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Sorption Kinetics and Isotherm Studies of Basic Dye Using Agricultural Waste: Silk Cotton Hull

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Abstract:- Finding out the effectiveness of Malachite Green dye removal is the aim of the present work by using Silk cotton hull an agricultural waste as an activated carbon. Even if various materials are used in the making of activated carbons ample availability and low cost of agricultural by-products create excellent source of raw materials for activated carbon. The Silk cotton hull activated carbon was prepared in the laboratory by carbonization followed by activation. To evaluate the influence of various experimental parameters like initial solution pH, contact time, initial concentration of dye and adsorbent dosage on the removal of Malachite Green dye from aqueous solution batch adsorption studies was performed. The concentration of the residual due was measured using UV visible spectrometer corresponding to the maximum adsorption for the dye solution. The equilibrium of adsorption data was interpreted by using the Langmuir and Freundlich isotherm and Kinetic studies for malachite green- Silk cotton hull batch adsorption system. Batch test showed that maximum of 92% of dye was removed when the dye concentration was 5 mg/L, at an adsorbent dose of 0.5 gm/L at dye pH 8 in 40 minutes. From the studies it is confirmed that the equilibrium data fitted very well with the both Freundlich and Langmuir isotherms. The maximum adsorption capacity of Silk cotton hull carbon was found to be 4.85 mg/g and pseudo second order kinetic model is more likely to predict the behavior over the whole experimental range of adsorption than pseudo-first order model. The intra particle diffusion model indicates that the intra particle diffusion is not the sole- rate determining step and also regression results indicate that the linear regression model give the best results. The above findings suggest that silk cotton hull can be effectively used for decontamination of dye containing wastewater.

Keywords*:* Silk cotton hull, adsorption, batch study, malachite green, isotherm, kinetics.

1. Introduction

The increase in global contamination of water systems with industrial and natural chemical compounds is a major environmental problem [1]. Out of many contaminants present in wastewater, such as acids, bases, toxic organic and inorganic dissolved solids and color, colors are considered the most undesirable and are mainly caused by dyes. The main source of dye is wastewater streams of many industrial sector, such as dying, textile, tannery, food processing and the paint industry; due their chemical composition they are resistant to fading on exposure light, water and many chemicals and there for difficult to remove dye once released into the environment [2]. The textile industry, a major consumer of water for several of its wet processing operations also a major producer of effluent wastewater containing dyes. Dyes though present in only small amounts are highly detectable and there are capable of causing serious problems to an aesthetic nature in the receiving water bodies. Discharge of dye bearing wastewater into natural streams has created significant concern, of impart toxicity, visibility and also presence of carcinogenic have been reported. Therefore, safe and effective treatment of dye containing wastewater by using low cost techniques is always a challenging task for the researchers and industries. More than 100000 dyes available in the trade with more than 7 X 10^5 tons of dyes are produced annually in the world and 1000 tons of these dyes are released annually into the aquatic system [3]. Dyes are classified into anionic (direct, acid and reactive dyes), cationic (basic dyes) and non-ionic (disperse dyes). Water-soluble anionic dyes (reactive dyes) are the most commonly dyes used due to their application ease, bright colors, and excellent color-fastness [4]. The removal of basic cationic dyes is important because, these dyes have high brilliance and intensity of color. They are highly visible even in a very low concentration and more toxic than acid dyes [5].

