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Equilibrium, Kinetics and Isothem Studies onthe Adsorption of Eosin Red and Malachite Green Using Activated Carbon from *Huracrepitans* Seed Shells

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Abstract: The activated carbon produced from *Hura crepitans* seed shell was effectively utilized as adsorbent for the removal of eosin red and malachite green from waste water. Thus the adsorption of eosin red, a typical acid dye and malachite green, a typical basic dye from synthetic waste water using *Hura crepitans* seed shell activated carbon was studied. The effect of adsorbent dosage, initial dye concentration and contact time was evaluated. The residual eosin red and malachite green concentration in solutions was determined using UV-visible spectrophotometer. All batch experiments were carried out at room temperature (± 2°C) using mechanical shaker that operates at 200 rpm. The results showed that the efficiency of dye adsorption increased with increase in amount of adsorbent, contact time, and with decrease in concentration of dye. The q_{max} for the adsorption of Malachite green was higher than that of Eosin red showing that MG were removed from waste water easily than ER. The results also showed that the adsorption of the two dyes follow pseudo-first order kinetics. Adsorption isotherm obtained for eosin red follows the Freundlichmodel while the adsorption isotherm obtained for Malachite green followed the Langmuir model.

Keywords: Adsorption, Eosin Red, Malachite Green, *Hura crepitans*, Equilibrium, Isotherms and Kinetics

1. Introduction

The discharge of dyes into water bodies and land surfaces has been one of the majorsources of water and land pollution. This discharge leads to the dissolution of contaminants into the water body this causes environmental pollution as some of the dyes and their metabolites are either toxic, mutagenic and carcinogenic and hence pose some potential health problem to human and aquatic animals. It also reduces the aesthetic value of the water. This is one of the disadvantages of dyes in water bodies [1]. There are number of ways to solve this problem of environmental pollution. These include coagulation, foam floatation, filtration, and ion exchange, aerobic and anaerobic treatment, advanced oxidation processes, solvent extraction, electrolysis, microbial reduction, activated sludge and adsorption. However, most of them are too expensive for most developing countries like Nigeria and their use is therefore restricted because of cost factors overriding the importance of pollution control [2].

Among all the above techniques, adsorption is now strongly favoured over the others because of its simplicity, cost effectiveness, ease of operation and good efficiency in the physical treatment of water. Conventional adsorbents are activated carbon, zeolites, and silica gels [3]. However, most of the commercially available adsorbents are expensive and are thus not utilized by the industries [4].

There are several examples of low cost adsorbents prepared from locally available raw-materials mainly from plant origin. An adsorbent such as activated carbon has been widely investigated for the adsorption of dyes. But drawback such as its high cost, limits its large scale application. There are extensive researches towards finding inexpensive and

effective alternatives to commercial activated carbon. Hence researchers have investigated low cost materials for the preparation of activated carbon. The determination of adsorption capacity is necessary and isprequisite for selecting adsorbent [5].

The aim and objectives of this present work is to use activated carbon prepared by Nsi *et al* [6] in the removal of eosin red (a typical acid dye) and malachite green, (a typical basic dye) from synthetic waste water and to determine the adsorption capacity, kinetics and isotherms of adsorption of these dyes by activated carbon prepared from *Hura crepitans* and to compare their extent of adsorption.

2. Materials and Methods

2.1. Preparation of Materials and Chemicals

The Eosin red dye and Malachite green dye were commercially obtained. The activated carbon prepared from *Hura crepitans* seed shells by Nsi*et al*., [6] was obtained and ground to a particle size range of 0.1-0.05mm and stored in an air tight container. Synthetic dye solution of eosin red with concentration 250mg/L was prepared as standard stock solution. This was carried out by dissolving 0.25 g of eosin red in 1000mL. Different concentrations of the dye were subsequently prepared by diluting the standard solution when necessary. The same procedures were also used for the preparation of malachite green solutions. All the sorption experiments were carried out at room temperature using mechanical shaker set at 200rpm and the post adsorption concentration was determine using UV-visible spectroscopy. All measurements were made at the wavelength corresponding to maximum adsorption and for eosin red (520nm) and malachite green (620nm).

