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Kinetics and Adsorption Studies of Tetracycline from Aqueous Solution Using Melon Husk

*[1]U. J. Ahile, [1]S. O. Adejo, [1]S.T. Ubwa, [2]T.B. Iorhuna, [1]R.L. Tyohemba, [1]M.G. Ikyagh and [1]P. I. Utange
1. Department of Chemistry, Benue State University, P.M.B. 102119, Makurdi, Nigeria
2. Department of Chemistry, Taraba State University, Jalingo
Corresponding Author:ujahile@gmail.com, +2348064049464

Abstract:*The adsorption of tetracycline from aqueous solution was carried out using melon husk as a low-cost adsorbent. The adsorbent was characterized using standard methods and values obtained were; pH = 7.80, bulk density = 0.43 g/mL, ash content = 2.2 %, moisture content = 8.27 %, attrition = 1%, and iodine number = 552 mg/g. Adsorption capacity was found to vary with initial concentration, adsorbent dosage, pH, contact time and temperature, the maximum adsorption capacity in each case was found to be at; 30 mg/L for concentration, 0.8 g for adsorbent dose, 5 for pH, 60 minutes for time and 30 °C for temperature. FTIR analysis was done to analyses the surface functional groups which shows a shift in the intensity the functional groups after the adsorbent was contacted with adsorbate indicative of an adsorption phenomenon,SEM analysis carried out revealed a rough and smooth morphology of the uncontacted and contacted adsorbent respectively. The experimental data judging from the R^2 values fitted best into the temkin isotherm. The fitting of tetracycline adsorption in to the pseudo second order kinetic model (R^2 of 0.9992).This result implies that melon shell is a good adsorbent for the removal of tetracycline from aqueous solution.*

Keywords*: Adsorption; tetracycline; melon husk; activated carbon; adsorbent isotherm.*

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I. Introduction

Tetracyclines (TCs) are among the antibiotics that are used extensively for disease control and in livestock feed for several decades due to their great therapeutic values [1]. The widespread use of TCs and other antibiotics has led to dissemination of these compounds into the water and soil environment [2]. Although environmental concentration of antibiotics maybe typically below the threshold levels to exhibit medicinal treatment effects on bacteria populations and other at-risk species, chronic exposure to low levels of antibiotics alone or along with other toxicants may still exert pressure on the development of antibiotics resistant bacteria such as tetracycline and minimize the effectiveness and the fate of tetracycline contaminants in the water-soil environment [3, 4].

Melon, (Cucumismelo L)., is an African herbaceous annual plant. It is a fruit of economic importance in both Nigeria and the world and largely cultivated in Benue State for its ediblefruit. Due to the high consumptionof melon, enormous amounts of the husk (as wasteproducts) are disposed, into the various environmental media inthe community. From an environmental viewpoint, theutilization of this agricultural waste as a low-cost sorbent for the removal of tetracycline is recommended [5].

Several methods have been employed for water treatment such as ion exchange, precipitation, membrane separation, electrolysis, advanced oxidation methods and adsorption to remove these recalcitrant wastes. The challenge is that most of these methods are expensive and requires high level of expertise. Hence, they are not applied by many end-users. For this reason, adsorption technology has gained a wider application due to its inherent low cost, simplicity in design, versatility and robustness [6].

Adsorption is a surface phenomenon which can be defined as the deposition of molecular species onto the surface. The molecular species that gets adsorbed on the surface is known as adsorbent while the surface on to which a specie is attached to is known as the as adsorbate. Several naturally occurring substances as adsorbents have continued to receive much attention as replacement for the commercial activated carbon. The greatly expanded interest on naturally occurring substances is attributed to the fact that they are readily available, eco-friendly, cheapand pose no threat to the environment. In addition, they are biodegradable and renewable sources of materials. The aim of this study was to evaluate the feasibility of using melon husk which is harmless, cheaper, and abundant agricultural raw material as a low-cost adsorbent for the removal of tetracycline from aqueous solution.

II. Materials AndMethods

2.1 Sample Collection and Preparation

Melon husks were collected from Wadata market along the river bank. It was washed, and sun-dried for three days, followed by pounding with mortar and pestle. The particle size was further reduced to fine powder using a grinding mill and subsequently, the powder was sieved through a 52 µm sieve to remove larger particles. The dried powder was chemically activated by steeping in a saturated solution of Ammonium chloride (NH_4Cl) for 24 hours, after which it was washed several times with distilled water and dried under room temperature. A 5 g of the powdered sample was weighed into a clean pre-weighed crucible. The crucible was introduced into a muffle furnace at 600 °C for 5 min after which the content was poured into a stainless-steel bowl and allowed to cool under room temperature [7].

