

Removal of Fluoride Ion from Water using Locally Produced Adsorbent

Ekine Aboiyaa A., Ikenyiri Patience N., Hezekiah-Braye O.

Abstract—This Research investigated the adsorption capacity of locally prepared adsorbents from Egg shells for the removal of fluoride ion in well water. It evaluated the performance of these adsorbents calcinated at 3000C and modified with 1.0M HNO₃ (trioxonitrate (v)) acid. Batch adsorber was used to allow for interaction between adsorbent (grounded Egg shells) with water containing fluoride ion. The batch experiment was performed with particle size of 2.12 μ m, contact time (60, 120, 180, 240, 300min), mass dosage (5g, 10g, 15g, 20g) and temperature (250C, 300C, 400C, 500C). The modified adsorbent was characterized to determine the physiochemical properties of grounded Egg shells (GE). Also, the chemical composition of the modified adsorbent was analyzed to determine the percentage of calcium element required for the uptake of the fluoride ions in water for calcium as 39.68% for grounded Egg shells (GE). Percentage adsorption increased with increase in contact time, mass dosage and temperature for the adsorbent. 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 for the grounded Egg shells (GE) reasonably described the adsorption process very well whereas the pseudo second order model was not suitable for a calcinations temperature of 3000C and particle size of 2.12 μ m. The adsorption isotherms were obtained from equilibrium experiment Performed at temperature of 25, 35, 45 and 550C. The result showed that Langmuir and Freundlich isotherm fitted 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_0 signified increased randomness with adsorption.

Index Terms—Defluoridation, Ground Water, Grounded Egg Shells, Fluoride, Adsorption, Water Treatment.

I. INTRODUCTION

Water is a chemical substance consisting of Hydrogen and Oxygen, linked by a covalent bond. It is a universal solvent and the main constituent of earth's streams, lakes and oceans, and the fluids of most living organism. Water is essential for life. This reveals that all creatures require water sufficiently and unpolluted water for survival. Today, the

quality and amount of water are of worry to man internationally on the ground that water is utilized day by day by billions of individuals around the globe. As indicated by the World Health Organization (WHO) enhancing drinking water quality is a noteworthy concern around the world, for human wellbeing to be ensured [1]. Therefore, water treatment is necessary for the removal of disease-causing agents or toxins- chemicals. These pollutants in drinking water are of concern because consumption of these contaminants at high concentration is harmful to human health. Thus, the need to control the risks to public health through systematic quality monitoring and surveillance [2].

According to the World Health Organization when fluoride concentration in water exceeds the limit of 1.5mg/L it becomes a contaminant in water [3]. Having fluoride ion content in drinking water is among the crucial issue to be tackled because both low and high concentrations of fluoride ion can affect human health. Report have it that dental cavities increases with fluoride ion concentration less than 0.5mg/l then when in excess it leads to severe health problems such as skeletal fluorosis and the degeneration of muscle fiber. 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 [4]. 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 [5]. We can conclude that, excess Fluoride is a pollutant of concern and treatment solution is required. Fluoride formation could be found naturally in groundwater when there exist slow dissolution of rocks or minerals which contains Sellaite (MgF₂), Fluorspar (CaF₂) and Cryolite (Na₃AlF₆) [6]. Also, anthropogenic activities can contaminate water sources (groundwater) with Flouride [7]. The use of pesticides and fertilizers containing Fluoride [8] or through the discharge of industrial effluents into water bodies [6]. In addition, industrial processes: cement and brick, electronic manufacturing process, aluminum smelting and refining amongst others, contaminates the groundwater with fluoride [5].

It is confirmed that the main source of water supply for human consumption in several countries is obtained from groundwater. Currently, there is a report of high fluoride ion content in water in more than twenty-six countries of the World-China, India, Sir Lanka, Africa [5], amongst others.

