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Utilization of Modified Cashew Nut Shell (Anacardium Occidentale) as an Adsorbent for the Removal of Synthetic Dye (C57) 4-Hydroxyl-3-Carboxy Phenylazophenylazo -2-Nitro-Toluene) From Aqueous Solution Via-Kinetics Approach

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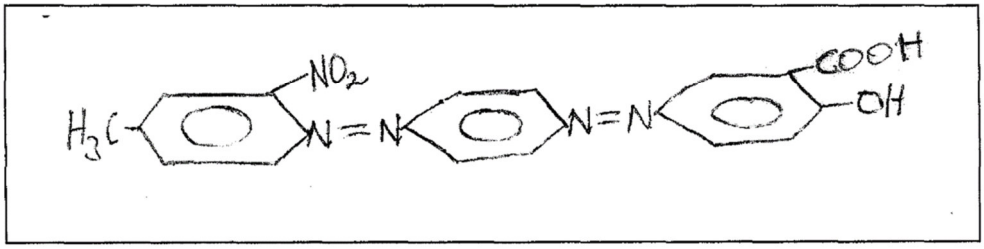
Abstract
The abatement of an azo-dye "4-hydroxyl-3-carboxylphenylazophenylazo-2-nitro toluene" with dye code C57 was carried out with the use of readily available and cheap adsorbent known as cashew nut shell (Anacareium occidentale) for the removal of the C57 dye from used water. The influence of the different system factors such as contact time, temperature, pH, dye ion concentration and adsorbent dosage were all investigated. The result showed the dye ion removal efficacy ncreases with time till optimum pion of 50 minutes (74.4&).The maximum dye adsorption occurred with 5g of the adsorbent resulting to maximum percentage removal of 73.5. optimum C57 Dye concentration was found to be 10mg/L with efficiency of 72%. low pH results to a positive change in H^+ concentration with % Removal of 63.9%, similarly the optimum dye removal was observed at 60^{0C} (333K) temperature resulting to 73.5% this maybe due to the chemical reaction the functional group of the cashew nut shell/C57. The Langmuir isotherm gave a smart linear graph with R^2 , q_{max} K_L and S_F values as 0.6013, 8.73L/g, 47.39, and 1.133 respectively, which was able to fit in better of than the Freundlich isotherm. Freundlich isotherm assumes the adsorption intensity of the adsorbent with K_F value of 15.95mg/g. Pseudo first and second order have K of 0.014 and 0.0041 respectively, whereas the later was able to fit in properly more than the former.

1.0 Introduction

The fabric industry and other industries release large quantity of dye in their discharges, especially the textiles according to Nabi Bidhendi *et al.,* (2007). In the same line Binupriya et al., (2009) reported that more than 70,000 tons of various kinds of coloured substances are synthesized over the world annually of which, about 30% are disposed as their effluents during the production processes (Cooper, 1993). These pigments damages the aquatic system where they are been discharged to as well as contributing majorly to the challenge of biological and chemical degradation resistance (Fu and Viraraghavan, 2002). Majority of these colored substances are Azo in nature. Azo dye are these synthetic substances that have one or more azo group (-N=N-) bond to the aromatic rings. The discharge of azo dyes into the aquatic system causes colouration of rivers and streams, toxic effect and the carcinogenicity of biotransformation products (Asiagwu *et al.,* 2012).

The methods for the removal of coloured materials can be grouped into three; physical, biological and chemical. The chemical means includes flocculation or coagulation, floatation and filtration, electro kinetic coagulation and so on. While the physical technique are: membrane filtration, adsorption and reverse osmosis. Biological technique which are known as biodegradation method such as microbial degradation are applied in the treatment of industrial wastewaters (Robinson *et al.,* 2001, Boyrarnoglu *et al.,* 2006 and Dabrowshi, 2009). All these conventional methods have several demerits like cost implicative and slow regeneration. The adsorptive way of dye treatment is better than any other techniques for polluted water treatment. It is simple, easy to perform and of low cost. It is also not hindered by toxic substances as stated by (Wu, 2007; Hassani *et al.,* 2008, Binupriya et al., 2009).

This present study is carried out to evaluate the possibility of using cashew nut shell to remove C57 dye from wastewater so as to develop a new low cost technique for the removal of coloured substances in wastewater or industrial effluents.



