

Kinetics, Equilibrium and Thermodynamics Studies of Fe³⁺ Ion Removal from Aqueous **Solutions Using Periwinkle Shell Activated Carbon**

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Abstract

Iron (III) adsorption from aqueous solutions unto periwinkle shell carbon (PSC) was studied using batch experiments. Activated periwinkle shell carbon was prepared (pyrolysed at 300°C and activated with nitric acid) and characterized to determine its physiochemical properties. Batch adsorption experiments were conducted to investigate the effects of process parameters (contact time, particle size, carbon dosage and pH of stock solution) on adsorption rate. Adsorption kinetics was tested using pseudo first and second order models. Adsorption Isotherms were analyzed using the Langmuir, Freundlich and Temkin isotherms while Thermodynamics parameters such as Enthalpy change (Δ H°), Entropy change (Δ S°) and Gibbs-free energy change (Δ G°) were determined. Results showed that adsorption rate increase with increase in contact time, adsorbent dose and pH and decreased with increase in particle size. Batch adsorption Kinetics experiments revealed that the mechanism of adsorption followed pseudo-second-order kinetic model. Isotherm data showed that the Langmuir isotherm accurately described the adsorption data indicating that adsorption process was mainly monolayer on a homogeneous adsorbent surface. Thermodynamic parameters results showed that adsorption process was endothermic with Enthalpy change (ΔH°): 222.91 kJ/mol; a positive Entropy change (ΔS°) of 19.19 kJ/mol, indicating an increase in the degree of freedom (or disorder) of the adsorbed species and a negative Gibb's free energy (ΔG°) at all temperature indicating that the adsorption process was spontaneous and favorable at high temperature.

Keywords

Adsorption, Iron Ions, Kinetics, Isotherm, Thermodynamics

1. Introduction

The contamination of groundwater with heavy metals particularly iron has been reported [1]. Iron is slowly released into ground water as naturally occurring and weathering iron bearing minerals and rocks infiltrating through the underlying formations are dissolved in the water and accumulates in the aquifers that serve as sources of ground water. Various products of industrial and human activities: Industrial effluents, acid-mine drainage, sewage, landfill leachate and agricultural activities also contribute iron to groundwater [2]. High content of iron in groundwater has been reported [3]. Although iron is an essential mineral for human, concentrations in ground water above the stipulated safe allowable limit makes ground water turbid, affects its domestic use (taste, color, odor) and affects its industrial applications. Oxidation of dissolved iron in water converts it to a red-brown solid which stains laundry and plumping fixtures, glassware, enhances the growth of iron bacteria, which forms dark-colored slime layers on the inner side of pipes and enhance corrosion of water pipes; excess iron deposits in the heart muscle can cause heart failure as well as abnormal heart rhythms [4].

Groundwater is the major source of industrial, domestic and drinking water supply in Nigeria [5] and major cities of Rivers State. UNESCO [6], reported that, more than five million people died every year in developing countries due the diseases associated to Water borne diseases. This has necessitated the stipulation of safe allowable maximum concentration limit for iron (0.3 mg/L) in ground water for drinking purpose by the World Health Organization (WHO) [7]. Treatment of the ground water supply is therefore recommended particularly when concentrations are above the stipulated allowable safe maximum.

Numerous processes abound for the removal of iron and indeed heavy metals from water and waste discharges. These methods include: solvent extraction [8], chemical precipitation [9], membrane process [10], adsorption [11] and ion-exchange [12]. However, Adsorption processes have been reported to be an efficient economical method and the primary methods for heavy metal removal [11], the other methods are more expensive and sometimes inefficient especially when the toxic heavy metals are present in low concentrations. Adsorption technique has found extensive applications in deodorization, purification of drinking water, treatment of waste water, separation of various organic and inorganic chemicals and the adsorption of heavy metals from aqueous solutions [13] using various materials as adsorbents: zeolites [14], silica [15], resins [16], biological adsorbents [17] and activated carbon [18] [19].

Adsorption using activated carbon as adsorbent has been found to be superior to other techniques because of its simplicity of design and capability to adsorb a broad range of pollutants or contaminant efficiently from aqueous or gaseous media [11]. Activated carbon (AC) is a porous material with exceptionally high surface area, large pore volume and well-developed internal micro porosity and wide spectrum of surface functional groups [27]. The use of low cost precursors such as agricultural wastes that are available in large amounts, renewable and with high carbon content for the sorption of heavy metals from solutions have been reported: rice hulls [20]; cotton stalks [21]; wood sawdust [22]; palm kernel shell [23]; almond shells, olive stones, and peach stones [24]; apple pulp [25]; sugarcane bagasse [26] and periwinkle shells [27]. Periwinkle shells have been reported [28] to have good adsorption capacity because of its polar functional groups (primary amines, hydroxyl, carboxylic acid, amide and phenolic groups. Periwinkle shell is an abundant waste material found in the riverine parts of the Niger Delta where its content (Lymneanetalensis) is an edible seafood.

The objective of this research is to investigate the use of periwinkle shells as an adsorbent for the removal of iron ions from groundwater. The activated carbon was produced from periwinkle shells (carbonization and activation with tri-oxo nitrate (V) acid), characterized and adsorption experiments of iron (III) from its aqueous solution performed. This was used to study the kinetics, equilibrium and thermodynamics of the adsorption process, thus generate the required data for parameters used in designing adsorber units for water purification.

