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Elephas Maximus Dung Activated Carbon as a Biosorbent for Methylene Blue Removal: Equilibrium and Kinetic Studies

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Abstract: Low cost activated carbon prepared from elephant dung by acid treatment (EDAC), was used as an eco friendly adsorbent for the removal of a cationic dye Methylene Blue (MB) from aqueous solution. Batch adsorption experiments were carried out by varying the initial dye concentration, adsorbent dosage and temperature. The optimum dosage of the adsorbent was found to be 100 mg. The equilibrium time was found to be 210 minutes for 40 mg/L and 150 minutes for 30 mg/L dye solutions. The adsorption kinetics was found to be best represented by Pseudo second order kinetic model. The mechanism of adsorption process was determined from intra particle diffusion model. The percent removal of the dye was increased with increase in temperature. The thermodynamic parameters like Gibb's Free energy change (ΔG), Entropy change (ΔS) and enthalpy change (ΔH) were calculated which indicated that MB adsorption process was endothermic and spontaneous.
Keywards : Elephant dung, Methylene Blue, Adsorption, Kinetics, Thermodynamics.

Introduction

Textile and dyeing industry effluent can create serious environmental pollution problems when they are discharged into water bodies. The untreated effluents possess toxic dyes and pigments which impart colour even at low concentration. These hazardous materials affect photosynthetic activity[1] because of reduced light penetration. So it is important to adopt some treatment methods before discharging the effluents into water to reduce the harmful effects. The methods employed for the removal of dyes from wastewaters include anaerobic decolourisation[2], chemical oxidation[3], reverse osmosis[4], ion exchange[5] and biological treatment methods[6]. These physico chemical methods are less efficient, expensive and produce wastes which are difficult to dispose. Among these methods, adsorption[7] onto activated carbon has been proven to be an effective method for the color removal in terms of initial cost, simplicity of design, easy operation and insensitivity to toxic substances[8]. Adsorption is more advantageous than the other conventional methods due to its sludge free clean process and high adsorption capacity for the colored particles. However, usage of commercial activated carbon for adsorption has some limitations like high cost and regeneration problems. This has necessitated the exploration of some effective, cheaper and easily available alternatives. Such alternatives include low cost activated carbons prepared from natural products like date pits[9], bagasse[10], fruit stones and nutshells[11], Jute fiber[12], rice husks[13], plum kernels[14] and coconut shells[15]. Activated carbons prepared from various products are widely used as adsorbents due to their high adsorption capacity, large surface area and micro porous structure. The wide usefulness of activated carbon as adsorbent is a result of their chemical and thermal stability. In this paper, an attempt has been made to use activated carbon prepared from elephant dung for the removal of MB from aqueous solution. Elephant dung is used to manufacture biogas, paper products and to make briquettes. Still a considerable amount of elephant dung goes unused. Elephant dung is disposed by dumping in landfills or by burning which causes environmental pollution problems. Therefore, use of elephant dung as a biosorbent will prove to be an effective application of the product. Further, the zero or negligible cost of elephant dung makes

this project feasible and cost effective for the removal of MB, a basic dye from aqueous solution. Among various classes of dyes basic dyes are the brightest class of soluble dyes. MB is a cationic dye used for dyeing cotton, wool and silk. It may cause eye burns to humans and animals on exposure. On inhalation it gives rise to breathing difficulties[16]. Therefore the treatment of effluent containing MB is important. The main objectives of the study are: Evaluating the possibility of using EDAC as a low cost adsorbent and studying its application to remove MB from wastewater through batch adsorption experiments; Studying the adsorption mechanism through kinetic and equilibrium data; Determining the thermodynamic parameters.

Materials and Methods

Adsorbate

Methylene Blue (CAS Number: 7220-79-3; Molecular formula: $C_{16}H_{18}N_3SCl$; Molecular weight: 319.85) was procured from Sigma Aldrich and it was used as received without further purification. A stock solution of the dye (1000 mg/L) was prepared by dissolving the dye in distilled water. Dilutions of required initial concentrations (30 and 40 mg/L) were made. The chemical structure of MB is represented in figure 1.

