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Methylene Blue Adsorption onto Coconut husks/Polylactide Blended Films: Equilibrium and Kinetic Studies

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Abstract
The removal of cationic methylene blue (MB) from aqueous solutions by coconut husks/polylactide blended films was studied in a batch system. Experiments were modeled as a function of contact time, initial dye concentration, ionic strength, adsorbent dose, temperature and initial solution p^H. Equilibrium data fitted the Langmuir isotherm model (R^2>0.9866) with monolayer adsorption capacity q_m = 16.34mg/g at 296K. Adsorption kinetics followed the pseudo-second model (R^2>0.9997) hence chemisorption rate limiting step was dominant. The results have shown viability of coconut husks/polylactide blended films for the removal of recalcitrant MB from both domestic and industrial wastewaters.

Key words: coconut husks, polylactide, methylene blue, isotherm, kinetics

1. Introduction

Increased global growth of textile industries has led to high volumes of dye laden wastewaters [1-3]. The annual global consumption of synthetic dyes by textile industries is in excess of 1.0 x 10^7 kilograms [4] with almost 1 million kilograms discharged into the aqueous environment [5]. Most synthetic dyes are aromatic in nature making them physical, chemical, thermal, biological and optical stable. Upon degradation, the dye products are toxic, carcinogenic and mutagenic to life forms [6, 7].

Methylene blue is a heterocyclic aromatic cationic dye widely used in the dyeing of paper, linen, textiles, bamboo and wood. It's stable and resistant to chemicals, physical stressors, and microorganisms. Exposure to MB causes increased heartbeat, shock, vomiting, cyanosis, jaundice, quadriplegia and tissue necrosis [8]. Hence, the removal of MB dye from textile wastewater is essential to protect the health of both aquatic and terrestrial ecosystems.

A variety of physical, chemical and biological treatment methods have been reported [9-11]. The choice of method is limited by cost, efficiency, release of secondary effluents and simplicity in design for operation [12-14]. Among the treatment methods, adsorption of dye molecules onto adsorbents such as biomass, clays and algae is the most preferred. It is simple, efficient and cost effective [10-12].

Recently, blending biopolymers with agricultural wastes has led to adsorbents with improved efficiency. Polylactide/spent brewery grains (SBGs) films have been applied to remove malachite green [15]. Blends of polyvinyl alcohol (PVA) with scleroglucan, cellulose microfibers and zein and Chitosan-g-poly (acrylic acid)/vermiculite hydrogel composites have shown potential for MB dye removal [16, 17]. In the present study coconut husks/polylactide blended films prepared by solvent-casting method using dichloromethane have been investigated for methylene blue adsorption.

Polylactide (PLA) is biodegradable aliphatic polyester with high strength, modulus thermoplastic and easily processed [18, 19]. Decreased production cost has diversified its application from biomedical to packaging, textile fibers and composite materials [20, 21]. Blending of PLA with other biopolymers has been found to enhance its properties [15, 22]. Coconut husks are agricultural wastes obtained from coconut trees that grow in low altitude areas along warm coastlines.

2. Experimetal Methods

2.1 Materials

Coconut husks were collected from Vuga in Kwale County, Kenya. They were ground into fine powder and washed with warm water until clean. Clean powder was soaked in distilled water, washed thoroughly and dried to constant weight in a thermostat oven at 313K for 8 hours. Dry powder was sieved into <300μm particle size and used in subsequent studies with polylactide (PLA). Equal masses of PLA and coconut husks powder were uniformly mixed in liquid dichloromethane. The mixture was then spread onto a thin film on a glass plate and dried at 313K in an oven for 8 hours. Dry films were removed and stored. Plain PLA films were prepared in dichloromethane as control.

Cationic methylene blue was purchased from Kobian Scientific-Kenya (Merck Manufacturers) and used without further purification. Experimental dye solutions were prepared from 1000mg/L MB stock solution.

2.2 Batch Adsorption Experiments

Experiments were carried out in triplicate at 296K by agitating a fixed mass of adsorbent with 50mL MB of known initial concentration and neutral pH in 250ml Erlenmeyer flasks on an orbital shaker preset at 300rpm. Effect of contact time on adsorption was studied using 0.125g of CH-PLA blended films with 26mg/L MB concentration and measuring residual dye concentration every 5 minutes at λ_{max} = 645nm using a UV/VIS spectrophotometer (Turner Model SP-850) for 120 minutes. The same procedure was repeated with Plain PLA films as control.

