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KINETIC MODEL FOR THE REMOVAL OF MALACHITE GREEN (DYE) FROM AQUEOUS SOLUTIONS USING PALM KERNEL SHELL

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ABSTRACT

Malachite dye is among the millions of dyes used in every aspect of our daily life. The adsorption kinetic of the pollutant (dye) from adsobate using palm kernel shell (Elaeis Guineasis) as the biomass was studied. From the several experimental parameters measured, the optimum adsorption occurred at 20 minutes giving 92.3%. Adsorption also decreased from 92.49% to 87.9% with increase in absorbent dosage giving the optimum dosage of 2g. Also increase in temperature decreased the adsorption from 95.6% to 92.7% having it optimum temperature to be 30^{o}C. Increase in dye ion concentration from 10-50mg/L also increased adsorption from 79.3% to 93.0%. There was a decrease in the percentage of dye removed for all the parameters investigated except for dye ion concentration. The value of S_F for Langmuir model is 0.232 and R^2 value is 0.6326 while for Freundlich model, the value of 1/n is 2.8092 and R^2 value is 0.9135 which indicate that Langmuir and Freundlich model are both good isotherm models because they have a S_F value of < 1 and 1/n value > 1. Pseudo second order model best fit the experimental data than pseudo first order having R^2 values of 1 and 0.5613 respectively. This shows that palm kernel shell can be used as an effective biomass for removing waste water from dye.

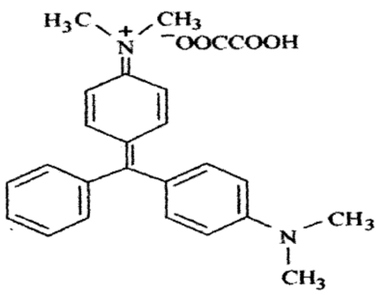
KEYWORDS: Malachite dye, removal, palm kernel shell and absorption kinetics.

INTRODUCTION

Pollution arising from industrial effluent has become a major concern owing to their toxicity and potential threat to human life and the environment (Thangamani *et al.*, 2007). Many industries uses dye materials to colour their products. However, the residual and unused dyes are discharged into the ecosystem, most especially the aquatic environment. Colour is one of the clearest indicators of water pollution (Hemlata *et al.*, 2007). Coloured substances are some of the important water pollutants that are generally contained in the effluents of the paper, rubber, textile, plastics, leather, pharmaceutical and cosmetic industries. These coloured substances are aesthetically displeasing and also inhibits sun light into the rivers and streams reducing photosynthetic reaction (Amina *et al., 2008).* The coloured substances are harmful to humans, hence their removal from industrial wastewater is of increasing importance.

The available technology for the removal of colour from industrial effluents includes coagulation, oxidation and adsorption, bio-treatment and ion exchange. Among these treatment options, adsorption technique have better potential in the removal of colour from industrial effluents (Asiagwu et al., 2012). Consequently, the application of biomasses like agricultural waste in the treatment of dye polluted aqueous bodies has been considered to be cheap and effective alternative for dye removal.

It is on this background, that this work was conducted to determine the optimum conditions for the removal of malachite green from industrial waste water using palm kernel shell as absorbent.



Structure of Malachite green Dye.

MATERIALS AND METHODS

Collection of sample and dye preparation
A basket of palm kernel was bought from a local market in delta state. It was washed and boiled to appropriate level to remove the pulp from the kernel. After removing the pulp, the palm kernel was cracked with the aid of a stone so as to be able to separate the palm kernel shell from the kernel fruit (endocarp). The palm kernel shell obtained was dried under the sun for seven days, before it was ground to smooth fine particle size. The ground samples were then sieved and preserved in air-light condition pending further use.

Preparation of the adsorbate
The adsorbate applied in this research was prepared by dissolving a known pure dye called (malachite green) gotten from commercial source in distilled water to the need experimental concentration for each of the parameter being conducted. For the case of contact time, absorbent dosage, temperature and pH, 0.20g of dye stock was weighed into 100ml of volumetric flask and made up to mark. 50ml was taken from each of them for their respective analysis. But for dye ion concentration; 0.1g, 0.2g, 0.3g, 0.4g and 0.5g was measured and made up to mark in a 100ml volumetric flask and 50ml was taken from each of them to be used for the analysis (Asiagwu *et al*., 2012).

