International Journal of Innovation in Science and Mathematics
Volume 5, Issue 4, ISSN (Online): 2347–9051

Kinetic Model for the Removal of Amaranth Dye from Aqueous Solution using Avocado Pear Seed as Biomass

A.K. Asiagwu*, M. A. Okposo, B. O. Peretomo-Clarke and C. K. Ojebah
*Department of Chemistry Delta State University, Abraka, Nigeria.
Department of science laboratory technology Delta State Polytechnics, Ozoro, Delta State, Nigeria
email id: drasiagwu@yahoo.com *; michael.okposo@gmail.com
*Corresponding author

Date of publication (dd/mm/yyyy): 17/07/2017

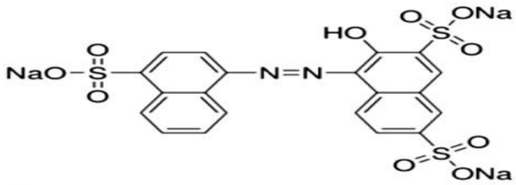
***Abstract* – This work presents the kinetic experiments carried out for the removal C57 as a basic dye from waste water using avocado pear seed waste biomass. The impacts of major variables governing the efficiency of the process such as temperature, interaction time, concentration, adsorbent dosage, and pH were checked. However the parameter impact result reflected that the quantity of the basic dye taken away increased from 0.194 – 0.212mg/g as the pear seed dosage was increased from 2000-6000 mg. In the same line the quantity of dye taken up increased from 0.198-0.202mg/g as increase interaction time changed from 20-40mins, thereafter the dye adsorbed decreased at a interaction time of 60 – 100 mins. Also, the dye adsorption capacity increased from 0.195-1.194mg/g with an increase in concentration of dye from 10mg/l – 50mg/l. the Langmuir and Freundlich models were applied to depict the adsorption efficiency. The squares of correlation coefficient (R^2) for both isotherms were 0.102 and 0.019 respectively. The basic dye abatement mechanism was analyzed using the linearized pseudo-first order and pseudo –second order kinetics having a correlation coefficient (R^2) of 0.336 and 0.999 respectively and the rate constant K_1 and K_2 were also determined. The experimental data was perfectly described by pseudo second-order adsorption kinetics.**

***Keywords* – Amaranth Dye, Dye Removal and Adsorption Kinetics.**

I. Introduction

The current challenge on environmental cleanliness has created the need to source for renewable and cost-impactive methods of waste water handing and management [1]. Most conventional techniques utilized in chemical precipitation, ion-exchange and so on are very expensive to afford by small and medium scale enterprise in Nigeria [2]. This circumstance has given rise to the intensified research on non-conventional methods that could be used in the treatment of contaminants in waste water like dyes and pigment [3].

Consequently, one of the non-conventional techniques that is being investigated is a '*mass transfer process, which involves the accumulation of substances at the interface of two phases*' [1,3]. Studies have shown that this adsorption process has excellent efficiency for the removal of organic compounds like colours (dye) in solution (3 4). It is in line of this forgoing research that this study is conducted to investigate the effectiveness in the application of avocado pear in the elimination of amaranth dye from its polluted solution.



Structure of amaranth dye

II. Materials and Methods

A. Sample Collection and Preparation of Avogadro Pear as Adsorbent

A collection of 10 fresh ripped avocado pear (persea Americana) seed were locally bought from Ubiaruku market in Ethiope East Local Government Area of Delta State. The samples were all washed and peeled to get the seed and were washed thoroughly with deionized water and dried for eight days. The dried pear seed were ground-up and screened through a sieve of 0.2 mm to eliminate the coarse particles and stored in an airtight container till the analysis.

B. Preparation of the Adsorbate (Dye-Solution)

The C57 (amaranth red) dye used for this investigation was already purified as procured from market. 20 mg of the dye was accurately weighed and dissolved in 1 liter of de-ionized water to form 20 mg/L as the stock adsorbate then the diluted to the required concentration for investigated.