2. Materials and Methods

2.1. Materials

The Periwinkle shell was obtained from Mile 3 market in Port Harcourt, Iron (III) oxide (Fe_2O_3) and the activation agent, nitric acid (HNO_3) were purchased from a chemical shop at the industrial chemical section of Mile 3 market, while distilled water was obtained from the Department of Chemistry laboratory, Rivers State University. All chemical reagents used were of analytical grades. The pyrolysis reaction was performed using the "pyrolysis setup" in the reaction kinetics laboratory of the Department of Chemical/Petrochemical Engineering, Rivers State University, Port-Harcourt, Rivers State, Nigeria. The activation of the carbon, characterization of the produced activated carbon and the batch adsorption experiments were also performed at the reaction kinetics laboratory.

2.2. Methods

Adsorbent Preparation

The periwinkle shell samples were washed several times with distilled water to remove sand and other surface impurities and sun dried.

Carbonization

The periwinkle shells were heated in a muffle furnace for 30 minutes to dry (free of water). A measured weight of the shells was introduced into the reactor and pyrolized at 300°C for three hours in the absence of air. A receiver was connected to the condenser to receive the distillates formed during the pyrolysis. The char material was cooled at room temperature before discharging into containers.

Carbon Activation

The carbonated material (carbon) from the periwinkle shells was crushed into powdered form using a crusher. A measured weight of the crushed sample was soaked in nitric acid of known concentration in a conical flask and stirred until the mixture turned a paste. The paste was heated in a muffle furnace at 800°C for 2 hours in the absence of air to increase the surface area of the charred sample; the activated carbon was cooled at room temperature, washed with distilled water until pH was approximately 7 (no change in color when tested with red litmus paper) indicating no trace of the nitric acid used. The char was dried for 6 hours, sieved with sieves of various sizes (75 um, 150 um, 212 um, 300 um, 600 um to obtain activated carbon of various particle sizes) and were stored in tight nylons.

Characterization of Produced Activated Carbon

The produced activated carbon was characterized by determining selected physiochemical properties such as oil yield, pH, carbon yield, moisture content, ash content, pore volume/porosity and bulk density following standard procedures as outlined in [19]. All results were the average of duplicate analysis.

Preparation of Heavy Metal (Iron (III) Oxide Fe₂O₃) Solution

The stock solution of Fe(III) was prepared by dissolving required quantity (80.7 g) of (Fe_2O_3) in known volume of distilled water. Different initial concentrations of Fe(III) solution was prepared by appropriate proper dilution of the stock solution.

Adsorption Experiment

Batch experiments were performed by adding known amounts of produced activated carbon to 50 mL of the iron III stock solution in a 100 mL conical flask. The conical flask containing the adsorbent (PSC) and the stock solution was placed in a rotary shaker and shaken at 150 rpm at room temperature (32°C) at different time periods at intervals of 20 minutes until equilibrium was attained(constant concentration of Iron (III) ion in the filtrate). The activated carbon was separated from the stock solution at each time interval by filtration using a Whatman number 41 filter paper. The concentration of iron (III) ion in the filtrate was analyzed at each time interval using an atomic absorption spectrophotometer (AAS). The Batch adsorption experiments were replicated trice.

The percentage of metal ion removed at each time interval was obtained using the relationship:

$$R\% = \left[\frac{C_o - C_t}{C_o}\right] \times 100 \tag{1}$$

The amount of metal ion adsorbed by the adsorbent at each time (t) was evaluated using the equation below;

$$q_{t} = \left[\frac{C_{o} - C_{t}}{W}\right] V \tag{2}$$

The adsorption capacity of the adsorbent was also calculated using the formula:

$$q_e = \left[\frac{C_o - C_e}{W}\right] V \tag{3}$$

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where: C_o = Initial concentration of Iron III ion present in waste water before adsorption.

 C_t = Final concentration of Iron III ion present after adsorption at time *t*.

 C_e = Concentration of Iron III ion in the filtrate when equilibrium was attained.

V = Volume of stock solution (mL).

W = Mass (g) of adsorbent used.

Effect of Process Parameters on Adsorption Rate

The effect of contact time on adsorption was studied by conducting the batch adsorption experiment with a known particle size and dose (weight) of adsorbent at different contact times from 20 to 120 minutes at 20-minutes interval. The effect of particle size on adsorption was studied by conducting the batch adsorption experiment with a known weight of adsorbent and fixed contact time for different particle sizes of 75 μ m, 150 μ m, 212 μ m, 300 μ m and 400 μ m of the activated carbon. The effect of adsorbent dose on adsorption was studied by conducting the batch adsorption experiment with a known particle size and contact time for different dosages of adsorbent (0.2 - 0.8 g). The effect of pH of stock solution on adsorption was studied by conducting the batch adsorption experiment with a known particle size, dose (weight) of adsorbent, fixed contact time at different pH values (1 - 5) of the stock solution. The pH of the solution was varied by dilution of the stock solution or by adding known volume of 0.1 M HCl or 0.1 M NaOH to stock solution as appropriate.

Adsorption Kinetics

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). Kinetic models have been used to correlate experimental data [29]. The pseudo first and second order kinetic equations were fitted to the experimental data to model the adsorption kinetics of Iron (III) adsorption onto periwinkle shell activated carbon. Kinetic models were used for goodness of fit of the experimental data using the correlation coefficient (R^2) as a measure of agreement between the experimental data.

