Kinetics of Batch Adsorption of Iron II Ions from Aqueous Solution using Activated Carbon from Nigerian Bamboo

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ABSTRACT

Kinetics of batch adsorption of iron II ions from aqueous solution using activated carbon from waste Nigerian based bamboo was studied. The bamboo was cut into sizes, washing and drying was carbonized at 400°C-500°C and activated at 800°C using nitric acid. The effect of process parameters such as particle size, carbon dosage, initial concentration of adsorbate and contact time were also investigated and were found to significantly affect the adsorption capacity. The adsorption process obeyed the Freundlich, Temkin and Langmuir isotherm model indicating a monolayer formation over the surface of the material. Langmuir isotherm had a better fit than Freundlich and Temkin models with maximum monolayer saturation capacity of 166.7 mg of iron II ions adsorbed per g of bamboo activated carbon. In order to determine the mechanism of sorption, kinetic data were modeled using the pseudo first order, pseudo second order kinetic equations, and intra-particle diffusion model. The pseudo second order equation was the best applicable model to describe the sorption process. Hence the pseudo second order kinetic reaction is the rate controlling step with some intra particle diffusion taking place.

Keywords: Nigerian Bamboo, Activated Carbon, Iron II ions, Adsorption Isotherm, Kinetics.

1. INTRODUCTION

Industrial activities such as tanning, mining, electroplating, refining, metallurgical operation and manufacturing have led to the release of toxic metal ions into the environment. These resulted in heavy metal pollution problems in the eco-system. Toxic metallic compounds do not only contaminate the water bodies like seas, lakes reservoirs and ponds but can also enter the underground water in traceable amounts. Unlike the organic pollutants which are biodegradable, heavy metals Fe, Zn, Ni are not biodegradable, thus making a source of great concern. Human health, agricultural development and the eco-systems are all at risk unless water and land system are effectively managed. Iron exists in two forms which are the iron (II) and iron (III) states. As a result of the toxicological effects of these metals, interest in heavy metal removal from waste water has been on the rise. Metals removal at low concentration is more effective via adsorption because of its economic feasibility [1]. This principle is mainly applicable for the removal of pollutants such as metal ions, dyes and other organic compounds from waste waters [2-3].

Ademiluyi and David –West [4] compared the effectiveness of three waste materials (waste Nigerian based bamboo, coconut shell and palm kernel shell) activated with different activating agents on the removal of heavy metals and reported that bamboo activated with nitric acid effectively remove zinc ions more than activated carbon produced from coconut shell and palm kernel shell. There was no investigation on the effect of some physio- chemical parameters such as particle size, carbon dosage, initial concentration and contact time on the adsorption of these metal ions on activated carbon from bamboo. Hence there is need to optimize and study the kinetics of the iron ions removal from aqueous solution using activated carbon from bamboo in a batch system.

Therefore, the objective of this work is to study the kinetics of the batch adsorption of iron II ions in aqueous solution using activated carbon from Nigerian bamboo. The effect of process parameters on the adsorption is also presented.

2. MATERIALS AND METHODS

2.1 Materials

The following materials and apparatus were used for this work: waste Nigeria based bamboo, Nitric acid was used as activating agents, A pyrolytic reactor was used for carbonization of the bamboo with condenser to condense other by products of the pyrolysis process. Other materials used are desiccators, crucibles, funnels, and filter papers. Two electronic weighing balance, Ohaus top loading balance (+0.01) was used to weigh the bamboo before
pyrolysis, while a more sensitive electronic analytical weighing balance (+0.001, Adams AFP 360L) was used for other analysis, retort stand, thermocouple with temperature sensor, spatula, crusher, sieves, measuring cylinders, and petri dishes etc.

2.2 Carbonization

Known weights of waste bamboo were cut into small sizes, washed, and dried as shown in Fig 1. They were carbonized differently in a pyrolysis reactor at about 400–500°C for about two hours after which the charred products were allowed to cool to room temperature. The charred material was crushed and sieved.