2.2 Characterization of Activated Carbon

The Bulk density was calculated in g/mL using the formula [8];

Bulk density =$\frac{massofdryactivatedcarbon \quad (g)}{volumeofpackeddrymaterial \quad (mL)}$ (1)

The attrition was calculated based on weight loss by the following expression [9];

Loss of attrition % = $\frac{(P_1-P_2)}{P_1} \times 100$ (2)

where: P_1 is initial mass and P_2 the final mass

Moisture Content which was calculated as weight loss from the equation below [10]

Moisture content $\frac{m_2-m_3}{m_2-m_1} \times 100$ (3)

where: $M_1$is weight of crucible, M_2, weight of crucible + sample before heating and M_3 the weight of crucible + sample after cooling

Ash is the inorganic residue remaining after the water and organic matter have been removed by heating, the total ash-content was calculated based on the expression [10];

$Ash\ (\%) = \frac{w_3-w_1}{w_2-w_1}100$ (4)

where;w_1 = weight of empty crucible (g), w_2 is weight of crucible + sample (g), w_3, weight after ashing (g)

Iodine value is the mass of iodine in grams that is consumed by 100 grams of chemical substance [10], iodine number was calculated using the formula;

$IAN = \frac{M_t(V_b-V_s)}{2m_a} \times A_{ri}$ (5)

where; M_t is the concentration of sodium thiosulphate solution, V_b, Average volume of sodium thiosulphate used as blank titration, V_s, Average volume of sodium thiosulphate used in titration of the aliquots, m_a, Mass of adsorbent used andA_{ri} the Relative atomic mass of iodine.

2.2 Batch equilibrium studies

The initial concentration of tetracycline was 1000 mg·L^{-1}, from which different concentrations of tetracycline was prepared. To estimate the applicability of melon husk as an adsorbent for the removal of tetracycline, 2g of carbonized melon husk was measured into a conical flask which contained 50mL of 50 mgL^{-1} of tetracycline. The flasks were shaken for one hour using a mechanical shaker under a constant temperature of 25 ± 2 °C, after which it was then filtered using Whatman filter paper (No. 42) and the filtrate was collected, the absorbance of the solution was taken using JENWAY spectrophotometer at 350 nm. The pH of the aqueous solution was adjusted to 3.0, 5.0, 7.0, 9.0, and 11.0. with varying initial concentrations of tetracycline ranging from 10 to 50 mgL^{-1} and then contacted with carbonized melon husk. The effect of the adsorbent dose was studied using 0.2, 0.4, 0.6, 0.8, and 1.0 g of the adsorbent with 50 mL of the antibiotic solution. The effect of contact time, and temperature on tetracycline removal was studied by contacting 2 g of carbonized melon husk with 50 mL of 50 mgL^{-1} of tetracycline at different time intervals and temperature respectively.

2.3 Adsorption Isotherm

Adsorption isotherm is described as the relationship between adsorption and aqueous concentration at a given temperature [11]. The equilibrium adsorption isotherm is fundamental in describing the interactive behaviour between adsorbate and adsorbent, and is important in the design of adsorption systems [12].

The Temkin model is linearly represented as equation (6) and generally applied in the form:

$q_e = blnA + blnC_e$ (6)

Where A (L/g) is maximum binding energy and B (J/mol) is heat of sorption. The value of A and B can be calculated from the slope and intercept of plot of qe against lnCe [13].

Freundlich equation gives a description of adsorption data over a restricted range of concentration, and is suitable for a multilayer adsorption. The linear form of Freundlich equation is [14];

$$lnq_e = lnK_f + \frac{1}{n} lnC_e \qquad (7)$$

Where; q_{eq} = is the adsorption capacity per unit mass adsorbent, K_f is a constant indicating the adsorption capacity and n is adsorption intensity and C_{eq} = Absorbent concentration in aqueous solution.