C. Experimental Processes

i. Impact of Interaction time on Adsorption

2000 mg of the pear seed powder were weighed into five various flasks this followed by addition of 50 ml of the prepared amaranth dye solution. The flasks were then labeled based on interaction time of 20, 40, 60, 80 and 100 mins. The flasks were covered and shake at the different time, the suspensions were filtered with the aid of filter paper. The ultraviolet spectrometer was adopted to ascertain the amaranth dye level of concentration **[5,6]**.

ii. Influence of Pear Seed Dosage on Dye Removal

2, 3, 4, 5 and 6g of the modified avocado pear were taken into five several flasks. The dye solution of 50 ml was measured into five different flasks, these were labeled for the following dosage 2, 3, 4, 5 and 6g. The tightly covered flasks were agitated for 20 mins and the suspensions were filtered using filter paper. The dye concentration was determined with the aid of ultraviolet spectrometer [5,6].

iii. Impact of Initial C57 (Amaranth Dye Ion) Concentration

50 ml of the initial C57 (amaranth dye) concentration of 10, 20, 30, 40 and 50 mg/L were used followed by the

International Journal of Innovation in Science and Mathematics
Volume 5, Issue 4, ISSN (Online): 2347–9051

addition of accurately measured 2 ± 0.01g modified adsorbent in five several flasks and jiggled for 20minutes. After which the outcome was filtered. The residual C57 dye level was determined using an ultraviolet spectrometer.

iv. Impact of Temperature on Dye Removal

The impact of temperature on amaranth dye elimination was conducted in line with the previous studies [6,7,8]. 2000 mg of modified avocado pear was taken accurately into five various flasks and 50 ml of amaranth dye (20 mg/L) was added into the flasks. The tightly covered flasks were heated at the varying temperature of 30^0, 40^0, 50^0, 60^0 and 70^0C with the aid experimental thermostatic water bath for 1200secs each, after which each of the flasks were removed from the water bath and jiggled for another 5 minutes. The filtered dye suspensions were investigated for dye concentration using ultraviolet spectrometer.

v. Impact of Ph on Dye Removal

Modified adsorbent of (2 ± 0.01g) taken into five separate flasks, this followed by the addition of 50 ml of aqueous C57 dye. The pH of the solution were adjusted to 2.0, .4.0, 6.0, 8.0 and 10.0 by adding a solution of HCl (0.1 M) or NaOH (0.1 M) and the pH readings were taken using pH meter. The flasks were then tightly covered and jiggled for another 20 minutes. The outcome were filtered via filter paper. The dye contents were measured with the aid of ultraviolet spectrometer.

III. Data Evaluation

A. Determination of Amaranth Dye Adsorption Potential

The quantity of amaranth dye eliminated by the Avogadro pear seed during the experiments was evaluated using the shown below.

$$q_e = \frac{(Ci - Cf)V}{M}$$

Where:

q_{eq} = amount of basic dye uptake onto the pear seed waste in (mg/g)

C_f = amount of basic dye left in adsorbate in (mg/L) at equilibrium

Ci = amount of basic dye in the adsorbate (mg/L) prior to the adsorption process

V = volume of C57 dye solution used (ml)

M = mass of pear seed used (g).

B. Kinetic Assessment of Experiment Data

The data obtained from the experiment was pinned to pseudo-first order and pseudo-second order model so as to determine the adsorption part way and the adsorption type.

The linearized pseudo-first order model is shown below.

$$In\ (q_e\text{-}q_t) = In\ q_e - Kt$$

Where:

qe = amount of basic dye uptake onto the pear seed waste in (mg/g)

q_t = quantity of basic dye abated at time t (mglg)

K_1 = Equilibrium constant

The linear plot of in (q_e - q_t) versus t confirms the model. The linear form of pseudo-second order model which has been also described previously (14, 12) is given as:

$$\frac{1}{q_t} = \frac{1}{h_o} + \frac{t}{q_t}$$

Where:

q_t = quantity of amaranth dye present on the adsorbent surface (mg/g) at any time t.

q_{eq} = The amount of dye ions adsorbed at equilibrium (mg/g) [12]

h_o = The initial amaranth adsorption capacity (mg/g min) [12]

The initial adsorption rate, h_o is defined as:

$$h_o = k_2 q_e^2$$

Where

K_2 is the pseudo- second order rate constant (g/mg min) [13].