Pseudo-First Order Kinetic Model

This model is associated with physical adsorption where the adsorption process is controlled by weak interactions between the adsorbate and the adsorbent surface [30].

The pseudo-first order rate equation by the Lagergren is given as:

$$\frac{\mathrm{d}q_t}{\mathrm{d}t} = K_1 \left(q_e - q_t \right) \tag{4}$$

where q_e and q_t are the adsorption capacities at equilibrium and at time t (mg·g⁻¹) respectively and K_1 is the pseudo-first order adsorption rate constant (L·min⁻¹). Integration at: t = 0 to t = t and $q_t = q_t$, gives the linear form of the equation as:

$$\log(q_e - q_t) = \log q_e - \frac{K_1}{2.303}t$$
(5)

The values of K_1 and q_e were obtained from the slope and intercept of the plot of $\log(q_e - q_t)$ versus *t* respectively.

The Pseudo-Second Order Kinetic Model

This model is based on the assumption that the adsorption is controlled by chemical adsorption-chemisorption (the rate of direct adsorption/desorption process seen as a kind of chemical reaction) [31]. The pseudo-second order kinetic model is given [32] as:

$$\frac{\mathrm{d}q_t}{\mathrm{d}t} = K_2 \left(q_e - q_t\right)^2 \tag{6}$$

Integration at: t = 0 to t = t and $q_t = q_t$, the linear form of the equation was obtained as:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$$
(7)

where $k_2(g \cdot mg^{-1} \cdot min^{-1})$ is the pseudo second order rate constant. The values of model parameters, q_e, k_2 were calculated from the slope and intercepts of the linear plot of $\frac{t}{q_t}$ vs t.

Adsorption Equilibrium Studies

Adsorption isotherms shows the relationship between the amount of adsorbed metal ions per unit of bio sorbent (adsorbent) (q_e) to the metal concentration in solution (C_e) at equilibrium at a given temperature, pressure, pH and total solute concentration [33]. Adsorption isotherm study was carried out at four different temperatures: 30°C, 40°C, 50°C and 60°C. The sorption equilibrium data from the experiments were fitted with the Langmuir, Freundlich, and Temkin isotherms models to describe the adsorption isotherm of Iron (III) ion on periwinkle shell activated carbon.

Langmuir Adsorption Isotherm

The Langmuir isothermmodel is based upon an assumption of monolayer adsorption (at maximum adsorption only a saturated monolayer of solute molecule is formed on the adsorbent surface) onto a homogeneous surface containing finite number of adsorption sites of uniform energies of adsorption, all adsorption occurs through the same mechanism with no transmigration of adsorbate in the plane of the surface (molecules of adsorbate do not deposit on other already adsorbed molecules of adsorbate, only on the free surface of the adsorbent) [33] [34]. The Non Linear form of the Langmuir isotherm is given as:

$$q_e = \frac{Q_o b C_e}{1 + b C_e} \tag{8}$$

The linearized form of this model is:

$$\frac{C_e}{q_e} = \frac{1}{Q_e b} + \frac{C_e}{Q_0} \tag{9}$$

The constants Q_o and b are the Langmuir constants representing the maximum adsorption capacity for the solid phase loading (mg·g⁻¹) and the nature of

adsorption and the shape of isotherm (L·mg⁻¹). These were evaluated from the slope and the intercept of the plot of $\left(\frac{C_e}{q_e}\right)$ vs C_e of the linear model. An essential feature of the Langmuir isotherm can be expressed in terms of a dimensionless separation factor or equilibrium parameter (R_L) defined [35] as:

$$R_L = \frac{1}{1 + bC_o} \tag{10}$$

where C_0 (mg·L⁻¹) is the initial amount of adsorbate and b (L·mg⁻¹) is the Langmuir constant described above. The value of R_L indicates whether the adsorption isotherm is unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$), or irreversible ($R_L = 0$).

Freundlich Adsorption Isotherm

The Freundlich isotherm model is based upon an assumption of multilayer adsorption onto a heterogeneous surface where the sorption energy distribution decreases exponentially [33]. The Non Linear form of this model takes the form:

$$q_e = K_f C_e^{1/n} \tag{11}$$

The linearized form of the model is:

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \tag{12}$$

where: K_f and 1/n are empirical constants related to adsorption capacity and adsorption efficiency. K_f is the Freundlich heterogeneous adsorbent constant and is the amount adsorbed at unit concentration, (mg·g⁻¹), *n* is Freundlich constant and is a measure of the intensity of adsorption. Where n > 1 indicates that affinity decrease with increasing adsorption density. These constants were evaluated from the slope and intercept of the linear model plot of $\log q_e$ versus $\log C_e$.

Temkim Adsorption Isotherm

The Temkim isotherm takes into account the interactions between adsorbents and metal ions to be adsorbed and is based on the assumption that the free energy of sorption is a function of the surface coverage where the heat of adsorption of all the molecules in a layer decreases linearly due to adsorbent-adsorbate interactions and that adsorption is characterized by a uniform distribution of binding energies, up to some maximum binding energy [36].

The isotherm is as follows:

$$q_e = B \ln K_T + B \ln C_e \tag{13}$$

A plot of q_e versus $\ln C_e$ enables the determination of the adsorption isotherm constants *B* and K_T from the slope and intercept respectively.