III. Results and Discussion

3.1 Characteristics of Activated Carbon

The characteristics of the activated carbon are presented in table 1. The low ash content of melon husk was found (2.2 %), as presented in the table 1 is as a result of high carbon yield. Raw materials used for the production of activated carbon are those with high carbon yield but low inorganic content [9]. A pH of 7.5 was obtained for the activated carbon, for most application pH of 6-8 is acceptable. The bulk density was obtained to be 0.48g/ cm^3. Bulk density affects infiltration and porosity, low bulk density is an indicator of high porosity and adsorbent compaction. Moisture content of activated carbon is often required to define and express its properties in relation to the net weight of the carbon. The moisture content of melon husk was found to be 8.27 % making it a good adsorbent with low moisture content. The attrition value of the melon husk was found to be 1% (table 1) this is indicative of the fact that melon husk can maintain its physical integrity and withstand frictional force imposed by back washing. The iodine adsorption number of melon husk was found to be 552 mg/g which indicates a reasonable pore volume [9].

Table 1 Physico-Chemical Characterization of Carbonized Melon Husk

Properties	**Values**
pH	7.80
Bulk density (g/mL)	0.48
Attrition (%)	1.00
Moisture content (%)	8.27
Ash content (%)	2.20
Iodine Number mg/g	552 .00

IV. Sem Analysis Result

Scanning electron microscope was used to study the physical morphology of the carbonized melon husk before and after contacting with adsorbate. In figures 1a, 2a, 3a reveals micrograph which appears to be rough with protrusions. The roughness of the surface is indicative of maximum surface area available for adsorption, However, surface coverage in the form of flake in figures 1b 2b, and 3b indicates the presence of the adsorbate (tetracycline)sorbed on the adsorbent. The difference in the interactive volume is an indication that there was an adsorption of the adsorbate on the surface of the adsorbent. Thus,the particle morphology, apparentlyreveals carbonized melon husk to be a suitable adsorbed [15].

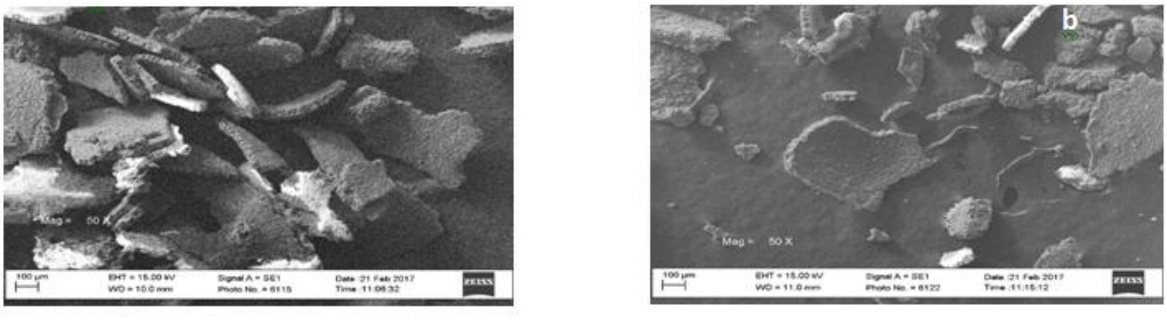

Figure 1: SEM Result of Carbonized Melon Husk before (a) and after (b) Contacting with Tetracycline at X50

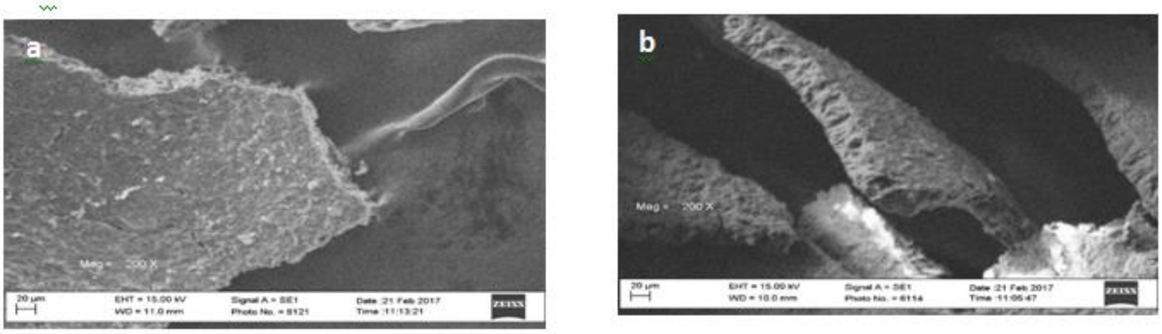

Figure:2 SEM Result of Carbonized Melon Husk before (a) and after (b) Contacting with Tetracycline at X200