Effect of initial dye concentration on adsorption was studied using 50mL dye of initial concentration varied from 20mg/L to 32mg/L in conjunction with 0.125g adsorbent and all other experimental conditions kept constant. Adsorbent dosage was increased from 0.1g to 0.175g. Initial MB pH was adjusted from 1.5 to 12.5 using 0.05M $HCl_{(aq)}$, 0.05M $NaOH_{(aq)}$ and distilled water.

Effect of temperature on adsorption was studied using 40ml of 26mg/L MB solutions and 0.125g CH-PLA blended films. Temperature was varied from 293K to 323K using metabolic shaking incubator (Dubnoff) preset at 400rpm and 25 minutes equilibration time.

Effect of salts on adsorption was studied using 25ml of 26mg/L initial MB concentrations added to seven 250ml Erlenmeyer flasks. To each of the flask, varying amounts 0.1M $NaCl_{(aq)}$ and distilled water were added followed by 0.125g of CH-PLA blended films and agitated at 300rpm on an orbital shaker for 40 minutes equilibration time.

2.3 Adsorption Isotherms

Adsorption isotherms were done at 296K where 50mL of MB solutions of different initial concentrations (20-32mg/L) were placed in a set of 250ml Erlenmeyer. About 0.125g of adsorbent was added to each flask containing dye solution and agitated at 300rpm on an orbital shaker for 60 minutes equilibration time. Residual dye concentration at equilibrium was measured at λ_{max} = 645nm using a UV/VIS spectrophotometer (Turner Model SP-850). The equilibrium adsorption capacity, q_e (mg/g) for the adsorbent was calculated using equation 1:

$$q_e = \frac{Co-Ce}{M} \times V \tag{1}$$

Where C_o and C_e are the initial and residual MB concentrations (mg/L) respectively while M is adsorbent weight (g) and V is the volume of solution (L).

3. Results and Discussions

3.1 Effects of Contact Time

The influence of contact time on MB adsorption is shown in figure 1. Dye uptake was rapid within initial 5 minutes due to higher number vacant adsorption sites on adsorbent surface [15, 23]. Adsorption equilibrium time was 60 minutes for CH-PLA blended films and 10 minutes for Plain PLA films. At equilibrium, the rate of dye adsorbing and desorbing from the adsorbent surface is almost constant. Hence any increase in contact time has less influence on adsorption. The amount of dye adsorbed at the equilibrium time reflects the maximum adsorption capacity of the specific adsorbent, q_e (mg/g), under the given operating conditions [24]. Similar observations have been reported by Abdallah and Taha, [25] on *Aspergillus fumigates*. Equilibrium adsorption capacity $q_{e,}$ for CH-PLA blended films and plain PLA films were 9.74mg/g and 1.72mg/g respectively. Plain PLA films have lower uptake of cationic MB dye molecules compared to the blended films. Chanzu *et al.*, [15] also demonstrated lower removal of cationic malachite green dye onto Plain PLA films compared to PLA/SBGs blended films. Hence this indicates that Plain PLA has low affinity for cationic dyes.

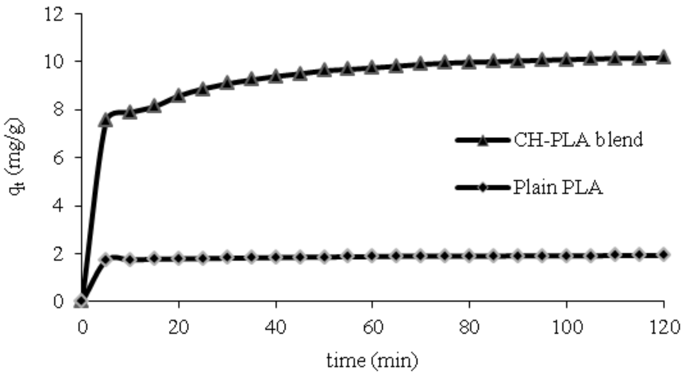

Fig 1: Effect of contact time for methylene blue adsorption

3.2 Effect of Initial Methylene Blue Concentration

The effect of initial MB dye concentration on adsorption was investigated and the results shown in figure 2. MB uptake increased with increasing initial dye concentration. At lower MB concentration, fractional adsorption (the ratio between the numbers of dye molecules to the number of available actives sites) is low and adsorption is independent of initial dye concentration. On the other hand the number of dye molecules is higher when concentration is increased resulting to a higher fractional adsorption hence increased uptake. Generally, it is the believed that a higher initial dye concentration provides greater driving force to overcome mass transfer resistance between the aqueous and solid surfaces hence enhancing sorption process [24].

