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Adsorption Efficiency of Ceiba Pentradenta Wood Waste onto Cationic Dye Removal

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Abstract: *Ceiba Pentradenta* wood waste activated carbon (CPAC) prepared under phosphoric acid (H_3PO_4) treatment to remove cationic dye (malachite green) from aqueous solutions was investigated. The influence of various factors such as initial dye concentration, pH, contact time, temperature and particle size were determined for the basic dye. Adsorption kinetics were verified by pseudo first order, pseudo second order and intra-particle diffusion models. The kinetic study fitted well with Pseudo second order model. Adsorption data was modeled using Langmuir and Freundlich adsorption isotherms. Thermodynamic parameter has also been evaluated and the values of ΔH^0, ΔS^0 and ΔG^0 were calculated. The structural and morphological features were characterized by SEM studies. The result indicated that the adsorbent could well be employed as a low cost adsorbent in wastewater treatment process for the removal of dye.

Key words: Activated carbon (CPAC), Malachite green, Adsorption isotherm, Equilibrium, Kinetic and Thermodynamic parameters.

1. Introduction:

Inorganic and organic environmental contaminants pose a serious problem to man and his environment because most of them do not undergo degradation[1]. Leather, textile, paper and pulp industries discharge a large quantity of highly coloured effluent containing dyes into nearby river streams or land without any vigorous treatment because conventional treatment methods are very expensive. Small amount of dye present in water (<1 mgL^{-1}) is highly visible and consequently undesirable[2]. Majority of these dyes are recalcitrant and usually take a long time to biodegrade. Moreover, it was that the intermediates formed during the biodegradation of these dyes which are more toxic than the original molecules[3]. Malachite Green is widely used as a direct dye for silk, wool, jute, leather, cotton, as well as in aquaculture as a parasiticide, in food, health, and other industries like fish breeding industry for control the fungus *saprolegnia*, which infects fish eggs in commercial aquaculture and the application of the cationic dye in the medical science is known[4]. The basic dye when discharged as effluent causes changes in the biological activity of aquatic life and poses hazard to human beings. This adverse effect of the dye induces cancer, acts as liver tumor enhancing agent and many more diseases[5]. Malachite green on direct contact with the skin leads to skin irritation with redness and pain[6]. The basic dyes could simultaneously exist in the equalization tank of a dye-house, hence it is of fundamental importance to remove them [7]. The research on dyeing wastewater treatment has often focused on basic dyes for three main reasons a) basic dyes represent an increasing market share, b) the fabrics dyed with basic dyes loose fastness on hydrolysis in alkaline dye bath and c) conventional wastewater treatment plants have a low removal efficiency for basic dyes, which leads to colored waterways [8,9].

Several physiochemical decolorisation processes such as reverse osmosis, membrane filtration; flocculation, adsorption etc., have been developed for treating these water effluents. Among the treatment options, adsorption has become one of the most effective and a comparable low cost method for the decolorization of colored wastewater effluents[10]. Adsorption is the process that involves the transfer of a mass of a fluid (adsorbate) onto the surface of an adsorbing solid (adsorbent). Activated carbons, which are usually used as an adsorbent, has excellent adsorption efficiency but its use is limited due to its high cost[11].Therefore, attempts to explore on alternate materials are being made, which are relatively inexpensive, abundant, and also efficient that can absorb the dye. The various precursor used for the adsorption of malachite green analyzed subsequently are rice husk[12], palm ash[13], pumice powder[14] and banana stalk [15]. Nteje clay have been investigated by some authors for its ability to remove colour pigments from palm oil [16–19].The present investigation was intended to experiment with CPAC for the removal of basic dye, namely malachite green and the data fitted well with the experimental values.

2. Experimental

2.1 Preparation of adsorbent (CPAC):

Based on chemical/physical treatment and preparation techniques, adsorption behavior of dye gets varied. CPAC was collected from local area in Erode and treated with phosphoric acid. The precursor material to be carbonized was soaked with phosphoric acid in the ratio of 1:1 at 80^0C for 48 hours. After 48 hours, the material was crushed well using mortar and the crushed material was kept aside for 12 hours. Further, the material was washed well with hot water until a neutral pH obtained and dried at 110^0C for 24 hours. The dried mass, subjected to carbonization process at 800^0C for about 10 minutes was again thermally activated at 400^0C for about 10 minutes in the presence of nitrogen atmosphere. The final product was ground well and used for subsequence analytical assessment [20]. The phosphoric acid hydrolyzed powders sieved to various mesh size of 75-180, 180-250 and 250-355 microns was used for sorption studies. The adsorbent was prepared once in stock, stored and used throughout the experiment.

2.2 Preparation of Malachite Green dye solutions:

Malachite Green and other chemicals used were of analytical grade. The materials after purification were prepared using recommended methods[21]. Distilled water was employed for preparing all the solutions and reagents. The stock solution was prepared by dissolving 1gm of the dye in 1000ml of double distilled water. The desired concentration of the dye can be prepared by diluting them to various concentrations. The characteristics of the dye are shown in table 1.

Table 1: Characteristics of Malachite Green:

Class	Basic
CI Number	42,000
Chemical Formula	$C_{50}H_{52}N_4O_8$
MW	927.03
λ_{max}	618 nm
pK_a	6.9
Solubility	Water
Melting point	137^0C

2.3 Experimental methods and measurements

The batch technique has been performed to obtain the rate and equilibrium data. Batch studies were performed at various temperatures (303K, 318K and 333K), varied particle size (75-180, 180-250 and 250-355 microns) and at concentration (20, 40 and 60 ppm) to attain equilibrium isotherm. The equilibrium time for CPAC was 200 min and the desired pH was 6 and pH_{ZPC} was 5.6. The dye concentration of the supernatant solution was analyzed using a spectrophotometer by monitoring the absorbance changes at wavelength of maximum absorbance (618 nm) in this adsorption experiments .The amount of dye adsorbed per gram of CPAC at equilibrium q_e (mg/g) and percentage dye removal were calculated with the following equation,

$$q_e = \frac{(C_0 - C_e)}{W} X\ V \quad - - - - - (1)$$

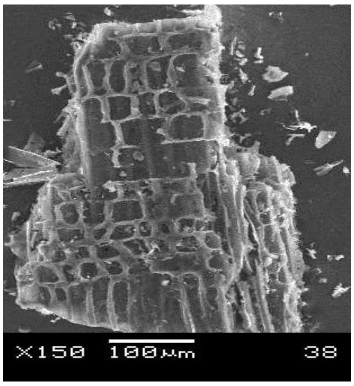
The percentage of dye removal (%R) in solution was calculated using equation 2.