Due to low biodegradability of color causing pollutants, physico-chemical methods have been commonly adopted for treatment of color bearing wastewater. Other conventional methods for treating wastewater containing dyes are chemical oxidation, radiation, ion exchange, reverse osmosis and adsorption. The process of adsorption as an edge over the other methods due to its sludge free clean operation and completely remove dyes, even for the diluting solution. Biowaste is an important sustainable source of adsorption activities for many harmful materials, such as hazardous metals/elements and organics. Activated carbons have been indigenously prepared by the various raw materials like bagasse, straw, fruit nuts, shells, hulls, agricultural byproducts. Although various materials are used in the production of commercial activated carbons, abundant availability and low cost of agricultural byproducts make them good candidature and source of raw materials for activated carbon. Adsorbents are the primary factor in adsorption, for which many substances have been utilized. Moreover, natural adsorbents are highly effective and scientific researchers have recently attracted attention. The advantages of adsorption are simplicity, efficient, high selectivity, high performance, inexpensive recovery of adsorbent and adsorbate, and efficient removal of contaminants [6]. The adsorption isotherm is widely used to elucidate the relationship between the amount of dye adsorbed at constant temperature and its concentration in equilibrium solution. It is an important tool of both theoretical and practical point of view. In order to optimize the adsorption design and also to predict its corresponding parameters. The parameters obtained from different isotherm models provide information about adsorption mechanism and the surface properties of the adsorbent. Linear regression coefficient is frequently used to determine the best fitting isotherm. [7]. The solute uptake rate can be described by adsorption kinetics, which is very important for designing suitable technologies of adsorption [8]. In recent years, adsorption mechanism involving kinetic-based models have been reported [9]. Attempts have therefore been made to utilize the silk cotton hull is a natural as well as agricultural waste material as alternative sorbent. silk cotton hull have no commercial usage and are not eaten by livestock. Moreover, the disposal of silk cotton hull results in environmental pollution. Hence, the utilization of silk cotton hull as an adsorbent to remove dyes from industrial effluent can greatly reduce the amount of waste produced.

A number of agricultural waste materials are being studied for the removal of different dyes from aqueous solutions at different operating conditions. Agricultural waste includes Boiler Bottom Ash [10], Maize Shell Carbon [11], Tripoli [9] and Guava Leaves [12]. In the present investigation, the application of silk cotton hull (Malyaceae) carbon as a low cost absorbent has been reported to be viable for removing cation dye from aqueous solution. The effect of various parameters such as initial dye concentration, adsorbent dosage, contact time and pH has been studied

2. Materials and Methodology

Preparation of adsorbent: silk cotton hull activated carbon was prepared by treating 4 parts of the silk cotton hull with 3 parts of concentrated sulfuric acid and keeping it in the hot air oven with the temperature being maintained in the range of 85° C - 100° C for a period of 24 hours. The carbonized material was washed well to remove excess acid and dried at 101° C. The dried material was subjected to thermal activation in the muffle furnace at 600° C for 30 minutes.

Preparation of adsorbate: Stock solution was prepared by dissolving appropriate quantity (1mg/L) of malachite green, a coloring reagent in distilled water. The stock solution was diluted as required to obtain a standard solution. The same was used throughout the experiment.

Specification of dye used:

Dye – Malachite green

Color – Bluish green

Type – Basic dye

Chemical formula – $C_{23}H_{24}CLN_2$

Molecular weight – 364.9

Wave length (λ) – 616nm

The adsorption experiments were carried out in a batch process by using aqueous solution of malachite green in the concentration range 1 - 6 mg/l, the other variable parameters were absorbent dose (0.25 - 0.75 gm/l), contact time (0 - 60minutes) and pH of the medium (2 –10). The concentrations were determined with the help of carefully prepared calibration curve with standard malachite green dye solution.

Equilibrium studies:

The amount of equilibrium adsorption q_e (mg/g) was obtained by

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

The dye removal percentage can be obtained as follows

$$= \frac{C_0 - C_e}{C_0} \times 100$$

Where *Co* and *Ce* (mg/L) are the liquid phase concentration of dye at initial and equilibrium condition, respectively, 'V' the volume of the solution (L) and 'W' is the mass of adsorbent used (g).

The kinetic experiments were performed using a procedure similar to the equilibrium studies. Kinetic studies were carried out to establish the effect of time on the adsorption process and to quantify the adsorption rate.

The amount of sorption at time t, q_t (mg/g) was calculated by

$$q_t = \frac{(C_0 - C_t)V}{W}$$

Where, *Ct* (mg/L) is the liquid phase concentration of dye at any time in mg/L.

3. Result and Discussions

3.1 Effect of initial concentration of Dye

The effect of initial dye concentration on adsorption of Malachite Green dye onto silk cotton hull carbon was investigated in the range of 1- 6 mg/L of the initial dye concentration. The adsorbent dose and agitation speed values were kept at 0.5 g/L and 100 rpm and study is carried out at natural pH (existing pH) for a contact time of 60 minutes at room temperature (27±2°C). From the Figure 1 it is evident that the maximum dye removal of 86 % has occurred at an initial dye concentration of 1 mg/L and decreased for further increase in initial dye concentration for Malachite Green dye.

At higher initial concentration the decrease in adsorption may be attributed to inadequate surface area for adsorption beyond saturation limit of basic dye.