Impact of palm kernel shell Dosage on Dye Removal
The impact of palm kernel shell Dosage on the adsorption of dye was done in line with previous work of (Asiagwu *et al*., 2012). 2,3,4,5 and 6g of the adsorbent were collected into 5 different flasks. 20mg/l of the adsorbate was prepared then 50ml of it was taken into the separate solutions. The flasks were labelled 2, 3, 4, 5 and 6g for dosage difference. The tightly covered flasks were stirred up for 20 minutes after which the suspensions were separated with the aid of Whitman's filter paper before it was centrifuged. The quantity of the dye removal were determined using UV spectrophotometer at 618nm wavelength.

Temperature Effect on Dye Adsorption
The place of temperature on dye adsorption was investigated according to the method as described by Mishra *et al.*, (2009) and Asiagwu, (2012a). The adsorbent of 2g was measured into 5 flasks separately. 20mg/l of the adsorbate was prepared whose 50ml was measured into the 5 flasks which were labeled based on different temperature values of 30, 40, 50, 60 and 70^{0}C. The flask respectively were then covered at their appropriate temperature were controlled with aid of thermostatic water bath at 20 minutes each. By the end, each of the flasks were removed from the bath stirred up for another 5 minutes. The suspensions were filtered with Whitman's filter paper and centrifuge. The malachite green level was determined using the UV spectrophotometer.

Dye Ion Concentration effects on Adsorption
Various standard malachite green solutions of 10, 20, 30, 40 and 50mg/l were prepared and 50cm^3 from each of the solution was added to the 2g of palm kernel shell in 5 different flasks and stirred up for 20 minutes. By the end of the time, the suspensions were filtered using Whitman's filter paper and centrifuged then the residue was analyzed using the UV spectrophotometer.

Degree of Dye Removed determination
The quantity of malachite green removed by the palm kernel shell during the batch process were evaluated using a mass balance equation expressed as shown below: (Asiagwu *et al.*, 2012, Asiagwu, 2012a).

$$Q_a = (C_b - C_c) * \frac{V_d}{M_e} \qquad \text{eqn i}$$

Where

Q_a = malachite green Dye concentration on the palm kernel shell at equilibrium (mg/g)

C_b = Initial malachite green dye concentration in solution (mg/l)

C_c = malachite Dye concentration in solution at equilibrium (mg/l)

V_d = Volume of malachite green dye solution used (ml)

M_e = Mass of the palm kernel shell used (g).

Kinetic analysis of Experimental Data
In order to know the mechanism of adsorption, the equations of pseudo-first order model and pseudo-second order model were used as in Asiagwu, (2012b):

The linear form of pseudo-first order model equation as depicted in Asiagwu, (2012a) is given below in eqn ii;

$$\ln(Q_{eq} - Q_t) = ln Q_{eq} - K_c t \qquad \text{eqn ii}$$

Where

Q_{eq} = Mass of malachite green equilibrium (mg/g)

Q_t = Mass of malachite green dye adsorbed at time t (mg/g)

K_c = Equilibrium constant

t = Time (minutes)

A linear flow of In (Q_{eq} – Q_t) against t reflects the model.

The linear form of pseudo –second order model equation as in Asiagwu, (2012) is given below in eqn iii:

$$\frac{t}{Q_a} = \frac{1}{H_i} + \frac{t}{Q_{eb}} \qquad \text{eqn iii}$$

Where

Q_a = Amount of malachite green adsorbed at time t (mg/g)

Q_{eb} = The initial amount of pollutant adsorbed at equilibrium (mg/g)

t = Time (minutes)

H_i = Initial adsorption capacity (mg/g)

The initial adsorption rate "H_i" is further defined by the equation

$H_i = K_2 Q_e^2$ eqn iv

Where K_2 = pseudo-second order rate constant (mg/g)

A linear flow of t/Q_a Vs t attest the model

RESULTS AND DISCUSSION

Contact Time effect on Dye Removal

Effects of contact time on the removed malachite green using palm kernel shell as waste biomass was studied between the time intervals of 20 to 100 min. The results is clearly shown in figure 1.

The amount of dye adsorbed decreased as the time increases from 20-100 minutes together with the percentage of dye removed in which maximum percentage of (92.3) was observed at the beginning of the experiment. This may be linked to the fact that as the dye solution is being stirred up at longer time, the palm kernel shell was unable to absorb more of the dye leading to decrease in the rate of adsorption.

