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Original Article

# ISOTHERM AND KINETIC STUDIES OF FLUORIDE REMOVAL ON ACTIVATED CARBON OBTAINED FROM COCONUT SHELL

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**ABSTRACT**

Objective: Activated carbon was prepared from coconut shell according to standard method. Langmuir and Freundlich isotherms, as well as pseudo-first-order and pseudo-second-order, were studied. Methods: Batch adsorption studies were carried out in a conical flask. A standard curve was obtained by preparing different concentrations of fluoride from 1 to 6 mg/L. Each adsorption parameter such as adsorbent dose, contact time, and pH was studied by applying a suitable amount of adsorbent to suitable volume of fluoride in a conical flask. The flask content was agitated and then filtered to obtain the filtrate. Then, 1ml of SPADNS reagent was added to the filtrate after which the absorbance of the solution was obtained at the wavelength of 570 nm using Uv/visible spectrophotometer. Results: The Freundlich isotherm confirmed a suitable match with the experimental information with high correlation coefficient. The kinetic parameters confirmed that the maximum favorable order for the adsorption technique is the pseudo-second-order kinetic. Conclusion: Outcomes showed that activated carbon prepared from coconut shell was very powerful in the defluoridation of water with approximately 73.1 % fluoride removal at a reaction time of 50 minutes, the temperature of 30°C, and an adsorbent dose of 1.5 g.

**Keywords:** Coconut Shell, Activated Carbon, Fluoride, Adsorbent, Adsorption, Kinetic, Studies.

## INTRODUCTION

Fluorine is one of the important components of teeth and bone. Its deficiency causes dental caries and excess leads to fluorosis. If the fluoride level in drinking water is below 0.5mg/L, it leads to dental caries. Concentrations above 2 mg/L level in drinking water leads to dental and skeletal fluorosis. Fluorosis is a problem in many parts of the world. The onset of fluorosis is not determined by fluoride, but a large number of agents, the climate of the area, host, and environmental factors determine its occurrence [1]. Fluoride exposure in humans is determined by fluoride concentration in drinking water, and duration of consumption [2, 3]. Normally the concentration of fluoride in raw water should be below 1.5mg/L, but groundwater may contain about 10 mg/L in areas rich in fluoride-containing minerals. According to the World health organization, WHO, the maximum allowable concentration of fluoride in drinking water is 1.5 mg/L [4]. To achieve this optimum limits set by the WHO, drinking water must be defluoridated before use. Defluoridation of water involves precipitation method (Lime treatment, Alum coagulation, and Nalgonda technique), Domestic defluoridation, and Adsorption/ion exchange method. But adsorption methods have been studied extensively by different authors using different adsorbents and proved to be fast and cost-effective [5-20]. Therefore, this study aimed to remove fluoride in a solution using activated carbon obtained from coconut shell.

### Reagents/Glass wares

The reagents, apparatus as well as equipment used were as follows: weighing balance, filter paper(what man No-1), pipette(10ml), aluminium foil, pH meter, motar and pestle, muffle furnance, hot plate(electric tung), measuring cylinder, oven, micrometer sieves, beakers, standard volumetric flasks, tap water, deionized water, and test tubes, : Hydrochloric acid (HCl), Acetic acid ($CH_3COOH$), SPADNS Reagent (2-parasulfophenylazo)-1,8-dihydroxy-3,6-naphthalene disulfanate), TISAB (Total Ionic Strength Adjustment Buffer), Sodium hydroxide(NaOH), Fluoride ion of known concentration, Phosphoric acid ($H_3PO_4$), Sulphuric acid ($H_2SO_4$), Sodium fluoride (NaF), Zirconyl chloride octahydrate, Sodium chloride (NaCl), Sodium citrate, concentrated acetic acid.

### Sample Collection

The sample of Montmorillonite clay was collected from Tallase town in Balanga Local Government Area of Gombe state, Nigeria.

### Preparation of Activated carbon and solutions

Both preparation of activated carbon and solution used in this project was prepared according to the method described by Wilson *et al.*, [9].

### Batch adsorption studies

Batch adsorption studies were carried out in a conical flask. A standard curve was obtained by preparing different concentrations of fluoride from 1 to 6 mg/L. Each adsorption parameter such as adsorbent dose, contact time, and pH was studied by applying a suitable amount of adsorbent to suitable volume of fluoride in a conical flask. The flask content was agitated and then filtered to obtain the filtrate. Then, 1ml of SPADNS reagent was added to the filtrate after which the absorbance of the solution was obtained at the wavelength of 570 nm using Uv/visible spectrophotometer. Concentrations of fluoride were calculated from the standard curve.

