PRODUCTION OF ADSORBENT FROM LOCAL RAW MATERIALS FOR THE REMOVAL OF FLUORIDE FROM WATER

Dagde K.K
Rivers State University
NIGERIA
dagde.kenneth@ust.edu.ng

Akpa J.G
Rivers State University
NIGERIA
akpa.jackson@ust.edu.ng

Ekine A.A
Rivers State University
NIGERIA
aboiyaaekine@yahoo.com

ABSTRACT

This study investigated the adsorption capacity of locally prepared adsorbents from Goat bones and Egg shells for the removal of fluoride ion in water. It evaluated the performance of these adsorbents calcined at 300^0C and modified with 1.0M HNO_3 (trioxonitrate (v)) acid. Batch adsorber was used to allow for interaction between adsorbents Bone char (BC) and Egg char (EC) with water containing fluoride ion. The batch experiment was performed with particle size of 2.12µm, contact time (60, 120, 180, 240, 300min), mass dosage (5g, 10g, 15g, 20g) and temperature (25^0C, 30^0C, 40^0C, 50^0C). The modified adsorbents were characterized to determine the physiochemical properties of Bone char (BC) and Egg char (EC). Also the chemical composition of both modified adsorbents were analyzed to determine the percentage of calcium element required for the uptake of the fluoride ions in water for calcium as 53.12% for BC and 39.68% for EC. Percentage adsorption increased with increase in contact time, mass dosage and temperature for both adsorbents. The adsorption capacity was also determined which also increased with increase in contact time, temperature but decreased with increase in mass dosage at constant time of 60minutes. The pseudo first-order, pseudo second order and intraparticle diffusion kinetic models were fitted into the experimental results. The results obtained indicated that the pseudo first order and intraparticle diffusion models reasonably described the adsorption process very well whereas the pseudo second order model was not suitable for a calcinations temperature of 300^0C and particle size of 2.12µm. The adsorption isotherms were obtained from equilibrium experiment carried out at temperature of 25, 35, 45 and 55^0C. The result showed that Langmuir and Freundlich isotherm fited perfectly the experimental data. However, the negative values of Gibb's free energy indicated that adsorption was favourable and the positive enthalpy change ΔH^0 revealed that adsorption process was endothermic while the positive value of the entropy change ΔS^O signified increased randomness with adsorption.

Keywords: Defluoridation, Bone char, Egg char, Fluoride, Adsorption, Water Treatment.

INTRODUCTION

Water is vital for life and every creature needs water to survive. This means plants and animal need water adequately and unpolluted water for survival. Today, the quality and quantity of water are of concern to man globally because water is used daily by billions of people around the world. According to the World Health Organization (WHO) improving drinking water quality is a major concern worldwide, for human health to be protected (WHO, 2004 cited in Garfi *et al*., 2016). Hence, there is a need for treatment or processing of drinking water and wastewater effluent to remove turbidity, organic matter, and pathogens that meet a specified goal, the standard set by regulating bodies (Crittenden et al., 2005 cited in Garfi *et al*, 2016).

According to Olugbade *et al*. (2017) the quality and accessibility of drinking water are of paramount importance. This drinking water had been reported by several works of literature to contain disease-causing agents or toxins-chemicals. Hence, there is a need to control the risks to public health through systematic quality monitoring and surveillance. Around the world, these identified chemicals in drinking water are of concern because consumption of these contaminants at high concentration is harmful to human health.

The presence of fluoride in drinking water is classified as a crucial issue because both low and high concentrations of fluoride can affect human health. The incidence of dental cavities increases with fluoride concentration less than 0.5mg/l while in excess it leads to severe health problems such as skeletal fluorosis and the degeneration of muscle fiber. According to the World Health Organization when fluoride concentration in water exceeds the limit of 1.5mg/L it becomes a contaminant in water (Wang *et al*., 2017). When water contaminated with fluoride above 1.5mg/L is consumed for a prolonged period it may result to health issues such as dental fluorosis, skeletal fluorosis, Muscle fiber generation and others (Mohapatra*et al*.,2009; Yadav *et al*,2013; Hermandez-Montoya et al, 2003; Bhatnagara *et al*., 2011 cited in Delgadilo-Velasco *et al*., 2017). Some other symptoms are stained teeth, bone diseases, tooth decay, stooped backs, crooked hands, and legs, non-skeletal fluorosis such as harmful effects to erythrocytes, ligaments, spermatozoa, thyroid glands and destruction of filaments in the muscles leading to muscle weakness. Also, the gastrointestinal system is affected causing gastric irritation such as nausea, vomiting and gastric pain (Spak *et al*., 1989 cited in Wong &Stenstrom, 2017). Thus, excess Fluoride is a pollutant of concern and treatment solution is needed. This fluoride could be found naturally in groundwater when there exist slow dissolution of rocks or minerals which contains Sellaite (MgF_2), Fluorspar (CaF_2)) and Cryolite (Na_3AlF_6) (Mohapatra *et al*., 2009 cited in Delgadillo- Velasco *et al* (2017). Furthermore, anthropogenic activities can contaminate water sources (groundwater) with Flouride (Yadav, *et al*., 2013 cited in Delgadillo- Velasco et al, 2017). The use of pesticides and fertilizers containing Fluoride (Tovar-Gomez *et al*., 2013) or through the discharge of industrial effluents into water bodies (Mohapatra *et al*., 2009; Bhatnagara *et al*., 2011; Kameda *et al*., 2015 cited in et al., 2017). In addition, industrial processes: cement and brick, electronic manufacturing process, aluminum smelting and refining amongst others, contaminates the groundwater with fluoride (Ramanathan, 2004; Nath& Dutta, 2015; Turner *et al*., 2005 cited in Wong & Stenstrom, 2017).

Moreover, it is established that the main source of water supply for human consumption in several countries is via the groundwater. Presently, there is a report of high fluoride content in water in twenty-six countries of the world- Meaning there are many areas around the world that have excess fluoride in drinking Water-China, India, Sir Lanka, Africa (Wong & Stenstrom, 2017), amongst others.

We need Potable water for consumption and the water that is not fit for drinking can be made potable by several methods of water treatment such as Coagulation, Flocculation, Sedimentation, filtration, adsorption, disinfection, reverse osmosis (Garfi *et al*.,2016) ceramic water filters (Lantagne *et al*., 2017). Cation exchange resin and Anion exchange resin amongst others. However, these methods are chosen depending on the areas of concern by the researcher and what is meant to be achieved at the end of the treatment. It is worthy of note that different concerns related to water consumption and wastewater effluent disposal over the years had led to the applications of several mechanisms to tackle the problems associated with drinking water and those emanating from wastewater treatment.

This work considers the use of bone char and egg shell (egg char) to achieve adsorption of fluoride in water because bone char had attracted much attention in wastewater treatment because of its advantages over other adsorbents. The advantages in considerations are low-cost and capacity for adsorbing a wide range of pollutants such as heavy metals, fluoride, arsenates, dyes. Also, regeneration of Bone char can be achieved by contacting the adsorbent with a basic solution (pH>12) (Medellin-Castillo et al., 2007). This quality makes Bone char an attractive adsorbent for environmental remediation.

Previous studies of Mlilo *et al.* (2010), Delgadillo- Velasco *et al.* (2017), Kofa *et al*., 2017, Yothin *et al.*, 2014, Medellin-Castillo *et al*, (2016) for removal of fluoride from water by adsorption method had considered the use of cow bones- per boiled bones as adsorbent, commercial synthetic, calcium pills, carmex bone char, clay, local furnace, among others and mostly synthetic water were used. The current work will be focused on using two adsorbent- Egg char and Bone char (made from fresh bones) to remove Fluoride ion from ground water in batch wire.

MATERIALS AND METHODS

Materials

The materials used for this experimental work were crusher, weighing balance, measuring cylinder (100ml and 1000ml) beakers, funnels, filter paper, protein bag, sieves, furnace, crucibles, thermometer, stirrer, Erlenmeyer flask, electric heater, pH meter, X-ray Fluorescence Spectrometer, oven, small pot, trioxonitrate (v) acid, sodium hydroxide, distilled water, water samples, - solar thermo elemental atomic absorption spectrophotometer (flame AAS).

Methods

Assorted goat bones were collected from the slaughter market, washed to remove sand, dirt's, and flesh and then sun dried while the eggshell was collected washed and dried under sunlight. There after bones and egg shell were crushed and characterized with EDX3600B X-ray Fluorescence Spectrometer to determine the chemical composition present in both samples. Both samples were weighed and heated in a furnace at temperature of 300℃ for an hour for the purpose of Calcination.