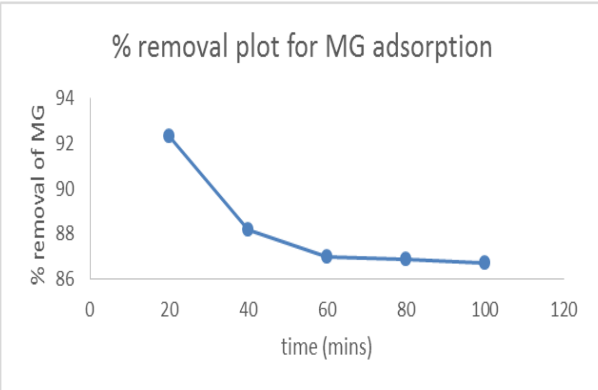


Fig. 1: Contact time on dye ion removal plot.

Adsorbent dosage effects on dye removal

Adsorbent dosage effect on the adsorption of malachite green using palm kernel shell as biomass was studies in which the amount of palm kernel shell was varied from 2 to 6g as shown below in figure 2. The study further shown that the efficiency of dye removal decreased from 92.49% to 87.9% as the adsorbent dosage was increased from 2 to 6g.

From the result obtained, it is evident that the amount of dye adsorbed decreases as the adsorbent dosage increases. It was also obtained from the results that the highest percentage of dye adsorbed was obtained at the adsorbent dosage of 2g. However similar observation has been made by some workers (Asiagwu, 2012a).

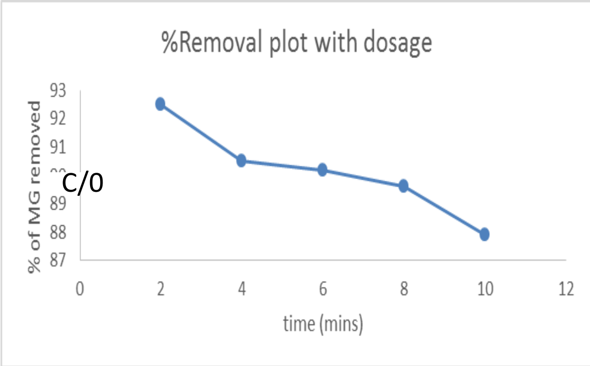


Fig. 2: A plot of adsorbent dosage on dye ion removal.

Effect of Temperature on the Removal of Malachite Dye

The dependence of temperature on the adsorption of malachite green using palm kernel shell as waste biomass was investigated within the temperature range of 30 -70^{0}C at intervals of 600 seconds. The results showed that the amount of dye adsorbed decreased with increase in temperature from 30 to 70^{0}C as shown in figure 3. It was also observed that the amount of dye adsorbed decreased as temperature is increased as well as the percentage of dye removed. It is also observed that the maximum percentage of dye removed (95.6%) was obtained at the minimum temperature of 30^{0}C.

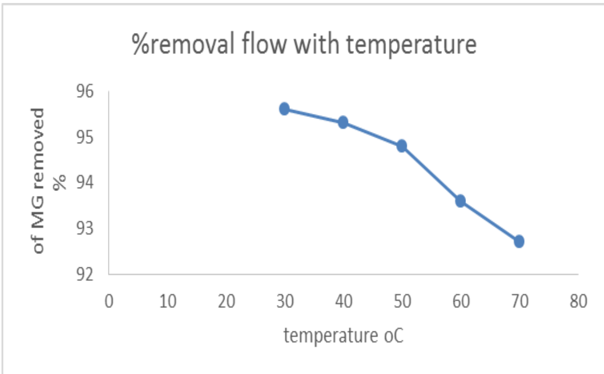


Fig. 3: A flow of temperature on the percentage removal of dye ion removal.

The place of Dye Ion Concentration on Adsorption

The dependence of dye ion concentration on the adsorption of malachite green using palm kernel shell is represented in figure 4 below.

From the results obtained the amount of dye adsorbed increased from 0.199-1.157 with increase in the dye ion concentration from 10-50. It was also obtained that the percentage of dye removed (93%) was obtained at the maximum concentration of 50 mg/g. This may be attributed to the fact that as the dye concentration is increasing, more of the dye will be available for adsorption by the adsorbent (Palm Kernel shell). This may also be linked to the effect of concentration gradient which controls most adsorption process (Mishra *et al.*, 2009, Asiagwu, 2012b).