The removal percentage of the adsorbate and the amount adsorbed, qe (mg/g), were calculated according to the following equation [9].

$$Removal\ \% = \frac{(C_i - C_e)x\,100}{C_o} \quad (1)$$

$$Amount\ adsorbed, q_e = \frac{(C_i - C_e)xV}{m} \quad (2)$$

Where Ci is the initial concentration of fluoride solution in mg/L, Ce is the equilibrium concentration of fluoride solution in mg/L, m is the mass of the adsorbent in grams, V is the volume of fluoride test solution in litters (L), and qe is the amount adsorbed in mg/g.

### Adsorption Isotherms

To perform the analysis of the adsorption process, isotherm is a vital tool. The experimental statistics have been analyzed with

Langmuir and Freundlich as the two most normally use isotherm fashions. Langmuir adsorption isotherm models the unmarried layer insurance of the adsorption surfaces and assumes that adsorption takes place on a homogeneous surface of the adsorbent [11]. Thus the linearized equation is given bellow,

$$\frac{C_e}{q_e} = \frac{1}{K_l q_{max}} + \frac{1}{q_{max}}.C_e \quad (3)$$

Where,

$C_e$= the equilibrium concentration of adsorbate (mg/L).

$q_e$=Is the equilibrium value of adsorbate adsorbed per unit weight of adsorbent (mg/g).

$q_{max}$=Is the maximum amount of adsorption corresponding to monomolecular layer coverage (mg/g).

$K_L$= Is the Langmuir constant and is related to measure of the affinity of the adsorbent (l/mg).

A linearized plot of $\frac{Ce}{qe}$ against $C_e$ yields a straight line graph which has an intercept and slope which correspond to $R_l = \frac{1}{1+C_oK_l}$ and $\frac{1}{q_{max}}$ respectively, from which the $q_{max}$ and $K_l$ can be calculated.

To verify the favourability of an adsorption procedure to Langmuir isotherm, the essential capabilities of the isotherm can be expressed in terms of a dimensionless constant called the separation element or equation parameter RL. The RL can be calculated using the subsequent equation;

$$R_l = \frac{1}{1+C_oK_l} \quad (4)$$

Where $C_o$ is the initial concentration.

The value of $R_l$ indicates that the isotherm is irreversible ($R_l$=0), favorable (0<$R_l$<1), linear ($R_l$=l), or unfavorable ($R_l$>1).

The Freundlich isotherm is an empirical equation employed to describe the heterogeneous machine; it assumes that the adsorption energy of an answer or ion binding to a domain on an adsorbent relies upon on whether or not or no longer the adjoining sites are already occupied.

The Freundlich isotherm is an empirical equation employed to describe the heterogeneous system; it assumes that the adsorption energy of a solution to a site on an adsorbent relies on whether or not the adjacent sites are already occupied.

The Freundlich equation is written as;

$$Logq_e = LogK + \frac{1}{n}\text{LogC}_e \quad (5)$$

Where, $q_e$ and $C_e$ are the equilibrium adsorption capacity of the adsorbent and the equilibrium concentration in the aqueous solution, respectively.

**Adsorption Kinetic**

To evaluate the mechanism of fluoride adsorption onto activated carbon, pseudo-first and pseudo-second-order kinetic models were considered as follows:

Pseudo-first order model is expressed by equation (6).

$$\log(q_e - q_e) = logq_e - \frac{K_1 t}{2.303} \quad (6)$$

Where $K_1$ is the Lagergren rate constant of adsorption (1/min).

The plot of log ($q_e$-$q_t$) against t, gives linear relationship from which $q_e$ and $K_1$ are determined from the intercept and slope of the plot respectively.

The pseudo-second-order is expressed by equation (7).

$$\frac{t}{q_e} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \quad (7)$$

Where $K_2$ is the second order rate constant of adsorption (g/mg min). The values of $K_2$ and $q_e$ are determined from the intercept and slope of the plot of $t/q_t$ against t.