IV. Results and Discussion

A. Impacts of Interaction time on Dye Adsorption

The result obtained from the experiment for the removal of dye is shown in Figure 2 below. As interaction time increased from 20-40 minutes, the contents of dye in aqueous solution removed by the biomass was observed to be high until a interaction time of 60 minutes was reached. After which the dye removed dropped and became partially constant. Also at a interaction time of 80 minutes, the amount of dye removed was increased until a interaction time of 100 minutes was also reached, after which the dye removed dropped again. The data collected on dye removal by biomass was relatively high at 20-40 minutes and the biomass was able to remove about 80% of the dye solution.

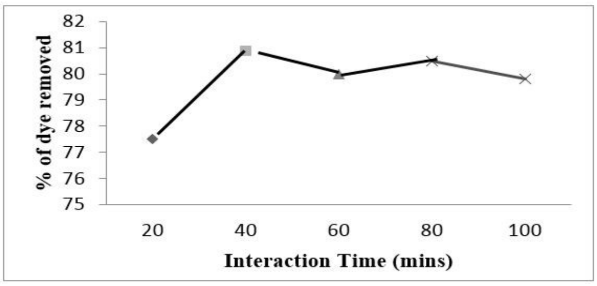


Fig. 2. Impact of Interaction Time on the adsorption of the dye by avocado pear seed adsorbent

B. Impact of Adsorbent Dosage on Dye Adsorption

The impact adsorbent dosage on dye removal is visualized in figure 3. The quantity of dye adsorbed exponentially increased from 0.194 mg/g to 0.212 mg/g with an increase in adsorbent surface area.

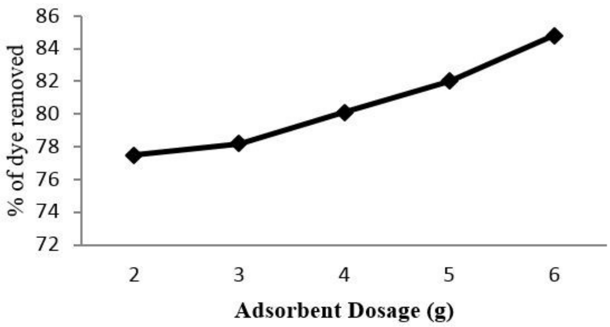


Fig 3. Impacts of adsorbent dosage on the adsorption of the dye by avocado pear seed

However, this increment could be connected to certain reasons according [10, 13,] the increase in dye removal is certain with increasing adsorbent dosage as the binding sites for adsorption increase. Some other workers have made similar report [6,7,8,910,13].

C. Impact of Concentration on Dye Removal

The result of amaranth red dye in aqueous solution adsorbed on avocado pear seed waste biomass was observed as shown in figure 4, that the percentage removal of the dye increased with increase in the concentration of dye solution from 0.195-1.194 mg/g with an increase in the concentration of dye from 10-50 mg/l having maximum adsorption of 1.194 mg/g at 50 mg/l.[13]

Nevertheless, the amaranth dye removal efficiency was found to increase with increase in initial dye concentration as shown in figure 4. This could be linked to the fact that as the concentration is increasing, more dye is available for adsorption on the adsorbent. This may be due to the impact of concentration gradient which is main factor governing the adsorption process [9,10,11,13].

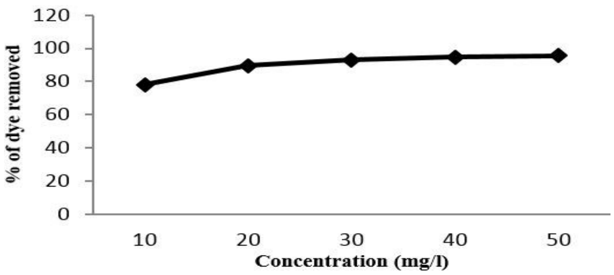


Fig. 4. Impact of concentration on the adsorption of the dye by avocado pear seed

D. Impact of Temperature on Dye Adsorption

The impact of temperature in the adsorption of dye is represented in figure5, in which the content of dye adsorbed decreases from 0.198-0.180 mg/g with increased in temperature from 30-70 ^{0}C.