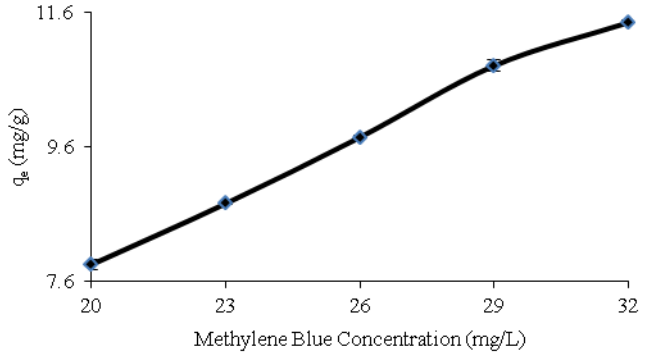

Fig 2: Effect of initial methylene blue concentration on adsorption

3.3 Effect of Initial Adsorbent Dose

Effect of adsorbent dose on adsorption was investigated using fixed initial MB concentration at 26mg/L while varying adsorbent dose from 0.1g to 0.175g. As shown in figure 3, equilibrium adsorption capacity, q_e (mg/g) decreases with an increase in adsorbent dose. At low adsorbent dose, surface active sites are readily accessible by dye molecules hence higher adsorption capacity. On the hand an increase in adsorbent dose increases number of surface active sites. However, overlapping of adsorbent particles hinders dye molecules access to surface active sites hence lower adsorption. Thus low adsorbent dose increases adsorption capacity [24].

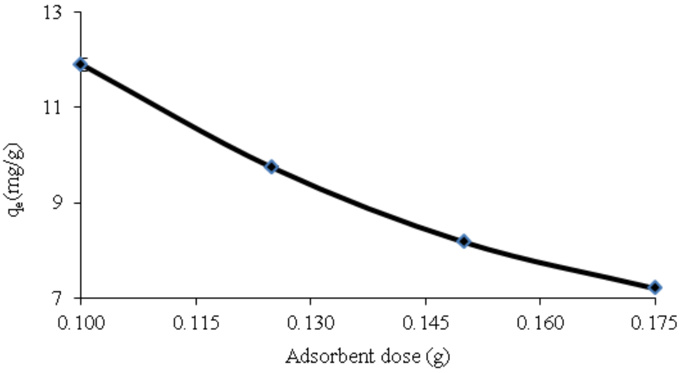

Fig 3: Effect of initial adsorbent dose on adsorption

3.4 Effect of Ionic Strength

Wastewaters especially from textile industries contain varying quantities of metal ions which significantly affect the adsorption process. In this study, volumes of distilled water and 0.1M $NaCl_{(aq)}$ were varied to alter the concentration of $Na^+_{(aq)}$ and $Cl^-_{(aq)}$ions in solution. These ions interact with dissociated dye molecules and compete to adsorb on adsorbent surfaces. About 25ml of 26mg/L initial MB at neutral p^H was used and all other experimental conditions kept constant. After equilibrium was attained, adsorption capacity of adsorbent was evaluated. Figure 4 shows that increased ionic strength lowers adsorption of MB. The decrease could be attributed to competition for available active sites between the cationic dye molecules and the positively charged $Na^+_{(aq)}$ being introduced [26]. A higher concentration of $Na^+_{(aq)}$ outnumber cationic dye molecules leading to decreased adsorption. Further smaller $Na^+_{(aq)}$ ions easily access anionic sites on adsorbent surface compared to the larger cationic dye molecules. It's also believed increased salt concentration expands the thickness of the electrical diffused double layer between adsorbate species and adsorbent surface. This expansion decreases electrostatic attraction of dye molecules to adsorbent surface hence low adsorption [15].