**RESULTS AND DISCUSSION**

**Effect of adsorbent dose**

The removal of the fluoride ion by adsorption onto activated Carbon adsorbent was studied by varying the dosage of activated carbon from the range of 0.5 to 2.5g/L. The experiment was done with a solution of 5mg/L of fluoride ion concentration, at agitation time of 60 minutes (1 hour), at a fixed pH of 7, and temperature of 30$^0$C. The results obtained Table 1, were plotted as percentage removal of the fluoride ion versus adsorbent doses, as shown in Figure 1. As can be inferred from the graphs that the percentage removal of the fluoride ion increases rapidly with increase in adsorbent dose, and after optimum dosage of 1.5g/L, there has been no significant change in the percentage removal of the fluoride ion. A similar result was reported by [21].

**Table 1: Effect of adsorbent dose**

| Adsorbent Dose (g) | $C_i$ (mg/L) | $C_e$ (mg/L) | $C_i$ – $C_e$ (mg/L) | % Removal |
|---|---|---|---|---|
| 0.5 | 5 | 1.174 | 3.826 | 76.5 |
| 1.0 | 5 | 1.043 | 3.957 | 79.1 |
| 1.5 | 5 | 0.913 | 4.087 | 81.7 |
| 2.0 | 5 | 1.304 | 3.696 | 73.9 |
| 2.5 | 5 | 1.347 | 3.653 | 73.1 |

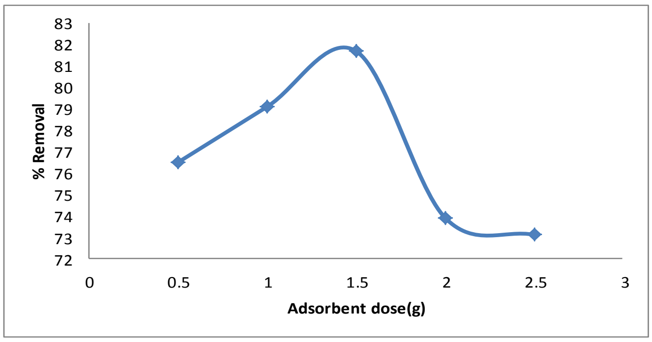


**Fig. 1: Effect of adsorbent dose graph for Flouride at adsorbate concentration of 5mg/L, the contact time of 50 (minute), the temperature of 25$^o$C and various adsorbent dosage of 0.5, 1.0, 1.5, 2.0 and 2.5 g**

**Effect of contact time**

In the adsorption system, contact time plays an important role in irrespective of the other experimental parameters affecting the adsorption kinetics. In order to study the effect of contact time, the adsorption experiments were conducted, and the extent of removal of the fluoride ion was known by varying the time from 10 to 60 mutes using a solution of 5mg/L fluoride ion concentration, at a fixed pH of 7, and temperature of 30$^0$C. The results obtained were plotted as percentage removal of fluoride versus contact time (minutes), as shown in Figure 2 and Table 2. As contact time increases at the initial stage, the percentage removal of the fluoride ion also increases rapidly. The equilibrium was reached after 50 minutes during which the rate of adsorption of fluoride onto the surface of the sorbent is equal to the rate of desorption. The rate of removal of the fluoride ion with time is higher at initial stages because of the availability of more active sites on the surface of the adsorbent, and with increase in contact time, the availability of the active sites on the surface of the adsorbent decreases and this result in the decrease of the fluoride ion removal rate by the adsorbent. From the observed results, the optimum contact time of activated carbon adsorbent was 50 minutes. The similar result was reported by [9].

**Table 2: Effect of contact time**

| Time (min) | Absorbent (g) | $C_i$ (mg/L) | $C_e$ (mg/L) | $C_i - C_e$ (mg/L) | % Removal |
|---|---|---|---|---|---|
| 10 | 1.5 | 5 | 1.826 | 3.174 | 63.5 |
| 20 | 1.5 | 5 | 1.522 | 3.478 | 69.6 |
| 30 | 1.5 | 5 | 1.174 | 3.826 | 76.5 |
| 40 | 1.5 | 5 | 1.043 | 3.957 | 79.1 |
| 50 | 1.5 | 5 | 0.783 | 4.217 | 84.3 |
| 60 | 1.5 | 5 | 0.800 | 4.200 | 84.0 |