Thermodynamic Studies

The thermodynamic behavior of the adsorption process was studied by determining parameters such as the Gibbs free energy change ΔG° (kJ/mol·K), the standard enthalpy change ΔH° (kJ/mol), and the standard entropy change ΔS° (J/mol·K) using the Van't Hoff equations:

$$\ln K_e = \frac{\Delta S^{\circ}}{R} - \frac{\Delta H^{\circ}}{RT}$$
(14)

$$\Delta G^{\circ} = \Delta H^{\circ} - T \Delta S^{\circ} \tag{15}$$

The distribution adsorption coefficient/equilibrium constant (K_c) of a metal ion adsorbed by an adsorbent (mL·g⁻¹) can be obtained from the equation given by [37] as:

j

$$K_e = \frac{mq_e}{VC_e} \tag{16}$$

where *R* is the universal gas constant (8.314 J·K⁻¹), *T* is the absolute temperature in Kelvin.

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

Adsorption experiments were conducted at different temperatures of 30°C, 40°C, 50°C and 60°C to obtain batch equilibrium data used in calculating the distribution adsorption coefficient/equilibrium constant (K_e) from equation (16) at these temperatures. The plot of $\ln K_e$ versus 1/T (Equation (14)) was used to calculate the values of ΔH° and ΔS° from the slope and intercept respectively. ΔG° was then obtained from Equation (15) for all temperatures.

3. Discussion of Results

3.1. Characterization of Activated Carbon

The characterization results of the produced activated carbon are given in **Table 1**.

Table 1 shows the properties of periwinkle shell activated carbon in comparison with those of activated carbon produced from bamboo, coconut shell and palm kernel shell as reported by [19]. This showed that periwinkle shell activated carbon had more carbon yield, less water content which increases sorption rate [38].

General Periwinkle Coconut Palm kernel Bamboo Characteristics shell Shell Shell Carbon Yield (%) 66.1 50 51 50.5 Moisture content (%) 0.223 2.44 5.18 2.38 Ash content (%) 14 8.27 6.13 6.44 Ph 6.6 6.64 6.63 6.1 Bulk density (g/cm³) 1.2 --Porosity 1.00 0.71 0.82 0.96

Table 1. Characterization of periwinkle shell activated carbon.

3.2. Effects of Process Parameters

3.2.1. Effect of Contact Time

The effects of contact time on adsorption (the percentage removal of Fe^{3+}) using various particle sizes are shown in **Figure 1**.

Figure 1 shows that for all particle sizes considered, the percentage of Fe (III) ion adsorbed increased with contact time.

3.2.2. Effect of Particle Size

The effects of particle size on adsorption (the percentage removal of Fe^{3+}) conducted at various contact times are shown in Figure 2.

Figure 2 shows that at all contact times of adsorption, the percentage of iron (III) ion adsorbed decreased with increase in particle size. The smaller the particle size of the activated carbon, the better the access to the surface area and the smaller the pore space which makes the activated carbon tends to retain more iron (III) ions.



Figure 1. Effect of contact time.



Figure 2. Effect of particle size.

3.2.3. Effect of Carbon Dosage

The effect of adsorbent dosage on adsorption (the percentage removal of Fe^{3+}) is shown in **Figure 3**.

Figure 3 shows that as the dosage (quantity of activated carbon used) increased, the amount of iron (III) ion in the stock solution adsorbed (percentage adsorbed) by the activated carbon increased; an increase in adsorbent dose increases the surface area and number of active sites of the activated carbon [39] available to the solute (iron (iii) oxide) for adsorption, thus increasing the rate of adsorption [40].

3.2.4. Effect of pH

The effect of pH of the stock solution on adsorption (the percentage removal of Fe^{3+}) is shown in **Figure 4**.

Extraction of metal ions from aqueous media by adsorption had been reported [41] to be usually pH dependent because pH affects the surface charge of adsorbents and the degree of ionization. The result shows that as the pH of the stock solution increases the percentage metal iron removed increased. The increase in percentage removal can be explained by the fact that at higher pH, the adsorbent surface is deprotonated and negatively charged; hence attraction between the positive metal cations occurred [42], thus increasing the adsorption rate.



Figure 3. Effect of carbon dosage.





3.3. Adsorption Kinetics

The plot of the pseudo first order rate ($\log(q_e - q_t)$ versus *t*) and pseudo second order rate ($\left(\frac{t}{q_t}\right)$ vs *t*) of the experimental data are shown in Figure 5 and Figure 6.

The parameters of the pseudo-first-order and pseudo-second-order models determined from the slopes and intercepts of **Figure 5** and **Figure 6** along with the corresponding correlation coefficients are listed in **Table 2**. The equilibrium amount adsorbed (q_e) from the experiment ($q_e exp$) and the calculated equilibrium amount ($q_e cal$) from the two models are also shown in **Table 2**.

Figure 5 and **Figure 6** shows that the plot of the second order model gives a better straight line with correlation coefficient R^2 of 0.9991compared to the



Figure 5. Pseudo-first-order-kinetics of Fe³⁺ ion adsorption onto PSC.



Figure 6. Pseudo-second-order-kinetics of Fe³⁺ ion adsorption onto PSC.