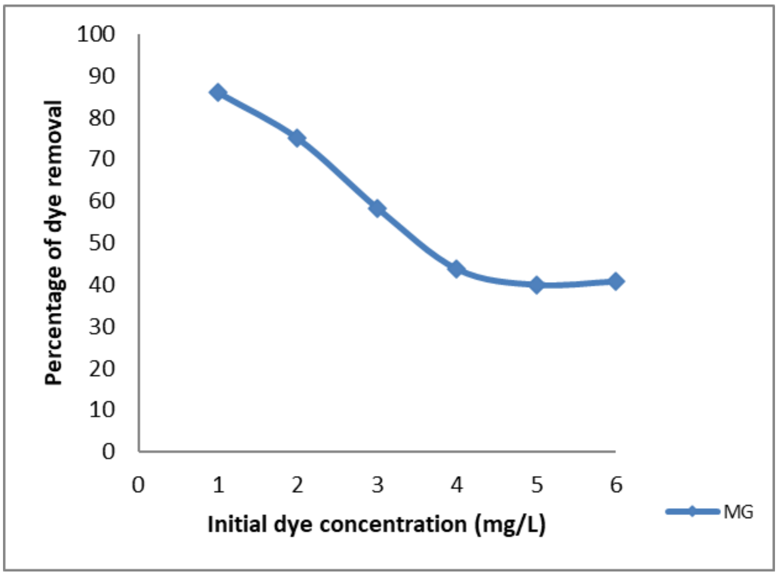

Figure 1: Effect of Dye concentration for the removal of dye

3.2 Effect of dosage of adsorbent

The effect of adsorbent dose on Malachite Green dye uptake capacity on silk cotton hull carbon was investigated with different adsorbent dose in the range of 0.25 - 0.75 g/L. Initial dye concentration and agitation speed values were kept at 1 mg/L and 100 rpm and experiments were carried out at natural pH (existing pH), contact time of 60 minutes, and at room temperature (27±2^{o}C). The influence of adsorbent dosage on dye removal by silk cotton hull carbon is presented in Figure 2. The percent removal of dye increases to 86 % with increase in adsorbent dose up to 0.5 g/L for Malachite Green dye and then it remains almost constant with increase in adsorbent dose.

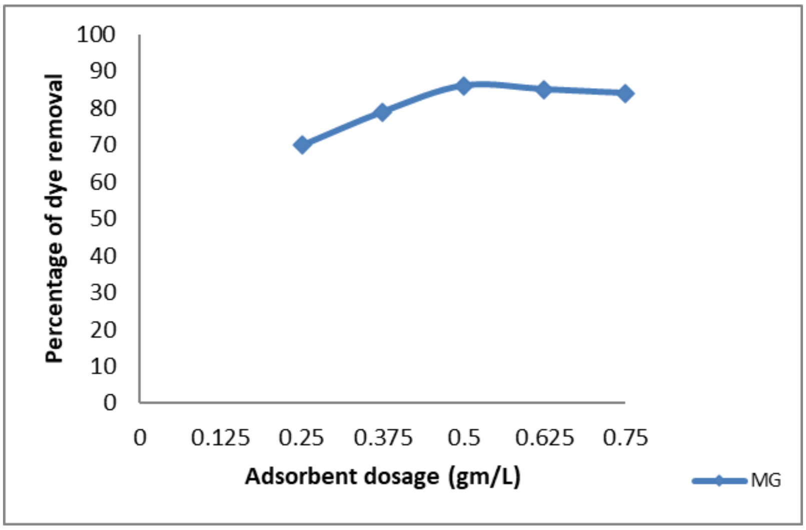

Figure 2: Removal of dye as a function of adsorbent dosage

The increase in the percentage of dye removal with adsorbent dosages could be attributed to increase in the adsorbent surface areas, augmenting the number of adsorption sites available for adsorption.

3.3 Effect of time

The effect of contact time on adsorption of Malachite Green onto silk cotton hull carbon was investigated in the range of 0 - 60 minutes. The adsorbent dose, initial dye concentration and agitation speed were kept at 0.5 g/L, 1 mg/ L and 100 rpm for Malachite Green dye, at natural pH (existing pH) and at room temperature (27±2^{o}C). The effect of contact time on uptake of dye is shown in Figure 3. The amount of Malachite Green dye adsorbed on silk cotton hull carbon increased with increase in contact time up to 40 minutes and the removal efficiency is 86 %. Thus, the time required to achieve a definite fraction of equilibrium adsorption was found to be 40 minutes for Malachite Green dye.