$$\%\ of\ dye\ Removal = (\frac{C_0 - C_e}{C_0})\ X\ 100 \quad - \ - - - - - (2)$$

3. Results and Discussion:

3.1 SEM Morphology:

The structural analysis of CPAC determined from the SEM photographs at various magnifications was shown below in Figure 1 and 2. SEM report shows that they have fissure, sharp boundaries and rough surface. The specific surface area of CPAC obtained from the BET measurements in N_2 atmosphere was found to enhances used for the dye adsorption to a greater extent. Physical properties and surface morphology of activated carbon influence the adsorption capacity. It is clear that the CPAC has considerable number of heterogeneous pores and can expect a good possibility of dye molecules to be trapped and adsorbed.



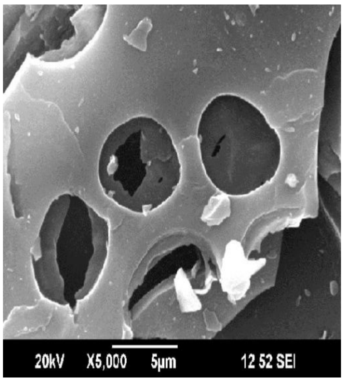


Figure1:SEM images of CPAC at X 150 Figure 2 : SEM image of CPAC at X5000

3.2 Characterization of adsorbent:

The physio-chemical characteristics of the adsorbent showed that they have a profound effect on the dye adsorption. Table 2 gives the characteristics of the adsorbent, CPAC

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Parameters	**Value**
pH	6
Moisture Content (%)	6
Ash Content (%)	7
Conductivity mS/cm	0.27
Specific Gravity (S)	1.39
Bulk Density (D)	0.3633
Porosity (%)	79.4
Matter soluble in Water (%)	1.45
Matter soluble in acid (%)	2.81
Carbon (%)	72.95
Hydrogen (%)	0.41
Nitrogen (%)	0.11
Sulphur (%)	ND
Oxygen (%)	26.53
Ion exchange capacity mg/l	0.52
Decolorizing Power mg/l	39
BET Surface Area m^2/g	380

3.3 Effect of pH:

The pH of the dye solution plays an important role in the whole adsorption process. As shown in Figure 3 consistent increase in adsorption capacity of the CPAC was observed as the pH increased from 2 - 6, and a marginal increase in uptake of dye was noticed at pH level beyond 6. As pH of the system decreased, the number of negatively charged adsorbent sites decreased and the number of positively charged surface sites increased, which did not favor the adsorption of positively charged dye cations due to electrostatic repulsion. In addition, low adsorption of malachite green at acidic pH might be due to the presence of excess H^+ ions competing with dye cations for the available adsorption sites.

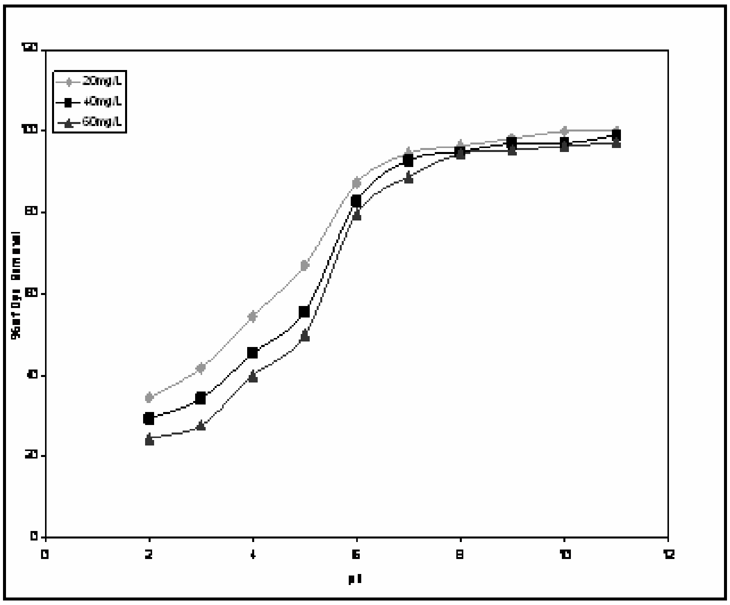

Figure 3: Effect of pH on the Initial dye concentration

3.4 Effect of particle size:

The particle size has a significant influence on the kinetic adsorption which occupy the adsorbate more in the break through curves.Normally the adsorption capacity is directly proportional to the particle diameter for non-porous adsorbents. The presence of a large number of smaller particles provides the adsorption system with a greater surface area available for the dye removal [22]. The particles size of 75-180, 180-250 and 250-355 microns were analyzed. It was observed that as the particle size decreased the amount of adsorbed dye increased, with subsequent decrease in equilibrium time. This is due to the larger external surface area available due to smaller particle, when the total mass of the adsorbent is constant[23]. The higher uptake of adsorbate is attributed to the size of the adsorbent per unit mass [24]. Figure 4 clearly shows that the adsorption of malachite green with smaller size particles was greater in magnitude than that of a larger sized particle. The breaking up of larger size particle to form smaller ones opens some tiny sealed channels that might then become available for adsorption and so the adsorption by smaller particles is higher than that by larger particles [25].