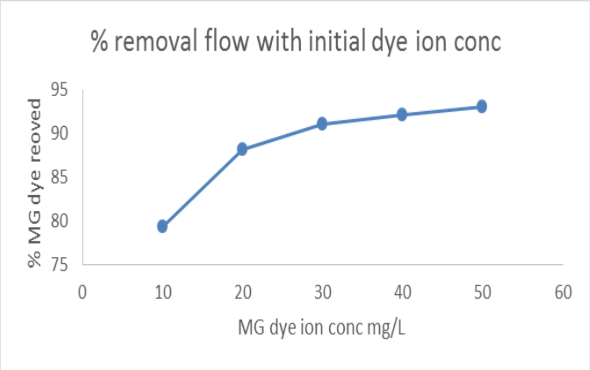


Fig. 4: A plot of dye ion concentration on adsorption.

Assessment of experimental data using Langmuir Isotherm

The Langmuir isotherm was used to estimate the maximum adsorption capacity conforming to complete monolayer on the palm kernel shell surface. The plots of (C_e/Q_e) Vs (C_e) as shown in figure 5 and the Langmuir isotherm parameters "Q_{max}" and the coefficient of determinations K_l are presented in the below in table 1.

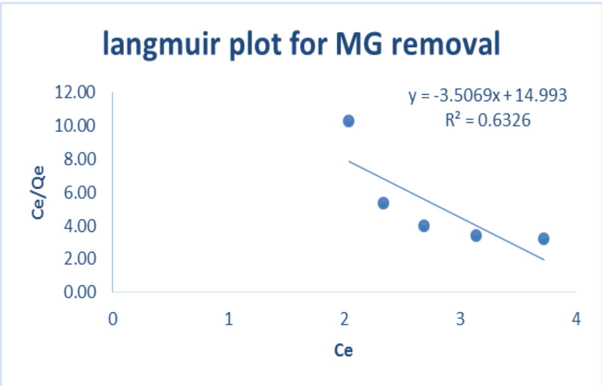


Fig. 5: Langmuir Equilibrium.

The value of the R^2 obtained suggests that the Langmuir isotherm provides a good fit for the adsorption. The favorability of adsorption of adsorbate on the palm kernel shell waste was concretized using the essential constants of the Langmuir equation defined in terms of a dimension constant known as the separation factor, S_F by Kumar et al., (2005) and Asiagwu, (2012b). The separation factor (S_F) is given as.

$$S_F = \frac{1}{1 \pm K_1 C_{iMG}}$$

Where

K_L = Langmuir isotherm constant

C_{iMG} = Initial MG dye ion concentration of 20mg/L

The parameters indicate the shape of the isotherm as follows

$S_F > 1$ = Unfavorable isotherm

S_F = 1 Linear isotherm

S_F = 0 irreversible isotherm

$0 < S_F < 1$ = Favorable isotherm

The separation factor for the dye was less than 1 indicating that palm kernel shell waste biomass appears to be an excellent adsorbent for malachite dye. The separation parameters and other Langmuir isotherm parameters are shown in table 1.

Table 1: Langmuir Equilibrium Isotherm Parameters.

Dye Ion	Q_m (mg^{-1})	K_L (Lg^{-1})	R^2	S_F
MG	0.285	0.0667	0.6326	0.232

Freundlich Model

The Freundlich model was invoked to measure the adsorption intensity of malachite green dye on the adsorbent system. Linearity of the plots of In Q_e against In C_e shows that the adsorption of malachite green dye assumed the Freundlich adsorption isotherm more than that of Langmuir as shown table 3 and figure 3 which shows the linear Freundlich sorption isotherm constant and (R^2 = 0.9135).

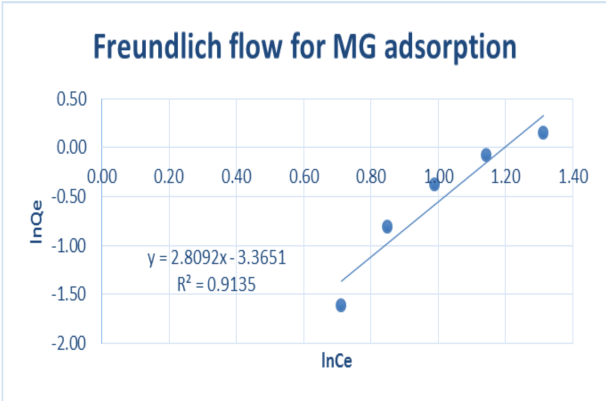


Fig. 6: Freundlich Equilibrium.

Table 4: Freundlich Equilibrium Isotherm Parameters.