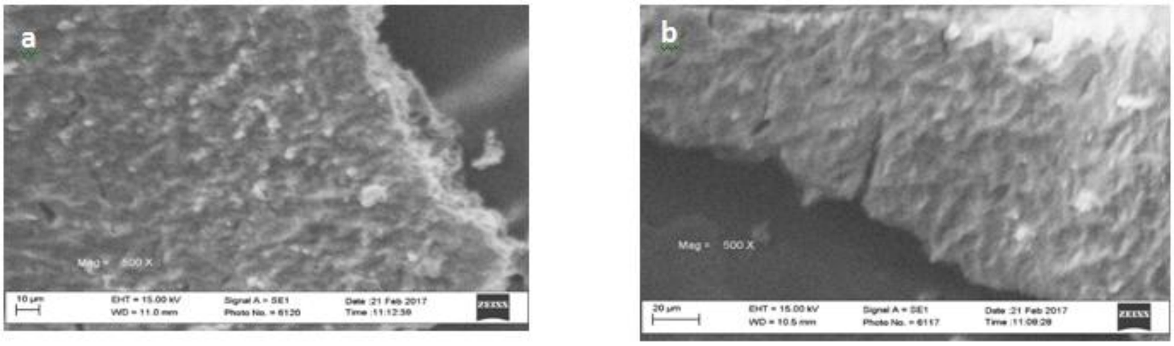

Figure 3: SEM Result of Carbonized Melon Husk before (a) and after (b) Contacting with Tetracycline at X500

Fourier Transform Infrared Spectroscopy (FTIR) Analysis

Since adsorption is a surface phenomenon which requires the adsorbate to stick to the surface of an adsorbent, the FTIR Spectrogram of carbonized melon husk was obtained to analyzethe surface functional group, fig 4a and b manifest the difference in functional groups before and after contacting with tetracycline. The FTIR of Carbonized melon husk before contacting with tetracycline exhibits O-H stretch, at 3743.92 corresponding to alcohol, phenols, C-H stretch at 2923.27 indicative of alkanes, H-C=O: C-H stretch at 2725.76 corresponding to aldehyde, C-H bend at 1462.72 corresponding to alkanes, C-H rock at 1376.80 indicative of alkanes, C-H wag (-CH_2X) at 1304.44 corresponding to alkyl halide, C-N stretch at 1154.29 corresponding to aliphatic amine, =C-H bend at 972.84 corresponding to alkenes and C-H rock at 721.84 corresponding to alkanes.

The FTIR spectra after contacting with tetracycline exhibits C-H stretch absorption peak at 2920.56 corresponding to alkane, H-C=O: C-H stretching vibration peak at 2725.76 indicative of aldehydes, C-H bend absorption peak at 1462.72 corresponding to alkanes, C-H rocks at 1376.80 corresponding to alkanes, C-H wag (-CH_2X) at 1304.44 indicative of alkyl halides, C-N stretch at 1154 indicative of aliphatic amine, =C-H bend at 972.20 corresponding to alkenes, and C-H rocks at 721.84 corresponding to alkanes.

The spectrum explains that some peaks were shifted while others have their intensity changed. The observed changes indicate the involvement of these functional group in the adsorption process. From the above results it was also observed that there is no complete shift in absorption and also that the increase in the intensity of the peak suggest that there is an addition of antibiotics which is an indication of physical adsorption.

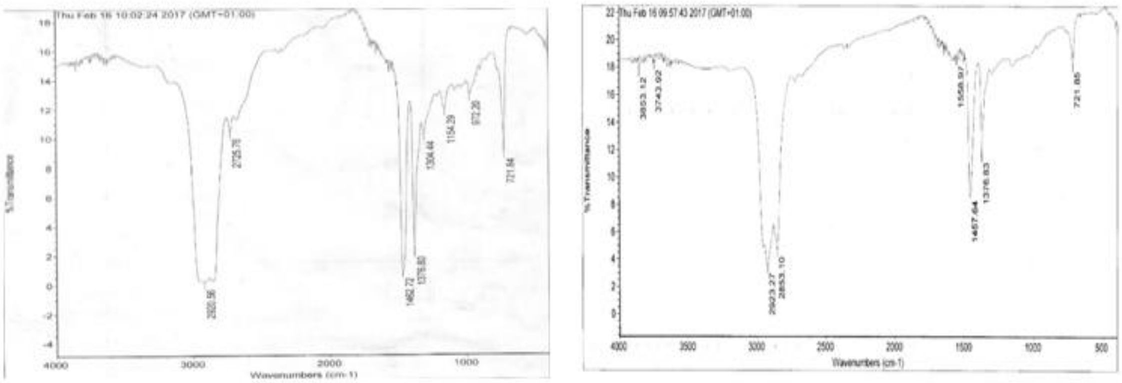

Figure 4: FTIR Result of Carbonized Melon Husk before (a) and after (b) Contacting with Tetracycline

