Kinetic and Equilibrium Studies For the Adsorption of Amoxicillin from Aqueous Solution on Carbonized Groundnut Shells


Abstract—Carbonized groundnut Shell was used for the adsorption of amoxicillin from aqueous solutions. The result for physico-chemical characterization show 6.28 for pH, 0.35 gml\(^{-1}\) for bulk density, 9.89\% for attrition, 4.20\% for moisture content, 44.6\% for ash content and 932 mg\(^{-1}\) of iodine value. The results of the batch adsorption studies gives the Maximum percentage removal of amoxicillin as 87.20\% at concentration of 80 mgL\(^{-1}\), 87.315\% at 4 hrs contact time and 87.64\% at 1.5 g of the adsorbent. The equilibrium adsorption was studied for Temkin, Freundlich and Tempkin. The Freundlich isotherm was found to be most favourable with R\(^2\) value of 0.9917, the kinetic was studied for both pseudo-first order and pseudo-second order kinetics, the result best fits in for pseudo-second order with R\(^2\) value of 1.000. The FT-IR results show functional group of alcohols, carboxyl, phenols, nitriles, alkynes, alkanes, alkyl halides and aliphatic amines. From the results obtained, the adsorbent proved to be an effective adsorbent for the removal of antibiotics from aqueous solutions.

Keywords—Adsorption, Amoxicillin, Groundnut shells, carbonized.

I. INTRODUCTION

Developing countries world over are faced with waste disposal problems. These waste are generated by anthropogenic activities [1]. Fresh water bodies which happen to be the major source of water for human activities (cooking, drinking, washing industrial use etc) is most affected as most of the generated wastes are disposed directly into the water body due to the absence or poor disposal facilities. These waste come from pharmaceutical, tamery, beverage, textile, chemical soap and detergent industries. Pharmaceutical wastes may contain antibiotics, anti-inflammators, tranquilizers, cosmetic ingredients, oil and grease, etc. Consequently, a large number of pharmaceutical products are present in water bodies thereby causing health challenges to potential consumers due to their lipophilic, non-biodegradable, biological and chemical nature [2].

In recent times, the scientific world has been confronted with a challenging problem of antibiotic resistance, occasioned by the use, misuse, overuse and improper disposal of antibiotics or their products by humans or pharmaceutical companies. Research has shown that almost every individual is resistant to one antibiotic or the other, even if he/she has not used same before. This may be as a result of bio-accumulation of antibiotics from water or other sources such as the food chain.

The emerging mechanisms of antibiotic resistance today have seriously hampered the treatment of certain infections [3]. There remain loopholes in curbing the problem of antibiotic resistance; therefore there is an urgent need to find available ways of solving this global problem.

Various ways which have been suggested by WHO to fight against antibiotic resistance such as medicine regulation, intersectional engagements, prevention of infection, technology innovation, service innovation knowledge and information. It is in the light of the above that the present research seeks to address the problem of antibiotic resistance by incorporating adsorption studies in the treatment of pharmaceutical waste.

The increase in antibiotic resistance occasioned by disposal of pharmaceutical waste that contains high amount of antibiotics which finds its way into the human system either through the food chain or when directly consumed resulting to health problems has called for concern [4]. The most challenging issue is the absence or improper waste treatment facility in our country.

One of the simplest methods of waste treatment is adsorption. This is primarily because it is economical, simple in design and effective [5]. Sorption studies have been applied widely in the removal of Heavy metals from systems [6,7] dyes [8] and pesticides [9] This work extends the concept of adsorption to removal of antibiotics from water.

The most commonly used adsorbent is activated carbon which is expensive and has a non-biodegradable attribute thereby resulting to environmental problems [10]. Hence alternative uses of low cost adsorbent from agricultural wastes which are readily available in the study area were utilised.

II. MATERIALS AND METHODS

A. Preparation of Amoxicillin Stock Solutions

1000 mgL\(^{-1}\) stock solution of amoxicillin was prepared by dissolving 1000 mg of amoxicillin capsule in distilled water and was made up to mark in a 1000 mL volumetric flask and was shaken and kept for serial dilution.