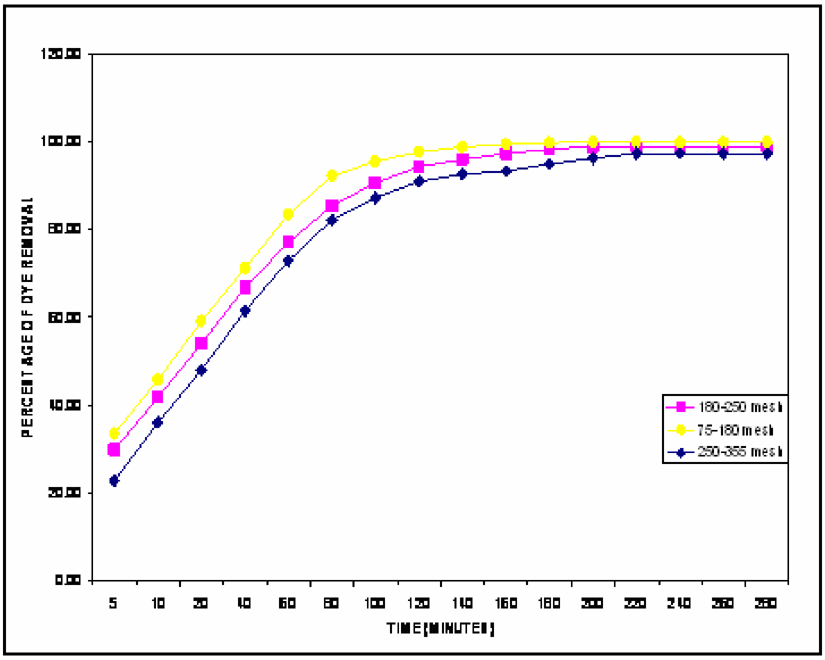

Figure 4: Effect of particle size on malachite green dye onto CPAC

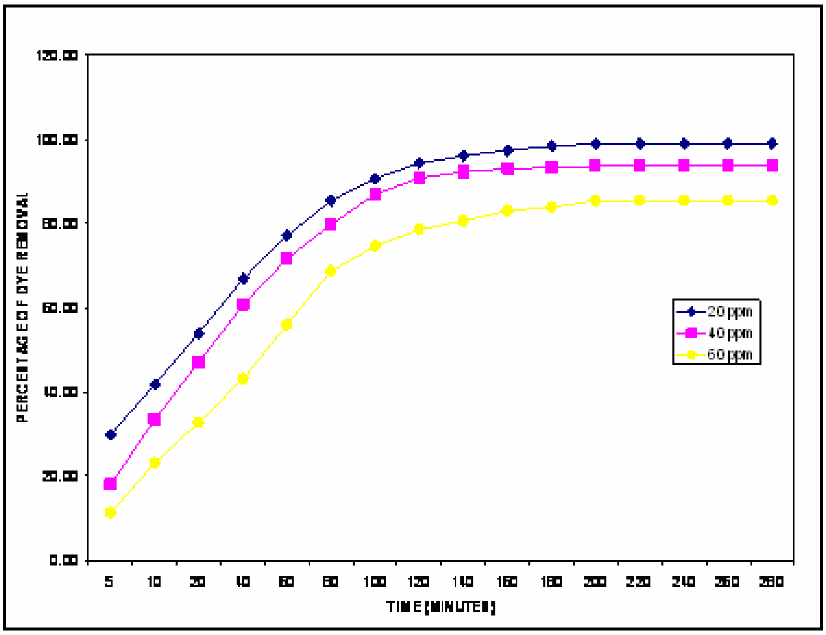

Figure 5: Effect of initial dye concentration on malachite green dye onto CPAC

3.5 Effect of contact time and initial concentration:

The contact time between the adsorbent and adsorbate, play a vital role in the dye adsorption. The equilibrium isotherm of the dye depends on temperature and pH of the adsorbent. The contact time is one of the major factors for the development of surface charge at the solid surface - interface. At lower concentration, the adsorption was more effective and as concentration increased the adsorption decreased. At 20ppm, the percentage of dye removed was found to be 99% and at 60ppm, it was found to be 85.4%. Figure 5 clearly show that as concentration increases the adsorption starts decreasing. The adsorption of dye amount increased with an increase in initial dye concentration. The reason was that, at a higher initial concentration, the driving force between the aqueous and solid phase enhanced and also the number of collision between dye ions and adsorbent increased. The reasons for decrease in adsorption at high concentration is due to low fractional adsorption. At low concentration, there were more number of sorption sites hence the adsorption increased. As the dye ratio increases , sorption sites becomes saturated, resulting in decrease in the sorption efficiency[26] and a rapid uptake of dye at lower concentration are due to surface mass transfer[27].After a lapse of time, the remaining surface sites are difficult to be occupied because of repulsion between the solute molecules of the solid and bulk phase. The equilibrium time required for malachite green was 200 minutes.

3.6 Effect of temperature:

The effect of rate constant for the removal of malachite green with initial concentration of 20 ppm and pH 6 experimented at various temperatures of 303K, 318K and 333K on CPAC signified well defined loss of dye removal efficiency. The percentage removal of dye decreased from to 99% to 80% as temperature increases from 303K to 333K at 20 ppm, which is shown in the figure 6, which indicates reaction to be exothermic. This can arise due to a tendency of the dye molecule to escape from solid phase to the bulk phase with an increase in temperature of solution [28].

The variation in the extent of adsorption with temperature may be explained on the basis of the change in chemical potential [29] which is related to the solubility of the adsorbate species which increases with an increase in temperature. Hence both solution and temperature depicts a measure of decrease in chemical potential at low temperature (303k) as inferred from figure 6.

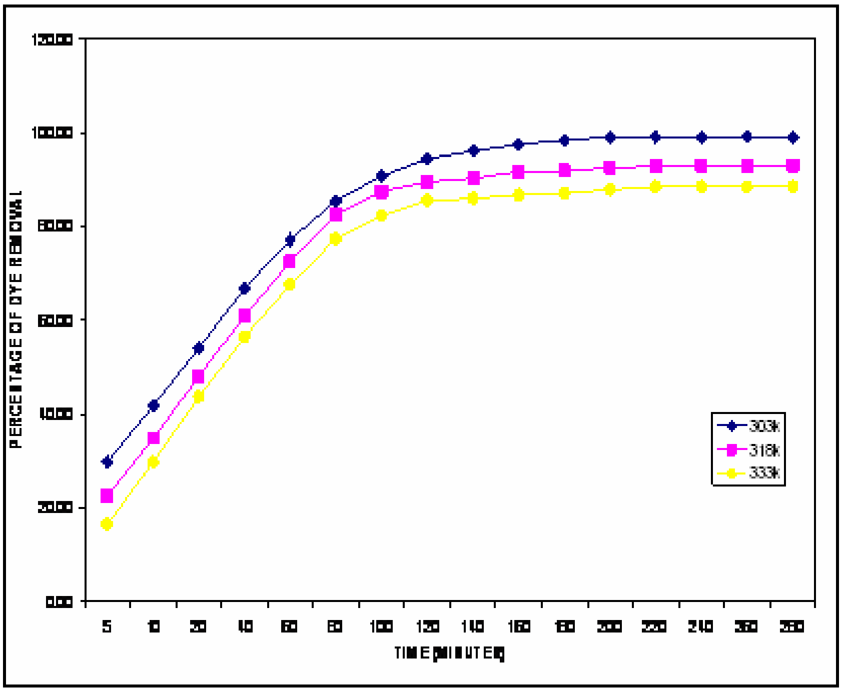

Figure 6: Effect of temperature on malachite green dye onto CPAC

3.7Adsorption kinetics:

The study of adsorption kinetics describes the mechanism and the potential rate controlling steps such as mass transport, pore diffusion and chemical reaction processes. Different kinetic models such as pseudo first order, pseudo second order, Elovich and intraparticle diffusion were applied to the experimental data to analyze the adsorption kinetics of malachite green were used to fit experimental data [30]. The experiments were carried out for time intervals varied from the 0 to 200 min at various temperatures of 303,318 and 333k at a fixed dye concentration of 20 ppm.

3.7.1 The pseudo first – order equation

The pseudo first - order equation (3) is generally expressed as follows.

$$\frac{dq_t}{dt} = k_1(q_e - q_t) \quad -----(3)$$

After integration and applying boundary conditions t =0 to t = t and qt= 0 to qt = qt, the integration form of equation (4) becomes.

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} X\, t \quad ------(4)$$

The value of log (q_e – q_t) were ploted against t. The plot of log (q_e – q_t) vs t should give a linear relationship from which k_1 and q_e can be determined from the slope and intercept of the plot respectively. The pseudo – first order kinetic constants are shown in Table 3. Figure 7 explains the pseudo first order plot. The k_L value increases as the temperature increases as reaction is exothermic in nature

Table 3 : Calculate Kinetic Parameters for the Adsorption of malachite green dye on CPAC

Dye	Temp K	Pseudo first order kinetics		First order reverse Kinectics			Elovih Model			Pseudo second order kinetics			
MALACHITE GREEN		k_L, min-1	R^2	K_C	K_B min-1	R^2	α, mgg-1 min-1	β gm-1	R^2	qe, mgg-1	K_2x 10^3 mgg-1min-1	h, mgg-1 min-1	R^2
	303	0.0251	0.985	99	0.025098	0.985	3.7757	0.2701	0.9783	10.6485	0.014637	0.60252	0.9988
	318	0.02535	0.9921	13.0845	0.025352	0.9815	3.2004	0.2673	0.968	10.0669	0.018802	0.52481	0.9987
	333	0.05566	0.9905	7.547	0.024167	0.9903	2.7882	0.2641	0.9688	9.70909	0.024598	0.43127	0.9984

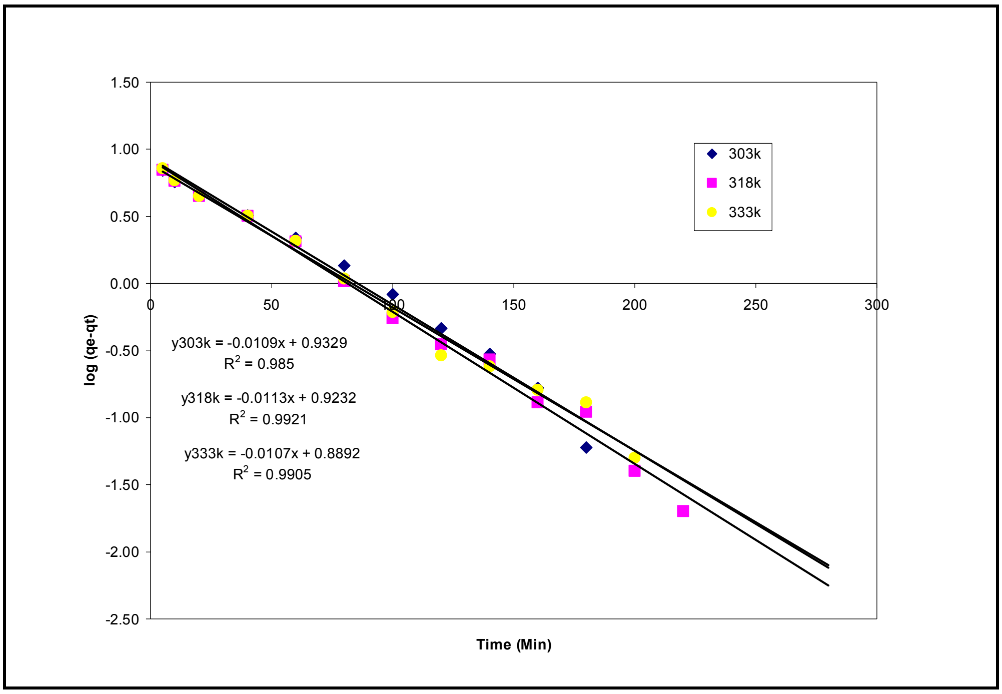

Figure 7: Effect of temperature on Pseudo-first order kinetics for the adsorption of Malachite Green dye onto CPAC.

3.7.2. The pseudo second – order equation.

The pseudo second – order adsorption kinetic rate equation is expressed as (5)

$$\frac{dq_t}{dt} = k_2(q_e - q_t)^2 \quad ------(5)$$

For the boundary conditions t = 0 to t = t and qt = 0 to qt = qt, the integrated form of equation (5) becomes.

$$\frac{1}{qe-qt} = \frac{1}{qe} + k_t \quad ------(6)$$

which is the integrated rate law for pseudo second – order reaction. Equation (6) can be rearranged to obtain equation (7), which has a linear form.

$$\frac{t}{q_t} = \frac{1}{k_2 q_e 2} + \frac{1}{q_e}(t) \quad -----(7)$$

Equations (6) and (7) become:

$$\left(\frac{t}{qt}\right) = \frac{1}{h} + \frac{1}{qe} \quad -----(8)$$

The plot of (t/qt) and t of equation (8) should give a linear relationship from which q_e and k_2 can be determined form the slope and intercept of the plot, respectively.

$$h = k_2 q_e^2 \text{-----} (9)$$

Figure 8 explain the pseudo second order plot exhibiting a linearity plot.