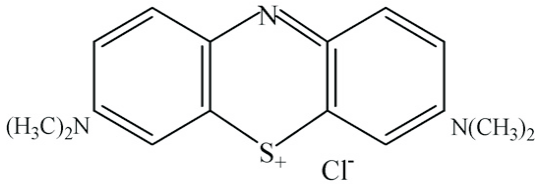

Figure 1: Structure of Methylene Blue

Adsorbent

Preparation and characterization of elephant dung activated carbon (EDAC) was reported in our previous paper[17].

Batch adsorption experiments

Batch adsorption experiments were carried out to study the kinetics of adsorption by agitating a known quantity of the adsorbent with 50 ml of dye solution of desired concentration in Labline shaking incubator at 120 rpm. After the achievement of equilibrium, the samples were withdrawn from the shaker, centrifuged and the clear solution was analyzed for residual dye concentration using Schimadzu UV-1700 PharmaSpec UV visible spectrophotometer. The effect of temperature on adsorption was studied at different temperatures (308 K, 318 K and 328 K) keeping all the other parameters constant. To study the effect of adsorbent dosage, 50 ml of dye solutions were agitated by varying adsorbent dosage ranging from 10 to 100 mg at room temperature. The amount of dye adsorbed (q_e) onto the adsorbent is calculated using the following equation.

$$q_e = (C_0-C_e)v/w$$

where, C_0 and C_e are the initial and equilibrium concentrations (mg/L) of the dye solution respectively. v is the volume of the dye solution (ml) and w is mass of the adsorbent used(mg).

Results And Discussion

Effect of initial concentration and time

The effect of contact time on the adsorption of MB by EDAC for different initial dye concentrations is shown in figure 2. A very rapid uptake had taken place in the initial stages and taken a longer period to reach equilibrium. The equilibrium time was 210 minutes for 40 mg/L, 150 minutes for 30 mg/L. Further, the amount of dye adsorbed increased with an increase in initial dye concentration. This is because, increased in initial concentration enhanced the driving force between the aqueous and solid phases and increased number of collisions between dye molecules and the adsorbent[18].

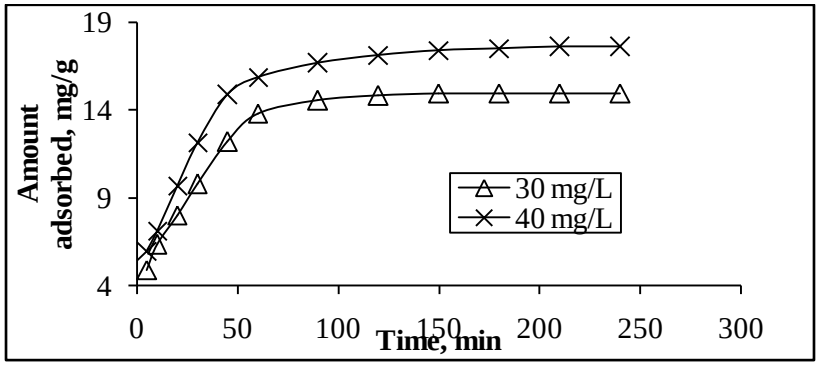

Figure 2: Effect of initial concentration

Effect of adsorbent dosage

The effect of adsorbent dosage on MB removal by EDAC is presented in figure 3. The percentage removal of dye was increased as the EDAC dose was increased from 10 mg to 100 mg. This is due to the increased surface area of the adsorbent and the availability of more number of adsorption sites[19].