Structure of the Dye
NAME: 4-hydrozyl, 3-carboxyl phenyl azo phenyl azo -2-nitro toluene
DYE CODE: C57

2.0 Materials and Methods

2.1 Sample Collection and cashew nut adsorbent preparation

A low cost adsorbent, cashew nut shell, was collected from a cashew tree from a neighbouring village in Obiaruku, Ukwuani Local Government Area, Delta State. The cashew nut shell is a waste material. It was rinsed using distilled water to remove all unwanted substance until a pH of 6.5-7 was obtained. It was dried at room temperature. This was then pelvurized to powder and sieved with si. The sieve shaker is like a vibrator having different sizes of sieves: 300 microns, 600 micron, 1.18mm, 2.3mm and 2.12 micron respective, which was able to sieve the biomass into different sizes. This was stored in a plastic container for further studies.

2.2 Preparation of dye solution and its properties and structure

The dye used in this present study is an azo-dye known as 4-hydroxyl, 3-carboxyl phenyl azo phenyl azo-2-nitrotoluene. This is a synthetic dye. 300ml of the C_{57} dye solution with dye concentration of 10mg/L was prepared in a flask with the aid of distilled water were 40ml of it was used for each analysis.

Properties

a. Elemental analysis;

Observed	Calculated
C, 61.50	61.53
H, 4.62	4.65
N, 21.50	21.53
O, 12.38	12.29

b. % yield of this azo is 32
c. It has a melting point of 162-164
d. Its ⋋max (nm) is 334,452
e. The Emax litre (mol an^{-1}) is 72,600

2.3 Variation of contact time on adsorption

the influence of resident time on the removal of C57 of a dye known as 4-hydroxyl, 3-carboxyl phenyl azo phenyl azo -2-nitrotoluene by cashew nut shell was determined.

The 0.002kg of the (cashew nut shell) was weighed into six several conical flasks labeled 20, 40, 50, 60, 80 and 100 minutes. The 10mg/L of dye concentration was prepared by dissolving 0.01g of the dye in $1dm^3$ of distilled water later 40ml of the C57 dye solution was taken into the 6 conical flasks respectively. These flasks were covered tightly and swirled. The suspensions were filtered with a Whitman No 45 filter paper at the end of each time interval and centrifuged. After which, the C57 dye concentration was measured with spectrum lab 22 spectrophotometer (Sathishkumar *et al.,* 2007).

2.4 Influence of adsorbent dosage on the removal of C57 dye in aqueous solution

The variation of adsorbent dosage on removal of a synthetic dye C57 (4-hydroxyl, 3-carboxyl phenl azo phenyl azo-2-nitro toluene) by cashew nut shell was determined in line with some other workers (Sathishkumar *et al.,* 2007). The 1g, 2g, 3g, 4g, and 5g were weigh into different flask. However 10mg/L of C57 dye concentration was prepared by dissolving 0.01g of the adsorbate in one litre of distilled water. The 40ml of the prepared dye was then taken into the 5 different conical flasks respectively. These flasks were covered and agitated for 20 minutes and then the suspension was filtered using filter paper and then centrifuged. The dye ion concentration was determined with the aid of spectrum lab 22 spectrophotometer.

2.5. Variation impact of C57 concentration on adsorption

The implication of dye concentration on adsorption was conducted following the method described by Sathishkumar *et al.,* 2007. Varying dye ionic concentration like 10mg/L, 20mg/L, 30mg/L, 40mg/L and 50mg/L were prepared and poured into different conical flask respectively. The 0.002kg of the cashew nut shell were measured into conical flasks differently. These flasks was covered and shaken for 20 minutes and the suspensions were filtered with filter paper and centrifuged. The dye ion concentration was determined with the aid of spectrum lab 22 spectrophotometer.

2.6. pH effect on adsorption of C57 dye in aqueous solution

The implication of pH on C57 dye removal from aqueous solution is carried following the method adopted by Sathishkumar *et al.,* 2007.