Activation of Adsorbent

The bone char and Egg char were then sieved to particle size of 2.12μm after the calcination process was performed, Then 180g of Bone char and Egg char was modified with 1.0M Solution of trioxonitrate(v) acid where 180g 0f both samples were separately added with 1000ml of 1.0M HNO_3 in Erlenmeyer flask which then heated up to 80℃ while being stirred continuously for 24 hours. The solution formed was allowed to cool and filtered with Whatman filter paper. The activated Bone char and Egg char were then oven dried and stored for subsequent use.

Characterization of Produced adsorbent

The activated Bone char and Egg char was characterized to determine the percentage of Calcium and Phosphorous in both samples with solar thermo elemental atomic absorption spectrophotometer (Flame AAS) and spectrophotometer respectively. Then the water sample was analyzed for initial fluoride content with the apparatus known as Spectrophotometer or Colour Comparator.

Physical properties of adsorbent

The physical characterization of the adsorbent is very important in order to classify them for specific applications. Samples' bulk destiny, moisture content, pore volume and porosity were determined as follows:

Bulk Density Determination

The bulk density of bone char and egg char were determined by calculating the ratio of the mass to the volume occupied. The procedure reported by Aneke and Okafor., 2004 was used in the work. Thus, two grams of sample was weighed (mass of the sample) and completely transferred into a measuring cylinder containing 10ml of distilled water (Volume of Water). The volume of the water displaced was recorded. The bulk density was therefore calculated using equation below:

$$\text{Bulk density} = \frac{Mass\ of\ sample}{Volume\ of\ Water\ displaced} \qquad (1)$$

Moisture Content Determination

The moisture content in each bone char and egg char were determined using the standard method prescribed in ASTM D2016-25. Two grams of sample -initial weight (Wi) was dried in an oven for 1.5hr at 105°C.The weight of the sample was determined at intervals until it became constant. This was taken as the final weight (W_f)

The moisture content was calculated as:

$$X_0(\%) = \frac{W_i - W_f}{W_i} \qquad (2)$$

where: X_0 = moisture content on wet basis, W_i = initial weight of the material (before drying), W_f = final weight of the material (after drying)

The Pore Volume and Porosity Determination

The pore volume and porosity of the bone char (BC) and egg char (EC) samples were determined using the procedure reported by Aneke and Okafor, 2004, Two grams of samples was weighed(w_i) and transferred into a 10ml measuring cylinder. The volume obtained after mixing was taken as the total volume of particle. This was further poured into a beaker containing 20ml of distilled water and was boiled for 5min to displace air in sample. The content in the beaker was filtered, superficially dried and weighted (w_f). The pore volume was thus calculated from equations:

$$\text{Pore volume} = \frac{W_f - W_i}{\rho_{H_2O}} \qquad (3)$$

where: w_i = initial weight of sample, w_f = final weight of sample,ρ_{H_2O} = density of water

The porosity of each sample was calculated from the equation:

$$\text{Porosity} = \frac{\text{Pore volume of the particle}}{\text{Total volume of the particle}} \qquad (4)$$

Surface Area Determination

Specific surface area (SSA) was calculated from the equation (Richardson et al., 2002):

$$SSA = \frac{q_m \times N_a \times a}{M} \qquad (5)$$

SSA = Specific surface area of adsorbent,q_m = maximum adsorption capacity on mono-Layer surface

NA = Avogaro's number = 6.02 x 10^{23} molecules/kmol, a = effective cross-section area occupied by one water molecule 0.114mm = 0.114x10^{-18}, M = molecular mass of water = 18 x 10^{-3}g/kmol

Adsorption Experiment

Batch experiment were carried out by adding 5g of activated Adsorbent of particle size 2.12μm into 500ml of solution containing 7.34928mg/l of Fluoride ion in an Erlenmeyer flasks placed on a hot plate stirrer and shaken at 300rpm at room temperature. The interaction was allowed for different time intervals of 60,120,180,240,300 minutes until equilibrium was established. The experiment was conducted with 5g of sample of both bone char (goat bone) and Egg char respectively. When the 5g of Bone char were placed into 500ml Erlenmeyer flasks and filled with 7.34928 mg/l of fluoride solution at room temperature. At each time interval aliquot of stock solution was removed from the flask and filtered using Whatman filter paper. The concentration of fluoride ion in the filtrate was analyzed using spectrophotometer. The amount of fluoride adsorbed by the adsorbents was calculated and graphed with the corresponding concentration of Fluoride.

Percentage Adsorption

The percentage of fluoride ion removed ($R\%$) at each time interval could be obtained by the relationship (Gurnorubon & Chukwunonso, 2018).

$$R\% = \left[\frac{C_o - C_t}{C_o}\right] \times 100$$

(6)

Where;

$C_{o=}$ is the initial fluoride concentration, C_t= is the concentration of fluoride at time (t)

Adsorption Capacity

The amount of fluoride ion adsorbed from the adsorbent at each time (t) was evaluated using the equation according to Gurnorubon and Chukwunonso (2018).

$$q_t = \left[\frac{C_o - C_t}{W}\right] V$$

(7)

where: $q_{t=}$ amount of fluoride ion adsorbed, V= volume of the solution (L), W= weight of the adsorbent (g)

The Adsorption capacity of the adsorbent was also calculated from the following relationship.

$$q_e = \left[\frac{C_o - C_e}{W}\right] V$$

(8)

Where: q_e = amount of fluoride ion adsorbed at equilibrium, C_e= is the concentration of fluoride at equilibrium.

According to Wong and Stenstrom (2017) the adsorptive capacity could be calculated from the relationship in equation (9).

$$\frac{X}{m} = (C_o - C_t)\, {}^{V}\!/_{m}$$

(9)

where: m = is the mass of the adsorbent used, , X is the mass of the fluoride absorbed $\left({}^{mg}\!/_{l}\right)$

Effect of Process Parameters on Adsorption Rate

Effect of Contact Time

The effect of contact time on adsorption was studied by conducting the batch adsorption experiment with a known particle size of 2.12μm and mass dosage (weight) of 5g of adsorbent at different times starting from 60 to 240minutes at 60 minutes interval.

Effect of Adsorbent Dosage

The effect of adsorbent dose on adsorption was studied by conducting the batch adsorption experiment with particle size of 2.12μm, and contact time of 60minutes for different dosages of adsorbent (5g, 10g, 15g and 20g).

Effect of Temperature

The effect of temperature on adsorption was studied by conducting the batch experiment with particle size of 2.12μm, of contact time of 60mins for different temperature range (25, 30, 40 50 ℃).

Adsorption Models

In Engineering, physical modeling is based on proposing empirical relations with large amount of experimental data and the relevant non-dimensional parameters using regression techniques (Babu& Ramakrishna, 2002). However, several kinetic and equilibrium models have been used in adsorption studies to fit the experimental data.

Adsorption Kinetic Model describes the solute uptake rate, which controls the residence time of adsorbate uptake at the solid-solution interface. This is a helpful mechanism in selection of optimum operating conditions for the full-scale batch process (Kalavathy *et al.*, 2005).

Adsorption Kinetics

The kinetic analysis was carried out to investigate the rate of adsorption, determine the mechanism of adsorption and the potential rate controlling steps (mass transport, pore diffusion or chemical reaction) (Gunorubon & Chukwunonso., 2018). The kinetic models had been used to correlate experimental data. Hence, pseudo first-order, pseudo second- order and intra-particle diffusion models equations were fitted to the experimental data to model the adsorption kinetics of Fluoride ions adsorption onto Bone char and Egg char. The essence of this, was to determine correlation coefficient (R^2) as a measure of agreement between the experimental data

Pseudo-First-Order-Model

The pseudo-first-order rate equation is generally expressed as follows:

$$\frac{dq_t}{dt} = K_t\left(q_e - q_t\right)$$

(10)

where: q_t = adsorption capacity at time, t (mg. g^{-1}), q_e = adsorption capacity at equilibrium (mg. g^{-1}), t = contact time (min), K_1 = pseudo-first-order rate constant (min^{-1})

After integrating and applying boundary conditions between limits, $q_t = 0$ at $t = 0$ and $q_t = q_t$ at t = t, equation (10) becomes (Gunorubon & chukwunonso, 2018).

$$q_t = q_e \left(1 - \exp \frac{K_1}{2.303} t\right)$$

(11)

$$\log_e\left(q_e - q_t\right) = \log_e\left(q_e\right) - \frac{K_1}{2.303} t$$

(12)

The plot of $\log_e$ (q_e-q_t) versus contact time (t), should give a linear relationship from which K_1 and q_e could be determined from the slope and intercept of the graph respectively.