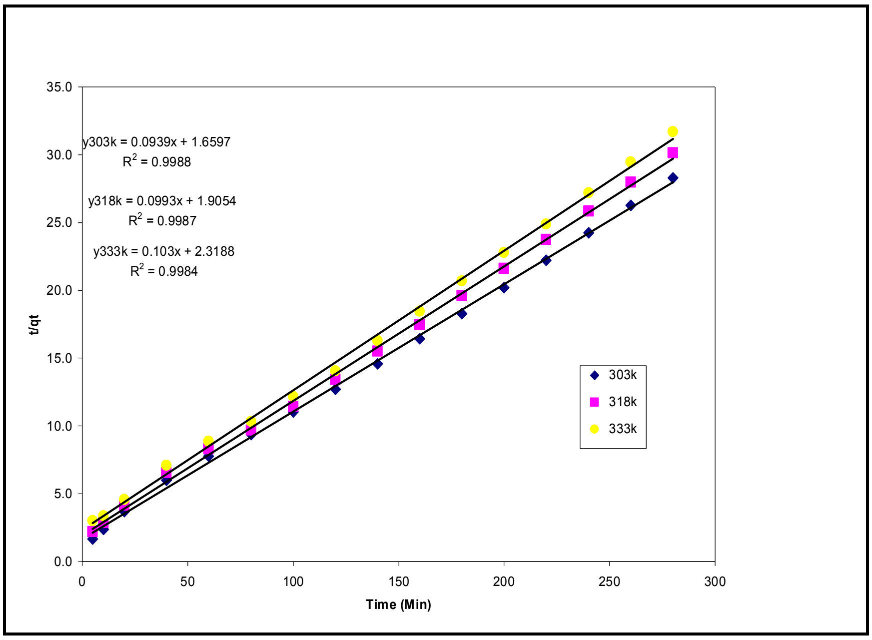

Figure 8: Effect of Temperature on Pseudo-second order kinetics for the adsorption of Malachite Green dye onto CPAC.

3.7.3. Elvoich Model Equation:

The Elovich model equation, which is used for systems in which the adsorbing surface is heterogenous

$$\frac{dqt}{dt} = \propto \exp(-\beta qt) \quad \text{-----} (10)$$

Integrating this equation at the appropriate boundary conditions and simplifying to a linear equation gives,

$$qt = \left(\frac{1}{\beta}\right)\ln(\alpha\beta) + \left(\frac{1}{\beta}\right) lnt \quad \text{-----} (11)$$

A plot of qt against ln t was used to calculate β and α from the slope and intercept respectively as given in Table 3.

The above kinetic data clearly shows that the pseudo second order model was found to fit well for the above basic dye malachite green.

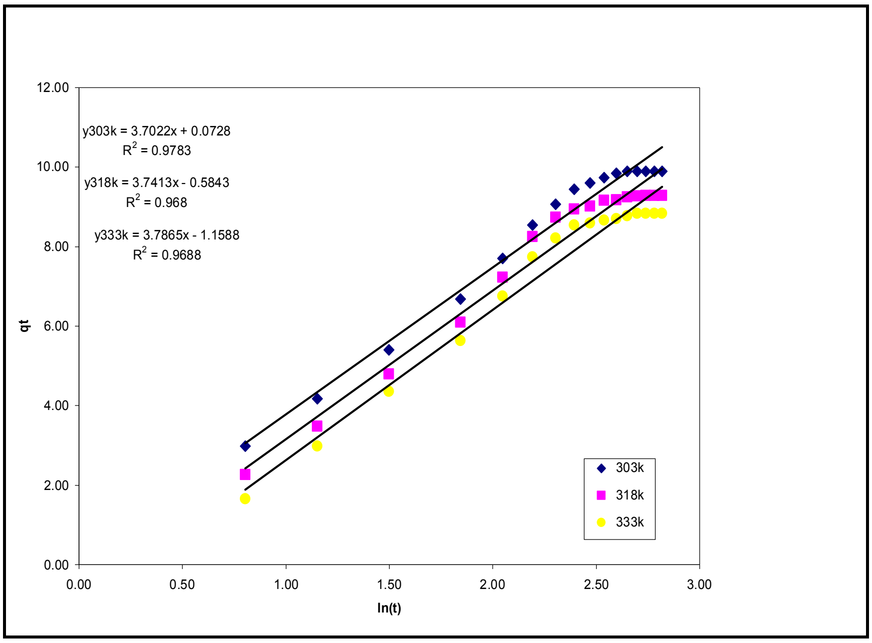

Figure 9: Effect of temperature on Elovich model for the adsorption of Malachite Green dye onto CPAC

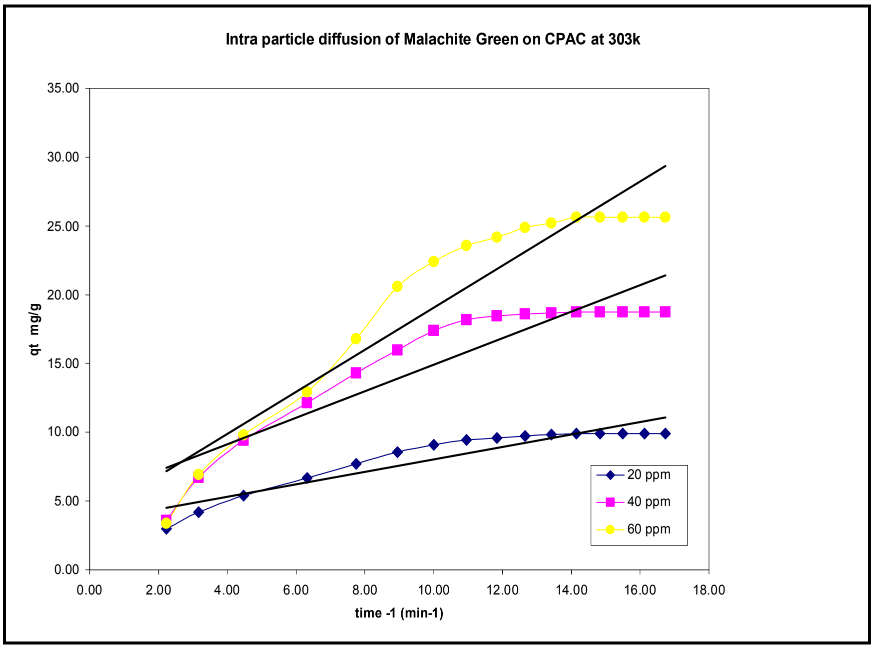

Figure 10: Effect of temperature on Intra particle diffusion model for the adsorption of Malachite Green dye onto CPAC