2.3 Chemical Activation

The carbonized waste bamboo, was weighed separately and poured in different beakers containing known quantity of trioxonitrate (v) acid. The best concentrations of the acid used for activation were already determined before this study. The content of the beakers was thoroughly mixed until a paste was formed. The paste of the samples were then transferred to crucibles and were placed in a Muffle furnace and heated at 800°C for two hours. The activated sample were then cooled at room temperature, washed with distilled water to a pH of 6-7, and dried in an oven at 105°C for three hours. The final products were sieved to different particle sizes and kept in an air tight polyethylene bags, ready for use.

![Fig 1. Waste bamboo before and after carbonization and activation](image)

2.4 Characterization of Activated Carbons

The waste Nigerian based bamboo, waste coconut shell, and waste palm kernel shell used in this work were characterized (iodine number, Methylene blue number, density, etc.), using the ASTM methods as described in the work of Ademiluyi et al. [4].

2.5 Adsorption iron II ions (Fe^{2+}) in Aqueous Solution on Activated Carbons from Bamboo

Stock solution of iron II solution was prepared by dissolving 1g of iron II salt into 1 litre of distilled water. 1g of activated carbon was measured and poured into known amount of the stock iron II salt solution inside the flask. The adsorption was carried out for 15mins and filtered. The above procedure was done for 30 minutes, 45 minutes, 60 minutes, 90 minutes, 120 minute till equilibrium was reached. The adsorption of iron in aqueous solution on bamboo activated carbon was carried out by optimizing various physicochemical parameters such as particle size, carbon dosage, initial concentration, contact time

The amount of iron ions in solution (i.e., Fe^{2+}) was determined using conductometric method from the filtrate after adsorption using waste Nigerian based bamboo. The work of Tanokkorn et al., revealed that at low concentrations, conductivity is linearly related to the different metal ion concentrations so that if just one metal is present its concentration is readily established through calibration. Hence a calibration curve of concentration versus conductivity was first prepared for iron ions in solution, before adsorption.

The amount of iron II ions adsorbed at equilibrium, $Q_e$ (mg/g) was determined using equation.

$$Q_e = \frac{(C_o - C_e)V}{m}$$  \hspace{1cm} (1)

and the percent adsorption (%) iron adsorbed was computed as follows [7]:

$$\text{Percent adsorption} (%) = \frac{(C_o - C_e)}{C_o} \times 100$$  \hspace{1cm} (2)

where $C_o$ and $C_e$ are the initial and equilibrium concentrations (mg/L), V volume of solution (L), $m$ the weight of activated carbon (g) and $C$ the solution concentration at the end of adsorption.

2.6 Isotherms Modeling

The most commonly used isotherms in adsorption studies to fit the experimental adsorption data were used namely: Langmuir, Freundlich and Temkin

- Langmuir isotherms are used for determining the isothermal behaviours of the adsorption processes. The Langmuir isotherm is expressed as [8]

$$\frac{C_e}{Q_e} = \frac{1}{K_L} + \frac{aLCe}{Q_e}$$  \hspace{1cm} (3)

where $Q_e$ is the amount of iron ions adsorbed per unit mass of adsorbent (mg/g) at equilibrium, $C_e$ is the equilibrium concentration of the adsorbate (mg/L), $K_L$ is a constant related to the affinity between the adsorbent and the adsorbate.
K_L/a_L = The theoretical monolayer saturation capacity Q_o

The values of Q_o and K_L can be determined by plotting C_e/Q_e versus C_e.

One of the most important parameter of the Langmuir isotherm model is the separation factor R_L, which is a dimensionless factor defined as [9]

\[ R_L = \frac{1}{1 + a_L C_o} \]  \hspace{1cm} (4)

where: C_o is the initial adsorbate concentration and a_L is the Langmuir constant related to the energy of adsorption. The values of R_L shows the shape of the isotherm to be either unfavorable (R_L > 1), favorable (0 < R_L < 1), linear (R_L = 1), or irreversible (R_L = 0).