Adsorption Studies

Effect of adsorbent dosage

In the batch adsorption process, the ratio of the solid to that of the solute is a very important factor in the determination of the capacity of adsorption. The effect of sorbent doses on the adsorption of melon husk has been shown in Figure 5which follows the prediction pattern of increasing percentage adsorption with increase in sorbent dose. From the results, the equilibrium was attained at an adsorbent dose of 0.8 beyond which adsorption dropped below equilibrium this indicates that the adsorption of tetracycline on the carbonized melon husk increases and reaches a maximum then desorption sets in. The increase in adsorption with a corresponding increase in sorbent dose could be as a result of the resistance to mass transfer of the adsorbate from the bulk liquid to the surface of the adsorbent

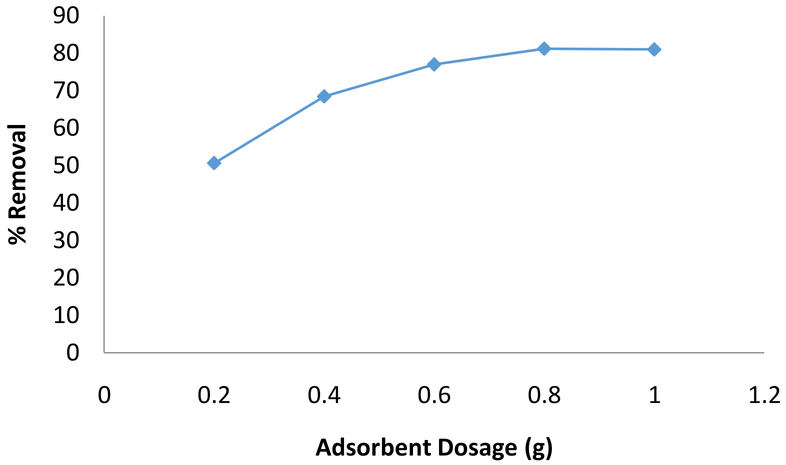

Figure 5: Effect of Adsorbent dose on the removal of tetracycline from melon husk

Effect of pH

Figure 6 gives a plot of the effect of pH on the adsorption of tetracycline on carbonized melon husk, from the graph it was observed that they were an increase in adsorption as pH increases from 3 -5 followed by a steady decrease as pH increases further, pH of 5 gives the optimum pH for the adsorption of tetracycline onto carbonized melon husk. pH is one of the most important variable affecting adsorption of substance on an adsorbent, this due to the fact that hydrogen ions themselves compete strongly with adsorbate. The adsorbate removal efficiency of melon husk at different pH values as shown in figure 2 shows optimal pH values around 2 - 4. The increase in the adsorbate removal with increase in pH values can be attributed to the fact that a decrease in competition between proton and the adsorbate molecules for the same functional groups and then the decrease in positive charge of the adsorbent which results in a lower electrostatic repulsion between the adsorbate and the surface.

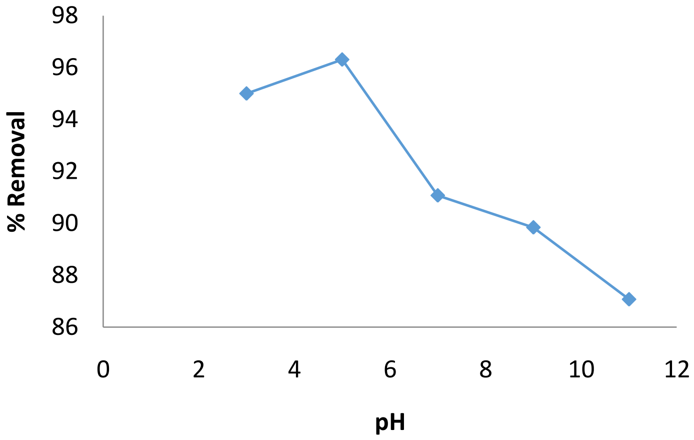

Figure 6: Effect of pH on the removal of tetracycline from melon husk

Effect of Contact Time

The effect of contact time on batch adsorption shows that adsorption increases from 30 minutes to 60 minutes after whichit decreasesto 120 minutes, this implies that equilibrium time was attained at 60 minutes since adsorption decreases afterwards, this is as a result of decrease in adsorption site with time.From the results, it can be observed that sorption takes place rapidly at the beginning of the reaction followed by a slower internal diffusion process, which may be the rate determining step. furthermore, the fast process at the beginning of the process can be accounted for by the fact that a large number of active sites are available for adsorption but after a sometime, the remaining active sites are difficult to be occupied as a result of the repulsion between the bulk phases and the solute molecules of the solid thus, increasing the equilibrium time.