Several methods of water treatment such as Coagulation,

Published on December 19, 2019

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Flocculation, Sedimentation, filtration, adsorption, disinfection, reverse osmosis [9] ceramic water filters [10]. Cation exchange resin and Anion exchange resin amongst others had been employed to generate Potable water for consumption from ground water and wastewater effluent. These methods are chosen based on the areas of concern by Individual researcher and what is meant to be achieved at the end of the treatment. Amongst the several mechanisms of the past applied in the removal of fluoride ion from ground water or wastewater, the focus of this work will be on adsorption.

This work considered the use grounded egg shell to achieve adsorption of fluoride in water. The advantages considered are low-cost and its capacity for adsorbing a wide range of pollutants such as heavy metals, fluoride, arsenates, dyes. Also, regeneration of grounded egg shell can be achieved by contacting the adsorbent with a basic solution (pH>12) [11].

Previous studies of [12], [4] [13], [14], [15], [11], 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, carmax bone char, clay, local furnace, Calcium Carbonate which has high cost of disposal among others and mostly synthetic water were used. The current work will be focused on using grounded Egg shells as adsorbent to remove Fluoride ion from ground water in batch wire because it is non corrosive, environmentally friendly and economical.

II. MATERIALS AND METHODS

A. 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).

B. Methods

Egg shells were collected, washed to remove sand, dirt's, and then sun dried. Thereafter, egg shells were crushed and characterized with EDX3600B X-ray Fluorescence Spectrometer to determine the chemical composition present in it. The sample was weighed and heated in a furnace at temperature of 300°C for an hour.

1) Activation of Adsorbent

The grounded Egg shells were then sieved to particle size of 2.12µm after the heating process was done. Then, 180g of grounded Egg shells was modified with 1.0M Solution of trioxonitrate (v) acid where 180g Of both samples were separately added with 1000ml of 1.0M HNO₃ in Erlenmeyer flask which then heated up to 80°C whiles being stirred continuously for few hours. The solution formed was allowed to cool and filtered with Whatman filter paper. The activated grounded Egg shells were then oven dried and stored for subsequent use.

2) Characterization of Produced adsorbent

The activated grounded Egg shell was characterized to determine the percentage of Calcium and Phosphorous in the sample 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.

3) 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:

4) Bulk Density Determination

The bulk density of grounded egg shells were determined by calculating the ratio of the mass to the volume occupied. The procedure reported by [10] 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:

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

5) Moisture Content Determination

The moisture content in each grounded egg shells were determined using the standard method prescribed in ASTM D2016-25. Two grams of sample -initial weight (W_i) 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:

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

where: X₀ = moisture content on wet basis, W_i = initial weight of the material (before drying), W_f = final weight of the material (after drying)

6) The Pore Volume and Porosity Determination

The pore volume and porosity of the grounded egg shells sample was determined using the procedure reported by [16], 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:

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

where: w_i = initial weight of sample, w_f = final weight of sample, ρ_{H₂O} = density of water

The porosity of the sample was calculated from the equation:

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

7) Surface Area Determination

Specific surface area (SSA) was calculated from the equation [19][20]:

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

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

N_a = Avogadro's number = 6.02×10^{23} molecules/kmol, a = effective cross-section area occupied by one water molecule $0.114\text{nm} = 0.114 \times 10^{-18}$, M = molecular mass of water = $18 \times 10^{-3}\text{g/kmol}$.

8) Adsorption Experiment

Batch experiment was carried out by adding 5g of activated Adsorbent of particle size $2.12\mu\text{m}$ into 500ml of solution containing 7.34928mg/l of Fluoride ion in an Erlenmeyer flask 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 grounded Egg shells. The 5g of grounded egg shells sample was 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.