- The linear form of the Freundlich isotherm is the earliest known relationship describing the adsorption equation and is often expressed as

\[ \log Q_e = \log K_f + \frac{1}{n} \log C_e \]  \hspace{1cm} (5)

K_f = The Freundlich constant related to the adsorption capacity

1/n = The Freundlich constant related to the adsorption intensity

- The Temkin isotherm is also often used to represent the equilibrium adsorptive behavior between two phases composing the adsorption system. The Temkin isotherm is expressed as [7]:

\[ Q_e = a + b \ln C_e \]  \hspace{1cm} (6)

where,

\[ a, b = \text{Constant related to energy and capacity of adsorption} \]

3. KINETIC STUDY

Three kinetic models were used in this study to model the adsorption of iron II ion on bamboo activated carbon namely: pseudo first order, pseudo second order and the intra particle diffusion models.

- The pseudo first order considers the rate of occupation of adsorption sites to be proportional to the number of unoccupied sites.

\[ \ln (Q_e - Q_t) = \ln Q_e - K t \]  \hspace{1cm} (7)

where, Q_e is the mass of metal adsorbed at equilibrium (mg/g), Q_t (mg/g) is the mass of metal adsorbed at time t and K is the first order reaction rate constant (L/min). A straight line of ln (Q_e - Q_t) versus t indicates the application of the first order kinetic model.

- The Pseudo Second order kinetic model for adsorption of iron is expressed as [10]:

\[ \frac{t}{Q_t} = \frac{1}{k_2 Q_e^2} + \frac{t}{Q_e} \]  \hspace{1cm} (8)

Intra -particle diffusion may be the rate determining step in batch adsorption process the uptake of adsorbate varies with the square root of the adsorption time [9]. so that

\[ Q_t = k_3 t^{0.5} + C \]  \hspace{1cm} (9)

A linear plot of Q_t versus t^{0.5} shows that the adsorption mechanism follows intra -particle diffusion and if the intra -particle diffusion is the rate controlling step if the line passes through the origin.

4. RESULTS AND DISCUSSION

4.1 Characterization of activated Carbon from Bamboo

Table 1 shows the characterization of activated Carbon from Bamboo used for the adsorption of iron II ions the bulk density, methylene blue adsorptive capacity, iodine number ( a measure of activity level and the micro pore content of the activated carbon; higher number indicates higher degree of activation ) ash content, compares favorably with references commercial activated carbons. The work of Ademiluyi and David-West [2] on effect of chemical activation on the adsorption of heavy metals using activated carbons from waste materials revealed that waste bamboo activated with HNO_3 can effectively be used to remove metal ions from waste streams and in different metal recovery processes than activated carbon from coconut shell and palm kernel shells.

4.2 Effect of Particle Size on the Batch Adsorption of Iron II ions in Aqueous Solution using Activated Bamboo Carbon
carbon, the particle size of the carbon should be within 75 – 150μm for effective adsorption for batch processes.

Table 1 Characterization of activated Carbon from Bamboo

<table>
<thead>
<tr>
<th>S/N</th>
<th>Parameters</th>
<th>Unit</th>
<th>Locally Made GAC</th>
<th>References activated carbon</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Bulk Density</td>
<td>g/cm³</td>
<td>0.458</td>
<td>0.2-0.6 Long and Criscione 11</td>
</tr>
<tr>
<td>2</td>
<td>Methylene Blue adsorptive capacity</td>
<td>mg/g</td>
<td>941.325</td>
<td>900-1100 [12]</td>
</tr>
<tr>
<td>3</td>
<td>Iodine number</td>
<td>g of iodine /kg of C.</td>
<td>1,197.45</td>
<td>500-1200 Long and Criscione [11]</td>
</tr>
<tr>
<td>4</td>
<td>Ash content</td>
<td>%</td>
<td>2.760</td>
<td>≤8 Melcalf and Eddy [13]</td>
</tr>
</tbody>
</table>