Varying 2g of the cashew nut shell were measured into 5 flasks respectively. Then 40ml of C57 dye solution were added followed by the adjustment of the pH to the range of 2.0, 4.0, 6.0, 8.0 and 10.0 with HCl (0.1M) or NaOH (0.1M) and then the pH readings were recorded from pH meter. These flasks were covered and then agitated for 20 minutes. The suspensions were then filtered using paper and centrifuged. The dye ion

concentration were assessed spectrum lab spectrophotometer.

2.7. The implications of change in temperature on dye adsorption

The influence of temperature on adsorption was conducted in line with the method earlier used by Sathishkumar *et al.,* (2007) and Asiagwu, (2012). The 0.002kg of the modified cashew nut shell was weighed into 5 separate flasks and then a 40ml of the C57 dye solution (10mg/L) was taken into the five flasks (Asiagwu, 2012). These flasks were covered and heated at different appropriate temperatures using thermostatic water bath, at 20 minutes each after which the flasks were removed from the water bath and gingled for another 5 minutes respectively. The suspension were filtered using filter paper and centrifuged. The dye ion concentration were obtained using spectrum lab 22 spectrophotometer.

3.0. Data Evaluation

3.1. Calculation of the Amount of Dye Removal

The amount of dye removed after the experiment was calculated using a modified mass balance equation as adopted by Uwanah et al., (2012) and shown below;

$q_{eC57} = (C_{iC57} — C_{fC57})$ x v/m ……. Eqn 1

Where;

q_{eC57} is the concentration of C57 dye adsorbed per unit weight of cashew nut shell powder (mg/g)

C_{fC57} is the equilibriumC57 dye concentration (mg/L)

C_{iC57} is the initial C57 dye ion concentration (mg/L)

M is the weight of cashew nut shell (g)

V is the volume of C57 dye solution (L)

3.1.1. Percentage of Dye Removed

The percentage removal of dye ion concentration by cashew nut shell was calculated using the equation described by as shown below.,

$\%R = \frac{C_{iC57} - C_{fC57}}{C_{iC57}}$ ……... Eqn 2

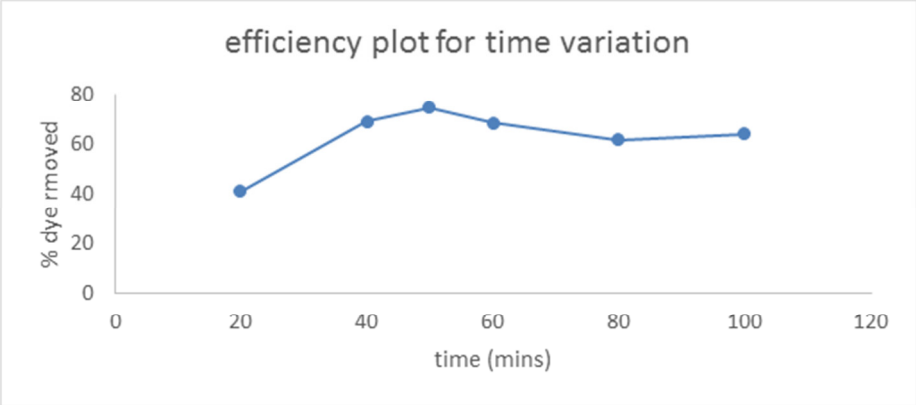
Where %R is the percent removal

C_{fC57} is the equilibrium concentration (mg/L)

C_{iC57} is the initial concentration (mg/L)

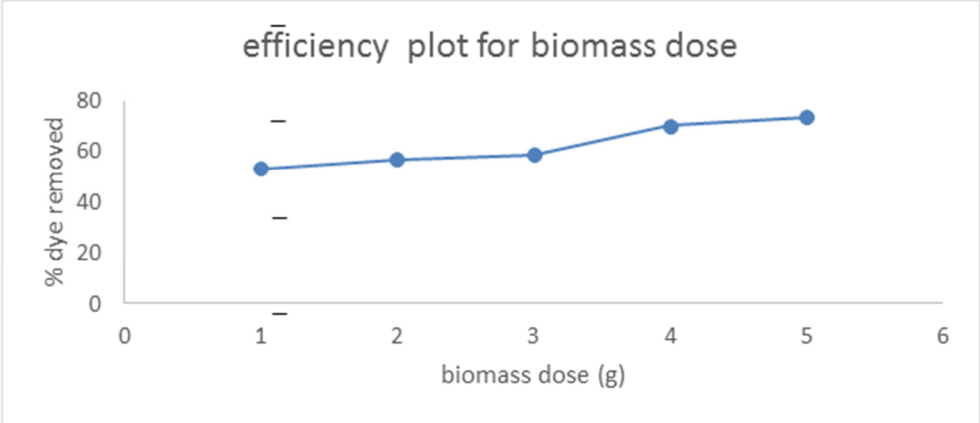
3.2. Variation of contact time on the removal of C57 in aqueous solution