9) Percentage Adsorption

The percentage of fluoride ion removed (R%) at each time interval could be obtained by the relationship [17].

$$R\% = \left[\frac{C_o - C_t}{C_o} \right] \times 100 \quad (6)$$

Where;

C_o = is the initial fluoride concentration, C_t = is the concentration of fluoride at time (t)

10) Adsorption Capacity

The amount of fluoride ion adsorbed from the adsorbent at each time (t) was evaluated using the equation according to (8).

$$q_t = \left[\frac{C_o - C_t}{W} \right] V \quad (7)$$

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.

$$q_e = \left[\frac{C_o - C_e}{W} \right] V \quad (8)$$

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

According to [5](23), the adsorptive capacity could be

calculated from the relationship in equation (9).

$$\frac{x}{m} = (C_o - C_t) V / m \quad (9)$$

where: m = is the mass of the adsorbent used, X is the mass of the fluoride absorbed (mg).

C. Effect of Process Parameters on Adsorption Rate

1) Effect of Contact Time

The effect of contact time on adsorption was considered by conducting the batch adsorption experiment with a known particle size of $2.12\mu\text{m}$ and mass dosage (weight) of 5g of adsorbent at different times starting from 60 to 240minutes at 60 minutes' interval.

2) Effect of Adsorbent Dosage

The effect of adsorbent dose on adsorption was considered by conducting the batch adsorption experiment with particle size of $2.12\mu\text{m}$, and contact time of 60minutes for different dosages of adsorbent (5g, 10g, 15g and 20g).

3) Effect of Temperature

The effect of temperature on adsorption was considered by conducting the batch experiment with particle size of $2.12\mu\text{m}$ of contact time of 60mins for different temperature range (25, 30, 40 50 °C).

D. Adsorption Models

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 [18].

1) Adsorption Kinetics

The kinetic analysis was performed to investigate the rate of adsorption, determine the mechanism of adsorption and the potential rate controlling steps (mass transport, pore diffusion or chemical reaction) [17]. 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 grounded Egg Shells. The essence of this, was to determine correlation coefficient (R^2) as a measure of agreement between the experimental data

2) Pseudo-First-Order-Model

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

$$\frac{dq_t}{dt} = K_1 (q_e - q_t) \quad (10)$$

where: q_t = adsorption capacity at time, $t(\text{mg.g}^{-1})$, 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 (8).

$$q_t = q_e \left(1 - \exp \left(-\frac{K_1}{2.303} t \right) \right) \quad (11)$$

$$\log_e(q_e - q_t) = \log_e(q_e) - \frac{K_1}{2.303} t \quad (12)$$

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.

3) Pseudo-Second-Order Model

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

$$\frac{dq_t}{dt} = K_2(q_e - q_t)^2 \quad (13)$$

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 (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 (24).

$$\left[\frac{t}{q_t}\right] = \frac{1}{K_2(q_e)^2} + \frac{1}{q_e} t \quad (14)$$

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.

4) Intraparticle Diffusion Model

This model is expressed as shown in equation (15)

$$q_t = k_{id} (t)^{0.5} + l \quad (15)$$

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, $\text{g(g.min)}^{-0.5}$

A plot of q_t versus $t^{0.5}$ gave a linear relationship, then l 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 [19].

5) 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 [17]. The adsorption isotherm experiment was performed at different temperatures of 25, 35, 45 and 55°C. Then, the sorption equilibrium data from the conducted batch experiments were fitted with the Langmuir and Freundlich Isotherm models in order to describe the adsorption Isotherm of Fluoride ion on grounded egg shell.

6) Langmuir Isotherms

The Langmuir model is expressed by the following equation below.

$$q_e = \frac{q_m K_L C_e}{1 + K_L C_e} \quad (16)$$

where: q_e = adsorption capacity at equilibrium ($\text{g H}_2\text{O.g}$

adsorbent-1), C_e = concentration in solution at equilibrium, K_L = Langmuir parameter, q_m = Langmuir parameter

Rearranging and linearizing equation (16) gives equation (17) as follows:

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{K_L q_m} \quad (17)$$

A plot of C_e/q_e versus C_e yields a straight-line graph with slope equivalent to $1/q_m$ and the intercept as from which K_L and q_m was 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 (RL), expressed as [20].

$$R_L = \frac{1}{1 + q_L C_0} \quad (18)$$

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 is (favourable), (linear adsorption), (irreversible) and (favourable).