4.3 Effect of Carbon Dosage on the Batch Adsorption of Iron II Ions in Aqueous Solution

Iron II ions in aqueous solution of known concentration was adsorbed using different carbon dosage of activated bamboo ranging from 0.1g – 1g in 100 ml of stock solution of iron II ions. The effect of carbon dosage on the adsorption of iron II ions using activated carbon from waste bamboo is presented in Fig 3. There was significant increase in the adsorption of iron II ions in solution as carbon dosage increased within adsorption time of 30min. Mehmet [14] reported similar findings during the removal of heavy metal adsorption by modified oak sawdust. This is due to the increased availability of active adsorption sites arising due to the increase in effective surface area resulting from the increases in dose of adsorbent or due to conglomeration of the adsorbent. Increasing the adsorbent dosage further, it was found that the optimum uptake of iron II ions requires about 4g of activated carbon from bamboo to adsorb 100% iron II ions in aqueous stock iron II solution.

4.4 Effect of Initial Concentration on the Adsorption of Iron II Ion using Bamboo Activated Carbon

The effect of initial concentration of iron II ions on adsorption of iron II ions using bamboo activated carbon is presented in Fig. 4. Adsorption of iron II ions in solution increase significantly with reduction in the initial concentration of iron II ions in solution. The initial concentration of adsorbate varied from 25mg/L to 200mg/L. The rate of adsorption decreased from 98% - 37% as the concentration of iron II ions increased from 25mg/L to 200mg/L within 30 mins of adsorption. This was expected and shows that there more reactive sites on the pore of bamboo activated carbon.

4.5 Effect of Contact Time on batch Adsorption of Iron II ions in Aqueous Solution

Figure 5 shows the effect of contact time on the adsorption of Iron II ions solution using activated carbon from bamboo. The concentrations of iron II ions in solution was varied from 25mg/L to 200mg/L and batch adsorption was carried out with 1g of activated bamboo. The percentage of iron II ions adsorbed increased with time until equilibrium was reached for each
concentrations. It is therefore evident from Fig 5 that at low concentration ranges the percent adsorption is high because of the availability of more reactive sites. At higher concentration of metal ion more and more surface sites are covered, the capacity of the adsorbent get exhausted due to non-availability of active surface sites. This leads to a fall in the percentage of metal ion adsorbed at higher concentration. It was observed that the percentage adsorption of iron (II) ion rapidly reached equilibrium at 30 minutes of contact for 25mg/L concentration, it increased to 100% implied that iron II (Fe$^{2+}$) ion was completely removed from aqueous solution at this concentration.

![Fig 4 Effect of initial concentration on the batch adsorption of Iron(ii) ion using activated Bamboo Carbon](image)

![Fig 5 Effect of contact time on the batch adsorption of Iron (ii) ions using activated carbon from Bamboo](image)

### 4.6 Adsorption Isotherm Equilibria

#### 4.6.1 Langmuir Adsorption Isotherm for Iron

The Langmuir adsorption isotherm for the adsorption of iron II ions on bamboo activated carbon is presented in Fig 6. The ratio of the equilibrium concentration to the ratio of the amount of iron adsorbed ($C_e/Q_e$) was plotted against the equilibrium concentration of iron ($C_e$). The linearity of the plot shows that Langmuir isotherm model can be used to predict the sorption of iron II ions on bamboo activated carbon. The Langmuir plots shows that there is increase in the rate of adsorption at different concentrations. This means that the lesser the concentration of the iron, the higher the adsorption of metal by the activated carbon. The Langmuir model assumes that the uptake of metal ions occurs on a homogeneous surface by monolayer adsorption without any interactions between adsorbed ions [15]. The Langmuir model parameters and the statistical fits of the adsorption data is presented in Table 2 and the correlation coefficient $R^2$ is greater than 0.89 which reveals' that the isotherm is consistent with Langmuir model.