Pseudo-Second-Order Model

The pseudo-second-order rate equation is expressed as shown

$$\frac{dqi}{dt} = K_2(q_e - q_t)^2$$

(13)

where: q_t = adsorption capacity at time t (mg. g^{-1}), q_e = adsorption capacity at equilibrium (mg. g^{-1}), t = contact time (min), K_2 = pseudo-second-order rate $constant_1$ g(g.min^{-1})
Integrating the equation between the boundary conditions, q_t = 0 at t = 0 and $q_t = q_t$ at t = t, the linearized model equation will be (Yasmin *et al.*, 2009).

$$\left[\frac{t}{q_t}\right] = \frac{1}{K_2(q_e)^2} + \frac{1}{q_e}t$$

(14)

The plot of (t/q_t) versus t of equation (14) gives a linear relationship from which q_e and K_2 could be determined from the slope and intercept of the graph respectively.

Intraparticle Diffusion Model
This model is expressed as shown in equation (15)

$$q_t = k_{id}\,(t)^{0.5} + l$$

(15)

where: q_t = adsorption capacity at time t (g.g^{-1}), t = contact time (min), l = boundary layer thickness, k_{id} = intraparticle diffusion rate factor, g(g.min)$^{-0.5}$
A plot of q_t versus $t^{0.5}$ gave a linear relationship, then I and K_{id} could be determined from the slope and intercept of the plot respectively. Higher values of 'l' depict higher adsorption capacities and higher values of k_{id} illustrates an enhancement in the rate of adsorption, whereas larger k_{id} values illustrate a better adsorption mechanism which is related to an improved bonding between the adsorbate and the adsorbent particles (Igwe *et al.*, 2008).

Adsorption Equilibrium Studies
The adsorption isotherms in this research shows the relationship between the amount of adsorbed fluoride ions per unit of bio sorbent(adsorbent) (q_e) to the fluoride concentration in the solution((c_e) at equilibrium at a given temperature, pressure, pH and total solute concentration(Gurunobon & Chukwunonso.,2018). The adsorption isotherm experiment was performed at different temperatures of 25, 35, 45 and55℃.Then, the sorption equilibrium data from the conducted batch experiments were fitted with the Langmuir and Freudlich Isotherm models in order to describe the adsorption Isotherm of Fluoride ion on Bone char and Egg char respectively.

Langmuir Isotherms
The Langmuir model is expressed by the following equation (Oke *et al.*, 2008).

$$q_e = \frac{q_m K_L C_e}{I + K_L C_e}$$

(16)

where: q_e = adsorption capacity at equilibrium (g H_2O.g $adsorbent^{-1}$), C_e = concentration in solution at equilibrium, K_L = Langmuir parameter, q_m = Langmuir parameter
Rearranging and linearising equation (16) gives equation (17) as follows:

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{K_L q_m}$$

(17)

A plot of $\frac{C_e}{q_e}$ versus C_e yields a straight line graph with slope equivalent to $\frac{1}{q_m}$ and the intercept as $\frac{1}{K_L q_m}$ from which K_L and q_m were determined.

The Langmuir model was developed for gas phase adsorption but sometimes it describes the liquid phase phenomenon reasonably well. Langmuir Isotherm could be expressed in terms of the dimensionless separation parameter (R_L), expressed as (Saswati and Ghosh, 2005).

$$R_L = \frac{1}{1+q_L C_o} \tag{18}$$

where: $R_L =$ Separation parameter, $q_L =$ Langmuir parameter, $C_0 =$Highest water concentration

This parameter has been used to predict how feasible an adsorption system is. If the value of $R_L > 1$ (favourable), $R_L = 1$ (linear adsorption), $R_L = 0$ (irreversible) and $0 < R_L < 1$ (favourable).

Freundlich Isotherm

Freundlich Isotherm was proposed by Freundlich. This isotherm is an empirical equilibrium relationship between heterogeneous surfaces, which often gives a more satisfactory correlation of experimental data. It assumes that the adsorption sites are distributed exponentially with respect to the heat of adsorption (Oke *et al.*, 2008). It can be expressed by equation (3.21).

$$q_e = K_f C_e^{\frac{1}{N_f}} \tag{19}$$

where:

q_e = adsorption capacity at equilibrium (g H_2O.g adsorbent^{-1}), C_e = concentration in solution at equilibrium (% W/W), K_f = Freundlich constant indicating adsorption capacity, N_F = Freundlich constant indicating adsorption intensity or surface heterogeneity (dimensionless)

The logarithmic linear form of Freundlich Isotherm may be expressed as follows

$$Log q_e = Log k_f + \frac{1}{N_f} Log C_e \tag{20}$$

A plot of Log_e versus $Log C_e$ gave a linear relationship. The Freundlich constants N_f and K_f were obtained from the slope and intercept of the plot respectively. The term $^1/_{N_f}$ indicates the intensity of adsorption, which in turn was ascribed to the distribution of heat of adsorption (Q) or surface heterogeneity factory (Y). N_f is a measure of performance of adsorbent. When the value of $^1/_{N_f} < 1$ (normal freundlich adsorption), $\frac{1}{N_f} > 1$ (cooperative adsorption) and $0 < {}^1/_{N_f} < 1$ (favourable adsorption).

It is generally accepted that the smaller values of $N_f(3-10)$ suggest better adsorption characteristics and formation of rather strong bond between the adsorbate and adsorbent (Oke *et al.*, 2008).

Thermodynamics Studies

In this research work the thermodynamics behavior of the adsorption process was studied by determining parameters like Gibbs free energy change ΔG^O(KJ/mol.k), the standard enthalpy change ΔH^O (KJ/mol), and the standard entropy change ΔS^O(J/mol.k) using the Van't Hoff equation.

$$Ink_{e=}\frac{\Delta S^O}{R}-\frac{\Delta H^O}{RT} \quad (21)$$

$$\Delta G^O = \Delta H^O - T\Delta S^O \quad (22)$$

The distribution adsorption coefficient/ equilibrium constant (K_e) of fluoride ion adsorbed by an adsorbent (mg/l) can be obtained from the equation given

$$K_e = \frac{mq_e}{VC_e} \quad (23)$$

where:

R is the universal gas constant(8.314J.K^{-1}), T is the absolute temperature in Kelvin.

Equilibrium concentration of adsorbed species in bulk phase (C_e) and adsorbent phase (q_e) at different temperatures were approximately correlated to estimate the thermodynamics parameters.

Adsorption experiment were conducted at different temperatures of 25, 35 45 and 55 ℃ to obtain batch equilibrium data used in calculating the distribution adsorption coefficient /equilibrium constant (K_e) from equation (23) at these temperatures. The plot of InK_e versus $\frac{1}{T}$ equation (21) was used to calculate the values of ΔH^O and ΔS^O from the slope and intercept respectively. $\Delta G^O$from equation (22) for all temperatures.

RESULTS AND DISCUSSION

Results

Chemical Composition

The activated bone char(BC) and Egg char(EC) studied were characterize after the modification with 1.0M HNO3 acid analysis of the calcium and phosphorous elements were analyzed because in previous analysis showed them as elements with higher composition. Thus, table 1 of the analysis showed Calcium (53.12%) and (39.68%) for Bone char and Egg char respectively while phosphorous was (4.08%) and (2.71%) in both adsorbent samples of Bone char and Egg char.

Table 1: Characterization of Activated Bone Char (BC) and Egg Char (EC)

Sample	Ca (%)	P (%)
Bone Char (BC)	53.12	4.08
Egg Char (EC)	39.68	2.71

Physiochemical Characteristics of Bone char and Egg char

The physical properties of two selected adsorbent (Bone char and Egg char) studied were presented in Table 2.

Table 2: The Physiochemical Properties of Activated Bone Char (BC) and Egg Char (EC)

	BC	EC
Moisture content	0.1275 (12.75%)	0.299 (29.93%)
Pore volume (g/ml)	0.202	0.547
Porosity	0.018	0.046
Bulk density (g/ml)	1.0	2.0
SSA (m^2/g)	2074.3	2074.3

The bulk densities of the samples were in the range of 1.0 -2.0g/ml. The bulk density of BC was lower than that of EC. Thus, higher bulk density means the adsorbent has high adsorption capacity (Aneke and Okafor, 2004).