Table 2. Adsorption Kinetic parameters for the adsorption of Fe^{3+} of periwinkle shell carbon.

| Pseu | ıdo-first-ord | er |] | Pseudo-seco | ond-order | | |
|-------------------------------------|---------------------------|--------|---------------------|----------------------|------------------------|--------|----------------------|
| $k_{_1}$ $\left(\min^{_{-1}} ight)$ | $q_{_e}cal.\ ({ m mg/g})$ | R^2 | k_2 (g/mg·min) | $q_{e}cal.$ (mg/g) | h $(mg/g \cdot min)$ | R^2 | $q_e exp.$ (mg/g) |
| 0.0405 | 10.0115 | 0.9338 | 0.000556 | 60.97 | | 0.9991 | 58.24 |

pseudo first order model with correlation coefficient R^2 of 0.9338. The calculated (theoretical) value of q_e from the pseudo second order model also agreed very well with the experimental values. Therefore, these results show that the pseudo second-order model was more reliable and accurate in correlating the experimental data compared to the pseudo first-order model. Hence the adsorption of Fe₂O₃ onto periwinkle shell activated carbon can be represented by a pseudo-second-order kinetic model which relies on the assumption that chemisorption may be the rate limiting step. In chemisorption, the metal ions stick to the adsorbent surface by forming a chemical (usually covalent) bond and finds sites that maximize their coordination number with the surface [43], Similar results of a second order kinetics was reported by [44] for the adsorption of copper from industrial waste waters by periwinkle shells activated carbon.

3.4. Adsorption Isotherm Studies

The plots of the Langmuir, Freundlich and Temkinisotherm models for adsorption data from adsorption experiment at equilibrium pH and a temperature of 30°C are shown in **Figures 7-9** respectively. The adsorption constants of these models determined from the slopes and intercepts of these figures along with the corresponding correlation coefficients are listed in **Table 3**. Similar plots of the Langmuir, Freundlich and Temkin isotherms models were made for adsorption experiments at temperatures of 40°C, 50°C and 60°C from where the adsorption constants and the corresponding correlation coefficients were determined. These are also listed in **Table 3**.



Figure 7. Langmuir isotherms for adsorption of Fe (III) ion onto PSC.

Table 3. Isotherm model constants and correlation coefficients for adsorption of Fe^{3+} on PSC.

| Temp (°C) | Langmuir Isotherms | | | | Freundlich Isotherm | | | Temkin Isotherm | | |
|--------------|--------------------|--------|---------|-------|---------------------|-------|--------|-----------------|-------|--------|
| | $Q_{_0}$ | b | R_{L} | R^2 | $k_{_f}$ | п | R^2 | A_{T} | В | R^2 |
| 30 | 48.251 | 0.3730 | 0.7686 | 0.994 | 3.197 | 2.628 | 0.8443 | 1.965 | 23.41 | 0.5541 |
| 40 | 49.781 | 0.3880 | 0.7615 | 0.989 | 3.315 | 2.616 | 0.8437 | 1.075 | 25.34 | 0.548 |
| 50 | 51.631 | 0.3990 | 0.7564 | 0.954 | 3.415 | 2.746 | 0.8389 | 1.032 | 26.62 | 0.533 |
| 60 | 53.347 | 0.4000 | 0.7560 | 0.917 | 3.457 | 2.759 | 0.8377 | 0.976 | 24.31 | 0.530 |



Figure 8. Freundlich isotherm for the adsorption of Fe³⁺ ions onto PSC.



Figure 9. Temkin isotherm for adsorption of iron (III) ions onto PSC.

Table 3 shows that the correlation co-efficient (R^2) of the Langmuir isotherm was closer to unity when compared to that of the Freundlich and Temkin isotherms at all temperatures the adsorption experiments were performed. Hence the Langmuir isothermf its the experimental equilibrium adsorption data of Fe³⁺ ions better than the Freundlich and Temkin isotherms, thus the Langmuir isotherm was most suitable for the data, followed by Freundlich then the Temkin isotherm. This suggest that the adsorption of Fe³⁺ ions on periwinkle shell activated carbon is a mono layer adsorption process on a homogeneous activated carbon surface. This agrees with the pseudo second order fit of the adsorption kinetics results with chemisorption (metal ions stick to the adsorbent surface) as the rate limiting step. The effect of the isotherm shape is seen in the values of the dimensionless separation factor (R_L). Table 3 shows that R_L values were between 0 and 1 at all temperatures, indicating that the adsorption process is favorable [favorable $(0 < R_1 < 1)$]. Table 3 also shows that the maximum adsorption capacity (Q_{o}) increases with temperature, confirming that adsorption of Fe³⁺ ions on periwinkle shell activated carbon increases with temperature.

Thermodynamic Studies

The relationship between $\ln K_e$ and 1/T is shown in Figure 10.

The thermodynamic parameters for the adsorption of Fe^{3+} ions calculated from Figure 10 and appropriate equations are given in Table 4.



Figure 10. Thermodynamic study for Fe³⁺ ions adsorption on PSC.