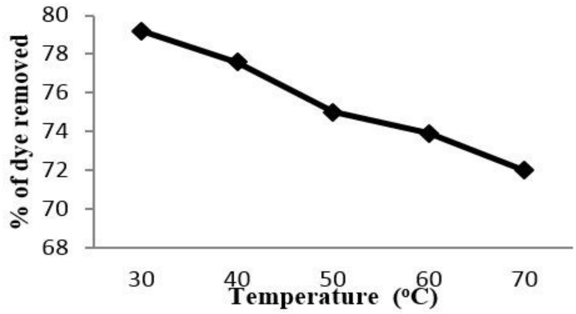


Fig 5. Impact of temperature on the adsorption of the dye by avocado pear seed

Figure 5 reveals percentage removal adsorption trend as a function of varying temperature. The result indicates that the adsorption of adsorbate pollutants on avocado pear seed decreased as temperature increases.

E. Impact of Ph on C57 Dye Adsorption

The pH of a solution is a crucial factor that affects the removal of the adsorbate[13]. The chemical characteristics of both adsorbate and adsorbent vary with pH[13]. Most plant materials are made up of complex organic residues such as lignin and cellulose that contain several types of polar functional groups [9,10,13]. These groups can be involved in chemical bonding and could be responsible for the cation-exchange characteristics of most biomaterials[13].

The pH dependence data of adsorption of the dye being investigated is shown in figure 6, it was observed that as the pH of pear seed solution changed from 2.0 to 10.0, the amount of dye adsorbed decreased from 0.227-0.188 mg/g.

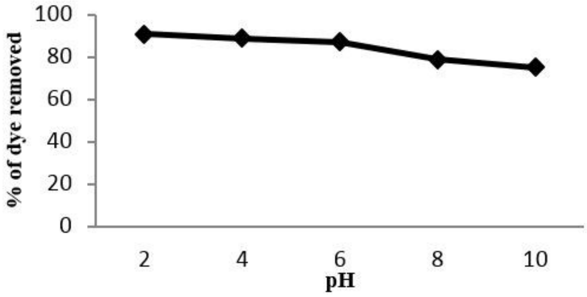


Fig. 6. Impact of pH on the adsorption of the dye by avocado pear seed

The result show in figure 6 indicates that the uptake of C57 dye on avocado pear seed increases in acid medium at pH 2. A close observation to this results was reported for colour removal [9,10]. The surface of the carbon becomes highly protonated under acidic conditions that influences the adsorption of dye in the anionic form. The increase in pH value caused a decrease in protonation of the surface, which led to a decrease in the net positive surface potential of sorbent.

V. Data Evaluation

A. Langmuir Isotherm

The graph of specific sorption (*Ce/qe*) against the equilibrium concentration (Ce) for amaranth red dye in aqueous solution is shown in fig 7 and the linear isotherm parameters shown in table 1.

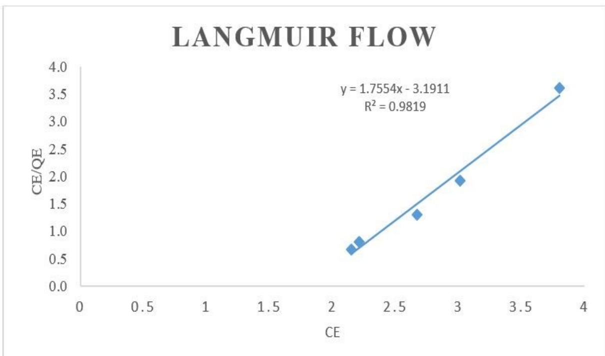


Fig 7. Langmuir equilibrium isotherm

The R^2 value indicates that the Langmuir isotherm displayed a good fit of the adsorption process. The favorability of the process were tested using the essential properties of the Langmuir isotherm model expressed in terms of a dimensionless constant called separation factor, S_F is defined by the following relationship.

$$S_f = \frac{1}{1+K_l C_o}$$

Where:
K_L = Langmuir isotherm constant
Co = initial dye ion concentration of 10 mg/l

The parameters indicate the shape of the isotherm as follows:
$S_f > 1$ Unfavourable isotherm
$S_f = 1$ Linear isotherm
$S_f = 0$ Irreversible isotherm
$0 < S_f < 1$ Favourable isotherm Source; Asiagwu[12]

The separation parameters for the dye is less than unity indicating that avocado seed waste biomass is a brilliant adsorbent for dye solution [12]. The separation parameters and other Langmuir isotherm parameters are shown in table 1 below:

Table 1. Linear Langmuir isotherm parameters

Dye solution	q_{max}(mg/g)	K_L (Lg^{-1})	R^2	S_f
Amaranth red	0.57	0.55	0.102	0.154

B. Freundlich Isotherm

The Freundlich isotherm was adopted to evaluate the adsorption intensity of the adsorbate on the adsorbent surface[13]. The linear Freundlich isotherms for the adsorption of the dye ion onto avocado are displayed in figure 8. The flow reveals that Freundlich isotherm is better model for the adsorption process under consideration compared to Langmuir [113, 14]. Table 2 shows the linear Freundlich sorption isotherm constant and the coefficient of determination (R^2).