Table 2 showed that the moisture content of the BC sample was lesser than the moisture content of the EC sample 12.75% was lesser than that of EC (29.9%). The lower the moisture content, the higher the adsorption capacity since water competes with organic molecules for active site on adsorbents such as carbon.

The pore volume of BC was 0.231g/ml while the porosity was 0.0193 and the pore volume of EC was 0.502g/ml while its porosity was 0.0456 as presented by Table.2. The higher pore volume and porosity indicates high adsorption capacity (Ademiluyi et al., 2008) while the bigger the surface area, the more effective the adsorbent.

Effect of Process Parameter

The effect of process parameter in this experiment considers the effect of contact time, the effect of adsorbent dose and the effect of temperature on adsorption.

Effect of Contact Time

The effect of contact time on adsorption (percentage removal of Fluoride F- ion) using known particle size 2.12μm and known adsorbent dosage (5g) is seen in Figure 1 for both samples of BC and EC. Thus, Figure 1 shows that the percentage adsorption of fluoride ion (F^-) increased gradually with contact time for both samples of activated Bone char (BC) and Egg char (EC).This indicate that both adsorbent had the capacity to remove fluoride ion from the solution.

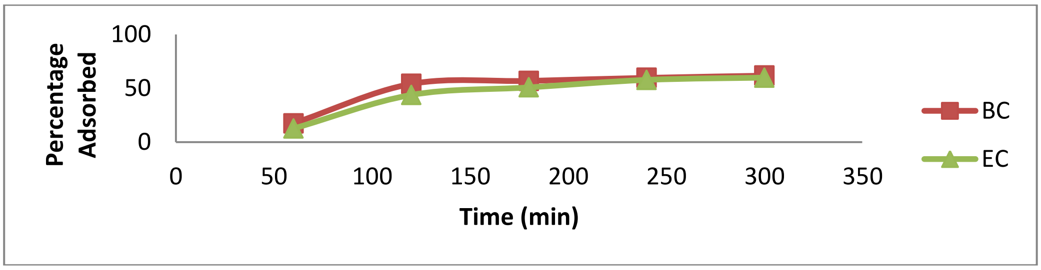

Figure 1: Effect of Contact Time

Effect of adsorbent dosage on adsorption

The effect of adsorbent dosage on adsorption (the percentage of fluoride removal) is shown in Figure 2

Figure 2 shows that as the dosage (quantity of adsorbent bone char (BC) and Egg char (EC)) used, increased the amount of fluoride ion in the stock solution adsorbed (percentage adsorbed) by activated BC and EC increased; increase in adsorbent dose increase the surface area and number of active sites of Bone char and Egg char available to the solute (fluoride ion) for adsorption, thus, increasing the rate of adsorption.

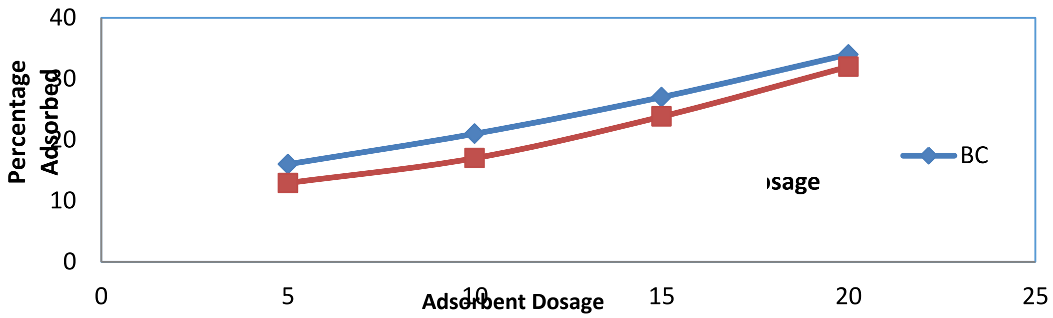

Figure 2: Effect of Adsorbent Dosage

Effect of Temperature on Adsorption

Temperature is another vital parameter affecting the adsorption process. The effect of temperature on adsorption (percentage of fluoride removal) by BC and EC using known particle size, dose and known contact time is shown in Figure 3

Figure 3 shows that increase in temperature for interaction between the adsorbents (BC and EC) respectively with the fluoride containing stock solution, increased the percentage of Fluoride absorbed.

Figure 3 showed that the percentage removal of Fluoride increased gradually as the temperature increases and this indicated that the adsorption reaction of fluoride was endothermic reaction. The adsorption percentage of fluoride ion was highest at room temperature with 74% for activated BC and 73.77% for activated EC. The mentioned percentage of fluoride was removed by the activated BC and EC from the initial concentration of fluoride.

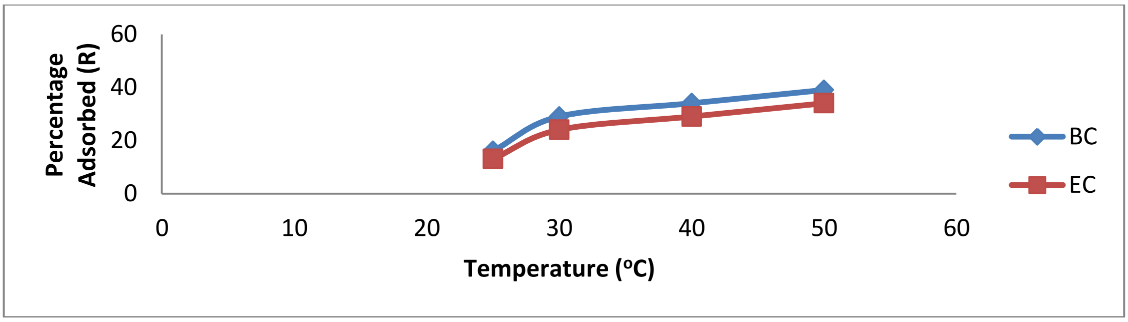

Figure 3: Effect of Temperature

Adsorption Capacity

Adsorption Capacity with Contact Time

Figure 4 shows the adsorption capacity (amount of fluoride adsorbed) with respect to contact time for 5g of the adsorbents Bone char(BC) and Egg char(EC). The result obtained indicates that increase in contact time had a corresponding increase in amount of fluoride adsorbed for both BC and EC respectively until equilibrium was established. Thus, at equilibrium the maximum adsorption was obtained.

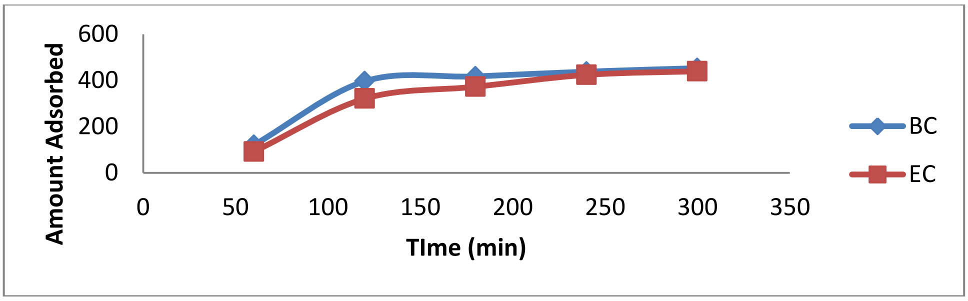

Figure 4: Adsorption Capacity with respect to contact time

Adsorption Capacity with adsorbent Dosage

Figure 4 was obtained from the experiment to determine the adsorption capacity (amount of fluoride ion) with respect to adsorbent dosage. The result obtained revealed that the adsorption capacity of fluoride (amount of fluoride adsorbed) from solution by Bone char(BC) and Egg char(EC) decreased as adsorbent dosage was increased from 5g to 20g at contact time of 60mins.

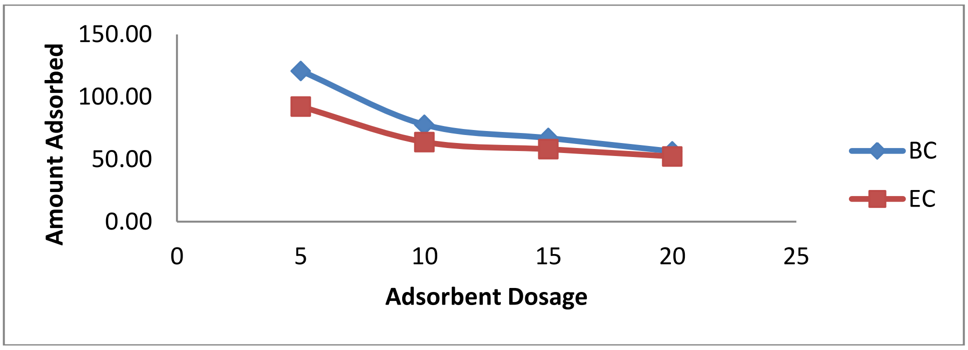

Figure 5: Adsorption Capacity with Adsorbent Dosage

Adsorption Capacity with Temperature

Figure 6 was the obtained from the experimental data of considering the amount of fluoride ion removed by adsorbents 5g of BC and EC with respect to increase temperature at a constant time of 60minutes.