The theoretical monolayer saturation capacity $Q_o$ for iron II adsorption on activated carbon from bamboo obtained from the slope of Fig 6 was 166.7 mg/g of carbon. Similar results was obtained during adsorption of Iron II on Thespesia populnea bark activated carbon by Prabakaran and Arivoli [15] but with a lower adsorption capacity $Q_o$ of 141.81mg/g as shown in Table 2. The separation factor ($R_L$) was determined from equation 4, the values were between 0.02 to 0.1 for adsorbate concentrations between 200mg/L to 50mg/L. Since $R_L$ is less than 1 for all the concentrations it means that adsorption process is favorable. Prabakaran and Arivoli [15] obtained separation factor ($R_L$) of 0.045 - 0.192 during adsorption of Iron II on Thespesia populnea bark activated carbon for adsorbate concentration between 125mg/L to 25mg/L. Comparing the adsorption capacity ($Q_o$) of iron II ions on bamboo activated carbon and with other reference carbons in Table 2 shows that bamboo activated carbon has very high affinity for iron II ions.

#### 4.6.2 Freundlich Adsorption Isotherm for Iron

Fig 7 shows the batch adsorption isotherm of iron ions on bamboo activated carbon at 30 °C. The log of $Q_e$ amount of iron adsorbed at equilibrium was plotted against the log of the equilibrium concentration $C_e$ of the metal ion adsorbed. The adsorption capacity $K_f$ and the adsorption intensity 1/n are obtained directly from the slopes and intercepts of the linear plot. The linearity of the plot and high correlation coefficient $R^2$ obtained (0.992) which is also greater than 0.89 reveals that the isotherm is consistent with Freundlich model. Atef [8] reported that $R^2$ greater than 0.89 shows that the adsorption data conforms with the model. The value of adsorption intensity ($n = 2.3$) is more than one for bamboo activated carbon, indicating the adsorption iron ion using
bamboo activated carbon. is more of chemisorptions than physical adsorption [16]

**4.7 Adsorption Kinetic Models**

Figures 9, 10 and 11 shows the kinetic plots for the adsorption of iron II ions on activated carbon from Bamboo using the pseudo first order, pseudo second order and the intra particle diffusion models at different concentrations. The linearity of the three plot shows that the adsorption mechanism is not only taken place at surface but combined with diffusion and chemisorption.

A linear relationship was also exhibited from the plot of amount of iron adsorbed ($Q_e$) at equilibrium against the natural logarithm of equilibrium concentration of iron ($\ln C_e$). Similarly the correlation coefficient $R^2$ (0.966) obtained for Temkin adsorption isotherm model for iron ions in Fig 8 and Table 2 shows that the Temkin model can also be used to predict the sorption of iron II ions using bamboo activated carbon.

**4.6.3 Temkin Adsorption Isotherm Model for Iron Ions**

**Fig 6. Langmuir adsorption isotherm for batch adsorption of iron II ions on bamboo activated carbon at 30°C**

**Fig 7 Freundlich adsorption isotherm for batch adsorption of iron ions on bamboo activated carbon at 30°C**

**Fig 8 Temkin adsorption isotherm for batch adsorption of iron ions on bamboo activated carbon at 30 °C**

**Fig 9 Pseudo first order kinetic plot for the batch adsorption of iron ions at different concentrations of adsorbate at 30 °C**