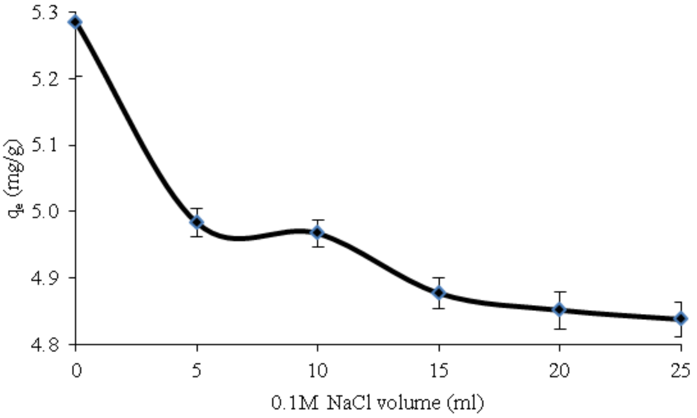

Fig 4: Effect of ionic strength on adsorption

3.5 Effect of Initial Methylene Blue p^H

Adsorption is normally p^H dependent. Initial p^H affects dye stability as well as surface characteristics of adsorbents [9, 15, 27]. The adsorption process was investigated over p^H range from 1.5 to 12.5. Figure 5 shows that an increase in p^H to 3.0 increases MB adsorption. This could be attributed to buildup of negative charge on the adsorbent surface which strongly attracts the cationic dye. At lower p^H, $H^+_{(aq)}$ compete with MB molecules for adsorption onto adsorbent anionic sites hence lower MB adsorption. However as p^H is increased from 3.0 to 12.5 there is a reduction in MB removal. The secondary formation of $NaCl_{(aq)}$ due to displacement of $Cl^-_{(aq)}$ from MB molecule with $NaOH_{(aq)}$ decreases dye adsorption. Increasing amounts of $NaCl_{(aq)}$ therefore increases small $Na^+_{(aq)}$ ions that compete with the cationic dye molecules for anionic sites on the adsorbent [28].

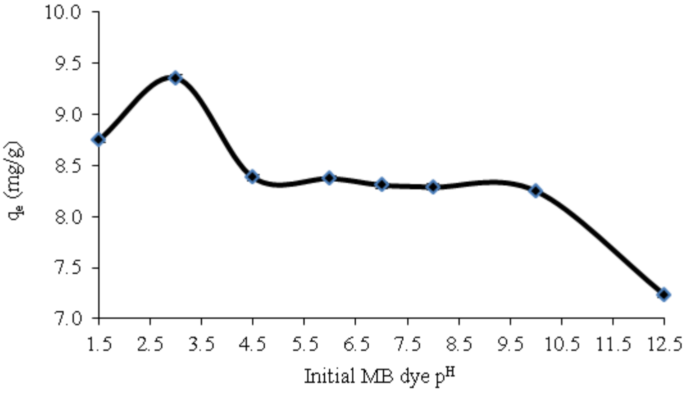

Fig 5: Effect of initial solution pH on adsorption

3.6 Effect of Temperature

Temperature has been found to alter the rate of dye molecules, viscosity of solution media and surface characteristics of adsorbent. The effect of temperature on the adsorption of MB onto CH-PLA was investigated within temperature range of 293-323K and the results shown in figure 6. The adsorption process was endothermic. An increase in temperature reduces viscosity of solution and causes activation of adsorbent surfaces which enhances the rate of diffusion of adsorbate molecules across the external boundary layer as well as in the internal pores of particles [29]. The endothermic nature on the adsorption of MB by adsorbents has also been reported by Sajab *et al*., [30] on oil palm empty fruit bunch fibers.

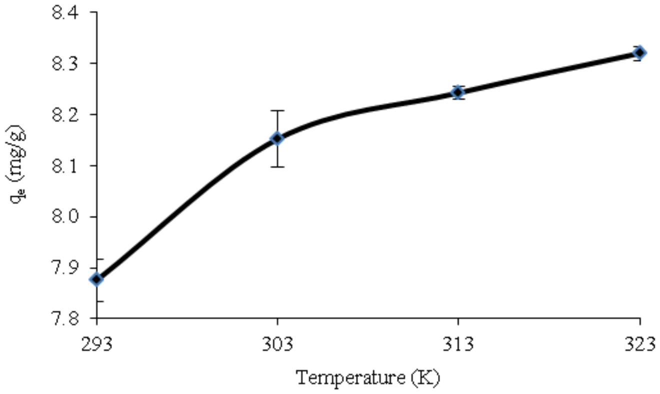

Fig 6: Effect of temperature on adsorption

3.7 Adsorption Isotherms

Isotherm models are used to describe the relationship between amounts of adsorbed dye with its equilibrium concentrations in solution. The Langmuir isotherm (equation 2) is based on the theoretical principle that only a monolayer exists on an adsorbent. Its linear form is written as [31]:

$$\frac{C_e}{q_e} = \frac{1}{q_m K_L} + \frac{C_e}{q_m} \qquad (2)$$

Main features of equation 2 are described by the dimensionless separation factor R_L given as:

$$R_L = \frac{1}{q_m K_L} \qquad (3)$$

Where C_e, q_e, q_m and K_L respectively are equilibrium dye concentration (mg/L), equilibrium adsorption capacity (mg/g), Langmuir monolayer constant (mg/g) and Langmuir constant for adsorption energy (L/mg).The shape of the isotherm can be described as unfavorable ($R_L > 1$), linear ($R_L = 1$), favorable ($0 < R_L < 1$) and irreversible ($R_L = 0$) [32]. A plot of $\frac{C_e}{q_e}$ against C_e is linear for a sorption process obeying the basis of this equation with q_m and K_L obtained from the slope and intercept respectively.

The Freundlich Isotherm assumes that dye uptake occurs on a heterogeneous surface by multilayer adsorption and amount of adsorbed adsorbate increases infinitely with an increase in concentration. The linear form of the Freundlich isotherm is presented in equation 4 [33]:

$$\log_{10} q_e = \log_{10} K_F + \frac{1}{n} \log_{10} C_e \qquad (4)$$

Where n and K_F are number of layers and Freundlich constant respectively. For a sorption process obeying this model, the plot of $\log_{10} q_e$ against $\log_{10} C_e$ is linear with K_F and n obtained from the intercept and slope respectively. Values of n between 1 and 10 indicate a favorable adsorption process [34] while higher K_F values indicate an easy uptake of dye from solution [35].

The isotherm parameters with regression coefficients presented in table 1 were obtained from linear plots of Langmuir isotherm (figure 7) and Freundlich isotherm (figure 8). The experimental data fits well to Langmuir isotherm model (R^2>0.9866) compared to Freundlich isotherm model (R^2>0.9722). Therefore adsorption process was favorable (R_L = 0.0805) and occurs through a monolayer formation (q_m = 16.34mg/g) on the adsorbent.

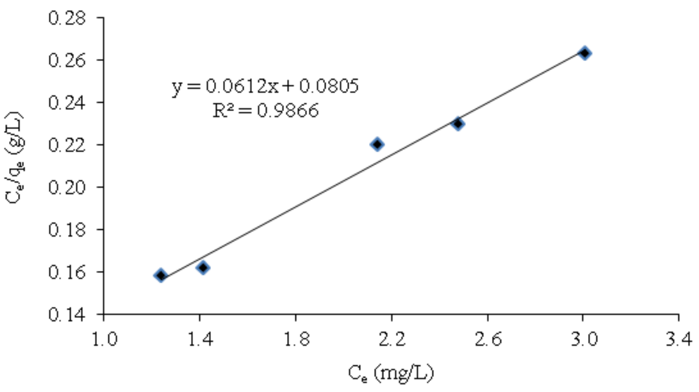

Fig 7: Langmuir isotherm plot

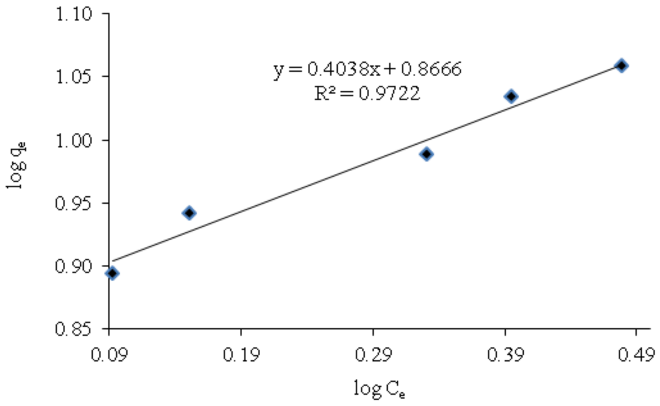

Fig 8: Freundlich isotherm plot

Table 1: Langmuir and Freundlich Isotherm Parameters

Langmuir Isotherm				Freundlich Isotherm		
q_m (mg/g)	**K_L (L/mg)**	**R^2**	**R_L**	**K_F (mg/g)**	**n (g/l)**	**R^2**
16.34	0.7602	0.9866	0.0805	7.36	2.4765	0.9722