The adsorption capacity (amount of fluoride adsorbed) from the solution by the adsorbent Bone char (BC) and Egg char(EC) with respect to temperature as shown Figure 6, indicates that increase in temperature gave corresponding increase in the amount of fluoride adsorbed by both adsorbents (BC and EC) until equilibrium will be established.

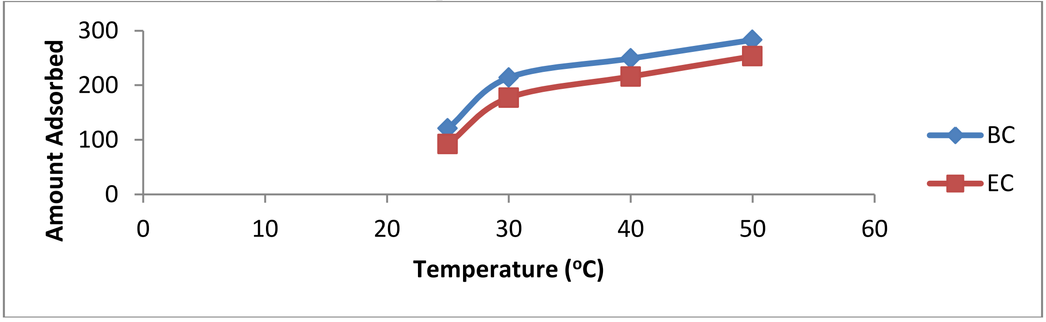

Figure 6: Adsorption Capacity with Temperature

Adsorption Kinetics

The kinetics of the adsorption process was monitored by following the adsorption capacity with contact time until equilibrium was achieved with concentration of fluoride remaining in water as 1.09 for BC and 1.92 for EC at q_e = 544.112 mg/g and 542.00mg/g respectively. Hence Figure 7-12 showed the kinetics behavior of both Adsorbent (BC and EC).

Intraparticle Diffusion Model

A Plot of q_t vs $t^{0.5}$ for the experimental data are shown in the Figure 7- 8. The intraparticle diffusion model revealed the mechanism involved in the adsorption process.

The first linear part of the curve is assumed to be attributed to boundary layer diffusion while the other part indicated the effect of intraparticle diffusion as presented in Figure 7. The plot did not pass through the origin indicating the influence of additional mechanism. This could probably be boundary layer influence, that is, external film resistance, resulting from vicious drag existing between the adsorbent surface and the solute in solution diffusing across its surface.

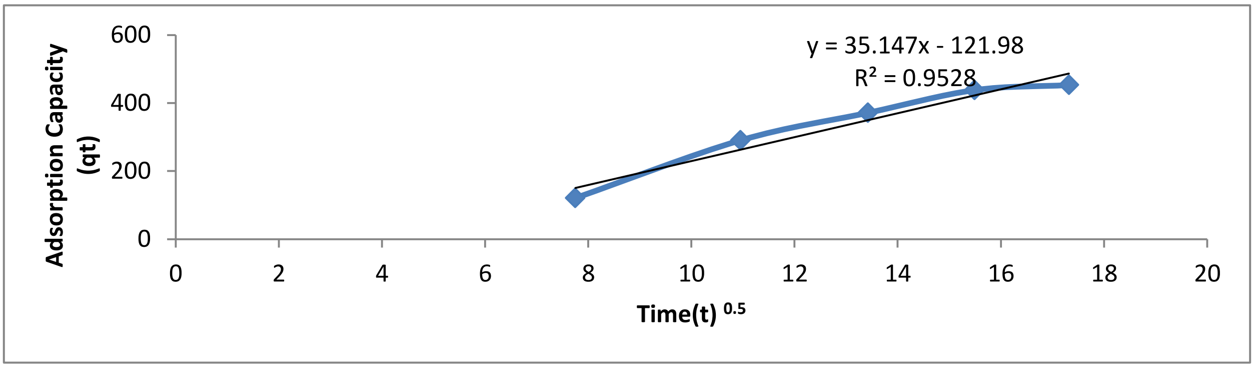

Figure 7: Intra Particle Diffusion Model for (BC)

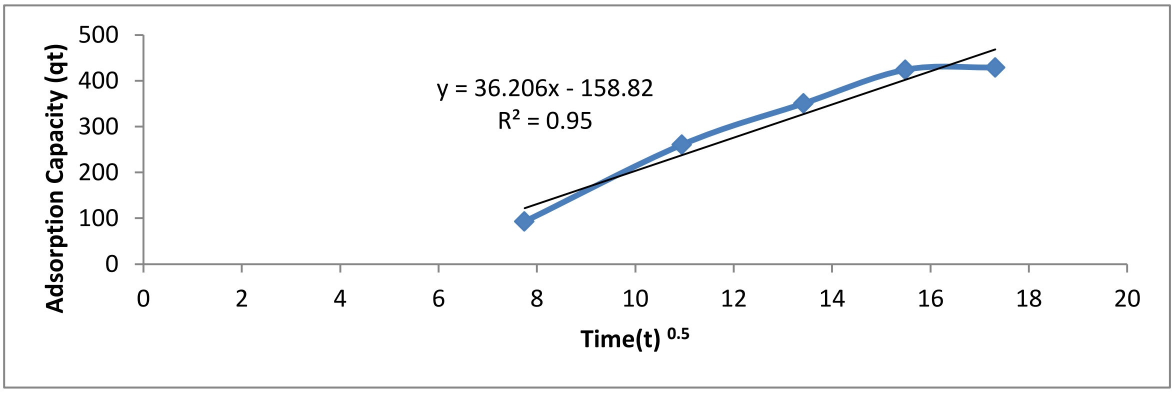

Figure 8: Intra Particle Diffusion Model for EC

The boundary layer thickness, 1, was 121.9 for Bone char (BC) and -158.8 for Egg char (EC). Larger values of ‘1’ showed improved bonding between sorbent and adsorbent particles, hence, higher adsorption capacity. Higher values of K_{id} of the Bone char (BC) and Egg char (EC) samples were 35.14 and 36.20. These results therefore showed that the sorption process was particle-diffusion controlled. Also, higher R^2 values implied higher accuracy, validity and good fitness of the model (Adie et al., 2010).

Pseudo-First Order Model

A Plot of the first order rate $\log(q_e - q_t)$ versus time (t) are shown in Figure 9-10.The parameter of the pseudo first order models were determined from the slope and intercepts of Figure 9 and 10 along with their corresponding correlation coefficients.

Figure 9-10 shows the graphs of Pseudo First- order model was used to evaluate the kinetics of the selected adsorbents (BC) and (EC). The Figure 9 showed that the adsorption process for BC followed the Pseudo first order Kinetics since the model fitted better into the experimental data than that of intraparticle diffusion and the Pseudo second order model. The calculated adsorption capacity values at equilibrium, $q_{e,cal}$ ($423.64^{mg}/_{g}$) of the pseudo first order for BC were closer to that of the experimental data, $q_{e,exp.}$ ($544.112^{mg}/_{g}$). However, higher values of $R^2 = 0.791$ implies higher accuracy, validity and good fitness of the model (Adie et al., 2010).