7) 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 [21]. It can be expressed by equation (19).

$$q_e = K_f C_e^{\frac{1}{N_f}} \quad (19)$$

where:

q_e = adsorption capacity at equilibrium ($\text{g H}_2\text{O.g}$ 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

$$\log q_e = \log K_f + \frac{1}{N_f} \log C_e \quad (20)$$

A plot of $\log q_e$ versus $\log C_e$ gave a linear relationship. The Freundlich constants K_f and $1/N_f$ 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 factor (Y). N_f is a measure of performance of adsorbent. When the value of $1/N_f < 1$ (normal freundlich adsorption), $1/N_f > 1$ (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 [21].

8) Thermodynamics Studies

In this research work the thermodynamics behavior of the adsorption process was studied by determining parameters like Gibbs free energy change ΔG^0 (KJ/mol.k), the standard enthalpy change ΔH^0 (KJ/mol), and the standard entropy change ΔS^0 (J/mol.k) using the Van't Hoff equation.

$$\ln K_e = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \quad (21)$$

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \quad (22)$$

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

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

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 performed at different temperatures of 25, 35 45 and 55°C 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 $\ln K_e$ versus $1/T$ equation (21) was used to calculate the values of ΔH^0 and ΔS^0 from the slope and intercept respectively and ΔG^0 from equation (22) for all temperatures.

III. RESULTS AND DISCUSSION

A. Chemical Composition

The activated grounded egg shells 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 I of the analysis showed (39.68%) for grounded Egg shells while phosphorous was (2.71%).

TABLE I: CHARACTERIZATION OF ACTIVATED GROUNDED EGG SHELLS

Sample	Ca (%)	P (%)
Egg Char (EC)	39.68	2.71

B. Physiochemical Characteristics of Grounded Egg Shell

The physical properties of adsorbent grounded Egg shells studied were presented in Table II.

TABLE II: THE PHYSIOCHEMICAL PROPERTIES OF ACTIVATED GROUNDED EGG SHELLS

	GE
Moisture content	0.299 (29.93%)
Pore volume (g/ml)	0.547
Porosity	0.046
Bulk density (g/ml)	2.0
SSA (m ² /g)	2074.3

The bulk density of the grounded Egg shells sample was

2.0g/ml. Thus, higher bulk density means the adsorbent has high adsorption capacity [16].

Table II showed that the moisture content of grounded Egg shells sample was (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 grounded Egg shell was 0.502g/ml while its porosity was 0.0456 as presented by Table II. The higher pore volume and porosity indicates high adsorption capacity [22] while the bigger the surface area, the more effective the adsorbent.

C. 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.

1) Effect of Contact Time

The effect of contact time on adsorption (percentage removal of Fluoride F⁻ ion) using known particle size 2.12 μ m and known adsorbent dosage (5g) is seen in Fig. 1 grounded Egg shells sample. Thus, Fig. 1 shows that the percentage adsorption of fluoride ion (F⁻) increased gradually with contact time for samples of activated grounded Egg Shell. This indicate that both adsorbents had the capacity to remove fluoride ion from the solution.