Table 4. Thermodynamic parameters for the adsorption of Fe³⁺ onto Periwinkle shell carbon (PSC).

| Temperature (°C) | $\Delta G^{\circ}(\mathrm{kJ/mol})$ | $\Delta H^{\circ}(kJ/mol)$ | $\Delta S^{\circ} (J/mol \cdot K)$ |
|------------------|-------------------------------------|----------------------------|------------------------------------|
| 30 | -5591.66 | | |
| 40 | -5783.56 | 222.91 | 19.19 |
| 50 | -5975.46 | | |
| 60 | -6167.36 | | |

The Gibb's free energy change of the process (ΔG°) were all negative and decreased with increase in temperature at all temperatures the experiments were conducted. This indicates that the adsorption mechanism of periwinkle shell activated carbon toward iron (III) is spontaneous in nature and thermodynamically favorable [45] and more favorable at higher temperatures [46]. This is in agreement with the favorable adsorption process predicted by the langmuir isotherm model which fitted most the adsorption isotherm data. The enthalpy change of the process (ΔH°) is positive, hence the process is endothermic. Therefore, adsorption capacity increase with temperature increase as predicted by the values of the maximum adsorption capacities (Q_a) from the langmuir isotherm model and in agreement with the Gibb's free energies obtained. The entropy change of the process (ΔS°) is positive. Entropy is defined as the degree of freedom or chaos of a system. The positive value of the entropy change indicates that the degree of freedom or randomness at the solid/liquid interface of the activated carbon increases during the adsorption of Fe³⁺ ions onto the active sites of the periwinkle shell activated carbon [47]. This is in agreement with the work of Saha & Chowdhury, [48] and explained to be because the mobility of adsorbate ions/molecules in the solution increase with increase in temperature and that the affinity of adsorbate on the adsorbent is higher at high temperatures.

4. Conclusion

The adsorption performance of periwinkle shell activated carbon for the removal

of iron (III) oxide from aqueous solution was investigated. The periwinkle shells were carbonized at a temperature of 300°C and activated using nitric acid. The produced activated carbon was characterized by determining its bulk density, pH level, porosity, carbon yield, moisture content and ash content. Batch experiments were carried out to investigate the effect of some process parameters such as: contact time, particle size, adsorbent dosage and the pH on adsorption rate. The adsorption rate increased with increase in contact time, adsorbent dosage and pH of aqueous solution (reduced with increase in acidity) and decrease with increase in particle size. The kinetics of Fe³⁺ adsorption onto periwinkle shell activated carbon obeys the pseudo-second-order model, suggesting that chemisorption is the rate-limiting step in the adsorption process. The adsorption equilibrium data fitted the Langmuir isotherm model in comparison to the Freundlich and Temkin isotherm models at the studied temperatures, therefore periwinkle shell activated carbon had a homogeneous surface with adsorption capacity increasing with increasing temperature. The dimensionless separation factor or equilibrium parameter (R_L) values calculated were greater than zero but less than 1, which showed that the adsorption process was favorable (Periwinkle shell activated carbon was an efficient adsorbent for Fe³⁺ ion removal). The thermodynamic parameters obtained indicated that the adsorption process of Fe⁺ ions was spontaneous (negative values of ΔG°) and endothermic in nature (positive ΔH°). The positive value of the entropy change (ΔS°) showed increased randomness with adsorption. Hence the adsorption process is thermodynamically favorable.

References

- Kamel, E.M. (2012) Simultaneous Removal of Iron and Manganese from Ground Water by Combined Photo-Electrochemical Method. *International Journal of Chemistry*, 2306-6415.
- [2] Singh, S. and Mosley, L.M. (2003) Trace Metal Levels in Drinking Water on Viti Levu, Fiji Islands. South Pacific Journal of Natural Science, 21, 31-34.
- [3] Todd, K. (1980) Groundwater Hydrology. 2nd Edition, John Wiley & Sons, New York.
- [4] Chakrabarti, B.K., Ghosh, H.N. and Sahana, S.N. (1984) Human Physiology. The New Book Stall, Calcutta, 547-548.
- [5] Longe, E.O., Malomo, S. and Olorunniwo, M.A. (1987) Hydrogeology of Lagos Metropolis. *Journal of African Earth Science*, 6, 163-174.
- [6] UNESCO (2007) Water Portal Newsletter. No. 161, Water-Related Diseases.
- USEPA (2000) Drinking Water Standards and Health Advisories, United States Environmental Protection Agency, Office of Water, Washington DC. http://www.epa.gov/OST
- [8] McDonald, C.W. and Bajwa, R.S. (1977) Removal of Toxic Metal Ions from Metal Finishing Waste Water by Solvent Extraction. *Separation Science*, 12, 435-445.
- [9] Linstedt, K.D., Houck, C.P. and O'Connor, J.T. (1971) Trace Element Removals in Advanced Waste Water Treatment Processes. *Journal of the Water Pollution Control Federation*, 43, 1507-1513.