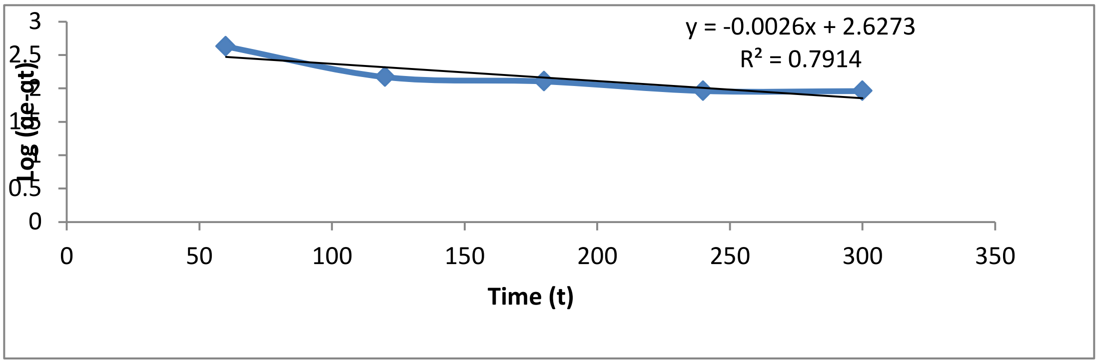

Figure 9: Pseudo first order for BC

Figure 10 the graphs of Pseudo First order model used to evaluate the kinetics of the selected adsorbents (BC) and (EC). The figure 10 shows that the adsorption process for EC followed the Pseudo first order Kinetics since the model fitted better into the experimental data than that of intra particle diffusion and the Pseudo second order model. The calculated adsorption capacity values at equilibrium, $q_{e,cal}$ ($533.33^{mg}/_{g}$) of the pseudo first order for EC were closer to that of the experimental data, $q_{e,exp.}$ ($542.215^{mg}/_{g}$). However, higher values of $R^2 = 0.930$ implied higher accuracy, validity and good fitness of the model (Adie et al., 2010). However, Pseudo first order model for Egg char correlation coefficient (R^2) values was higher than of Bone char (BC).

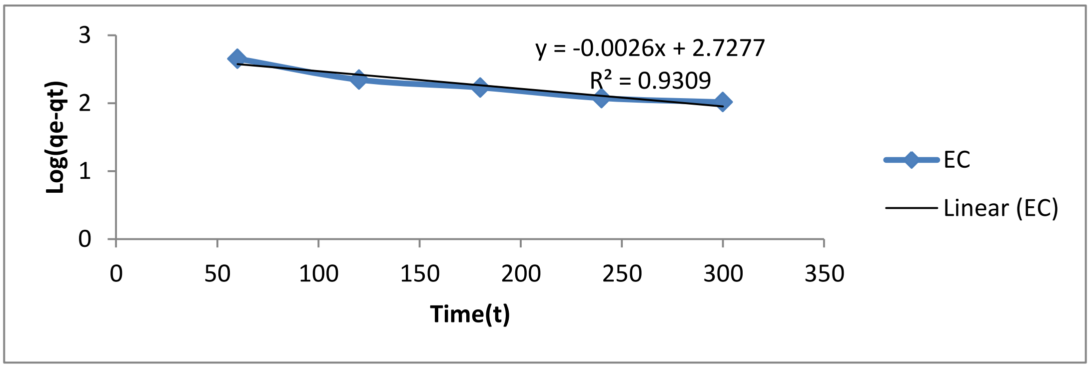

Figure 10: Pseudo first order model for EC

Pseudo-Second Order Model

A Plot of the second order rate ${}^{t}/_{q_t}$ versus time (t) of the experimental data are presented in Figure 11 and 12 for Bone Char (BC) and Egg char (BC) respectively. The parameter of the pseudo first order models was determined from the slope and intercepts of figure 11and 12 along with their corresponding correlation coefficients.

Figure 11 -12, shows the graphs of Pseudo- second order models used to evaluate the kinetics for the adsorbents Bone char and Egg char respectively. But, the Figure 11 signifies the adsorption process followed by Bone char (BC) which $q_{e,calc}$(1000mg/g) was far higher than the experimental values obtained $q_{e,exp}$ (544.112mg/g) and the R^2 =0.464 which was far from unity. This indicated that the experimental data does not fit into the of the pseudo-second order kinetics model.

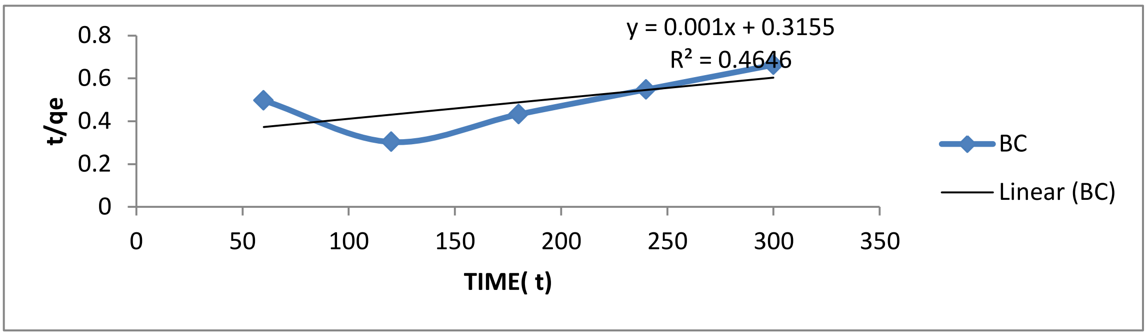

Figure 11: Pseudo second order model for BC

Figure 11-12, are the graphs of Pseudo- second order models used to evaluate the kinetics for the adsorbents Bone char and Egg char respectively. But, the Figure 3.12 signifies the adsorption process followed by Bone char (BC) which $q_{e,calc}$(0.00mg/g) is far lower than the experimental values obtained $q_{e,exp}$ (544.112mg/g) presented on table 3.11 and the R^2 =0.113 which is far from unity. This indicated that the experimental data does not fit into the of the pseudo-second order kinetics model.

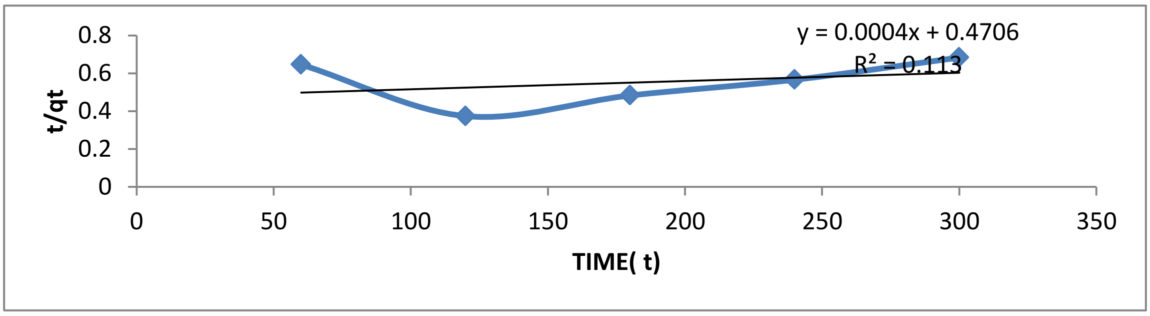

Figure 12: Pseudo Second Order Model for EC

The Pseudo –First order model has better fit with the experimental data with higher squared correlation coefficients (R^2 = 0.930) for EC and (R^2 =0.791) for BC followed by Intraparticle diffusion with (R^2 = 0.876) for EC and(R^2= 0.747) for BC. The Pseudo Second –Order model does not fit the experimental data because of its R^2 values. Thus, the results shows that pseudo –First order kinetic model is the most suitable for describing the kinetic of Bone char and Egg char calcined at 300℃ , followed by the Intraparticle diffusion.

Adsorption Isotherm

The plot of Langmuir and Freundlich adsorption isotherm models for adsorption data from the experiment at equilibrium at temperatures of 25, 35 45 and 55℃ are shown in Figure 13-16. The adsorption constants of these models were determined from the slopes and intercepts with its corresponding correlations coefficients are given by figure 13 - 16.

The plots and estimated adsorption parameters of the adsorbents by the Langmuir and Freundlich isotherms were presented in Figure13-14.The Langmuir parameter (q_m =500) for BC while the K_L =2.0, R_L =-0.073 and the correlation coefficients R^2=0.989. The R^2value for BC is close to unity indicating that the experimental data fit the Langmuir Isotherm model. More so the value of separation parameter R_L =-0.073 calculated lies within (0<R_L<1) which indicates favourable adsorption for Bone char sample (BC).