**Figures 9, 10 and 11 also revealed the concentration of adsorbate affected the adsorption and diffusion process greatly since the slope and intercept are not the same at the different concentrations. The pseudo second order kinetic model gave a higher correlation coefficient $R^2$ than the pseudo first order and the intra particle diffusion models as shown in Table 3.**
Though a linear plot of $Q_t$ versus $t^{0.5}$ in Fig 11 shows that the adsorption mechanism follows intra-particle diffusion and if the intra-particle diffusion is the rate controlling step, the line of the plot in Fig 11 will pass through the origin. The values obtained from the intercept (-5.855, -5.423, and 0.499) of the intra-particle diffusion kinetic model at different adsorbate concentrations are not the same as shown in Fig 11 and did not pass through the origin which indicated intra-particle diffusion is not the rate controlling step. Thus pseudo second order kinetic is the rate controlling step. Also the values of the intercept of Fig 11 at the different concentrations gives an idea of the thickness of the boundary layer; the larger the intercept the thicker the boundary layer effect [18]. The values obtained from the intercept from Fig 11 at low adsorbate concentration (<150mg/L) was -5.855, and -5.423 are insignificant. At higher adsorbate concentration 200mg/L the intercept was small (0.499), which revealed that the boundary layer will not be thick. Hence the pseudo second order kinetic reaction is the rate controlling step with some intra-particle diffusion taking place. 

5. CONCLUSION

Kinetics of batch adsorption of iron II ions from aqueous solution using activated carbon from waste Nigerian based bamboo has been investigated. The amount of iron II ions adsorbed was found to vary significantly with process parameters such as particle size, carbon dosage, initial concentration of adsorbate and contact time. The adsorption process follows Langmuir, Freundlich and Temkin isotherms but a better sorption fit using Langmuir isotherm model was obtained indicating a monolayer formation over a surface of the material. The monolayer saturation capacity of 166.7 mg of iron II ions adsorbed per g of bamboo activated carbon was obtained and found to be higher than monolayer saturation capacity of other adsorbent used for iron II ions adsorption. Adsorption kinetics was modelled using the pseudo first order, pseudo second order kinetic equations, and intra-particle diffusion models. Sorption kinetics showed good agreement of the experimental data. The pseudo second order kinetic reaction is the rate controlling step with some intra-particle diffusion taking place.

The high adsorption intensity of bamboo activated carbon and its affinity for iron II ions can help solve many adsorption challenges in the industry and in water purification processes.

Table 2  Isotherm models and their constant values for adsorption of iron from aqueous solution using activated carbons from bamboo

<table>
<thead>
<tr>
<th>Isotherms/Constants</th>
<th>Activated carbon from Present study</th>
<th>Reference activated carbon</th>
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</thead>
<tbody>
<tr>
<td></td>
<td>Bamboo</td>
<td>Thespesia bark [15]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Wild Jack bark [17]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Jambul bark [17]</td>
</tr>
<tr>
<td>Kinetic Model</td>
<td>100mg/L</td>
<td>150mg/L</td>
</tr>
<tr>
<td>-----------------------</td>
<td>---------</td>
<td>---------</td>
</tr>
<tr>
<td>Pseudo first order</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$Q_e$ (mg/g)</td>
<td>132.2</td>
<td>150.8</td>
</tr>
<tr>
<td>$K_2$</td>
<td>0.05</td>
<td>0.036</td>
</tr>
<tr>
<td>$R^2$</td>
<td>0.987</td>
<td>0.970</td>
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<tr>
<td>Pseudo second order</td>
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<td></td>
</tr>
<tr>
<td>$Q_e$</td>
<td>100</td>
<td>166.7</td>
</tr>
<tr>
<td>$K_2$</td>
<td>0.0004</td>
<td>0.000206</td>
</tr>
<tr>
<td>$R^2$</td>
<td>0.926</td>
<td>0.976</td>
</tr>
<tr>
<td>Intra particle diffusion</td>
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<tr>
<td>$K_2$</td>
<td>10.24</td>
<td>14.68</td>
</tr>
<tr>
<td>$C$</td>
<td>-5.855</td>
<td>-5.423</td>
</tr>
<tr>
<td>$R^2$</td>
<td>0.926</td>
<td>0.976</td>
</tr>
</tbody>
</table>

Table 3 Kinetic parameters for the batch adsorption of iron ions at different concentrations of adsorbate at 30°C

REFERENCES