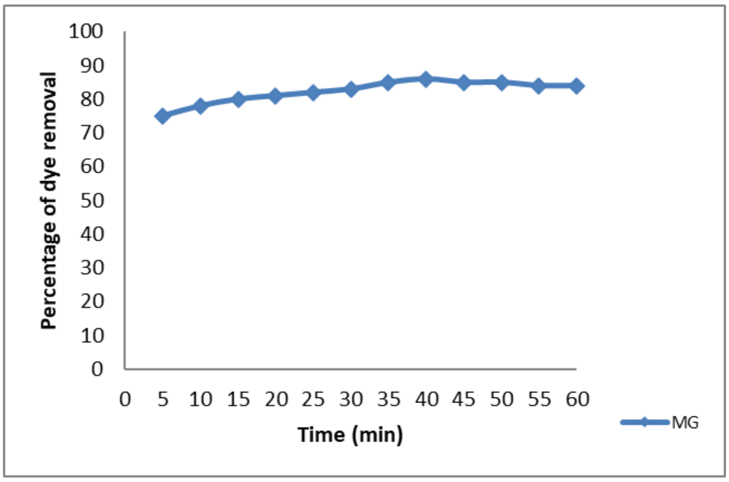

Figure 3: Effect of contact time for the removal of dye.

Generally, the rate of removal of dye increases with an increase in contact time to a certain extent. Further increase in contact time does not increase the uptake due to deposition of dyes on the available adsorption site on adsorbent material

3.4 Effect of pH

The effect of pH 2 - 10 on adsorption of Malachite Green dye from a solution onto silk cotton hull carbon was investigated for contact time in the range of 0 - 60 minutes. While adsorbent dose, initial dye concentration and agitation speed were kept at 0.5 g/L, 1 mg/ L and 100 rpm for Malachite Green dye at room temperature (27±2oC). The percentage of removal of basic Malachite Green dye by silk cotton hull carbon at different pH values for a contact time of 0 - 60 minutes is plotted in Figure 4. The removal percentage of Malachite Green dye by silk cotton hull carbon increased from 76 % to 92 % for an increase in pH of solution from 2 to 10, while the optimum pH value for the maximum dye removal was found to be 8 for a contact time of 40 minutes.

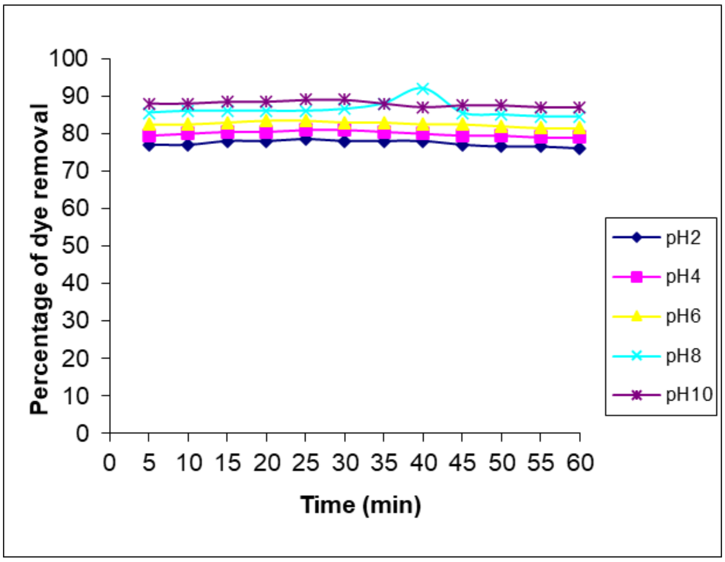

Figure 4: Effect of pH for the removal of dye.

For cationic dyes, lower adsorption of dye at acidic pH is probably due to the presence of excess H^+ ions competing with the cation groups on the dye for adsorption sites. As surface charge density decreases with an increase in the solution pH, the electrostatic repulsion between the positively charged dye and the surface of the adsorbent is lowered, which may result in an increase in the extent of adsorption.

3.5 Adsorption Isotherms

Adsorption isotherms help in describing how molecules of adsorbate interact with adsorbent surface. Equilibrium adsorption equations are required in the design of an adsorption system and their subsequent optimization.