B. Preparation of Carbonized Groundnut Shells

Fresh groundnuts were obtained in railway market in Makurdi, Benue State. The groundnut was washed to remove the sand particles and sundried for 48 hrs after which the husk were removed and pounded by mortar and pestle, it was ground by a blender and sieved through 52 µm sieve, it was...
steeped into ammonium chloride (NH₄Cl) for 24 hrs after which it was rinsed several times with distilled water and dried at room temperature. The groundnut shells was carbonized at 350 °C using a muffle furnace and crucibles for 20 minutes. The activated groundnut shell was then washed with distilled water to remove the ash particles, dried in the laboratory and kept for further use.

C. Preparation of 0.05 M Iodine Solution

20 g of iodate free potassium iodine was dissolved in 30 – 40 mL of distilled water, 12.7 g of resublimed iodine was weighed on a rough balance and transferred into the concentrated potassium iodine solution and shaken until iodine dissolved. The solution was made up to mark with distilled water in a 1000 mL volumetric flask and was kept in a cool dark place.

D. Preparation and standardization of 0.1 M sodium thiosulphate solutions

2.4 g of sodium thiosulphate were weighed into 70 mL of distilled water, it was transferred into a volumetric flask of 100 mL, filled up to mark with distilled water and was shaken to homogenize the solution. 50 mL aliquots of standard iodate solution 0.1 M were pipette into 25 mL conical flask, 2 g of iodate-free potassium iodate (KI) were introduced into the solution 0.1 M were pipette into 25 mL conical flask, 2 g of potassium iodate were weighed into 25 mL of conical flask and swirled to hasten the solution. 2 mL of 6 M HCl were added and were titrated immediately with standard iodate solution: 50 mL aliquots of standard iodate solution: 2.4 g of sodium thiosulphate were weighed into 70 mL of distilled water, it was transferred into a volumetric flask of 100 mL, filled up to mark with distilled water and was shaken to homogenize the solution. 50 mL aliquots of standard iodate solution 0.1 M were pipette into 25 mL conical flask, 2 g of iodate-free potassium iodate (KI) were introduced into the solution 0.1 M were pipette into 25 mL conical flask, 2 g of potassium iodate were weighed into 25 mL of conical flask and swirled to hasten the solution. 2 mL of 6 M HCl were added and were titrated immediately with thiosulphate solution until the solution becomes pale yellow. 5 mL of starch indicator were added and titrated at constant stirring to the disappearance of the blue colour.

E. Preparation of Starch Indicator

1 g of starch was added into 100 mL boiling water. It was stirred and allowed to cool.

F. Preparation and standardization of 0.1 M potassium iodate solution:

21.4 g of potassium iodate were weighed into 100 mL of distilled water. 25 mL of potassium iodate were weighed into 100 mL of distilled water. 25 mL of potassium iodate solution were diluted with 100 mL of distilled water, to about 20 mL of this solution, 2 g of potassium iodide and 10 mL of 1 M sulphuric acid were added. It was titrated with 0.1 M sodium thiosulphate using 1 mL of starch indicator added towards the end of the titration.

G. Preparation of 6 M hydrochloric acid:

146.81 g of hydrochloric acid were measured and taken into 100 mL volumetric flask and was diluted to mark with distilled water.

H. Preparation of 0.1M Hydrochloric Acid

2.44 cm³ of hydrochloric acid were measured into 100 mL volumetric flask; it was diluted with distilled water up to mark.

I. Fourier Transform Infrared Spectroscopy

A small portion of adsorbent was scanned by the FT-IR spectrometer, the mixing solution of both the adsorbate and adsorbent were scanned through the FTIR spectrometer.

J. Batch Adsorption Studies:

Batch adsorption studies were carried out to obtain the rate of adsorption and equilibrium data. This was performed at varying concentrations, adsorbent doses and contact time. A calibration curve was obtained by a Uv-Visible adsorption spectrophotometer at concentrations from 20 mgL⁻¹ to 100 mgL⁻¹.

K. Contact Time:

The effect of contact time was studied at time intervals of 1,2,3,4 hrs at room temperature using 50 mL of 80 mgL⁻¹ of the solution with carbonize groundnut shell of 2.5 g in a beaker dipped in a thermostat water bath, it was filtered and analyzed using a Uv-Visible spectrophotometer.