- [10] Cartwright, P.S. (1981) Reverse Osmosis and Ultrafiltration in the Plating Shop. *Plating Surf Fin*, 68, 40-45.
- [11] Ahmad, A.A., Hameed, B.H. and Aziz, N. (2006) Adsorption of Direct Dye on Palm Ash: Kinetic and Equilibrium Modelling. *Journal of Hazardous Materials*, **94**, 1-10.
- [12] Knocke, W.R., Clevenger, T., Ghosh, M.M. and Novak, J.T. (1978) Recovery of Metals from Electroplating Waste Waters. *Proceedings of the 33rd Purdue Industrial Waste Conference*, **33**, 415-426.
- [13] Yin, C.Y., Aroua, M.K. and Daud, W.M.A.W. (2007) Review of Modifications of Activated Carbon for Enhancing Contaminant Uptakes from Aqueous Solutions. *Separation and Purification Technology*, **52**, 403-415. https://doi.org/10.1016/j.seppur.2006.06.009
- [14] Pasinli, T., Eroglu, A.E. and Shahwan, T. (2005) Preconcentration and Atomic Spectrometric Determination of Rare Earth Elements (REEs) in Natural Water Samples by Inductively Coupled Plasma Atomic Emission Spectrometry. *Analytica Chimica Acta*, 547, 42-49. https://doi.org/10.1016/j.aca.2005.04.076
- [15] Mashhadizadeh, M.H., Pesteh, M., Talakesh, M., Sheikhshoaie, I. and Mazloum, M. (2008) Solid Phase Extraction of Copper (II) by Sorption on Octadecyl Silica Membrane Disk Modified with a New Schiff Base and Determination with Atomic Absorption Spectrometry. *Spectrochimica Acta Part B: Atomic Spectroscopy*, **63**, 885-888. <u>https://doi.org/10.1016/j.sab.2008.03.018</u>
- [16] Dave, S.R., Kaur, H. and Menon, S.K. (2010) Selective Solid-Phase Extraction of Rare Earth Elements by the Chemically Modified Amberlite XAD-4 Resin with Azacrown Ether. *Reactive and Functional Polymers*, **70**, 692-698. https://doi.org/10.1016/j.reactfunctpolym.2010.05.011
- [17] Diniz, V. and Volesky, B. (2005) Biosorption of La, Eu and Yb using Sargassum Biomass. Water Research, 39, 239-247. <u>https://doi.org/10.1016/j.watres.2004.09.009</u>
- [18] Marwani, H.M., Albishri, H.M., Jalal, T.A. and Soliman, E.M. (2012) Activated Carbon Immobilized Dithizone Phase for Selective Adsorption and Determination of Gold(III). *Desalination and Water Treatment*, **45**, 128-135. https://doi.org/10.1080/19443994.2012.692019
- [19] Akpa, J.G. and Nmegbu, C.G.J. (2014) Adsorption of Benzene on Activated Carbon from Agricultural Waste Materials. *Chemical Science Research Journal*, 4, 34-40.
- [20] Teker, M. and Mustafa, I. (1999) Adsorption of Copper and Cadmiumions by Activated Carbon from Rice Hulls. *Turkish Journal of Chemistry*, 23, 185-191.
- [21] Girgis, B.S. and Ishak, M.F. (1999) Activated Carbon from Cotton Stalks by Impregnation with Phosphoric Acid. *Materials Letters*, **39**, 107-114. https://doi.org/10.1016/S0167-577X(98)00225-0
- [22] Bogdanka, R., Zarko, K., Mile, K. and Marina, S. (2007) Adsorption of Heavy Metals from Electroplating Wastewater by Wood Sawdust. *Bioresource Technology*, 98, 402-409. <u>https://doi.org/10.1016/j.biortech.2005.12.014</u>
- [23] Tumin, N., Delaila, A.L., Chuah, Z.Z. and Suraya, A.R. (2008) Adsorption of Copper from Aqueous solution by Elais Giuneensis Kernel Activated Carbon. *Journal of Engineering Science and Technology*, 3, 180-189.
- [24] Ferro-Garcia, M.A., Rivera-Utrilla, J. and Bautista-Toledo, I. (1990) Removal of Lead from Water by Activated Carbons. *Carbon*, 28, 545-552. <u>https://doi.org/10.1016/0008-6223(90)90051-Y</u>
- [25] Saurez, G.F., Martinez, A.A. and Tascon, J.M.D. (2002) Pyrolysis of Apple Pulp: Chemical Activation with Phosphoric Acid. *Journal of Analytical and Applied Py-*