2.2. Equilibrium Studies

The effect of activated carbon dosage on the equilibrium uptake of the two dyes was investigated using various quantities of the adsorbent (0.1-0.5g) in 100ml of 250mg/L of the dye solution. The shaking time was 1 hour. The effect of dye concentration was investigated by adding a fixed amount of the adsorbent into 250 mL conical flask containing 100mL of each dye solution of varying concentrations (50 – 250 mg/L). The shaking time was 1 hour. The adsorption experiment was also carried out by adding a fixed amount of the adsorbent into 250mL conical flask containing 100mL of the dye solution and shaking for varying contact time. This was carried out to investigate the effect of contact time on the dye adsorption. The contact times used were 20, 40, 60, 80, 100, and 120 minutes.

After each experiment, the post adsorption concentration was determined using UV- visible spectroscopy. The adsorption efficiency of each experiment was determined using

$$\text{Adsorption efficiency} = \frac{C_o - C}{Co} \text{ x } 100\%$$

The solute intake per unit mass of activated carbon q_e*(mg/g)* was calculated using adsorption system mass balance given as.

$$q_e = \frac{v(C_o - C)}{m}$$

Where V = volume of solution (mL),
m = amount of dry adsorbent (g)
C_o= initial concentration (mg/L),
C= final concentration (mg/L)

2.3. Determination of Adsorption Isotherm

Equilibrium adsorption isotherms are used to show the relationship between adsorbate concentration in solution and the amount of the adsorbent at equilibrium [7]. Isotherm models provide fundamental information on the sorption mechanism and heterogeneity of the adsorbent.

The isotherms models determined in this work are the Langmuir and Freundlich isotherms.

2.3.1. Langmuir Isotherm

This isotherm model describes monolayer adsorption onto the surface of an adsorbent with a finite number of identical adsorption sites. It assumes that adsorption occurs at specific homogenous sites within the adsorbent and no interaction between the adsorbent sites, the model is expressed as

$$\frac{1}{qe} = \frac{1}{q_{max}} + \frac{1}{q_{max} K_L} \cdot \frac{1}{Ce}$$

Where q_e is the quantity of dye adsorbed in (mg/g) at equilibrium. It corresponds to complete monolayer coverage. *Ce*is the equilibrium concentration of the adsorbate (mg/L), $K_L$is the Langmuir constant related to the energy of the adsorption (L/mg), $q_{max}$is the maximum sorption of the adsorbate from solution (mg/g). $q_{max}$and $K_L$were determined from the intercept and slope of the plot of $1/q_e$ against 1/Ce.

From Langmuir isotherm, $R_L$values was obtained which is expressed as

$$R_L = \frac{1}{1 + K_L C_0}$$

Adsorption is said to be favourable if $0 < R_L < 1$ and unfavorable if $R_L > 1$

2.3.2. Freundlich Isotherm

Freundlich isotherm is an empirical equation used to describe the heterogeneity of the adsorbent surface which is an indication that then binding sites are not equivalent or dependent.

The linear form of the equation is given as

$$\log q_e = \log K_f + 1/n \log c_e$$

Where q_e is the quantity of the adsorbate adsorbed at equilibrium (mg/g), Ce is the equilibrium concentration of the adsorbate (mg/L), K_f is the empirical constant that

provides an indication of the overall adsorption capacity (mg/g). 1/n is a dimensionless quantity; it is the sorption intensity of adsorbate into adsorbent or surface heterogeneity. The value of 1/n ranges from 0-1 and the closer the value to zero, the more heterogeneous the adsorbent surface [8].

2.4. Kinetic Modeling of Adsorption

The kinetic of adsorption was investigated using pseudo-first order and pseudo- second order rate equations.

2.4.1. The Pseudo –First Order or LagergernEquation

This is based on the assumption that the rate of adsorption site occupation is proportional to the number of unoccupied sites.