The linear form of the Freundlich isotherm appears to produce a smart description for the adsorption process under consideration based on the value of R^2.

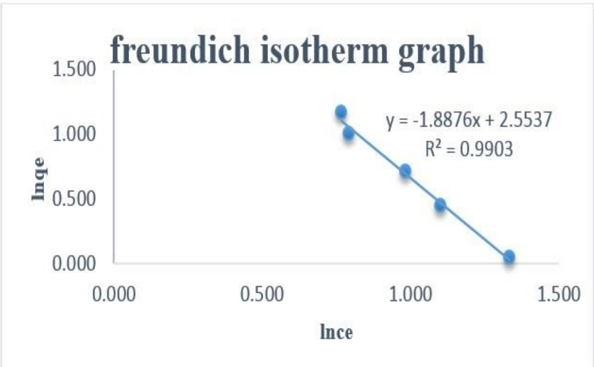


Fig. 4.8. Freundlich Equilibrium Isotherm

Table 2: Freundlich isotherm constant

Dye ion	1/n	N	K_f	R^2
Amaranth red	1.888	0.53	12.86	0.9903

VI. Adsorption Kinetics

A. Pseudo-First Order Model

The kinetic of adsorption is one of the most important factor in predicting the rate at which adsorption takes place for a given system[12].

Graph (q_e-q_t) against t as shown in figure 8 gave the pseudo-first order kinetics. From the flow evident, it is observed that the relationship between dye ion diffusivity, in (q_e-q_t) and time (t) is linear Which attests the model[14]. The value of coefficient of determination R^2 is shown and the value indicates that pseudo first order model provides a good description for the adsorption of amaranth red dye on avocado pear seed waste biomass.

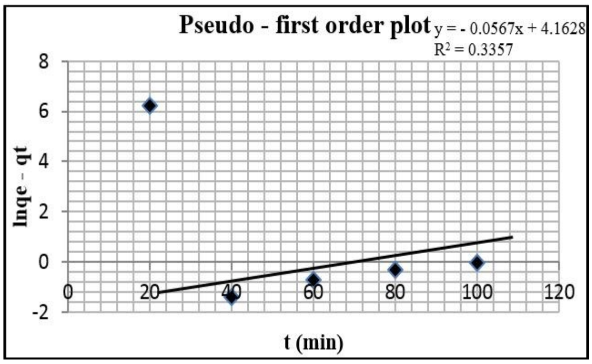


Fig. 9. Pseudo - first order plot

Table 3. Values of pseudo-first order kinetic parameter

Dye ion	K	Qe(mg/g)	R^2
Amaranth red	0.057	0.016	0.336

However, in confirming the linearity of the pseudo-first order the same trend has been observed for the adsorption of basic dye on strongly chelating polymer[11].

B. Pseudo-Second Order Model

A plot of t/qt against t is presented in figure 10 which gave the pseudo-second order kinetics. From the plot, it is observed that the relationship between t/qt and t is linear which verify the model[14]. Also, h_o, q_{eq}, k_2 and R^2 are shown in table 4, based on the value of coefficient of determination R^2. It is evident that pseudo-second order model provide a better description for the adsorption process than pseudo-first order model. This observation has been reported for the adsorption of dyes from coloured textiles wastewater by orange peels adsorbent [1,12,14].