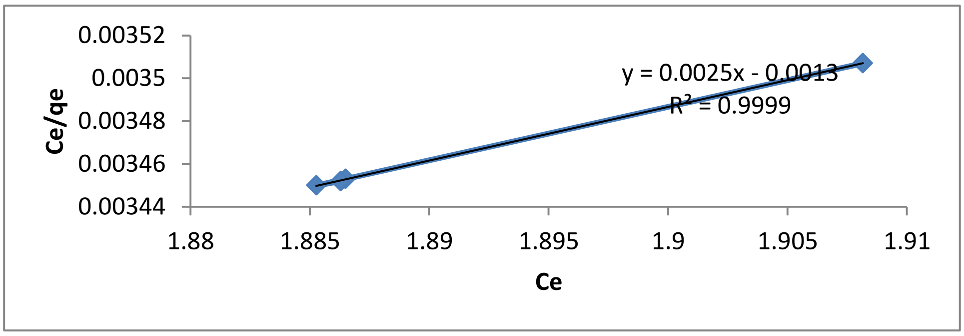

Figure 13: Determination of Langmuir Isotherm for Bone Char (BC)

The plots and estimated adsorption parameters of the adsorbents by the Langmuir and Freundlich isotherms are presented in Figure 13-16. The Langmuir parameter (q_m =500) for BC while the K_L =2.0, R_L =-0.073 and the correlation coefficients R^2=0.999. The R^2value for BC is close to unity which revealed that the experimental data fit the Langmuir Isotherm model. More so the value of separation parameter R_L =-0.073 calculated lies within (0<R_L<1) which indicates favourable adsorption for Egg char sample (EC).

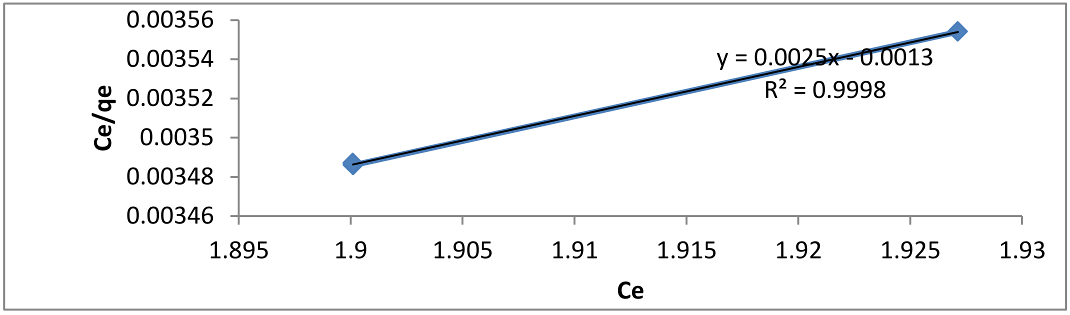

Figure 14: Determination of Langmuir Isotherm for Egg Char (EC)

The Freundlich Isotherm of Bone char (BC) was presented in Figure15 for BC, The performance of both adsorbent is measured by the Freundlichterm($^1/_{N_f}$) .The calculation based on figure 15 showed that $^1/_{N_f}$ = -0.348 for BC where (0<$^1/_{N_f}$<1) signifying favourable adsorption.

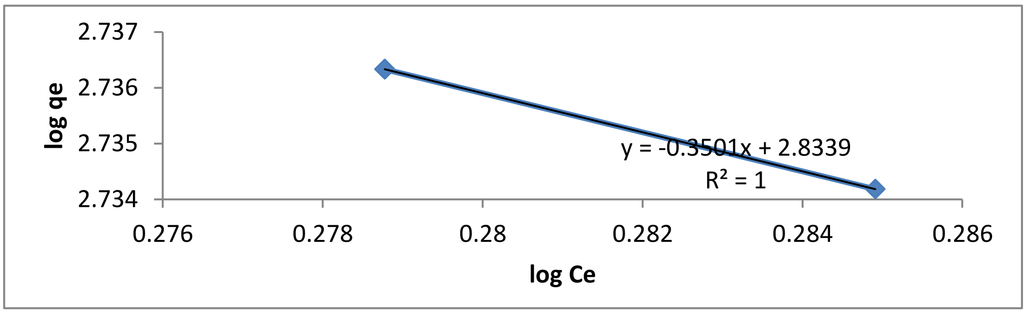

Figure 15: Determination of Freundlich Isotherm for BC

The Freundlich Isotherm for Egg char (EC) is presented in Figure 16. The performance of both adsorbent was measured by the freundlich term ($^1/_{N_f}$). The calculation based on figure 16 showed that $^1/_{N_f}$ = -0.350 for EC where (0<$^1/_{N_f}$<1) signifying favourable adsorption. The correlation coefficient (R^2) of Freundlich Isotherm is unity when compared to the Langmuir Isotherm at all temperatures. The Freundlich Isotherm fits most suitable for Egg char (EC) and Bone char followed by Langmuir Isotherm for both adsorbents sample.

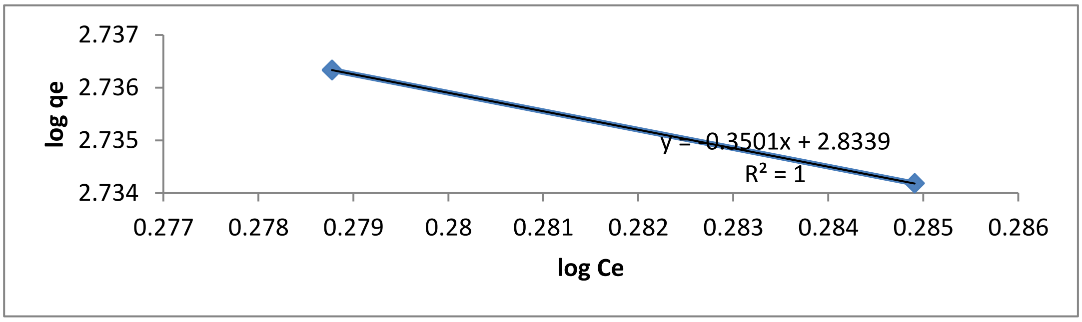

Figure 16: Determination of Freundlich Isotherm for EC

Thermodynamic Studies

Figure 17 and 18 showed the relationship between Ink_e and $^1/_T$. Thermodynamic parameters for the adsorption of fluoride ion was calculated to determine enthalpy, entropy and Gibbs free energy.The Gibbs free energy change of the process(ΔG^0) were all negatives and decreased with increase in temperature. This signifies that the adsorption mechanism of Bone char(BC) and Egg char(EC) towards fluoride ion is spontaneous in nature and thermodynamically favorable (Goswami & Ghosh.,2005 cited in Gunorubon & chukwunonso.,2018) and more favorable at higher temperatures (Zaki et al.,2000 cited Gunorubon & chukwunonso.,2018).

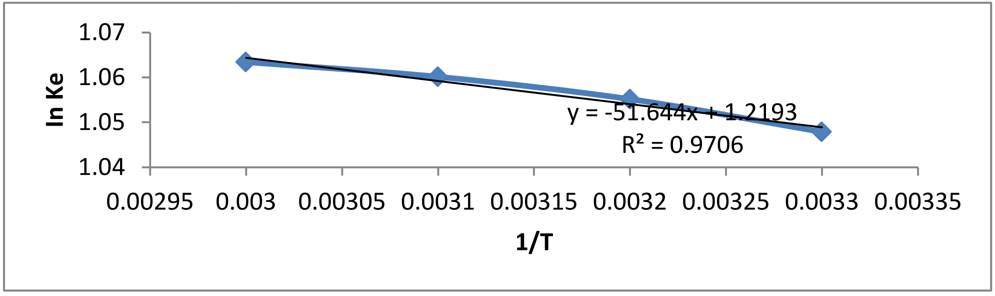

Figure 17: Thermodynamics Study for Fluoride ions adsorption on Bone Char (BC)

The enthalpy change of the process is positive, hence the process is endothermic. Thus, adsorption capacity increased with increase in temperature as predicted by the values of the maximum adsorption capacities q_m from Langmuir iso- therm model and in agreement with the Gibbs energies obtained**.** The entropy (ΔS^0) change of the process is positive indicating that the degree of freedom or randomness at the solid /liquid interface increased during the adsorption of fluoride ions onto the active site of the adsorbate. (Gupta.,1998 cited Gunorubon & chukwunonso.,2018). However, this agrees with the works of Saha & Chowdhury (2011) cited in Gunorubon & chukwunonso.,2018 and explained the mobility of the adsorbate ions/molecules in the solution increase with increase in temperature.