The linear form of the Lagergen equation is given as

$$\log(q_e - q_t) = \log q_e - \left(\frac{k_1 t}{2.303}\right)$$

Where K_1 (Min^{-1}) is the rate constant and q_e and q_e are the amounts of dye adsorbed at time t(Min) and equilibrium respectively. The model presented a good fit to the kinetic model based on the regression coefficient, r^2. In order to obtain the rate constants, a plot of $\log(q_e\text{-}q_t)$ was plotted against t.

2.4.2. The Pseudo-Second Order Kinetic Model

The model is based on the assumption that chemisorptions are the rate determining step. The linearised form of pseudo-second order kinetics is given as

$$\frac{t}{qt} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t$$

A plot of t/qt against t was used in determining the rate constant of the equation.

3. Results and Discussion

The following are the results obtained from the experiment.

3.1. Effect of Adsorbent Dosage

The results obtained from this experiment are presented in Table 1. It was observed that there is an increase in percentage adsorption with increase in the adsorbent dosage. This can be attributed to the increase in adsorptive surface area and hence availability of more adsorption sites for the adsorbate [9]. Our previous work on the adsorption of dyes using activated carbon prepared from different raw materials also had similar results [6,10, 11].

Table 1. *Effect of adsorbent dosage on adsorption.*

EosinRed			Malachite Green		
Dosage (mg)	**Post adsorption concentration (mg/L)**	**Efficiency (%)**	**Dosage (mg)**	**Post adsorption concentration (mg/L)**	**Efficiency (%)**
0.1	238.41	4.63	0.1	231.97	7.20
0.2	200.97	19.61	0.2	203.29	18.68
0.3	101.49	59.40	0.3	155.30	37.88
0.4	64.71	74.11	0.4	107.48	57.01
0.5	62.71	74.93	0.5	40.71	83.71

3.2. Effect of Initial Concentration of Dye

The effect of initial concentration of the dye solutions on adsorption efficiency is presented in Table 2. The percentage of adsorption was found to increase with decrease in the concentration of the dye. This is due to the fact that the percentage adsorption is an inverse function of the initial concentration of the dye. Moreover, at lower concentrations, there are sufficient active sites that the adsorbate can easily occupy.

Table 2. *Effect of ConcentrationonAdsorption.*

EosinRed			Malachite Green		
Concentration (mg/L)	**Post Adsorption Concentration (mg/L)**	**Efficiency (%)**	**Concentration (mg/L)**	**Post Adsorption Concentration (mg/L)**	**Efficiency (%)**
50	35.38	24.24	50	17.10	67.79
100	90.79	9.21	100	52.42	47.58
150	136.09	9.27	150	128.205	14.52
200	197.90	1.05	200	169.88	15.06
250	247.38	1.048	250	235.69	5.72

3.3. Effect of Contact Time

The results of this experiment are presented in Table 3. It was observed that the percentage adsorption slightly increases with increases in contact time. The adsorption efficiency was very low; this may be due to the nature of raw material, method of preparation of the activated carbon and the high concentration of the adsorbate

Table 3. *Effect of Contact Time.*

EosinRed			Malachite Green		
Time (Mins)	**Post Adsorption Concentration (mg/L)**	**Efficiency (%)**	**Time (Min.)**	**Post Adsorption Concentration (mg/L)**	**Efficiency (%)**
20	247.96	0.82	20	244.69	2.12
40	247.72	0.91	40	240.71	3.72
60	247.48	1.01	60	238.55	4.58
80	247.24	1.10	80	231.66	7.33
100	247.01	1.16	100	229.34	8.26
120	246.65	1.34	120	228.07	8.77

3.4. Isotherm Modeling

The results obtained from the experiment were analyzed using the Freundlich and Langmuir isotherms and the plots of these isotherm models are presented in Figure 1-4 and the derived parameters are given in Table 4 and 5. The adsorption of Eosin red by activated carbon prepared from *Hura crepitans* seed shell gives low linear regression values R^2 for both Langmuir and Freundlich isotherms. The R^2 for Langmuir and Freundlich isotherms were 0.751 and 0.857 respectively. These values are somewhat less than unity which suggests that the adsorbent is not suitable for the adsorption of this particular adsorbate. However the isotherm models for malachite green gives a good fit for Langmuir isotherm. The linear regression values R^2 obtained were 0.961 and 0.909 for Langmuir and Freundlich isotherms respectively. The result gives a better fit for the Langmuir model.