L. Concentration:

A mass of 2.5 g of the adsorbent was contacted with 50 mL of amoxicillin solution of concentrations 20, 40, 60, 80 mgL⁻¹ using thermostat water bath maintained at 25 °C, this was filtered and analyzed using a Uv-Visible spectrophotometer.

M. Adsorbent Dosage:

Sample of Carbonized groundnut shell of mass 0.5 g, 1.5 g, 2.0 g, 2.5 g was added to 50 mL of amoxicillin solution (80 mgL⁻¹), it was stirred by a mechanical shaker for 4 hrs, it was filtered and analyzed using a Uv-Visible spectrophotometer.

III. RESULTS AND DISCUSSION

A. Physico-Chemical Parameters

Table 1 show the results of physico-chemical parameters of the carbonised groundnut shells. From the results, The pH was 6.28, bulk density 0.35 gL⁻¹. The attrition 9.89%. The moisture content was 4.20%. while The ash content was 44.65%. The iodine number was 932 mgg⁻¹. the results shows that the carbonised groundnut shells is a good adsorbent for adsorption studies [13].

B. FT-IR Result

The structure of amoxicillin consist of lone pairs of electrons on the Sulphur (S), Nitrogen (N), and Oxygen (O) which can co-ordinate other electrons to bonding. The FT-IR spectra of carbonized groundnut shell show characteristic bands at 3754.56 cm⁻¹ due to 0 – H stretch bond indicating alcoholic and phenols functional groups, 3218.34 cm⁻¹ represent C (triple bond) N stretching of amides, 2923.36 cm⁻¹ represent C-H stretching of alkenes, 2923.36 cm⁻¹ represent C-H stretching of alkynes, 2855.46 cm⁻¹ represent C-H stretching of alkanes, 2360.59 cm⁻¹ represent C-H bending of alkenes, 2360.59 cm⁻¹ represent C-H bending of alkynes, 2266.43 cm⁻¹ represent C=O stretching of carboxylic acid, 2100.59 cm⁻¹ represent C=O stretching of ketones, 1716.52 cm⁻¹ represent C=O stretching of carboxylic acid, 1604.52 cm⁻¹ represent C=O stretching of amides, 1374.56 cm⁻¹ represent C=O stretching of amides, 1114.89 cm⁻¹ represent C-H wagging of alkenes, 923.79 cm⁻¹ represent C-H wagging of alkynes, 798.56 cm⁻¹ represent C-H wagging of alkanes, 405.06 cm⁻¹ represent C- Br stretch of alkyl halides, 405.06 cm⁻¹ represent characteristic Raman shifts.

This implies that carbonized groundnut shell is a good adsorbent for the adsorption of amoxicillin, more over the observed increase in the intensity of the peaks suggests that
there is addition of the antibiotic to the adsorbent and since there is no complete shift in adsorption, this mechanism is suggestive of physical adsorption [13].

C. Adsorption Isotherms

The adsorption capacities of the adsorbent were studied using adsorption models. In this study, the Langmuir, Freundlich and Tempkin isotherms were studied on the adsorption of amoxicillin on carbonized groundnut shell. The adsorption isotherms can be expressed as

\[
\begin{align*}
\text{Langmuir} & \quad \frac{1}{q_e} = \frac{1}{q_m K \Gamma e} + \frac{1}{q_m} \\
\text{Freundlich} & \quad \ln q_e = \ln K_f + \frac{1}{n} \ln C_e \\
\text{Tempkin} & \quad \frac{-2a q_e}{2.303} = \log K + \log C_e
\end{align*}
\]

The result from plots indicate $R^2 = 0.9917$, 0.9374 and 0.9246 for Freundlich, Tempkin and Langmuir respectively.

To determine whether the adsorption of amoxicillin on carbonized groundnut shell was favourable, the values of $R_L$ and $n$ for Langmuir and Freundlich were evaluated. The results indicate that $R_L = 2.5 \times 10^{-5}$ and $n = 1$. The works of Musa et al. [14] indicate that if $R_L$ is less than unity, then adsorption is favourable. This indicates that the adsorption of amoxicillin on carbonized groundnut shell is favourable by Langmuir, Freundlich and Tempkin isotherms respectively. But in terms of $R^2$, Freundlich is more favourable than Langmuir and Tempkin. This agrees with other researches [14] which has value of 0.4128, 0.4587 and 23. For $\frac{1}{n}$, $R_L = \frac{R}{R_T}$. This implies that carbonized groundnut shell is a good adsorbent for amoxicillin.