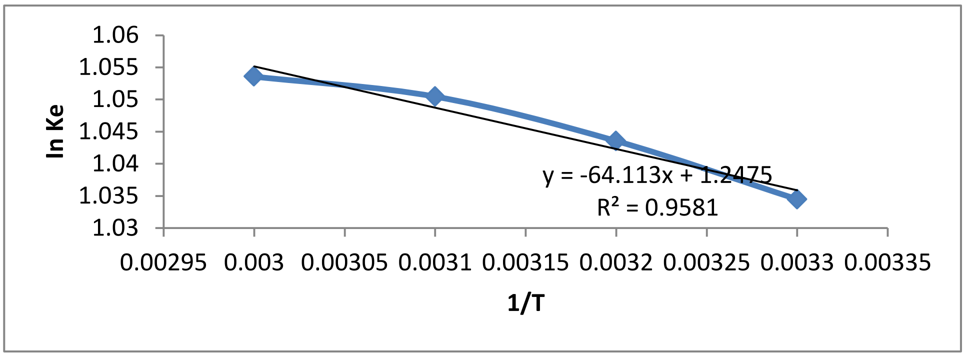

Figure 18: Thermodynamics Study for Fluoride ions adsorption on Egg Char (EC)

CONCLUSION

The production of activated Bone char and Egg char from Goat bones and Egg shell were carried out and modified with 1.0M HNO_3 trioxonitrate (v) acid. The activated Bone char and egg char was utilized for the removal of fluoride ion from water sample. From the experimental information obtained, it has been shown in this investigation that activated Bone char and Egg char of particle size of 2.12μm produced from animal waste (goat bones) and agricultural waste (Egg shell) could selectively adsorb fluoride ion from water. The performance investigated was based on adsorption capacity, Percentage removal of fluoride ion, effect of process parameter. Kinetic models, Adsorption Isotherm and thermodynamic parameters studies were utilized. The result obtained revealed that Percentage adsorption increased with increase in contact time for both adsorbents (BC and EC), increased with increased in mass dosage and increased with increase in temperature. The adsorption capacity was determined which increase with increase in contact time, increased with increase in temperature and decreased with increase in mass dosage. The mechanism of sorption indicated that the pseudo first order equation was the best applicable model to describe the sorption process. Hence, the pseudo first order kinetics is the rate controlling step with some intra particle diffusion. Both the Freundlich and Langmuir Isotherms were found to correlate the Batch adsorption equilibrium data. The experimental data for the adsorption process fitted perfectly into the Langmuir and Freundlich equations. The thermodynamic parameters studied were Gibb's free energy, enthalpy and entropy. The negative, positive and positive values of Gibb's free energy, enthalpy and entropy respectively indicated that the adsorption process was favourable, endothermic and increased in randomness.

REFERENCES

Ademiluyi,T.F, Audu, T.O.K,Njobuenwu,D. & Akpan,F.E (2008) Effect of Variety on the heat coefficient during drying of Fermented ground Cassava, International journal of Food Science and Technology,43,1181-1186.

Aneke, N.A & Okafor, J.O. Proceedings of the Nigerian Society of Chemical Engineers, 35th Annual Conference, Kaduna, Nigeria, 2005.

Babu,B.V& Ramakrishna, V.(2002) Applicability of Regression Techniques for Physical Modelling: A Case Study on Adsorption in Wastewater Treatment. Proceedings of International Symposium and 55th Annual Session of Indian Institute of Chemical Engineering, December19-22, Hyderabad.

Beita- Sandi, W.&Karanfil (2017) Removal of both N-nitrosodimethylamine and trihalomethanes Precursors in a Single Treatment using ion Exchange Resins. *Water Research*, 124, 20-28.

Crittenden, B.D & Thomas, W.J (1998) Adsorption Technology and Design Butterworth Heinemann, Oxford, 1-30.

Delgadillo-Velasco, L., Hermandez-Montoya, V., Cervantes, F.J., Moran, M.A & Lira-Berlanga, D.(2017) Bone Char with antibacterial properties for fluoride removal: Preparation, Characterization and Water treatment. *Journal of Environmental Management*, 201, 277-285.

Garfi, M., Cadena, E., Sanchez-Ramos, D. & Ferrer, I.(2016) Comparing Conventional Water Treatment, Reverse Osmosis and Mineral Water in Glass and Plastic Bottles. *Journal of Cleaner Production*, 137, 997-1003.

Gunorubon, A. J. &Chukwunonso, N. (2018). Kinetics, Equilibrium and Thermodynamics Studies of Fe^{3+} Ion Removal from Aqueous Solutions Using Periwinkle Shell Activated Carbon, *Advances in Chemical Engineering & Science, 8,* 49-66.

Freundlich,H.(1926) Colloid and Capillary Chemistry, Science Research Publishing

Kalavathy, M.H., Karthikeyan, T., Rajgopal, S & Miranda, J.R.(2005) Kinetics and Isotherm Studies of Cu(11) Adsorption onto H_3PO_4, Activated Rubber Wood Sawdust, Journal of Colloid and interface Science, United States, 292:354-362.

Kofa, G.P., Gomdje, V.H., Telegang, C., &Koungou, S.N. (2017) Removal of Fluoride From Water by Adsorption onto Fired Clay Pots: Kinetics and Equilibrium Studies. *Journal of Applied Studies,* 2017(2017), 1-7. Available at: https://doi.org/10.1155/2017/6254683

Lantagne, D., Rayner, J., Mittelman, A., & Pennell, K. (2017) Comment on “A re-assement of the Safety of Silver in Household Water Treatment: Rapid Systematic Review of Mammalian in Vivo Genotoxicity Studies’’. Environmental Health, 12(121) 1-4.

lgwe, J.C., Abia, A. A &lbeh, C.A. (2008) Adsorption Kinetics and Intraparticulate Diffusivities of Hg, As andPb Ions on Unmodified and Thiolated Coconut Fiber. International Journal of Environmental Science and Technology, Iran 5(1): 83-92

Li, Y., Yang, S., Jiang, Q., Fang, J., Wang, W. & Wang, Y. (2018) The Adsorptive Removal of Fluoride from Aqueous Solution by Modification Sludge: Optimal Using Response Surface Methodology: *International Journal of Environmental Research and Public Health*,15,826,1-12.

Medellin-Castillo, N.A., Padilla-Ortega, E., Tovar-Garcia, L. N., Leyva-Ramos.,R., Ocampo-Perez, R.,Carrasco-Marin, F.&Berber-Mendoza, M.S.(2016) Removal of Fluoride from Aqueous Solution Using Acid and Thermally Treated Bone Char, *Researchgate*,1-12.Retrieved:https://www.researchgate.net/publication/305952439.

Mlilo, T.B., Bruson, L.R. & Sabatini, D. A. (2010) Arsenic and Fluoride Removal using Simple Materials. *Journal of Environmental Engineering*, 391-398.

Oke, L.A., Olarinoye, N.O. &Adewusi, S.R.A. (2008) Adsorption Kinetics for Arsenic Removal from Aqueous Solutions by Untreated Powdered Eggshell. Adsorption, Netherlands.14, 73-83

Olugbade, E.A, Ojesola, F.F &Giwa, A. (2017) Treatment of Borehole Water Using MoringaOleifera Seed and Activated Carbon, *International Journal of Engineering Research in Africa*, 32, 62-75.

Razi, A., Rohazriny, R. &Naimah, I. (2015) Properties of Waste Eggshell as Calcium Oxide Catalyst, *Applied Mechanics and Materials*,754-755pp171-175,doi:10.4028/www.science.net/AMM.754-755.171

Richardson, J.K., Harker, J.H &Backhurst, J.R (2002) Particle Technology and Separation Process. Vol .2, 5thEdn, Butterworth-Heineman, Oxford, 970-1047

Saswati, G. & Ghosh, U.C. (2005) Studies on Adsorption Behaviour of Cr (vi) onto Synthetic Hydrox Stannic Oxide. Water, SA, South Africa, 31(14), 597-602.

Tovar-Gomez, R., Moreno-Virgen, M.R.,Dena-Aguilar, J.A., Hermandez-Montoya, V., Bonilla-Petriciolet, A. & ,Montes-Moran, M.A.(2013)Modeling of Fixed Bed Adsorption of Fluoride on Bone Char Using a Hybrid Neural Network Approach. *Chemical Engineering Journal*, 228, 1098-1109.

Volesky, B. (2001) Detoxication of Metal- Bearing Effluents: Biosorption for the Next Country, Hydrometallurgy, Netherlands, 59, 203-216.

Wong, E.Y. &Stenstrom, M.K.(2017) Onsite Defluoridation System for Drinking Water Treatment using Calcium Carbonate. *Journal of Environmental Management*.

Yasmin, H ., Chakravarty,A.k.,Shankar, N.C, Mazumder.T(2009) Comparison of Efficacy of Turmeric and Commercial Curcumin in Immunological Function and Gene Regulation, *International journal of Pharmacology*.

Yothin, M., Sunisa, S., Surat, M. & Deanna, D.(2014) Defluoridation with Locally Produced Thai Bone Char, *Advances in Environmental Chemistry*,2014,1-9,Retrieved:www.hindawi.com/journals/aec/2014/483