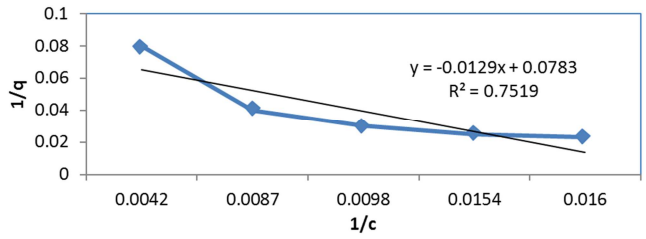

Figure 1. *Langmuir Isotherm for ER Adsorption.*

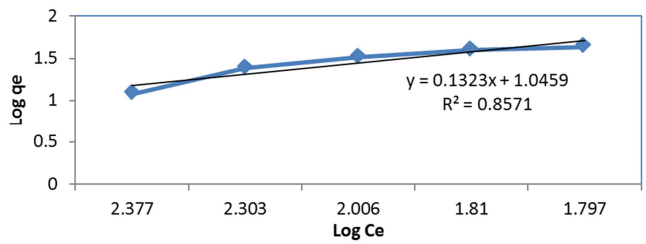

Figure 2. *Freundlichisotherm for ER Adsorption.*

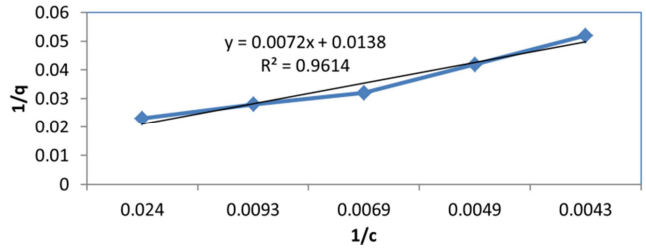

Figure 3. *Langmuir Isotherm for MG Adsorption.*

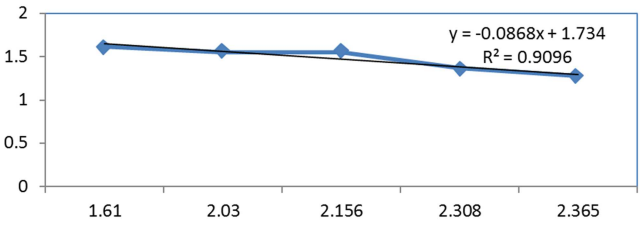

Figure 4. *FreundlichisothermforMG adsorption.*

Table 4. *Isotherm parameters for adsorption ER and MG.*

Isotherm parameter	Adsorption of eosin red	Adsorption of malachite green
LANGMUIR		
q_{max} (mg/g)	12.82	76.92
K_L (L/mg)	6.510	1098
R_L	0.000615	0.0000036
R^2	0.75	0.961
FREUNDLICH		
K_f	11.09	54.20
1/n	0.132	0.086
R^2	0.857	0.909

3.5. Kinetic Modeling

The kinetic studies carried out for the adsorption for ER and MG are presented in Figure 5-8. The kinetic data obtained are presented in Table 5. Eosin red adsorption gives a good linear plot for both the pseudo-first order and pseudo-second order kinetic models. The R^2 values for the plots were 0.980 and 0.970 for the pseudo-first order and pseudo-second order kinetic models respectively. The linear regression values R^2 obtained from the kinetic data of Malachite green were 0.922 and 0.599 for the pseudo-first order and pseudo-second order models respectively. Form the linear regression values R^2, it is seen that the adsorption of both dyes follows first order kinetics. However the kinetic study was more favorable for the adsorption of ER than MG since its R^2 tends to unity.