The well-known linearized form of Freundlich isotherm can be expressed as

$$\log(q_e) = \log k_F + \frac{1}{n}\log(C_e) \quad (1)$$

Where q_e is the amount of dye absorbed per unit weight of the absorbent (mg/gm), C_e is the equilibrium concentration of the dye in aqueous solution (mg/L), k and n are constants depending upon the nature of absorbent and dye absorbed (Table 1). The lined plots in Figure 5 between Log q_e and Log C_e show the applicability of Freundlich isotherms. The value of n between 0 – 10 indicating that adsorption is efficient.

The linear form of Langmuir isotherm can be represented by the following equation

$$\frac{C_e}{q_e} = \frac{1}{Q_0 b} + \frac{C_e}{Q_0} \quad (2)$$

Where C_e is initial dye concentration (mg/L), q_e is the amount absorbed at equilibrium time per unit absorbent (mg/gm) and Q_0 and b is Langmuir constants related to adsorption capacity and energy of adsorption respectively. The lined plots in Figure 6 between C_e/q_e and C_e show the applicability of Langmuir isotherms. The value of dimensionless equilibrium parameter R_L, where R_L is equal to $1/(1+bC_0)$, where C_0 is the initial dye concentration, lie between 0-1(Table 1), showing favorable absorption of dyes on the adsorbent.

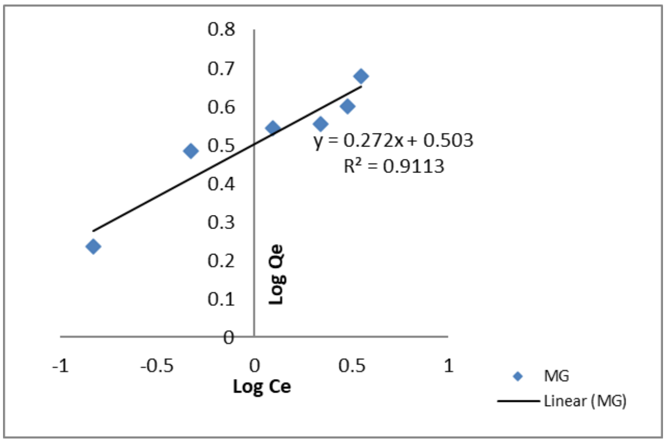

Figure 5: Freundlich isotherms for Silk cotton hull carbon

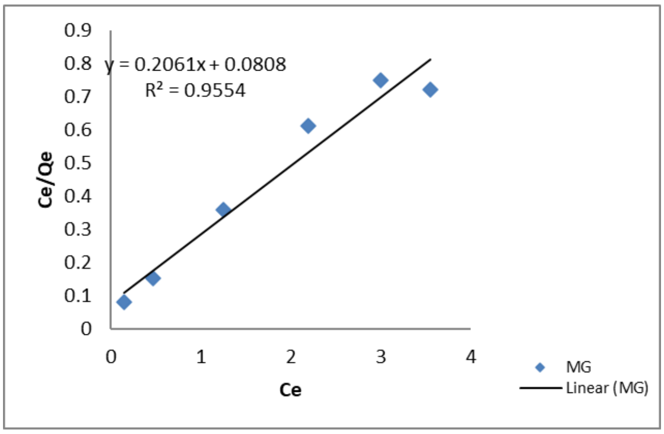

Figure 6: Langmuir isotherms for Silk cotton hull carbon

The values of $k_{F,}$ n and R^2 are found to be 1.658 (mg/g)(L/g)1/n, 3.669 and 0.911 respectively for Malachite Green dye. From the studies it was found that, for Malachite Green dye removal using silk cotton hull carbon, the value of n is such that $1/n < 1$ which indicates that the adsorption is favorable. (Table 1).

From the Table 1, values of Q_o, b, R_L and R^2 for adsorption of Malachite Green are found to be 4.85 (mg/g), 2.575 (L/mg), 0.060 and 0.955 respectively. The adsorption capacity of silk cotton hull carbon for malachite green dye is 4.85 mg/g.

Table 1: Parameters of Freundlich and Langmuir isotherms for Malachite Green (MG) dye on silk cotton hull carbon

Freundlich isotherm				Langmuir isotherm			
Dyes	k_F(mg/g)(L/g)1/n	n	R^2	Q_o(mg/g)	b (L/mg)	R^2	R_L
MG	1.658	3.669	0.911	4.85	2.575	0.955	0.060

Table 1 shows the batch absorption studies of Malachite Green

Followed the both Freundlich and Langmuir isotherms.