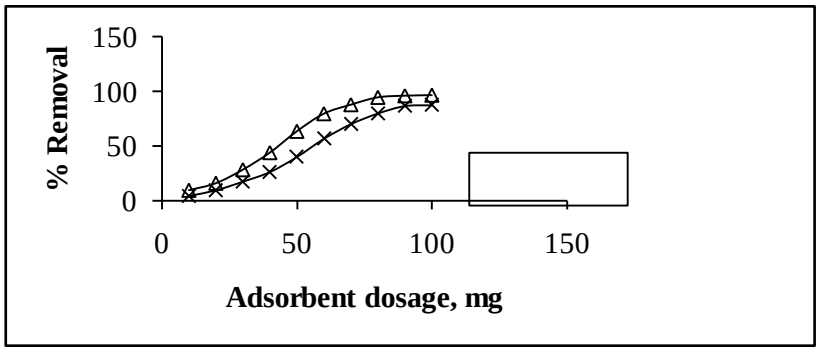

Figure 3: Effect of adsorbent dose

Effect of temperature

The effect of temperature on percentage removal of MB is shown in figure 4. The effect of temperature on the adsorption of MB was examined by carrying out experiments at 308 K, 318K and 328K with 50 ml of 40 mg/L dye solution with 100 mg adsorbent. From the results it was observed that the percentage removal of the dye increased as the temperature was increased. When the temperature is increased, the mobility of the dye molecules increased and the retarding forces on the diffusing ions decreased, thereby increasing the sorption capacity of the adsorbent[20]. The enhancement of adsorption capacity of the adsorbent at high temperatures was also attributed to the enlargement of pore size and activation of the adsorbent surface[21].

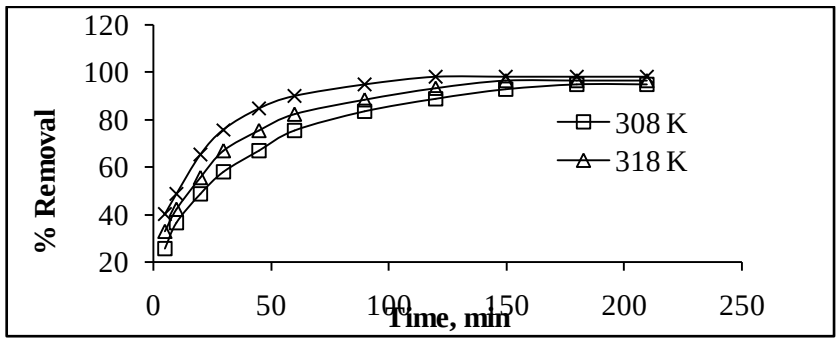

Figure 4: Effect of temperature

Adsorption kinetics

Pseudo first order, Pseudo second order and intra particle diffusion and were applied to the experimental data to analyze the adsorption kinetics of MB. The results of all the kinetic models are presented in table 1.

Table 1 Kinetic parameters

Concentration (mg/L)	**30**	**40**
Pseudo first order kinetic model		
k_1x10^{-2} (min^{-1})	3.915	2.533
$q_{e.cal}$ (mg/g)	11.939	14.125
$q_{e.exp}$ (mg/g)	14.934	17.605
r^2	0.993	0.991
Pseudo second order kinetic model		
k_2x10^{-3}(g/mg.min)	4.067	3.586
$q_{e.cal}$ (mg/g)	16.393	19.230
r^2	0.997	0.998
Intra particle diffusion model		
k_{id} (g/mg.$min^{1/2}$)	1.797	1.920
r^2	0.998	0.973

Pseudo first order kinetic model

Pseudo first order equation can be expressed as follows[22].

$\log(q_e-q_t)=\log q_e-(k_1/2.303)t$

Where, q_e and q_t are the amounts of dye adsorbed at equilibrium and at time‘t’ respectively. k_1 is the Pseudo first order rate constant. The plot (Figure 5) of $\log(q_e-q_t)$ versus t indicates that the first order kinetic model is not best suited.