rolysis, 63, 283-301. https://doi.org/10.1016/S0165-2370(01)00160-7

- [26] Mohamed, E.F., El-Hashemy, M.A., Abdel-Latif, N.M. and Shetaya, W.H. (2015) Production of Sugarcane Bagasse-Based Activated Carbon for Formaldehyde Gas Removal from Potted Plants Exposure Chamber. *Journal of the Air & Waste Management Association*, 65, 1413-1420. https://doi.org/10.1080/10962247.2015.1100141
- [27] Okuo, J.M. and Ozioko, A. (2001) Adsorption of Lead and Mercury Ions on Chemically Treated Periwinkle Shells. *Journal of Chemical Society of Nigeria*, **26**, 60-65.
- [28] Okuo, J.M. (2006) Removal of Heavy Metal Ions by Blended Periwinkle Shells. Journal of Applied Sciences, 6, 567-571. <u>https://doi.org/10.3923/jas.2006.567.571</u>
- [29] Rao, M.M., Kumar Reddy, D.H.K., Venkateswarlu, P. and Seshaiah, K. (2009) Removal of Mercury from Aqueous Solutions using Activated Carbon Prepared from Agricultural By-Product/Waste. *Journal of Environmental Management*, 90, 634-643. <u>https://doi.org/10.1016/j.jenvman.2007.12.019</u>
- [30] Radnia, H., Ghoreyshi, A.A., Younesi, H. and Najafpour, G.D. (2012) Adsorption of Fe (II) Ions from Aqueous Phase by Chitosan Adsorbent: Equilibrium, Kinetic and Thermodynamic Studies. *Desalination and Water Treatment*, **50**, 348-359. <u>https://doi.org/10.1080/19443994.2012.720112</u>
- [31] Ho, Y.S. and Mckay, G. (2000) The Kinetics of Sorption of Divalent Metal Ions onto Sphagnum Moss Peat. Water Research, 34, 735-742. https://doi.org/10.1016/S0043-1354(99)00232-8
- [32] Ho, Y.S. and Mckay, G. (1999) Pseudo-Second Order Model for Sorption Processes. *Process Biochemistry*, 34, 451-465. <u>https://doi.org/10.1016/S0032-9592(98)00112-5</u>
- [33] Kumar, P.S., Vincent, C., Kirthika, K. and Kumar, K.S. (2010) Kinetics and Equilibrium Studies of Pb²⁺ Ion Removal from Aqueous Solutions by Use of Nano-Silversol-Coated Activated Carbon. *Brazilian Journal of Chemical Engineering*, 27, 339-346.
- [34] Ho, Y.S., Wase, D.A.J. and Forster, C.F. (1994) The Adsorption of Divalent Copper Ions from Aqueous Solution by Sphagnum Moss Peat. *Process Safety and Environmental Protection*, 72, 185-194.
- [35] Marwani, H.M., Albishri, H.M., Jalal, T.A. and Soliman, E.M. (2017) Study of Isotherm and Kinetic Models of Lanthanum Adsorption on Activated Carbon Loaded with Recently Synthesized Schiff's Base. *Arabian Journal of Chemistry*, 10, S1032-S1040. <u>https://doi.org/10.1016/j.arabjc.2013.01.008</u>
- [36] Ayawei, N., Ebelegi, N.A. and Wankasi, D. (2017) Comparative Sorption Studies of Dyes and Metal Ions by Ni/Al-Layered Double Hydroxide. *International Journal of Materials and Chemistry*, 7, 25-35.
- [37] Han, D.M., Fang, G.Z. and Yan, X.P. (2005) Preparation and Evaluation of a Molecularly Imprinted Sol-Gel Material for On-Line Solid-Phase Extraction Coupled with High Performance Liquid Chromatography for the Determination of Trace Pentachlorophenol in Water Samples. *Journal of Chromatography A*, **1100**, 131-136. https://doi.org/10.1016/j.chroma.2005.09.035
- [38] Sinha, N., Subramanian, V., Jose, M.T. and Venkatraman, B. (2016) Effect of Moisture Content on Surface Area of Activated Charcoal Used in Nuclear Industries. *Proceedings of the International Conference on Radiological Safety in Workplace*, *Nuclear Facilities and Environment*, Kalpakkam, 22-25 February 2016, 22-25.
- [39] Ladhe, U.V., Wankhede, S.K., Patil, V.T. and Patil, P.R. (2011) Adsorption of Eriochrome Black-T from Aqueous Solutions on Activated Carbon Prepared from Mosambi Peel. *Journal of Applied Sciences in Environmental Sanitation*, 6, 149-154.

- [40] Arivoli, S., Hema, M. and Martin, P.D. (2009) Adsorption of Malachite Green onto Carbon Prepared from Borassus Bark. *Science and Engineering*, 34, 31-43.
- [41] Zhang, L., Chang, X., Zhai, Y., He, Q., Huang, X., Hu, Z. and Jiang, N. (2008) Selective Solid Phase Extraction of Trace Sc(III) from Environmental Samples using Silica Gel Modified with 4-(2-morinyldiazenyl)-N-(3-(trimethylsilyl) propyl) Benzamide. *Analytica Chimica Acta*, **629**, 84-91.
- [42] Bernard, E., Jimoh, A. and Odigure, J.O. (2013) Heavy Metals Removal from Industrial Wastewater by Activated Carbon Prepared from Coconut Shell. *Research Journal of Chemical Science*, 3, 3-9.
- [43] Atkins, P.W. (1995) Physical Chemistry. 5th Edition, Oxford University Press, Oxford.
- [44] Badmus, M.A.O., Audu, T.O.K. and Anyata, B. (2007) Removal of Copper from Industrial Waste Water by Activation Carbon Prepared from Periwinkle Shells. *Korean Journal of Chemical Engineering*, 24, 246-256. https://doi.org/10.1007/s11814-007-5049-5
- [45] Goswami, S. and Ghosh, U.C. (2005) Studies on Adsorption Behavior of Cr (VI) onto Synthetic Hydrous Stanniz Oxide. *Water SA*, 31, 597-602.
- [46] Zaki, A.B., El-Sheikh, M.Y., Evans, J. and El-Safty, S.A. (2000) Kinetics and Mechanism of the Sorption of Some Aro-Matic Amines onto Amberlite IRA-904 Anion-Exchange Resin. *Journal of Colloid and Interface Science*, 221, 58-63. https://doi.org/10.1006/jcis.1999.6553
- [47] Gupta, V.K. (1998) Equilibrium Uptake, Sorption Dynamics, Process Development, and Column Operations for the Removal of Copper and Nickel from Aqueous Solution and Wastewater using Activated Slag, a Low-Cost Adsorbent. *Industrial & Engineering Chemistry Research*, **37**, 192-202. https://doi.org/10.1021/ie9703898
- [48] Saha, P. and Chowdhury, S. (2011) Insight into Adsorption Thermodynamics. In-Tech, Vienna. <u>https://doi.org/10.5772/13474</u>