3.6.4 Intraparticle diffusion model:

The intra-particle diffusion model checks the possibility of the adsorbate diffusing into the interior pores of the adsorbent after initially being adsorbed on the surface of the adsorbent [31]. The kinetic model propounded by Weber and Morris is given by,

$$qt = \boldsymbol{k}_{int} t^{1/2} + \boldsymbol{c} \;\; ----- \;\; (12)$$

where K_{int} is the intra-particle diffusion constant and c is the intercept of the line which is proportional to the boundary layer thickness.

The plot of qt against $t^{1/2}$ was used to calculate the intra-particle diffusion constants, K_{int} and c. The high values of the correlation coefficient R^2 for the adsorption indicate that the adsorption of malachite green followed the intra-particle diffusion but, since the linear plot did not pass through the origin, then the intra-particle diffusion though involved in the adsorption process, is not the rate-controlling step.

3.8. Adsorption isotherm:

The commonly used isotherms for non-linear equilibrium between amounts of basic dye on adsorbed the acid treated CPAC (q_e) and equilibrium concentration of solution (C_e) at a temperature of (303K, 318K & 333K) is investigated. Langmuir equation was found valid for monolayer sorption onto a homogeneous surface with a finite number of identical sites.

3.8.1 Langmuir model:

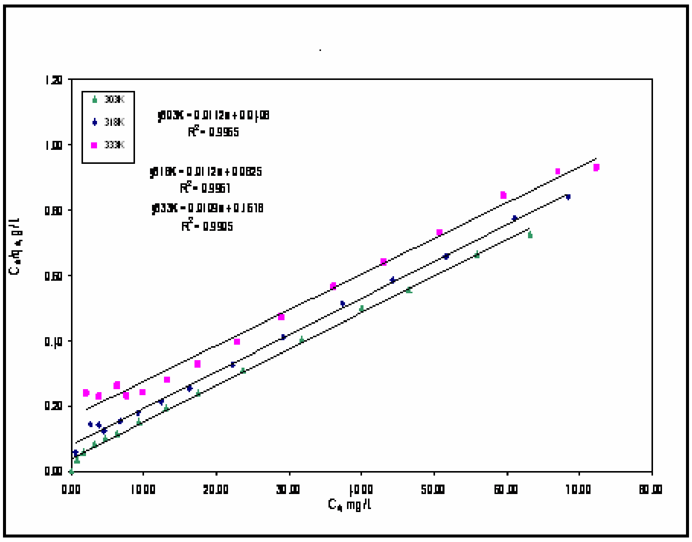

Figure 11 Langmuir plot for malachite green dye onto CPAC, 100 mg; V, 50 ml; pH, 6; temperature at 303K,318K and 333K)

The adsorption isotherm for CPAC waste have been investigated.100mg of the adsorbent was taken with 50 ml of the aqueous solution of the dye at various concentration (10-150 ppm) at a fixed pH of 6. The bottles were placed in orbital shaker at 200 rpm until equilibrium was obtained. The experiment was carried out at different temperature viz.303, 318 and 333K.

Table 4 : Calculated Langmuir equilibrium isotherm of malachite green dye on CPAC

Temp K	Q_o mg/g	K_L l/mg	R^2
303	91.53181	24.53465	0.9965
318	89.57646	12.11682	0.9967
333	89.15475	5.960125	0.9905

The Langmuir isotherm equations [32] have been used for the determination of adsorption isotherm to optimize the design of an adsorption system to remove basic dyes and also it is important to establish a most appropriate correlation from the equilibrium curves. The Langmuir adsorption, which is valid for monolayer adsorption, depends on the assumption that the intermolecular forces decrease rapidly with distance, and consequently predicts the existence of monolayer coverage of the adsorbate at the outer surface of the adsorbent. The Langmuir equation is given in the following equation [13].

$$\frac{C_e}{q_e} = \frac{1}{Q_0 b} + \frac{1}{Q_0} C_e \qquad ------(13)$$

The constants can be evaluated from the intercepts and the slopes of the linear plots of C_e/q_e versus C_e (as shown in Figure 12). The adsorption data for CPAC states that it shows a monolayer of adsorption.

From Table 3 the R^2 value (≥ 0.99) indicated that the adsorption data of the dye onto the adsorbent at all the three temperatures studied obtained a good fit for the Langmuir isotherm model. The maximum monolayer adsorption capacity of adsorbent onto the adsorbate decreased with increase in solution temperature from 303K to 333K, respectively. The Q_0 values show that the adsorption capacity of CPAC adsorbent was highly comparable to the adsorption capacities of some other low-cost adsorbent materials for Malachite Green [33-34]. In order to determine the Langmuir adsorption process is favorable or unfavorable, a dimensionless constant separation factor or R_L is defined according the equation

$$R_L = \frac{1}{1+bc_0} ------(14)$$

The calculated R_L values of malachite green is found to be between 0.412, 0.3835 and 0.3250 at various temperature viz 303,318 and 333k. The R_L value indicates the type of the isotherm to be ($0< R_L <1$), unfavorable at ($R_L >1$), linear ($R_L =1$) or irreversible ($R_L =0$)