The effect of contact time was carried out to determine the equilibrium time required for the adsorption of the C57 synthetic dye and was varied between the intervals of (20 to 100 mins). It is shown that the rate of removal of the dye increased with increase in contact time to an extent. This is shown in figure 1. However,further increase in contact time indicated no increase in the uptake of dye due to deposition of C57 dyes on the adsorption sites of the adsorbent material and the strong force of attraction between the C57 dye molecules and the cashew nut shell (adsorbent) hence the optimum time recorded was 50 minutes giving 74.4% C57 dye removal.



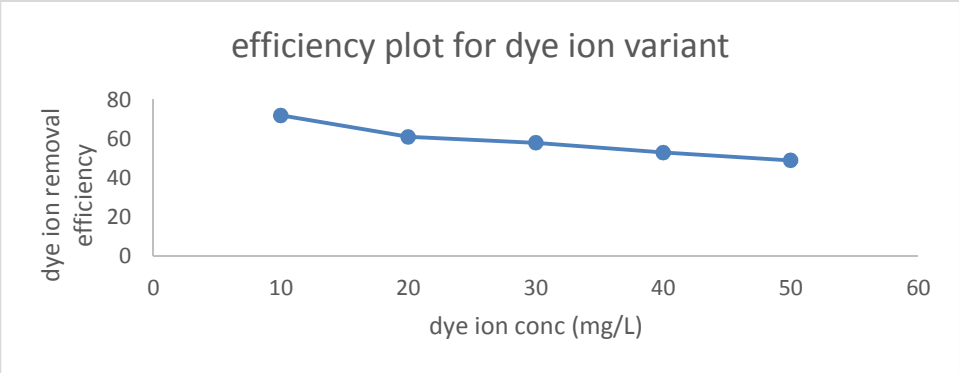
3.3. Influence of Adsorbent Dosage on C_{57} dye removal from aqueous solution

The influence of adsorbent dosage on adsorption of the synthetic dye indicated that an increase in adsorbent dosage of cashew nut shell leads to an increase in the amount of dye removed as represented in figure 2. The maximum dye adsorption was at 5g of the adsorbent with maximum percentage of dye removed of 73.6%.



3.4. Influence of dye ion concentration on adsorption

The implication of dye concentration on adsorption showed that the amount of dye removed increased only at C57 dye concentration of 10mg/L but decreased with an increases in dye concentration, after which there was an increase in the amount adsorbed as shown in figure 3. Increase in dye concentration of C57 influences its adsorption uptake. This can be attributed to an increase in the driving forces of the concentration gradient when there is increase in dye concentration of C57, however high amount of C57 dye decreaces the adsorbent efficiency this maybe attribute to non presence of unoccupied adsorbent active site.



3.5. Variation of pH on adsorption

The implication pH on adsorption as studied revealed that the maximum C57 dye removal was obtained at acidic pH. Low pH usually resultss to increase in proton concentration in the system and the surface of the adsorbent will become more positive charge by absorbing this proton(H^+) as the cashew nut shell acquires a positive charge at acidic pH, a significantly strong electrostatic attraction could appear between the positively charged adsorbent surface and the C57 dye molecule resulting to maximum adsorption of dye hence the optimum pH is 6 , as shown in figure 4 below.