3.6 Kinetic studies

Adsorption is a physicochemical process that involves mass transfer of a solute from liquid phase to the adsorbent surface. In order to investigate the controlling mechanisms of the adsorption processes like mass transfer and chemical reactions, pseudo first-order, pseudo second-order kinetic studies and Intra particle diffusion equation are used to test the experimental data.

A simple kinetic analysis of adsorption is the first order rate expression given by Lagergren:

$$\log(q_e - q_t) = \log q_e - \frac{k_1}{2.303} t \tag{3}$$

Where q_e and q_t are the amounts of adsorbate adsorbed (mg g−1) at equilibrium and at time t in minute, respectively, and k_1 is the rate constant of adsorption (min−1). Values of k_1 were calculated from the plots of log (qe −qt) vs. t (Figure 7).

The table 2 shows that the correlation coefficients for pseudo first- order were low (0.8792) and the predicted values of qe;cal were not reasonably close to experimental qe;exp values, suggesting the insufficiency of pseudo-first-order model to fit the kinetic data.

The second order kinetic model is expressed as:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \tag{4}$$

Where k_2 (min gmg−1) is the rate constant of second order adsorption.

The parameters k_2 and q_e can be obtained from the plot of (t/q_t) vs. t (Figure 8), that should show a linear relationship. Also, this model is more likely to predict the behavior over the whole experimental range of adsorption than pseudo-first order model. The correlation coefficient is close to 1.0 (Table 2).

Hence, it could be concluded that the pseudo-second-order model better represented the adsorption kinetics. The results revealed that the pseudo second-order model was the best one in describing the kinetics of malachite green adsorbed onto silk cotton hull carbon.

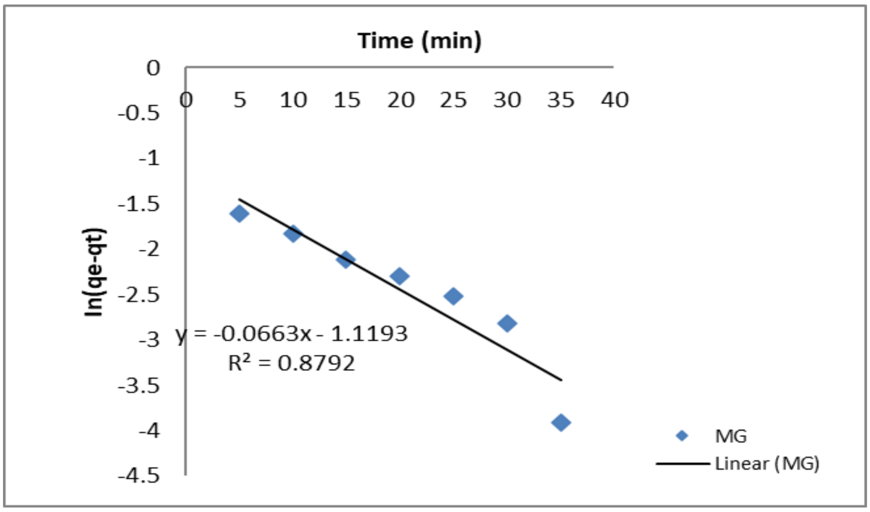

Figure 7: Pseudo-first order kinetic plot for the adsorption of malachite green on silk cotton hull carbon