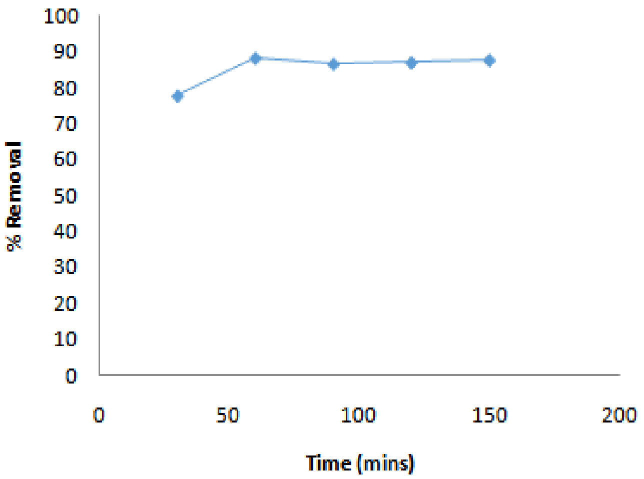

Figure 7: Effect of contact time on the removal of tetracycline from melon husk

Effect of Concentration

The experimental results on the effect of concentration on batch adsorption shows an increase in adsorption with an increase in concentration. The rapid adsorption then gave rise to a slower uptake at 20 mg/L. this can be attributed to the concentration gradient created at the beginning of the process as a result of the concentration of the solute in the solution and at the adsorbent surface. This can therefore be accounted for by fact that the adsorbate loading increases on the surface of the adsorbent, hence the concentration gradient reduces giving rise to a slower adsorption process. When the concentration of the adsorbate became higher the active site of the carbonized melon husk wassurrounded by more adsorbate molecules and the process of adsorption was carried out sufficiently leading to equilibrium 60 mg/L.

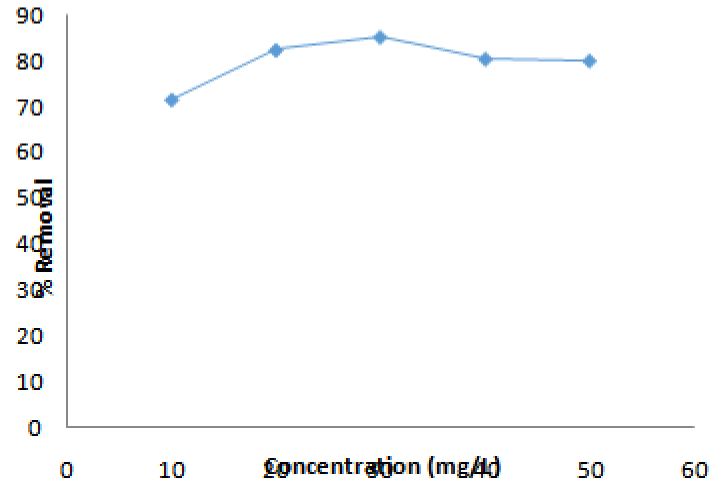

Figure 8: Effect of concentration on the removal of tetracycline from melon husk

Effect of Temperature

The experimental results of the effect of temperature on the adsorption of tetracycline on carbonized melon husk show a rapid decrease in the adsorption of the adsorbate onto the adsorbent as the temperature increases from 30 °C – 40 °C and increases from 40 °C – 70 °C. From the graph it can be clearly seen that the optimum operating temperature for the adsorption process is at 30 °C.