3.8.2 Freundlich Model

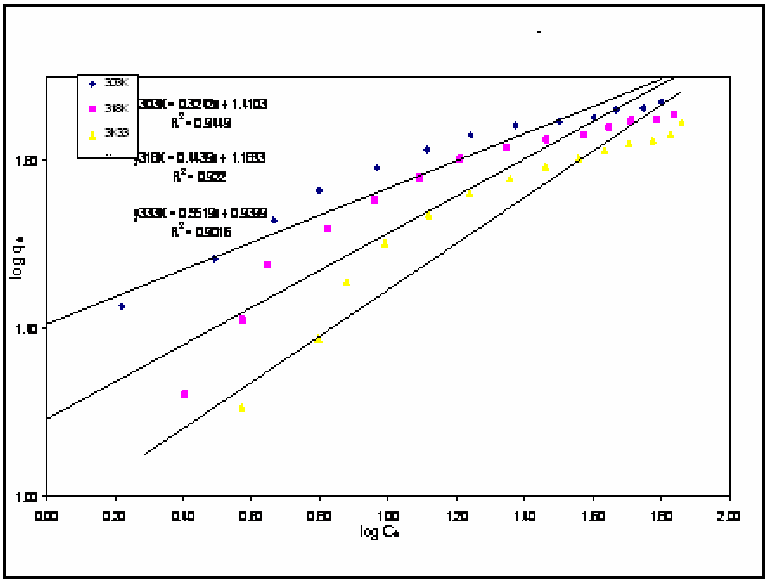

Figure 12. Frendlich plot for malachite green dye onto CPAC, 100 mg; V, 50 ml; pH, 6; temperature, 303K, 318K and 333K)

Table 5: Calculated Frendulich Equilibrium isotherm of Malachite Green on CPAC

Temperature K	N	K_f	R^2
303	3.0843	25.7205	0.9449
318	2.2528	15.2524	0.922
333	1.8119	8.70824	0.9016

At Equilibrium conditions, the adsorbed amount, q_e can also be predicted by using the Freundlich equation (15).

$$q_e = K_f C_e^{1/n} ------(15)$$

A logarithmic form of the above equation is

$$\log q_e = \log K_f + \left(\frac{1}{n}\right)\log C_e ------(16)$$

The values of n and K_f were determined from the plot log Ce vs log qe .
where, K_f is Freundlich constant related to the sorption capacity and 1/n is Freundlich constant related to the energy heterogeneity of the system and the size of the adsorbed, molecule ranging between 0 and 1, becoming more heterogeneous as its value gets closer to zero. The Freundlich equation [35] predicts that the dye concentration on the adsorbent will increase so long as there is an increase in the dye concentration in the

liquid. The experimental evidence indicates that an isotherm is reached at a limiting value of the solid phase concentration. The equation itself does not have any real physical significance.

Freundlich isotherm fits well into the data . The calculated Freundlich isotherm constants at 303, 318 and 333K are as shown in Table 5. The value of Freundlich exponent are lying in the range of 1 - 10, indicate favorable adsorption.

3.8.3 Adsorption Thermodynamics:

Table 6: Evaluation of Thermodynamic parameters

Temp	ΔH^0 $Jk^{-1}mole^{-1}$	ΔS^0 $Jk^{-1}mole^{-1}$	ΔG^0 $Jk^{-1}mole^{-1}$
303K	-7.456174	103.81	-8061.467
318K			-6595.334
333K			-4942.125

Thermodynamic parameters provide information of inherent energetic changes associated with adsorption. The thermodynamic adsorption parameters to be characterized are standard enthalpy (ΔH^0), standard free energy (ΔG^0), and standard entropy (ΔS^0).The values of ΔH^0, ΔG^0 and ΔS^0 are calculated by using equation 17 & 18.

$$\ln K_L = \frac{\Delta S^0}{R} - \frac{\Delta H^0}{RT} \quad ----- (17)$$

$$\Delta G^0 = -RT \ln K_L \quad ----- (18)$$

where R= (8.314J/mol K) is the universal gas constant, T(K)is the absolute solution temperature, and K_L (L/mg)is the Langmuir isotherm constant. ΔH^0 and ΔS^0 can be ascertained as the gradient and intercept derived from the plot of ln K_L versus 1/T, respectively.

Table 4 reported the values of ΔH^0, ΔG^0 and $\Delta S^0$for adsorption of Malachite green Dye on CPAC. The negative ΔH^0 value shows that the adsorption of Malachite Green dye onto CPAC was exothermic in nature, which supported the results obtained earlier where the Malachite Green dye uptakes increase with increase in solution temperature. The positive value of ΔS^0 describes increasing degree of freedom and randomness during the adsorption process at the solid-liquid interface with some structural changes in the adsorbate and adsorbent. This phenomenon had also been observed in the adsorption of azo-dye Orange II by titanic aerogel [36] and direct dyes by carbon nanotubes [37].For the standard free energy, ΔG^0 values were negative which describes the condition of spontaneous nature of the adsorption processes at the range of temperature studied.

5. Conclusion:

Adsorption of basic dye malachite green on the CPAC was found to be dependent on the pH, (The optimal pH of malachite green was 6), temperature and concentration of adsorbent. Thermodynamic parameters obtained for the adsorbent accounts for feasibility of the process at each concentration. Adsorption equilibriums were reached within 200 min contact time for basic dye used in this test. The kinetics of malachite green adsorption on adsorbent was found to follow a pseudo second -order rate equation. The Freundlich, and Langmuir isotherm prediction of equilibrium isotherm were tested on for the adsorption of malachite Green on CPAC and the result showed that the Langmuir isotherm was the best fit.

6. References:

1. Gładysz-Płaska, A , M. Majdan, S. Pikus, and D.Sternik, 2012. "Simultaneous adsorption of chromium (VI) and phenol on natural red clay modified by HDTMA," *Chemical Engineering Journal*, vol. 179,pp. 140–150.
2. Sun, Q. and L.Yung 2003, The adsorption of basic dyes from aqueous solution on modified peat- resin particle, *Water resource*, 37, pp 1535-1544.