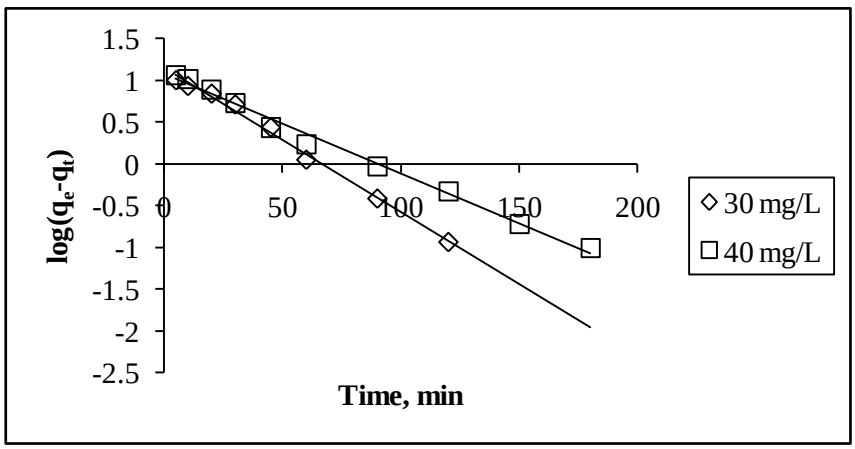

Figure 5: Pseudo first order kinetic model

Pseudo second order kinetic model

Pseudo second order kinetic model can be represented in the following form[23].

$t/q_t= 1/ k_2q_e^2 + (1/q_e)\ t$

where, k_2 is the rate constant of Pseudo second order adsorption (g/mg.min). q_e is the equilibrium adsorption capacity(mg/g). A plot of t/q_t versus t gives a linear relationship which proves that the adsorption follows Pseudo second order kinetics. q_e and k_2 can be calculated from the slope and intercept of the plot (Figure 6). The equilibrium sorption capacity q_e, increases and Pseudo second order rate constants decreases

with increase in initial dye concentration. The correlation coefficient r^2 values are higher than Pseudo first order kinetic values.

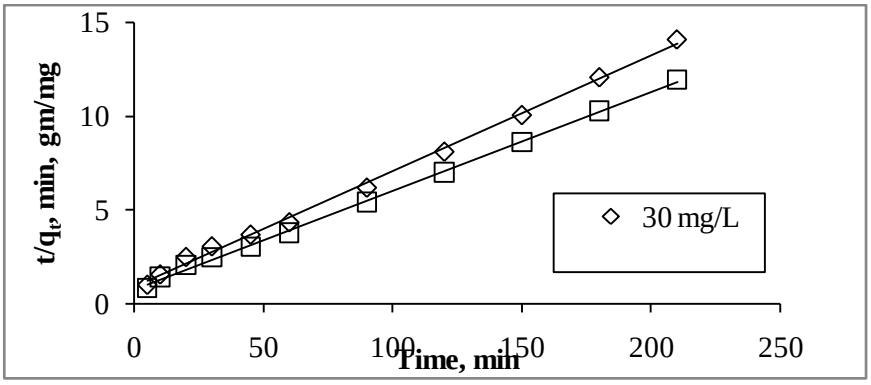

Figure 6: Pseudo second order kinetic model

Intra particle diffusion model

In the adsorption process, initial adsorption takes place on the surface of the adsorbent. In addition to that, there is a possibility of the dye molecules to diffuse into the pores of the adsorbent. Weber and Morris[24] suggested the following kinetic model to investigate intraparticle diffusion mechanism. According to this theory,

$q_t = k_d \, .t^{1/2}$

where, k_d (g/mg.min$^{1/2}$) is the intraparticle diffusion rate constant, calculated by plotting q_t versus $t^{1/2}$ (Figure 7). The plots are multi linear and there are three different portions, indicating the different stages in adsorption. The first sharper portion represents the external mass transfer. The second portion is the gradual adsorption stage where intraparticle diffusion is rate limiting. The third portion is the final equilibrium stage where, intraparticle diffusion starts to slow down due to low adsorbate concentration left in the solution[25]. As the lines do not pass through the origin, it is understood that intraparticle diffusion is not the only rate controlling step[26]. The values of k_d was determined from the slope of the second linear portion of the plot q_t versus $t^{1/2}$.