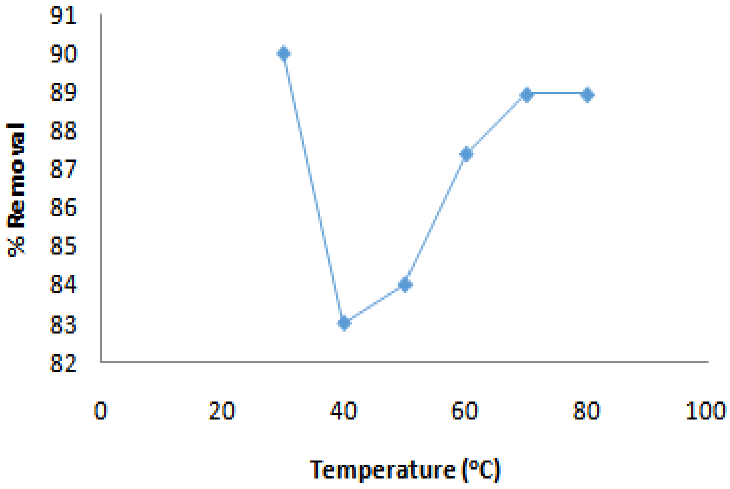

Figure 9: Effect of temperature on the removal of tetracycline from melon husk

Equilibrium Isotherm Models

Adsorption properties and equilibrium data, commonly known as sorption isotherms, describe how adsorbate ions interact with adsorbent particles and are thus critical in optimizing the use of solid materials. An important step in the analysis of the data is carried out by fitting them to different isotherm models to find the suitable model that can be used to design purpose. Two isotherms were tested for to determine fit of the results to the experimental results, namely; the Freundlich isotherm and theTemkin isotherm [5].

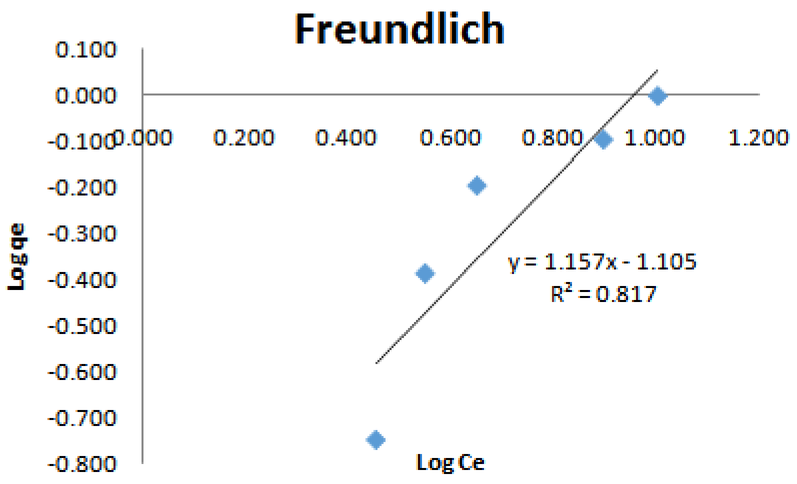

Figure 3 Freundlich Isotherm for the adsorption of tetracycline by melon husk.

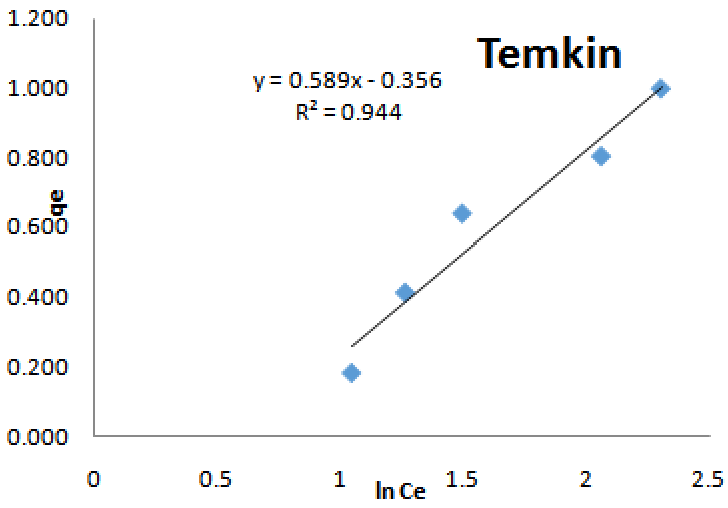

Figure 4: Temkin Isotherm for the adsorption of tetracycline by melon husk

In the freundlich model, the regression correlation coefficient (R^2) was found to be 0.8172 and that of temkin model was found to be 0.9449. both agrees with the experimental data but the higher R^2 value of temkinmodel implies that the equilibrium data agrees well with the temkin model which assumes that the heat of adsorption of all molecules in the layer would decrease linearly with increase coverage of the adsorbent surface and that adsorption is characterized by a uniform distribution of binding energies.