3. Kumar,S V. Gunasekar, and V. Ponnusami, "Removal of methylene blue from aqueous effluent using fixed bed of groundnut shell powder," *Journal of Chemistry*, vol. 2013, pp. 1–5, 2012
4. Srivastava, S., Sinha, R., & Roy, D. Toxicological effects of malachite green.Aquatic Toxicology, 66, 319–329 ,2004.
5. Sharma.Y, B. Singh, and Uma, Fast removal of malachite green by adsorption on rice husk activated carbon, open environ,"Journal of Pollution Toxicol., vol. 1, pp. 74–78, 2009.
6. Pan.X and D. Zhang, 2009."Removal of malachite green from water by firmiana simplex wood fiber,"*Electronic Journal of Biotechnology,* vol. 12, no. 4, pp. 9–10.
7. Chiou, M.S, H.Y.Li, 2003 Adsorption behavior of reactive dye in aqueous solution on chemical cross-linked chitosan beads. *Chemosphere 50*, 1095–1105.
8. Zollinger, H. 1987 Color Chemistry: Synthesis, Properties and Applications of Organic *Dyes and Pigments*; John Wiley & Sons, Inc.: Hoboken, NJ, USA.
9. Allègre. C, P. Moulin, M. Maisseu, F. Charbit, 2006. Treatment and reuse of reactive dyeing effluents. *J. Membr. Sci. 269*, 15–34.
10. Iqbal M. J. and M. N. Ashiq, 2007 "Thermodynamics of adsorption of dyes from aqueous media on activated charcoal," *J. Res. Sci,* vol. 18, no. 2, pp. 91–99.
11. Ladhe U, S. Wankhede, V. Patil, and P. Patil, 2011 "Adsorption of eriochrome black-T from aqueous solutions on activated carbon prepared from mosambi peel,"*Journal of Applied Sciences in Environmental Sanitation,* vol. 6, no. 2, pp. 149–154.
12. Vadivelan, V. & V.K.Kumar 2005. Equilibrium, kinetics, mechanism, and process design for the sorption of methylene blue onto rice husk. *Journal of Colloid and Interface Science.* 286, 90–100.
13. Ahmad, A.A., B.H Hameed and N.Aziz 2007. Adsorption of direct dye on palm ash: Kinetic and equilibrium modeling. *Journal of Hazardous Materials*. 141 ,70–76.
14. Feryal, A. 2005. Adsorption of basic dyes from aqueous solution onto pumice powder. *Journal of Colloid and Interface Science*. 286, 455–458.
15. Hameed, B.H., D.K. Mahmoud, & A.L.Ahmad 2008. Sorption equilibrium and kinetics of basic dye from aqueous solution using banana stalk waste. *Journal of Hazardous Materials.* 158, 499–506.
16. Ajemba R. O. and O. D. Onukwuli, 2013 "Adsorptive removal of colour pigment from palm oil using acid activated Nteje clay. Kinetics, equilibrium and thermodynamics," *Physicochemical Problems of Mineral Processing*, vol. 49, no. 1.
17. Nwabanne. J and F. Ekwu, 2013 "Decolourization of palm oil by Nigerian local clay: A study of Adsorption isotherms and bleaching kinetics," *Int. J. Multidiscipl. Sci. Eng*, vol. 4, no. 1, pp. 20–25,
18. Ajemba, R 2012"Enhancement Of Physicochemical Properties Of Nteje Clay To Increase Its Bleaching Performance Using Acid Activation," *International Journal of Engineering Research and Applications*, vol. 2, no. 4, pp. 281–288.
19. Nwabanne.J and F. Ekwu, 2013 "Experimental design methodology applied to bleaching of palm oil using local clay," *International Journal of Applied*, vol. 3, no. 4, pp. 69–77.
20. Nasser,M.M., and M.S. El-Geundi,1991, *J Chem Biotechnology,* 50**,** 257,1991.
21. Vogel A, 1961 A Text Book of Quantitative Inorganic Analysis,3rd ed., Longman, London.
22. Boutemedjeta & Oualid Hamdaoui Sihem, 2000. *Desalination water treatment*, 8,201.
23. Khattri, S.D., M.K.Singh, 2000. Colour removal from synthetic dye wastewater using a bioadsorbent, *Water Air Soil Pollut.* 120 283-294.
24. Liew .A.G, etal ,2005. Azo dye removal by adsorption using waste biomass: surgcane bagasse, *Int.J.Eng.Technol.*2(1) 8-13.
25. Khattri, S.D. and M.K.Singh 1998, Colour removal from aqueous solution by adsorption, *Indian J.Chem.Technol.* 5(4) ,230-234.
26. Lagergren S,1898 .Zur theorie der sogenannten adsorption gelöster stoffe. Kungliga Svenska Vetenskapsakademiens. Handlingar, 24 : 1-39.
27. Weber W.J.and C.J.Morris, 1963 Kinetic of Adsorption on Carbon from Solution, *J.Sanit .Engg.Div.,* 89:31-60.
28. Ozer.D, G.Dursum,A. Ozer, 2007. Methylene blue adsorption from aqueous solution by dehydrated peanut hull, *J.Hazard .Meter.*144, 179-1179.
29. Ho Y S,G. Mckay, D A J Wase, CF Foster 2000, Study of the sorption of divalent metal ions on to peat, *Adsorp. Sci .Technol*, 18: 639-650.
30. Ekpete .O and M. H. Jnr, 2011 "Kinetic sorption study of phenol onto activated carbon derived from fluted pumpkin stem waste," *ARPN Journal of Engineering and Applied science*, vol. 6, no. 6, pp. 43–49.

31. Sivakumar P and P. Palanisamy, 2009. “Adsorption Studies of basic red 29 by a non conventional activated carbon prepared from Euphorbia Antiquorum,” International Journal of Chem Tech Research, vol. 1,no. 3, pp. 502–510.
32. Langmuir I, 1918.The adsorption of gases on plane surfaces of glass, mica and platinum.J. Am.Chem. Soc, 40: 1361-1403.
33. G. Mckay, J.F. Porter, G.R. Prasad, The removal of dye colours from aqueous solutions by adsorption on low-cost materials, Water Air Soil Pollut. 114 (1999) 423–438.
34. I.A. Rahman, B. Saad, S. Shaidan, E.S. Sya Rizal, Adsorption characteristics of malachite green on activated carbon derived from rice husks produced by chemical–thermal process, Biores. Technol. 96 (2005) 1578–1583.
35. Freundlich H, 1926.Colloid and Chemistry, London.Methuen.
36. Abramian.L and H. el-Rassy, , 2009 “Adsorption kinetics and thermodynamics of azo-dye Orange II onto highly porous titania aerogel,” *Chemical Engineering Journal*,vol.150,no.2-3,pp. 403–410.
37. Kuo, C.-Y, C.-H. Wu, and J.-Y. Wu, 2008 “Adsorption of direct dyes from aqueous solutions by carbon nanotubes: determination of equilibrium, kinetics and thermodynamics parameters,” *Journal of Colloid and Interface Science* ,vol.327,no.2,pp.308–315.

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