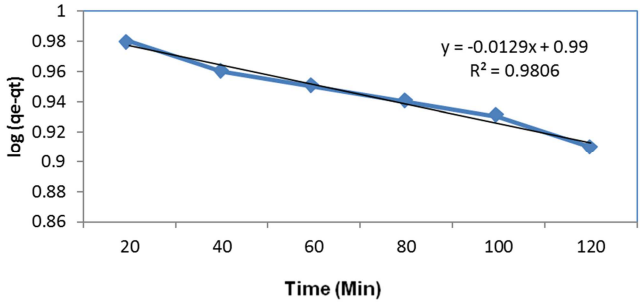

Figure 5. *Pseudo-first order kinetics for ER Adsorption.*

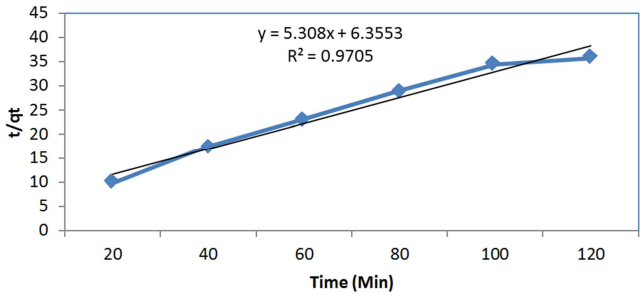

Figure 6. *Pseudo-second order kinetics for ER Adsorption.*

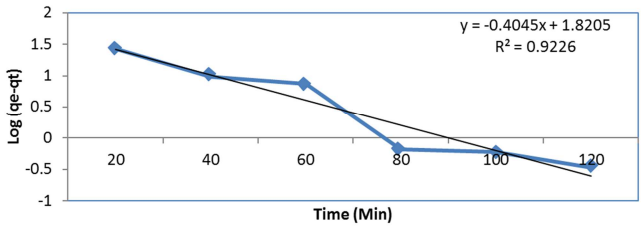

Figure 7. *Pseudo-first order kinetics for MG adsorption.*

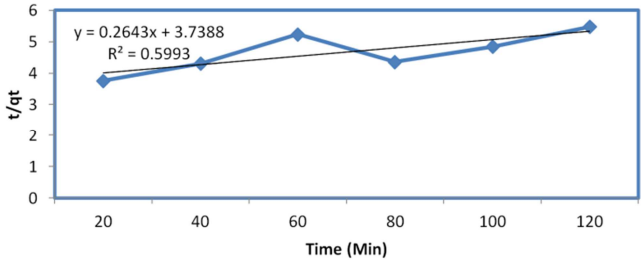

Figure 8. *Pseudo-second order kinetics for MG Adsorption.*

Table 5. *Kinetic Data for the Adsorption of ER and MG.*

Kinetic Model	Eosin red	Malachite green
Pseudo-first order		
Rate constant	0.027	0.93
R^2	0.980	0.922
Pseudo-second order		
Rate constant	0.839	0.0186
R^2	0.970	0.599

4. Conclusion

This study indicates that activated carbon prepared from *Hura crepitans* seed shell was able to remove malachite green, a typical basic dye than eosin red, a typical acid dye. The adsorption of these dyes was found to depend on adsorbent dosage, initial dye concentration, and contact time. It further indicates that the adsorption depended on the nature of the adsorbate.

The R^2 value obtained for the Langmuir and Freundlich models for the adsorption of eosin red were relatively low. However, the Freundlich model gave a better fit than Langmuir model. The adsorption of malachite green resulted in high value of R^2 for both the Langmuir and Freundlichmodels, however Langmuir model fitted more.

However, the kinetic of adsorption of both dyes fitted the pseudo- first order than pseudo-second order kinetic models.

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