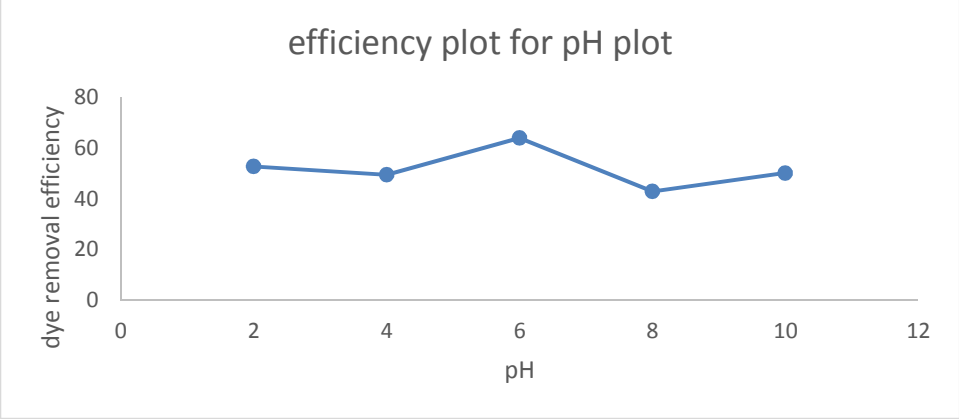


Figure 4: Influence of pH on the adsorption of C57 dye from aqueous solution.

3.6. Results of temperature variation on adsorption

The influence of temperature on C57 dye adsorption was studied within the range of temperatures 30-70^{0}c (303-343K) at the interval of 10^{0C}. It was observed that increase in the temperature increased the amount of dye adsorbed up to 60^{0}c as shown in the figure 5. This could be due to the chemical reaction occurring between the functional groups of the adsorbate/adsorbent

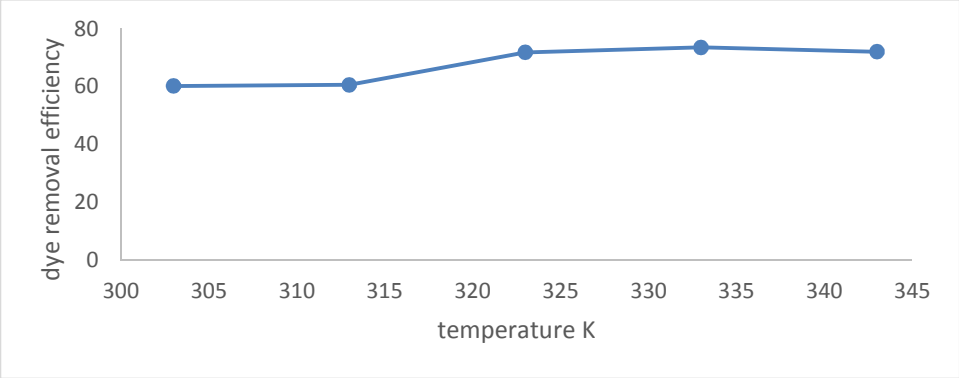


Figure 6: Influence of temperature variation on adsorption of C57 dye from aqueous solution

4.0. Isothermal studies.

The experimental output were subjected to the following isothermal investigations under the influence of initial adsorbate variations.

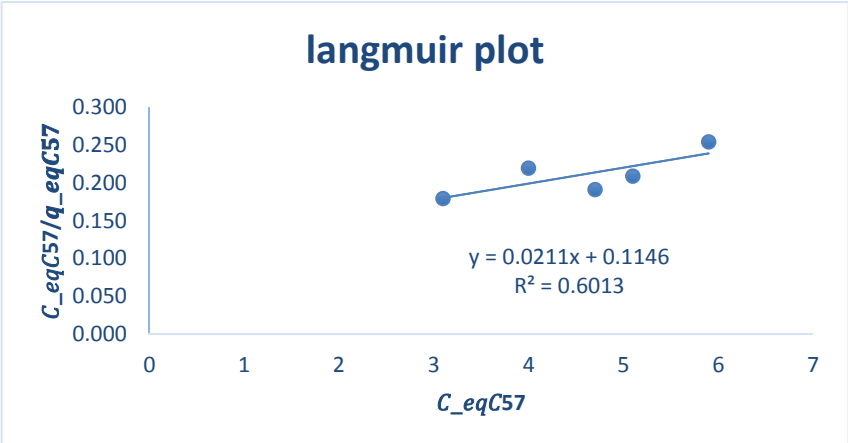
4.1. Langmuir Model

The Langmuir isotherm assumes a monorayer coverage and contains binding energy between surface and adsorbate. The mathematical expression below represents the model,

$$\frac{C_{eqC57}}{q_{eqC57}} = \frac{1}{q_{max} * ae} + \frac{C_{eqC57}}{q_{max}} \quad \text{..... eqn 3}$$

where q_{eqC57} is the amount of C57 dye removed in mg/g, C_{eqC57} is the final concentration of C57 dye at equilibrium, q_{max} and ae are Langmuir constants relating adsorption capacity and energy respectively, $K_{LC57} = q_{max} * ae$