3.8 Adsorption Kinetics

To describe the adsorption mechanism experimental data was fitted to kinetic models. Adsorption kinetics was investigated using pseudo-first-order kinetics, pseudo-second-order kinetics and intra-particle diffusion models. The Lagergren [36] pseudo-first order kinetics model is presented in equation 5 as:

$$\log\,(q_e - q_t) = \log\,q_e + \frac{K_1}{2.303}t \quad (5)$$

Where q_t, K_1 and t are adsorption capacity at a given time (mg/g), pseudo-first order adsorption rate constant (min^{-1}) and time (min) respectively. A linear plot of $\log\,(q_e - q_t)$ against t, gives q_e (mg/g) as intercept and K_1 from slope.

The linear form of the Lagergren pseudo-second order kinetics model described by Ho and Mckay [37] is given in equation 6 as:

$$\frac{t}{q_t} = \frac{1}{K_2 q_e^2} + \frac{t}{q_e} \quad (6)$$

Where K_2 is the pseudo-second order adsorption rate constant ($gmin^{-1}mg^{-1}$). The linear plot of $\frac{t}{q_t}$ against t, enables calculation of q_e (mg/g) from the slope and intercept K_2. The kinetic parameters for the linear plots of pseudo-first-order (figure 9) and pseudo-second-order (figure 10) are shown in table 2. The adsorption of MB onto coconut husks/polylactide films follows pseudo-second-order kinetics since $q_{e,exp}$ are in agreement with $q_{e,cal}$ (table 2) and higher correlation coefficient (R^2>0.9997). Hence the adsorption of MB through pseudo-second order kinetics implies that the rate limiting step during adsorption is based on chemisorption. Therefore the adsorption rate was dependent on both concentration of dye molecules and surface characteristics of the adsorbent.

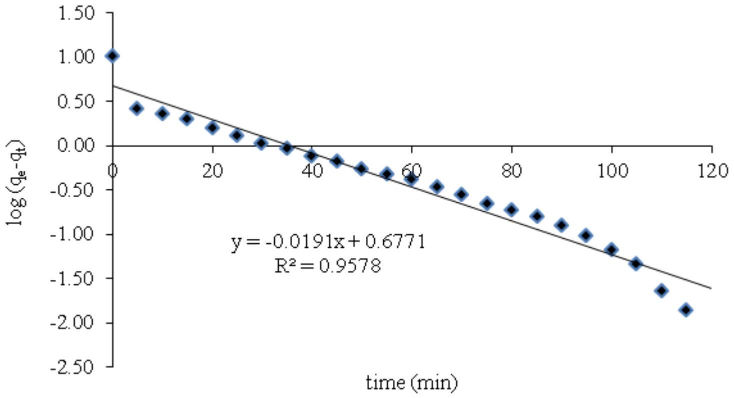

Fig 9: Pseudo-first order kinetics model

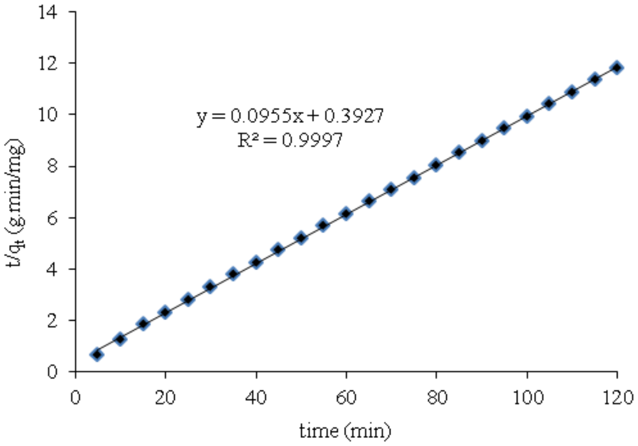

Fig 10: Pseudo-second order kinetics model

Table 2: Kinetic Parameters for Adsorption of MB dye onto Coconut Husks/Polylactide Films

