

Serial No.	T, K	ΔG^0, kJ/mol	ΔH^0, kJ/mol	ΔS^0,J mol^{-1} K^{-1}
1	293	-9.86	25.2215	92.24
2	303	-10.23		
3	313	-12.45		
4	323	-14.12		
5	333	-11.45		
6	343	-12.76		
7	353	-12.98		

Table 4: Thermodynamic parameters for the adsorption of fluoride onto Activated bio-char.

Regeneration Study

The regeneration study of adsorbent in de-fluoridation method is very significant. As the bio-char from food waste demonstrated higher de-fluoridation efficiency (91.24%), so its desorption study was determined by 5 adsorption-desorption cycles. The present adsorption-desorption study was carried out with 100 ml of 50 $mg{\cdot}L^{-1}$ of synthetic fluoride solution at the starting of each cycle. The study was investigated with 1% sodium hydroxide as desorbing agent. The adsorption capacities of each cycle were 90.92%, 87.46%, 84.13%, 80.01%, and 77.53%. These experimental results (Figure 10) represents that bio-char prepared from food waste can be reused for de-fluoridation in water.

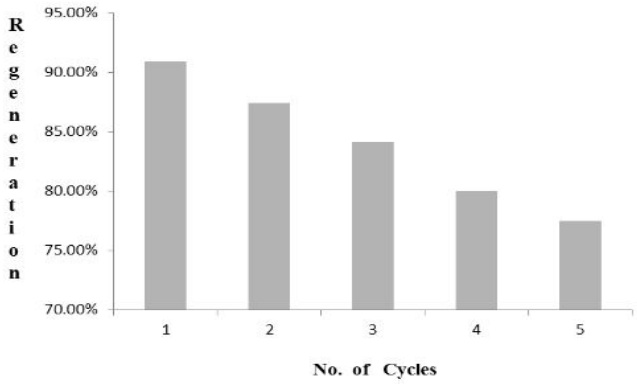

Figure 10: Regeneration% of Activated Bio-char.

Comparative Adsorption Capacity, Isotherm of Various Adsorbents with Activated Bio-Char Synthesized in this Study

Sorbent	Maximum adsorbent capacity	Isotherm	Reference
Activated Carbon (Rice straw)	18.9 $mg{\cdot}g^{-1}$	Langmuir	[19]
Activated Carbon (*Moringa indica*)	0.2314 $mg{\cdot}g^{-1}$	Langmuir	[20]
Activated carbon (*Acacia farnesiana*)	2.622 $mg{\cdot}g^{-1}$	Freundlich	[21]
Activated carbon (*Pithacelobium dulce*)	1.9333 $mg{\cdot}g^{-1}$	Freundlich	[22]
Activated carbon (*Arachis hypogaea*)	14.79 $mg{\cdot}g^{-1}$	Freundlich	[23]
Activated carbon (*Cynodon dactylon*)	4.755 $mg{\cdot}g^{-1}$	Langmuir	[24]
Activated carbon (*Anacardium occidentale*)	1.95 $mg{\cdot}g^{-1}$	Langmuir	[25]
Activated carbon (pecan nut shells)	2.3 $mg{\cdot}g^{-1}$	Langmuir	[26]
Graphene	48.31 $mg{\cdot}g^{-1}$	Langmuir	[27]
Activated bio-char from food waste	49.47 $mg{\cdot}g^{-1}$	Langmuir	Present study

Conclusion

The present investigation deals with the aim of de-fluoridation study by adsorption process onto activated bio-char from food waste. The adsorption studies were carried out as a function of temperature, contact time and adsorbent dose. The following con-

clusions may be drawn on the basis of the study:

- It is proved that the adsorption equilibrium data are satisfactorily fitted to the Langmuir adsorption model rather than Freundlich isotherm model at different temperatures.
- The obtained experimental results are well fitted to pseudo-second order kinetic model.
- Thermodynamic parameters such as change in Gibbs free energy (ΔG0), enthalpy (ΔH0), and entropy (ΔS0) were determined from thermodynamic studies.
- The nature of the adsorption mechanism is endothermic and spontaneous which is experimentally proved.

As food waste is easily available, therefore synthesized activated bio-char from urban food waste may be useful adsorbent for de-fluoridation in waste water.

Acknowledgment

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