The graph of specific adsorption (Ce/qe) against the equilibrium concentration (ce) are shown in fig 6 representing Langmuir model. The R^2 value and the SF constants as represented in table 1 and figure 6, shows that



For the linear Langmuir isotherm parameters

$$S_f = \frac{1}{1 + K_{L * Ci\ C57}} \quad \text{.....eqn 4}$$

K_{LC57} =Langmuir isotherm = 8.73
$C_{i\ C57}$ = initial dye ion concentration 10mg/I

Table 1 Langmuir constants for the adsorption process

Dye ion	q_{max} (mg^{-1})	K_L (Lg^{-1})	B	S_F	R^2
Values	47.39	8.73	0.184	1.133	0.6013

4.2. Freundlich isotherm

The Freundlich model assumes the adsorption intensity of the adsorbate on the adsorbent surface, which is represented by equation; $\boldsymbol{q_{eqC57}} = K_{fC57}(C_{eqC57})^{1/n}$ where 1/n is the adsorption intensity of C57 dye onto the adsorbent indicating the system favourability

K_F is a constant for the system relaring to the afsorption capacity (mg/g)

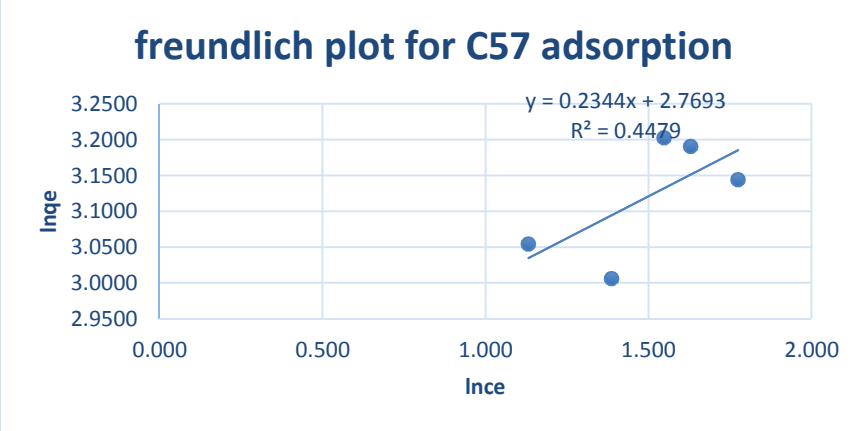


Figure 7: Freundlich isotherm describing the adsorption process.

Result from table 2 and figure 7 is an evident that Freundlich isotherm.

Linear plot poorly fitted the experimental data than Langmuir model

Table 2: Freundlich isotherm constants

Dye ion	1/n	N	K_F	R^2
Values	0.2344	4.27	15.95	0.44479

5.0. Adsorption Kinetics

5.1. Pseudo First Order model

The graph of In (qe-qt) against time gives the pseudo first order model. This gives the relationship between dye ion diffusivity, In (qe-qt) and time is linear which confirm the model, as shown in figure 8 below