Pseudo-first order				**Pseudo-second order**			**Intra-particle Diffusion**		
$q_{e,exp}$ **(mg/g)**	$q_{e,cal.}$ **(mg/g)**	K_1 **(min^{-1})**	R^2	$q_{e,cal.}$ **(mg/g)**	K_2 **(gmin^{-1}mg^{-1})**	R^2	$K_{diff.}$ **(mg/g)**	**C(mg/g)**	R^2
10.15	4.75	0.044	0.9578	10.47	0.0232	0.9997	0.1855	8.24	0.9428

According to Weber and Morris [38], intra-particle diffusion processes are normally expressed in terms of the square root of time. The intra-particle diffusion process model is given in equation 7 as:

$$q_t = K_{diff.}\, t^{1/2} + C \qquad (7)$$

Where $K_{diff.}$ is intra-particle diffusion rate constant ($mgg^{-1}min^{-1/2}$) and C represents boundary layer thickness. Intra-particle diffusion is normally a slow process preceded by mass transport of adsorbate molecules to adsorbent surface. Mass transport resistance could be eliminated for a well agitated system. If intra-particle diffusion is rate controlling then the plot of q_t against $t^{1/2}$ is linear with slope giving $K_{diff.}$ and C from intercept. If C is close to zero then diffusion is the only rate limiting step [39]. Higher C values indicate greater contribution of surface sorption in rate determining step. Figure 11 gives the intra-particle diffusion plot for MB adsorption onto coconut husks/polylactide blended films.

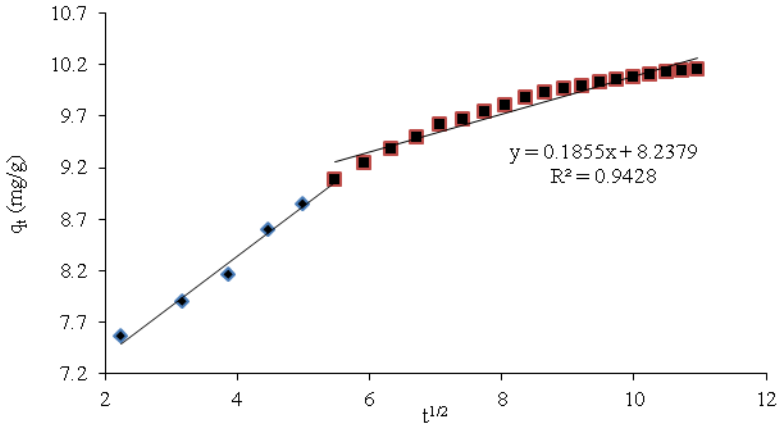

Fig 11: Intra-particle diffusion model

Two steps characterize the adsorption process. The first initial rapid step is correlated with the boundary layer diffusion of adsorbate. This is followed by a gradual adsorption of MB molecules where intra-particle diffusion is rate controlling. The linear curves do not pass through the origin hence intra-particle diffusion is not the only rate controlling step. Therefore more than one process affects adsorption process [40-42].

The intra-particle diffusion parameters obtained in the second step adsorption process presented in table 2 shows that the boundary layer thickness C is 8.24mg/g indicating greater contributions of surface sorption in the rate controlling step. Therefore, the adsorption of MB is a multi-step process involving adsorption on the external surface and diffusion into the interior [43].

4. Conclusions

The adsorption of methylene blue was influenced by several operational factors such as contact time, temperature and solution p^H. Adsorbent adsorption capacity at equilibrium increased with increase in temperature, initial dye concentration and contact time. However increased adsorbent dosage and ionic strength lowers adsorption capacity of adsorbent. Maximum adsorption was found at $p^H<3$ and decreased at higher p^H. The experimental data agrees well with the Langmuir model ($R^2>0.9866$). On the basis of the Langmuir model, the monolayer adsorption capacity for the adsorbent, q_m is 16.34mg/g at 296K. The adsorption process follows pseudo-second kinetics model ($R^2>0.9997$) hence chemisorption. Thus adsorption of MB onto coconut husks/polylactide blended films is influenced both by number of surface active sites on adsorbent as well as dye concentration.

The plot of adsorption capacity, q_t (mg/g) against $t^{1/2}$ for intra-particle diffusion depicts a multi-linearity process. Therefore, intra-particle diffusion was not the only rate controlling step and adsorption process is multi-step involving adsorption on the external surface and diffusion into the interior.

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6. References

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