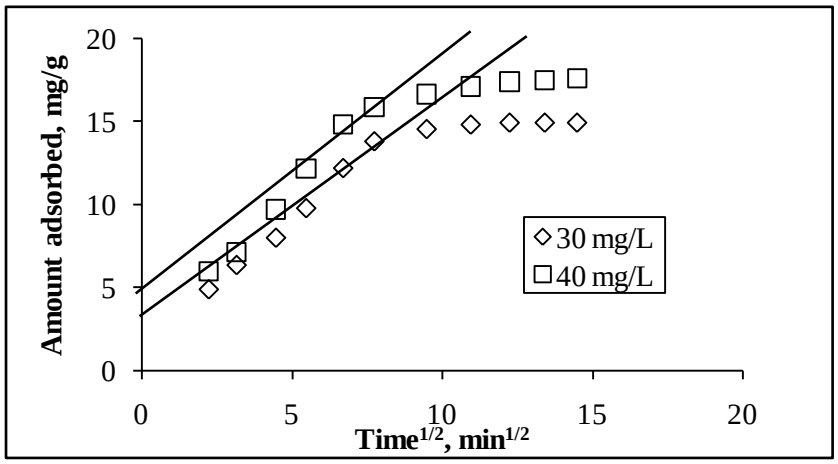

Figure 7: Intra particle diffusion model

Thermodynamics

The thermodynamic parameters such as change in free energy change (ΔG), enthalpy change (ΔH) and entropy change (ΔS) play an important role in determining the feasibility, spontaneity and heat change for adsorption process. These parameters are calculated using the following equation[27].

$\Delta G = - RT \ln k_c$

Where, R is the Universal gas constant (8.314 J $K^{-1}mol^{-1}$); T is the temperature (Kelvin); k_c is the distribution coefficient. The value of k_c is obtained from the following equation[28].

$k_c = q_e / C_e$

Where, q_e is the concentration of the dye in the solid phase and C_e is the concentration of the dye in solution phase. The Gibb's free energy change is calculated from the following equation.

$\Delta G = \Delta H - T \Delta S$

The equation can also be written as

$\ln K_c = \Delta S/R - \Delta H/RT$

The thermodynamic parameters ΔH and ΔS are obtained from the slope and intercept of the plot (Figure 8) $\ln k_c$ versus 1/T respectively. The negative ΔG values obtained are 11.254, 11.619 and 11.984 kJ/mol at 308, 318 and 328K respectively. It is understood that negative ΔG values decreased as the temperature was increased. This confirmed that the adsorption process was feasible and spontaneous. The positive value of ΔH (7.812 J/K/mol) suggested that the sorption process was endothermic[29]. The positive values of ΔS (36.514 J/K/mol) proved the increased randomness at the solid solution interface during adsorption process[30].

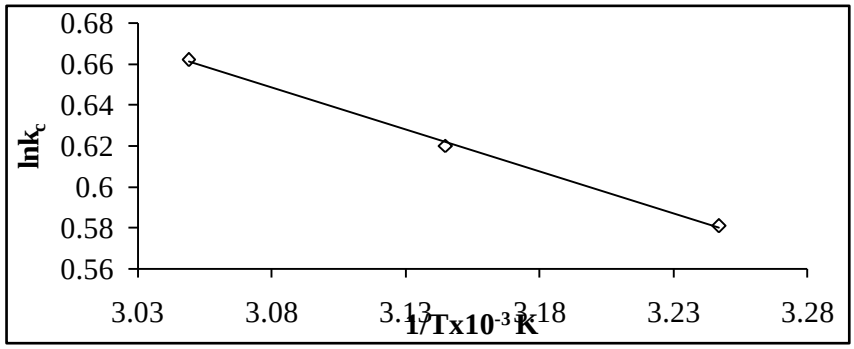

Figure 8: Vont Hoff's plot

Conclusions

Sulphuric acid treated EDAC was prepared and characterized by various physical and chemical methods. From the experiments, it is concluded that EDAC can be used as an effective adsorbent for the removal of MB from aqueous solution due to its easy availability, negligible cost and dye uptake capacity. From the batch adsorption studies, the percent removal of dye was dependent on contact time, initial dye concentration, adsorbent dosage and temperature. The equilibrium time was found to be 210 minutes for 40 mg/L and 150 minutes for 30 mg/L dye solutions. The optimum adsorbent dosage was found to be 100 mg. The kinetics of adsorption process was investigated using pseudo first order kinetic model and pseudo second order kinetic model. The results showed that the adsorption process followed pseudo second order kinetic model. Mechanism of adsorption was explained by intraparticle diffusion model. Negative ΔG and positive ΔS values suggested that the adsorption process was spontaneous and endothermic in nature.

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