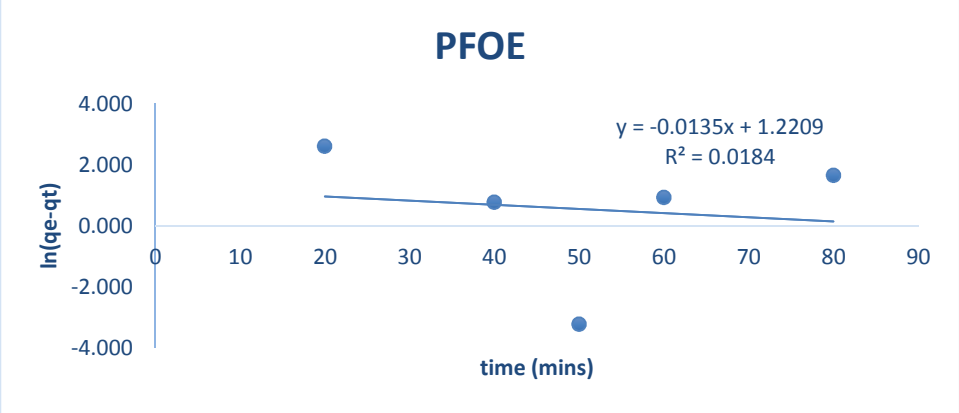


Figure 8: Pseudo first order kinetic used to study the adsorption process

Table 3: Linear form of pseudo first order model

Dye ion	K_1	$\boldsymbol{q_{eqC57}}$ (mgg^{-1})
Values	0.014	0.061

5.2 Pseudo second order Model

The second order rate constant where used to calculate the initial sorption rate given by $h_{C57}=K_2q_e^2$. A plot of t/qt vs t gives a linear relationship.

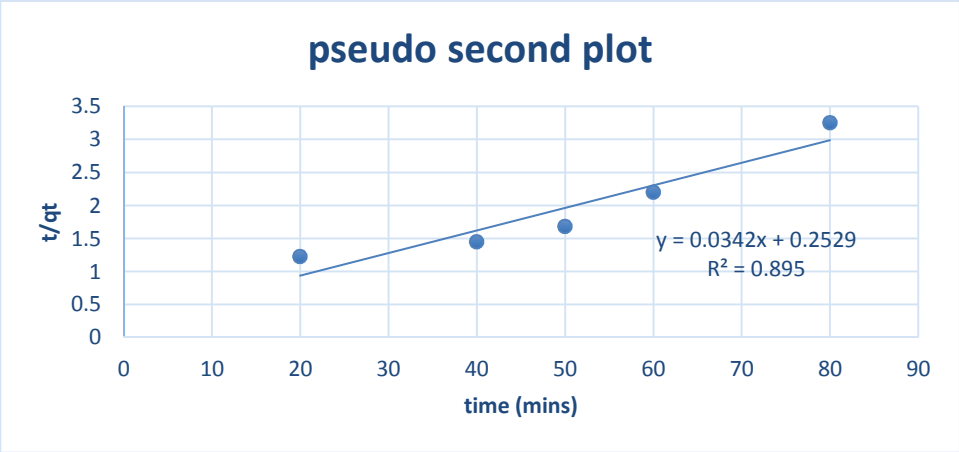


Figure 9: Pseudo-second order kinetics employed to study the adsorption process

Table 4: Linear form of pseudo second order model

Dye ion	h_{C57}	K_2	$q_{eqC57}\ exp$	q_{eqC57}cal	R^2
Values	3.95	0.0041	29.8	29.24	0.895

From the table 4 above, the PSOE is a better fit for the experimental data than the PFOE, this is evident in closeness of the exp. Qeq = 29.8 and the model predicted value f 29.24 as well as the high value of R^2 = o.895, similar observation was summited by Asiagwu et al., (2017).

6.0. CONCLUSION

The adsorption of an azo-dye (4 hydroxyl-3-carboxyphenylazophenylazo-2-nitrotoluene) onto locally available adsorbent (cashew nut shell) has been investigated under varying conditions like time, adsorbent dosage, dye concentration, pH and temperature respectively. The value of C57 dye removed increased with increase in contact time to some extent and decreased after with a longer period of shaking. The adsorbent dosage and temperature increased with an increase in adsorbent dosage (cashew nut shell) and temperature. The dye concentration shows that the amount of dye removed increased only at dye concentration of 10mg/L. it was also evident that the maximum dye adsorbed was at high acid and high basic pH. The equilibrium data was fitted into the Langmuir and Freundlich isotherm where by the Langmuir isotherm model assume uniform energies of adsorption onto the surface without transmigration of adsorbate in the plane of the surface with R^2 = 0.601. The kinetic data showed that the pseudo kinetic model of which the pseudo second order model gave a good correlation of R^2 = 0.895 for the adsorption process with predicted equilibrium concentration of C57 adsorbed of 29.24 which is a close call to experimental value of 29,76.

Cashew nut shell is therefore a low —cost locally available adsorbent which successfully adsorbed dye form wastewater.

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