Freundlich constants	K_{maxf} mg/g	1/n	N	R^2
Values	28.94	2.8092	0.356	0.9135

From table 4 above the value of 1/n is larger than 1 (1/n>1) which is a pointer of favourable adsorption, hence it is a confirmation of Langmuir favorability observation (Kumar et al., 2016).

Adsorption Kinetics

The kinetics of adsorption is one of the most important factor in evaluating the rate at which adsorption takes place (Asiagwu, 2012a). It can be provided as pseudo-first order and pseudo-second order respectively.

Pseudo - First Order Model

A graph of In (Q_e - Q_t) Vs *t* is shown in figure 7 expresses the pseudo first order equation. From the flow, it is true that the relationship between the malachite green removal and time (t/mins) is linear which confirms the model. In table 4 the coefficient of determination R^2

is shown and it indicates that pseudo first order model appear to be a good equation for the adsorption of palm kernel shell biomass.

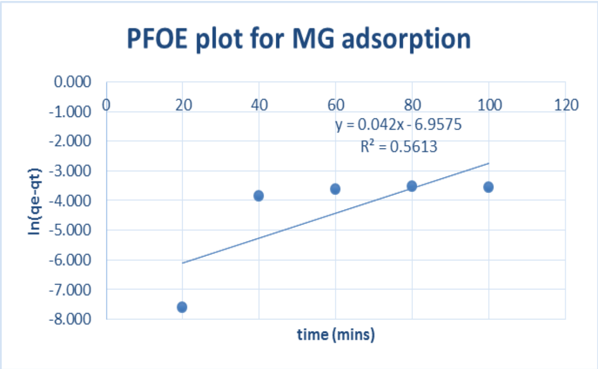


Fig. 7: Pseudo – first order graph.

Table 5: Values of Pseudo first order kinetic parameter.

PFOE parameters	K_t	Q_{eq} (mgg^{-1})	R^2
	0.042	0.0009515	0.5613

Pseudo – Second Order Model (PSOM)

A plot of t/Q_t against *t* as shown in figure 8 describes the pseudo second order kinetics (Asiagwu, 2012a). From the flow, it was observed that the interaction between t/Q_t and *t* is linear which confirms the PSOM. the initial adsorption rate "Hi", the equilibrium adsorption capacity, pseudo second order rate constant, and the coefficient of determination are represented in table 6. Based on the coefficient of determination $R^2 = 1$, it is evident that pseudo second order model provides a better description for the adsorption process better than pseudo – first order model. Similar observation were made by Che, (2004) and Asiagwu, 2012a for the removal of basic blue, and direct red types using clay based and activated carbon adsorbents.

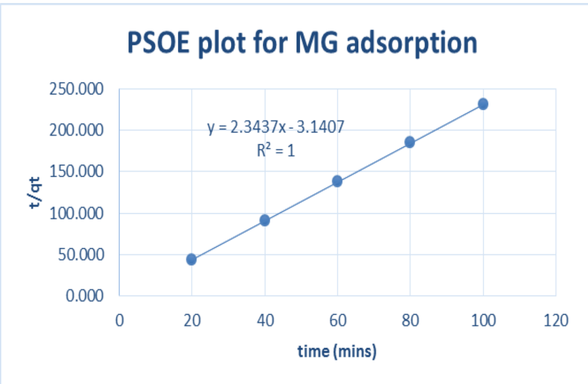


Fig. 8: Pseudo – second order plot.

Table 6: Values of pseudo –first order kinetic parameter.

PSOE parameters	H_i	K_2	Q_{eq} (mmg)	R^2
	-0.3184	-1.7475	0.4268	1

CONCLUSION

The dependence of adsorbent dosage, temperature, contact time and dye ion concentration on the removal of malachite dye from aqueous solution using palm kernel shell has been investigated. The study revealed that increase in temperature contact time, adsorbent dosage increased the rate removal of malachite green from aqueous solution. Similarly, the variation in these physical properties lead to increase in the percentage of dye removal.

The Langmuir isotherm revealed that adsorption of malachite green using palm kernel shell waste biomass was favourable as confirmed by Freundlich model. This implies that palm kernel shell could be used to remove malachite green dye from wastewater. The pseudo – second order model provided the more appropriate description of malachite green dye removed from wastewater, using palm kernel shell. Summarily, the data obtained from the experimental run showed that palm kernel waste biomass was successful as adsorbent for the removal of malachite green from waste water and may serve as an alternative adsorbent to other conventional techniques. Hence, Palm kernel shell is not only inexpensive and readily available but it also has the potential for dye removal from wastewater.

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