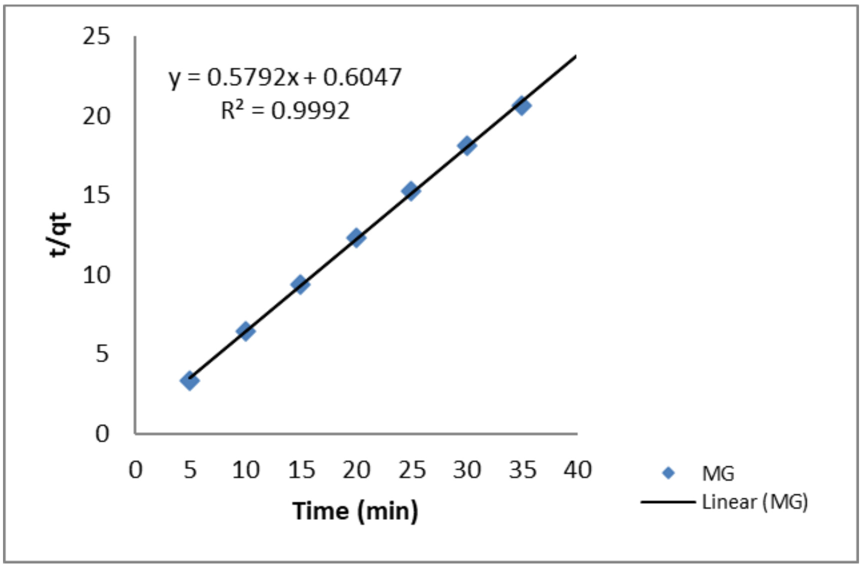

Figure 8: Pseudo-second order kinetic plot for the adsorption of malachite green on silk cotton hull carbon

Table 2: Pseudo first order and pseudo second order kinetic constants for the adsorption of Malachite Green onto silk cotton hull carbon

Dyes	q_e exp (mg/g)	k_1(min^{-1})	q_e cal (mg/g)	R^2	k_2(g mg^{-1}min^{-1})	q_e cal (mg/g)	R^2
MG	1.72	0.0663	3.06	0.8792	0.957	1.72	0.9992

3.7 Intra particle diffusion model

The intra particle diffusion is the rate controlling step when negligible diffusion of the liquid film surrounding the adsorbent. The intra particle diffusion is investigated with its mathematical expression as follows:

$$q_t = k_p t^{0.5} + C \quad (5)$$

Where q_t is the fraction dye uptake (mg/g) at time t, k_p is the intra-particle-diffusion rate constant (mg/ (g min) and C is the intercept (mg/g). The plot of qt versus $t^{0.5}$ will give k_p as slope and C as intercept (Figure 9).

The values of the diffusion rate constant, *C* and the regression coefficients R^2 are given in Table 3.

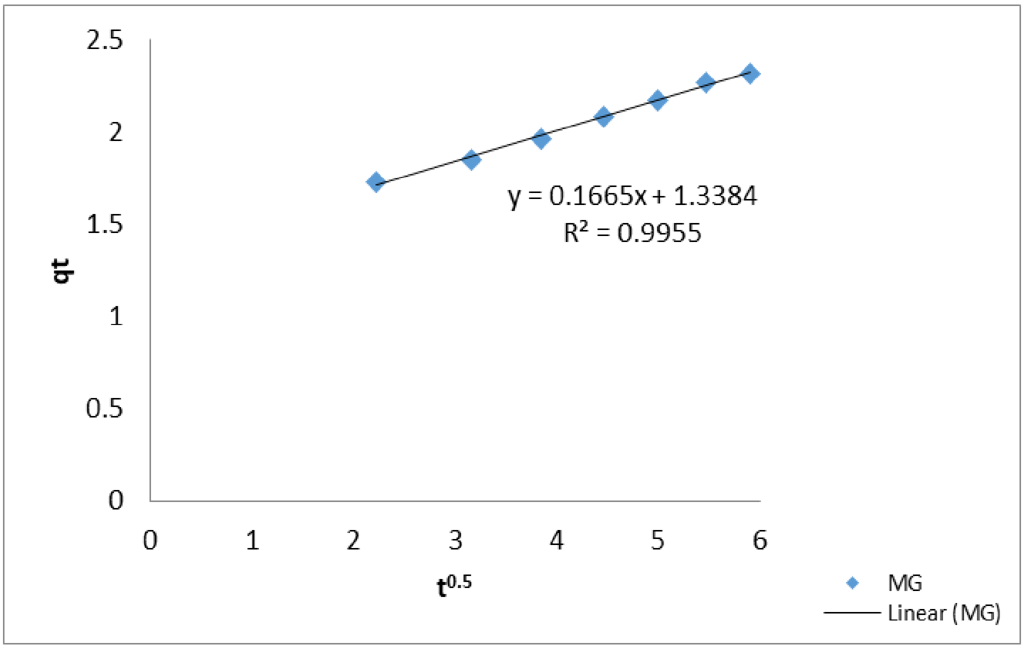

Figure.9: Intraparticle diffusion kinetic model for the adsorption of MG on silk cotton hull carbon

Table 3: Intra particle model parameters for the adsorption of Malachite Green onto silk cotton hull carbon

DYE	k_p (mg g^{-1} $min^{-0.5}$)	*C*	R^2
MG	0.1665	1.3384	0.9955

The plot shows the straight line not from the origin indicates that the intra particle diffusion is not the sole- rate determining step. It can also be confirmed on the basis of C value. However, if $C \neq 0$, indicates that the adsorption process is rather complex and involves more than one diffusive resistance and represents the thickness of the boundary layer, the larger the intercept, the greater the effect of the boundary layer.