Kinetic model

The kinetics of tetracycline adsorption by melon husk was studied, Kinetic models are used to determine the rate of the adsorption process. Two kinetic models: pseudo-first-order and pseudo-second-order [16, 17]were used to investigate the adsorptionprocess of tetracycline by melon husk.

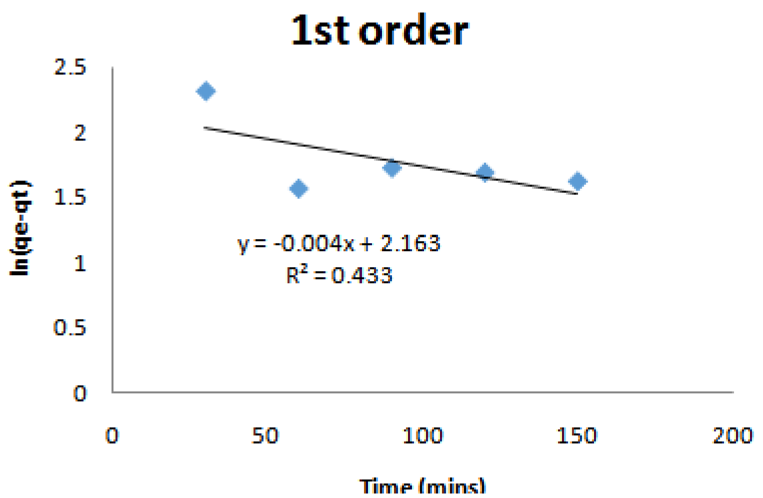

Figure 5: First order kinetics for the adsorption of tetracycline by melon husk

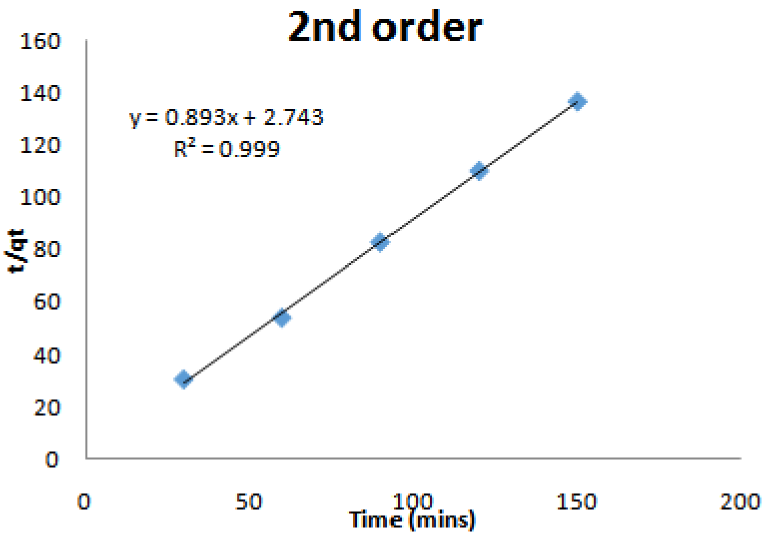

Figure 6: Second order kinetics for the adsorption of tetracycline by melon husk

The correlation coefficient (R^2) was 0.4331 for first order, this R^2 value is not in agreement with the experimental data, suggesting that tetracycline adsorption did not fit the pseudo first order model. On the order hand the R^2 value for pseudo second was 0.9992 which agrees well with the experimental data. Thus, the higher R^2 value indicates that the pseudo second kinetics model is suitable to describe the kinetic adsorption process of tetracycline better than pseudo first order kinetics. These suggest that during the adsorption of tetracycline on melon husk there was chemisorption due to the sharing of electron between the adsorbent surface and the adsorbate.

V. Conclusion

The study successfully preparedactivated from melon husk and removal of tetracycline from aqueous solution was achieved. The shift in FTIR spectrum confirms tetracycline adsorption onto carbonized melon husk, the physical morphology examine by SEM analysis shows physical adsorption on the surface of the carbonized melon husk, two adsorption isotherms namely Freundlich and Temkin were used to analyzed the data which gives the following R^2 values of 0.8172 and 0.9449 respectively but the Temkin model is more suitable because of the higher R^2. Furthermore, the kinetic study was done using the pseudo first order and pseudo second order of which the pseudo second order was well fitted to the experimental data. Results indicate that activated melon husk,a low-cost adsorbent is a promising solution to the removal of tetracycline from aqueous solution.

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