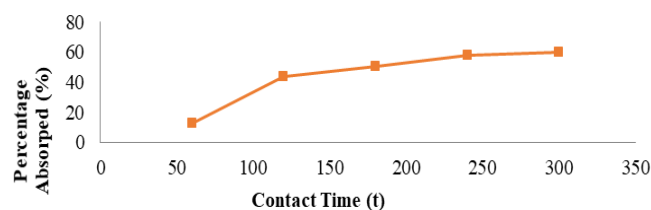


Fig. 1. Effect of Contact Time

2) Effect of adsorbent dosage

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

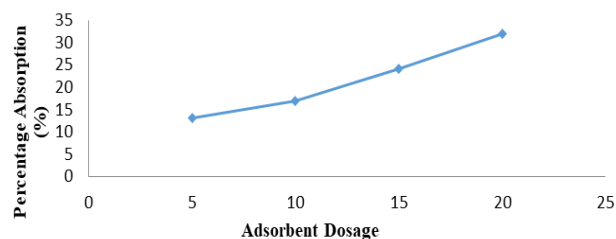


Fig. 2. Effect of adsorbent dosage

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

3) Effect of Temperature

Temperature is an important parameter affecting the adsorption process. The effect of temperature on adsorption (percentage of fluoride removal) by grounded Egg shells using known particle size, dose and known contact time is

shown in Fig. 3

Fig. 3 shows that increase in temperature for interaction between the adsorbent (grounded Egg shells) with the fluoride containing stock solution, increased the percentage of Fluoride absorbed.

Fig. 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 of 73.77% for activated grounded Egg shells. The mentioned percentage of fluoride was removed by the activated grounded Egg shells from the initial concentration of fluoride.

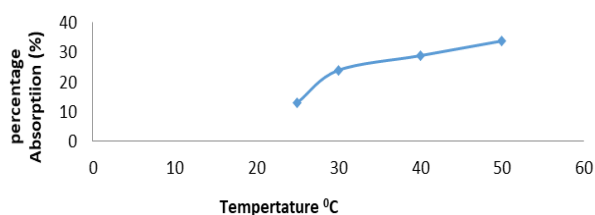


Fig. 3. Effect of Temperature.

4) Adsorption Capacity

Fig. 4 shows the adsorption capacity (amount of fluoride adsorbed) with respect to contact time for 5g of the adsorbent ground Egg shells (GE). The result obtained indicates that increase in contact time had a corresponding increase in amount of fluoride adsorbed for (GE) until equilibrium was established. Thus, at equilibrium the maximum adsorption was obtained.

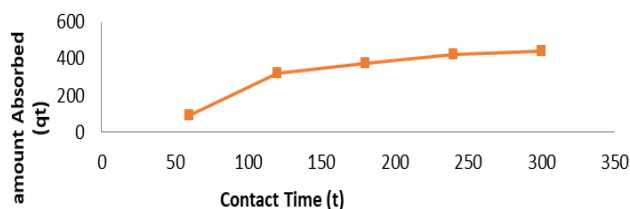


Fig. 4. Adsorption Capacity with respect to contact time.

Fig. 5 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 grounded Egg shells (GE) decreased as adsorbent dosage was increased from 5g to 20g at contact time of 60mins.

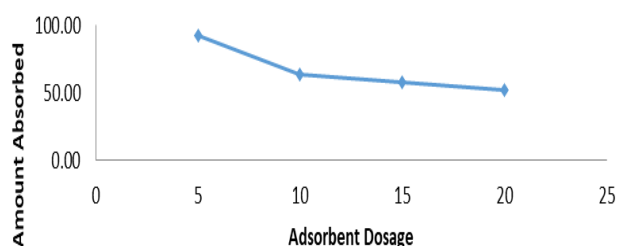


Fig. 5. Adsorption Capacity with Adsorbent Dosage

Fig. 6 was the obtained from the experimental data of considering the amount of fluoride ion removed by adsorbent 5g of grounded Egg shells (GE) with respect to increase temperature at a constant time of 60minutes.

The adsorption capacity (amount of fluoride adsorbed) from the solution by the adsorbent grounded Egg shell (GE) with respect to temperature as shown Fig. 6, indicates that increase in temperature gave corresponding increase in the amount of fluoride adsorbed by adsorbent (GE) until equilibrium will be established.