D. Kinetics of Adsorption

The kinetic of adsorption was investigated using the lagergren first order plots and the pseudo-second order model as represented equation 4 and 5

\[
\ln (q_e - q) = q_e - k_1 t
\]

\[
\frac{t}{q} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}
\]

A plot of $\ln (q_e - q)$ against $t$ will give a slope $k$. Similarly, plot of $t/q$ against $t$ will give the values of $k_2$ and $q_e$. The results of the kinetics of adsorption give $R^2$ values of 0.617 for pseudo first order and 1.00 for pseudo second order kinetics. From the values of the $R^2$, the pseudo second order is more favourable showing that the adsorption phenomenon followed the second order. Moreover, the values of the rate constants were found to be 0.197 for pseudo first order and -89.687 for pseudo second order, proving that pseudo second order is more favourable than pseudo first order [15].

E. Batch Adsorption Studies

The batch adsorption was carried out using concentration, contact time and adsorbent dose. The result of the effect of contact time, presented in Fig. 10, however indicate that at time intervals of 2, 3 and 4 hrs, the adsorption was at equilibrium. This shows that adsorption of amoxicillin on carbonized groundnut shells beyond 2 hrs resulted in no further removal of amoxicillin since internal saturations of pores occurs [16].

The results for adsorbent dose presented in Fig. 9 shows that equilibrium is attained at an adsorbent dose of 1.5 g beyond which adsorption dropped below the equilibrium. This indicates that the adsorption of amoxicillin on carbonized groundnut shells increases and reaches a maximum then desorption sets in [16]. In general these results imply that carbonized groundnut shell is good for adsorption of amoxicillin antibiotics.

![Fig. 1 FTIR Result of Carbonized Groundnut Shells](http://dx.doi.org/10.17758/IAAST.A0515011)

![Fig. 2 FTIR Result of Carbonized Groundnut Shells contacted with Amoxicillin](http://dx.doi.org/10.17758/IAAST.A0515011)

**TABLE I**

<table>
<thead>
<tr>
<th>Physical-Chemical Characterization of the Adsorbent</th>
</tr>
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<tbody>
<tr>
<td>Properties</td>
</tr>
<tr>
<td>pH</td>
</tr>
<tr>
<td>Bulk density, gmL(^{-1})</td>
</tr>
<tr>
<td>Attrition, %</td>
</tr>
<tr>
<td>Moisture content, %</td>
</tr>
<tr>
<td>Ash content, %</td>
</tr>
<tr>
<td>Iodine Number mg/g</td>
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</tbody>
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http://dx.doi.org/10.17758/IAAST.A0515011
Fig. 3 The plot of Freundlich isotherm

\[ y = 26.552x - 26.691 \]
\[ R^2 = 0.9917 \]

Log Ce vs log Qe

Fig. 4 The plot of Tempkin isotherm

\[ y = 15.899x - 35.739 \]
\[ R^2 = 0.9374 \]

Qe vs LnCe

Fig. 5 The plot of Langmuir isotherm

\[ y = -55.129x + 568.99 \]
\[ R^2 = 0.9246 \]

Ce/Qe vs Ce

Fig. 6 The plot of pseudo first order kinetics

\[ y = 0.4265x + 0.0102 \]
\[ R^2 = 1 \]

1/Qt vs Time (Hours)

Fig. 7 The plot of pseudo second order kinetics

\[ y = 0.4265x + 0.0102 \]
\[ R^2 = 1 \]

0.2
0.4
0.6
0.8
1
Log Qe

Log Ce

Fig. 8 The plot of effect of concentration

% Removal vs Concentration (mg/L)

Fig. 9 The plot of effect of adsorbent dosage

% Removal vs Adsorbent dosage (g)
Fig. 10 The plot of effect of contact time

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One of the simplest methods of waste treatment is adsorption. This is primarily because it is economical, simple in design and effective. Sorption studies have been applied widely in the removal of Heavy metals from systems, dyes, and pesticides; this work extends the concept of adsorption to removal of antibiotics from water.