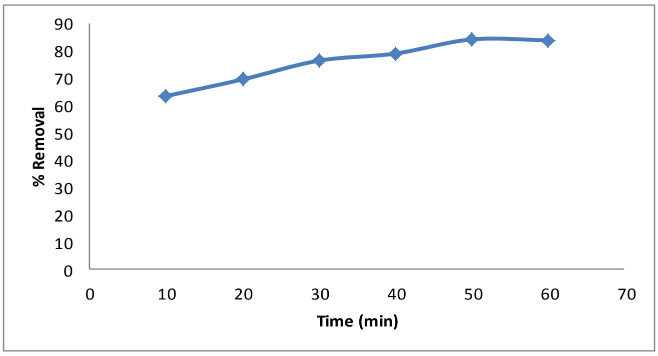


**Fig. 2: Effect of contact time graph for Fluoride at an adsorbent dose 2.0 g, initial Fluoride concentration of 5 mg/L, the temperature of 25°C, the various contact time of 10, 20, 30, 40, and 50 minutes**

### Effect of pH

The effect of pH of fluoride ion solution on the removal of the fluoride ion from aqueous solution was studied by varying the pH from 2-12. The optimum parameters applied include; 5mg/L of fluoride ion concentration, the contact time of 50 minutes, adsorbent dose of 1.5g, and at the temperature of 30°C. The results obtained were plotted as percentage removal of the fluoride ion versus pH, as shown in Figure 3 and Table 3. The maximum removal was observed at a pH value of 7. A similar result was reported by [22] in which the maximum removal percentage of 70% was achieved at a pH value of 7.

**Table 3: Effect of pH**

| pH | Absorbent (g) | Time (min) | $C_i$ (mg/L) | $C_e$ (mg/L) | $C_i - C_e$ (mg/L) | % Removal |
|---|---|---|---|---|---|---|
| 2 | 1.5 | 50 | 5 | 2.217 | 2.783 | 55.7 |
| 4 | 1.5 | 50 | 5 | 1.867 | 3.131 | 62.6 |
| 7 | 1.5 | 50 | 5 | 1.347 | 3.653 | 73.1 |
| 10 | 1.5 | 50 | 5 | 2.391 | 2.609 | 52.2 |
| 12 | 1.5 | 50 | 5 | 2.652 | 2.348 | 46.9 |

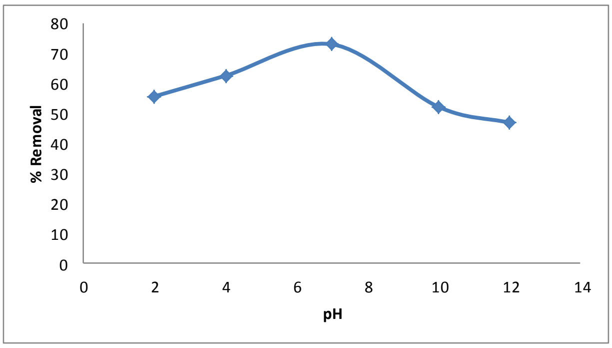


**Fig. 3: Effect of pH graph for Fluoride at an adsorbent dose 2.0 g, initial Fluoride concentration of 5 mg/L, the temperature of 25°C, the contact time of 50 minutes, and various pH of 2, 4, 7, 10 and 12**

### Kinetics of Adsorption

The kinetics parameters are presented in Table 4 for both pseudo-first-order and pseudo-second order, whereas the graphs are shown in Figure 4 and 5, respectively. From the results, pseudo-second fitted well to experimental data.

**Table 4: Kinetic parameters of the Fluoride adsorption on Activated Carbon.**

| Adsorbent | Pseudo-first order | | | Pseudo-Second order | | |
|---|---|---|---|---|---|---|
| | $K_1$(i/min) | $q_e$(g/mg) | $R^2$ | $K_2$ (g/mg min) | $q_e$(g/mg) | $R^2$ |
| Activated Carbon | 0.2361 | 2438.9337 | 0.9447 | 0.0024 | 76.3359 | 0.9958 |