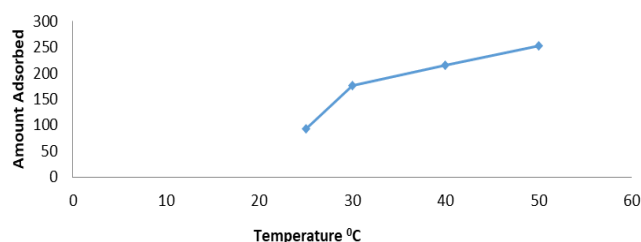


Fig. 6. Adsorption Capacity with Temperature

D. 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 was 1.92mg/L for grounded Egg Shells (GE) at $q_e = 542.00$ mg/g. Hence Fig. 7-9 showed the kinetics behavior of Adsorbent (grounded Egg shells).

1) Intraparticle Diffusion Model

A Plot of q_t vs $t^{0.5}$ for the experimental data are shown in the Fig. 7. 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 Fig. 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.

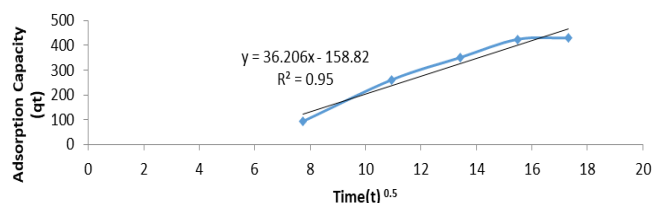


Fig. 7. Intra Particle Diffusion Model for GE

The boundary layer thickness, 1 , was -158.8 for grounded Egg shells. Larger values of ' 1 ' showed improved bonding between sorbent and adsorbent particles, hence, higher adsorption capacity. Higher values of K_{id} for the grounded Egg shells (GE) samples 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 [23]

2) Pseudo-First Order Model

A Plot of the first order rate $\log(q_e - q_t)$ versus time (t) are shown in Fig. 8. The parameter of the pseudo first order models were determined from the slope and intercepts of Fig. 8 along with the corresponding correlation coefficient.

Fig. 8 shows the graphs of Pseudo First order model used to evaluate the kinetics of the adsorbent (grounded Egg

shells). Fig. 8 shows that the adsorption process for grounded Egg shells 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, $q(e,cal)$ (533.33mg/g) of the pseudo first order for EC were closer to that of the experimental data, $q(e,exp.)$ (542.215mg/g). However, higher values of $R^2=0.930$ implied higher accuracy, validity and good fitness of the model [23].

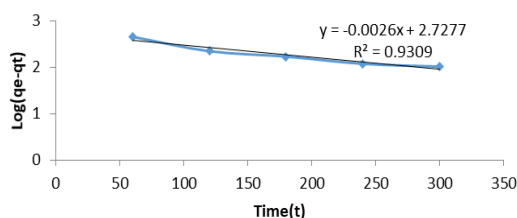


Fig. 8. Pseudo first order model for GE

3) Pseudo-Second Order Model

A Plot of the second order rate t/q_t versus time (t) of the experimental data was presented in Fig. 9 for grounded Egg shell. The parameter of the Pseudo- first order models was determined from the slope and intercepts of Fig. 9 along with their corresponding correlation coefficient.

But, the Fig. 9 signifies the adsorption process followed by grounded Egg shells which $q(e,calc)(0.00mg/g)$ is far lower than the experimental values obtained $q(e,exp)$ (544.112mg/g) presented on Fig. 9 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.

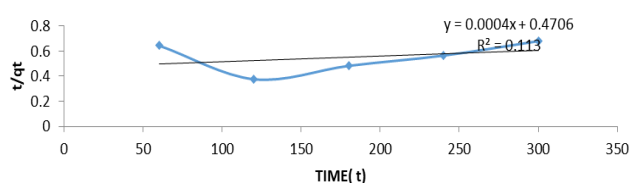


Fig. 9. Pseudo Second Order Model for grounded Egg shells (GE)

The Pseudo-First order model has better fit with the experimental data with higher squared correlation coefficients ($R^2 = 0.930$) for grounded Egg shells followed by Intraparticle diffusion with ($R^2 = 0.876$) for grounded Egg shells. The Pseudo Second -Order model does not fit the experimental data because of its R^2 values. Thus, the results show that pseudo -First order kinetic model is the most suitable for describing the kinetic of Egg shells calcined at 300°C, followed by the Intraparticle diffusion.