3.8 Regression analysis

The estimated linear model interrelating percentage of color removal with the controlling parameters is express in the following Equations 6 and 7 for malachite green dye.

Y =A0+A1X1+A2X2 (6)

Y=75.30909+0.021X1+1.366667X2 (7)

Where, X1= contact time in minutes, X2= pH of dye solution and Y= percentage of color removal.

From the model, the most significant controlling parameter of the system affecting percentage of color removal is the pH of the dye solution and the least significant parameter is the contact time for Malachite Green dye for silk cotton hull carbon.

From correlation matrix correlation of percentage of color removal to pH is 1.366667 and for contact time is 0.021 for Malachite Green dye adsorption onto silk cotton hull carbon.

From the figures the R^2 evaluated as 0.9296 Malachite Green dye (Figure.10) adsorption onto silk cotton hull. The results indicate that the linear regression model gives the best results (R^2 nearly equal to 1).

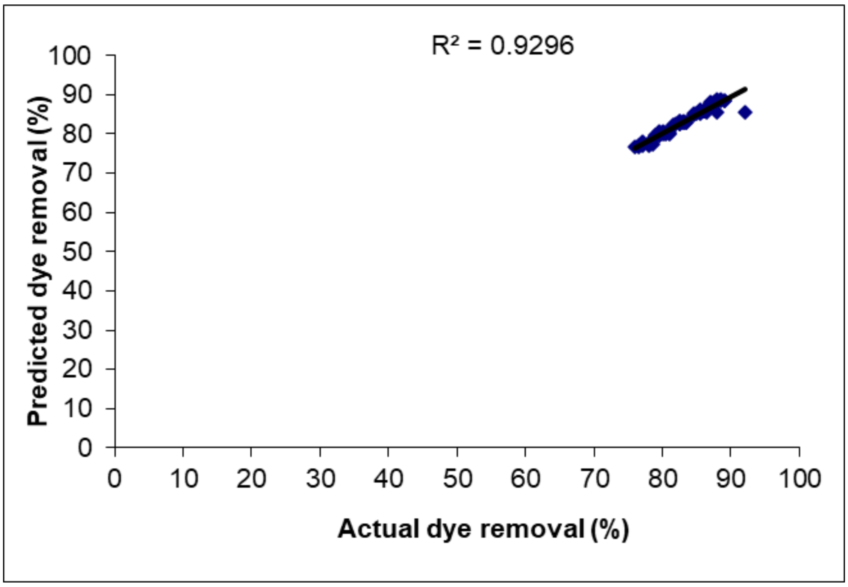

Figure 10: Linear regression plot showing observed and predicted percentage color removal of MG on silk cotton hull carbon

4. Conclusion

The present investigation explores the effect of various experimental conditions on adsorption efficiency along with kinetic and equilibrium studies. Experimental results showed that silk cotton hull was effective for the removal of Malachite Green from aqueous solutions. The silk cotton hull used as a new low-cost adsorbent for dye removal from effluents was found to be efficient and capable of removing 92% of dye when the dye concentration was 5 mg/L, at an adsorbent dose of 0.5 gm/L at dye pH 8 in 40 minutes. From the studies it is confirmed that the equilibrium data fitted very well with the both Freundlich and Langmuir isotherms. The maximum adsorption capacity of Silk cotton hull carbon was found to be 4.85 mg/g and pseudo second order kinetic model is more likely to predict the behavior over the whole experimental range of adsorption than pseudo-first order model. The intra particle diffusion model indicates that the intra particle diffusion is not the sole- rate determining step. The results indicate that the linear regression model give the best results (R^2 nearly equal to 1). The material used in this work is basically an agricultural waste, is cheap and locally available, it can be expected as an economically viable and promising adsorbent for the removal of basic dye from aqueous solutions.

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