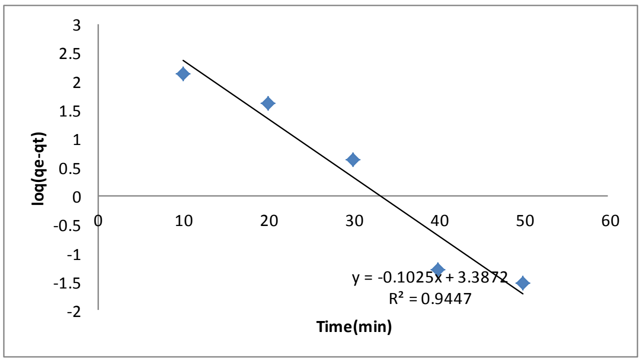


**Fig. 4: Pseudo-first order kinetic plot**

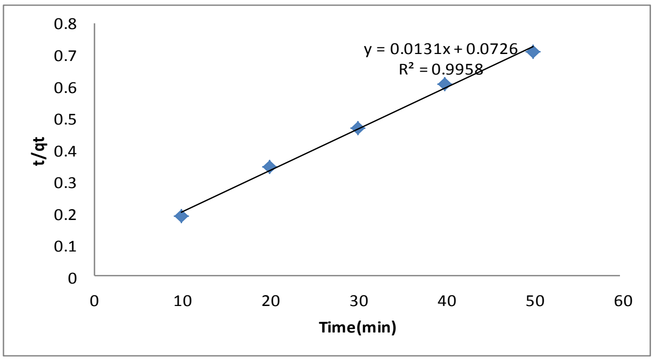


**Fig. 5: Pseudo-second order kinetic plot**

**Adsorption Isotherms**

Langmuir and Freundlich Isotherms were investigated. Figure 6 and 7 describe Langmuir and Freundlich Isotherm respectively. The Isotherm parameters for both Langmuir and Freundlich are shown in Table 5. The Freundlich isotherm showed the best fit with the experimental data with the high correlation coefficient. Even though the high correlation coefficient was observed in Langmuir Isotherm, the negative value of the slope disproved Langmuir theory. This indicates the inadequacy of the isotherm model to explain the adsorption process since these constants are indicative of the surface binding energy and monolayer coverage [23-25].

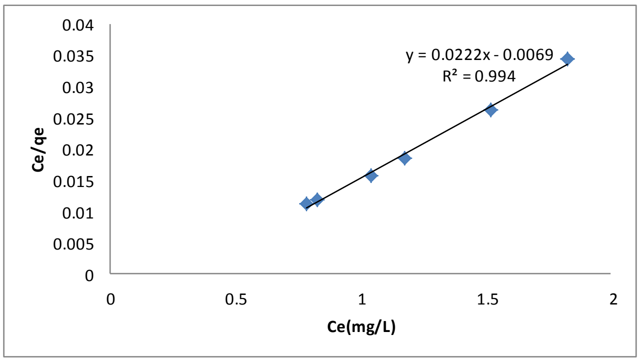


**Fig. 6: Langmuir plot**

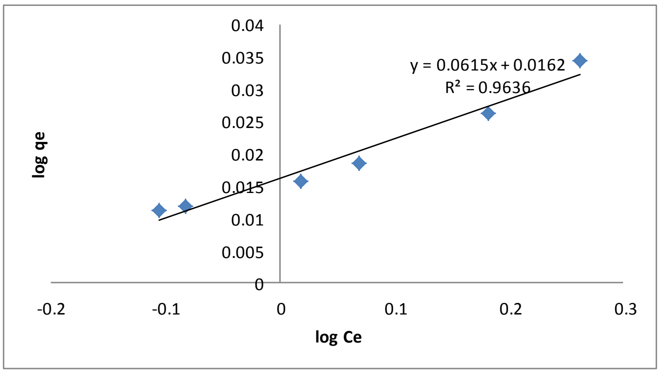


**Fig. 7: Freundlich plot**

**Table 5: Isotherm adsorption parameters**

| Absorbent | Langmuir | | | Freundlich | | |
|---|---|---|---|---|---|---|
| Activated | $K_L$ | $q_e$ | $R^2$ | $K_f$ | 1/n | $R^2$ |
| Carbon | -3.2174 | 45.045 | 0.994 | 1.038 | 0.0615 | 0.964 |

**CONCLUSION**

The Isotherm and kinetic parameters of the adsorption or removal of fluoride on activated carbon was determined. The results showed defluoridation by activated coconut shell carbon was favourable. The kinetic parameters showed that the most favourable order for the adsorption process is the pseudo-second order reaction. The highest percentage of fluoride removal by activated carbon is 73.1 at an exposure time of 50 minutes, which can be said to be very effective in fluoride removal.

**CONFLICT OF INTEREST**

No conflict of interest

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