E. 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°C are shown in Fig. 10-11. The adsorption constants of these models were determined from the slopes and intercepts with its corresponding correlations coefficients are given by Fig. 10-11

The plots and estimated adsorption parameters of the adsorbent by the Langmuir and Freundlich isotherms are

presented in Fig. 10-11. The Langmuir parameter ($q(m)=500$) for grounded Egg shell while the $K(L)=2.0$, $R(L) = -0.073$ and the correlation coefficients $R^2=0.999$. The R^2 value for grounded Egg shells 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 favorable adsorption for grounded Egg shell sample.

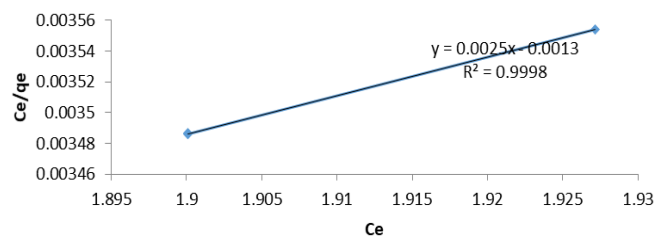


Fig. 10. Determination of Langmuir Isotherm for Egg Shells)

The Freundlich Isotherm for activated grounded Egg shells is presented in Fig. 11. The performance of the adsorbent was measured by the freundlich term ($1/N_f$). The calculation based on Fig. 11 showed that $1/(N_f) = -0.350$ for activated grounded Egg shell 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 activated Egg shell followed by Langmuir Isotherm.

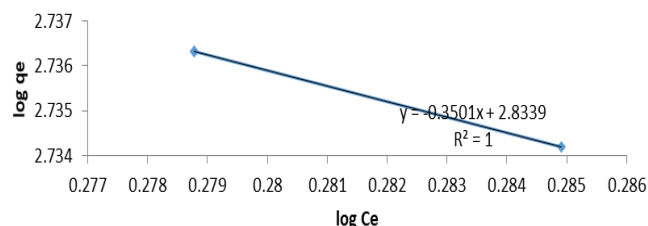


Fig. 11. Determination of Freundlich Isotherm for GE

F. Thermodynamic Studies

Fig. 16 showed the relationship between $\ln k_e$ 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 activated grounded Egg shells towards fluoride ion is spontaneous in nature and thermodynamically favorable [19] and more favorable at higher temperatures [19].

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 isotherm 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 [17]. However, this agrees with the works of [19] and explained the mobility of the adsorbate ions/molecules in the solution

increase with increase in temperature.

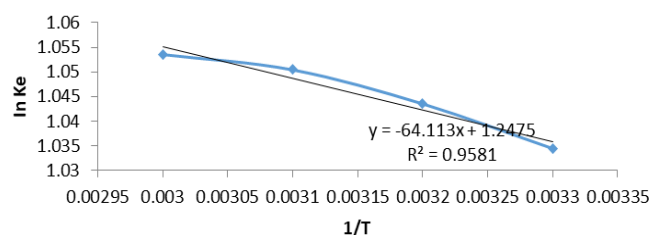


Fig. 12. Thermodynamics Study for Fluoride ions adsorption on Egg Shells (GE).

IV. CONCLUSION

The production of activated grounded Egg shells were carried out and modified with 1.0M HNO₃ trioxonitrate (v) acid. The activated grounded 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 grounded Egg shells of particle size of 2.12μm produced from agricultural waste (Egg shells) 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 the adsorbent (grounded Egg shells), 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.

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