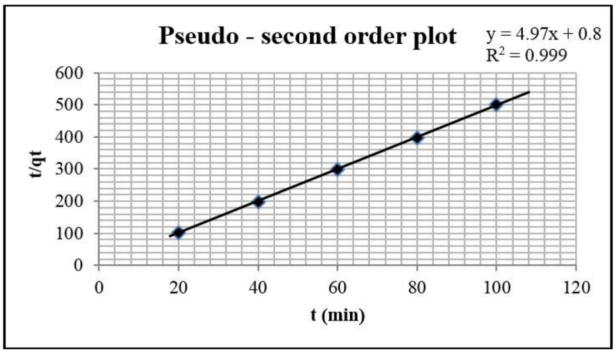


Fig. 4.10. Pseudo -second order plot

Table 4. values of pseudo order kinetic parameters

Dye ion	Ho (mg/g/min)	K_2 (mg/g/min)	Qe (mg/g)	R^2
Amaranth red	1.250	30.940	0.201	0.999

VII. Conclusion

The kinetics of sorption, and isotherm of azo dye (amaranth red) on avocado pear seed (persea Americana) has been studied. It was found out that as time increased the amount of dye adsorbed also increased, but later reduces at as interaction time of 100minutes. The adsorption capacity of the adsorbent and the sorption process could also be seen as a reaction where by the azo dye distribute itself between the aqueous solution and the adsorbent. The kinetic studies proved that the second order kinetic was the best applicable model.

The Langmuir and Freundlich models were also revealed that avocado pear seed is suitable to remove amaranth dye from waste water or aqueous solution. Thus, the biomass is a good adsorbent for the removal of the dye in aqueous solution.

Reference

[1] Arami, M.; Limaee, N.Y.; Mahmood N.M.; Tabrizi, N.S. (2005). “Removal of dyes from coloured textile wastewater by orange peels adsorption. Equilibrium and kinetic studies. *Journal of colloids interface science.* 288, 371-376.

[2] Adamson, A.W. Physical chemistry of surface. Wiley New York. 2001.

[3] Che, A.Y. Adsorption studies of dyes using clay-based and activated carbon adsorbent. *Malaysia journal of analytical science.* 2004. 1 (17), 142-168.

[4] Chiang, H.L.; Lin K.H.; Chen, S.Y.; Choa, C.G.; Pan, S.D. Dye adsorption on biosolid adsorbents. Province, Rhode Island, USA. 2004. 11-16.

[5] Gardea-Torresaday, J.L.; Tang, L.; Salvador, J.M. Methyl red adsorption by esterified and unesterified factors of sphagnum peat moss and it’s different humic substances. *J. hazard matter.* 1996. 4, 191-206.

[6] Mishra, S.; Prakash, D.J.; Ramakrishma, G. Characterization and utilization of malua oil cake. A new adsorbent for removal of Congo red dye from aqueous phase. *Electronic journal of environmental, agricultural and food chemistry*, 2009. 8 (6), 425-436.

[7] Arslanogwu, F.N.; Kar, F.; Arisan, M.. Adsorption of dark coloured compounds from peach pulp by using powdered activated carbon. *Journal of food engineering.* 2005. 71, 156-163.

[8] Horsfall, M.; Abia, A.A.; Spiff, A.I. Removal of Cu (ii) and Zn (ii) ions from wastewater by cassava (manihot esculenta) waste biomass. *African journal of biotechnology.* 2003. 2 (10), 360-364.

[9] Ho, Y.S.; Chiu, W.T.; Chiang, C.W. (2005). Regression analysis for the sorption isotherms of basic dye on sugarcane dust, *Bioresource technol*. 96(11), 1285-1291.

[10] Ho, Y.S.; Chiang, T.H.; Hsteh, Y.M. Removal of basic dye from aqueous solution using tree fern as a biosorbent process, *Biochem*. 2006. 40 (1), 119-124.

[11] Gunmany, A. Adsorption of basic dye on strongly chelating polymer: Batch kinetic studies. *Iranian polymer journal.* 2002. 11(4), 237-244.

[12] Asiagwu, A.K. (2012). Sorption model for the removal of 1-Naphthy Amine Dye from aqueous solution using orange peel as Biomass. Journal of international Environ metal application and sciences,7(4); 700-708.

[13] Owanah, H., Izinyon, O.C and Asiagwu., A.K. (2012). Sorption model ans kinetic assessment of Ultramarine blue removal using modified cassava peels. Journal of civil and environmental engineering. 2;121. Dox;10.4172/2165-784x.1000121.

[14] Asiagwu, A.K. (2012). Sorption kinetics of Pb (II) and Cd(II) ions via biomass surface of plantain peel waste. IJRRAS, 13(2); 626-635.