

Adsorption Kinetics of Malachite Green Dye Removal from Aqueous Solution by using Banana Stem



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Abstract: This research work goals at searching the effectiveness of Malachite Green dye removal using banana stem, an agricultural waste as an activated carbon. The banana stem activated carbon was made ready in the laboratory by carbonization followed by activation. Adsorption studies were carried out to check the effect of various experimental conditions like different pH values, varying contact time, initial concentration of dye and changing banana stem carbon dosage on the removal of Malachite Green dye from aqueous solution at constant Temperature and agitation speed. The equilibrium experimental data were used for applicability of Langmuir and Freundlich isotherm models and the kinetic models. Batch test showed that maximum of 99% of dye was removed when the dye concentration was 2 mg/L, at an adsorbent dose of 0.75 gm/L at dye pH 8 in 45 minutes. From the obtained results it is validated that the equilibrium data's favorable for both Freundlich and Langmuir isotherms. Maximum adsorption capacity of banana stem carbon on malachite green dye was found to be 8.29 mg/g. It was prevailing that the adsorption process followed the pseudo-second-order rate kinetics. It was observed that intra particle diffusion is not the only rate-limiting step in this adsorption system but also regression results indicate that the linear regression model gives the best results. The above observations recommend that Banana stem carbon can be competently implemented for removal of malachite green dye from aqueous solution in the adsorption treatment processes.

Keywords: Banana Stem, Adsorption, Batch Study, Malachite Green Dye, Isotherm, Kinetics.

I. INTRODUCTION

The major environmental crisis arises from increase in global contamination of water bodies with industrial and natural chemical compounds [1]. Due to growing industrialization, modernization, urbanization, technology our world is leading to new high perception but the fare which we reimburse or will pay in time ahead is definitely going to be too much [2].

A higher percentage of dyes from the industrial waste water are being released into aquatic environment system and polluted the natural water bodies. Control measures to treat the dye wastewater are done by government, users and the dye manufacturers [3]. Dyes are usually used in

some of the industries such as textiles, tannery, food processing, etc., in their manufacturing process to color their end products [4].

The disposal of colored wastewater without sufficient treatment into the water bodies is polluting the receiving water bodies. Due to their carcinogenicity, dye contaminated water effecting human health through food chain. So, it is very essential to bring down the concentration of dyes such that environmental agencies may accept the same [5].

Different treatment methods have been put forward for the dye removal from textile waste water, which includes photocatalytic, electrochemical degradation, ultrafiltration, ion exchange, biological treatment and adsorption on activated carbon. Among all treatment methods, adsorption looks to be promising for the removal of colors from dye bearing wastewater. Adsorption of a toxic chemicals from the industrial wastewater using a raw material and subsequent easy desorption of it, in case of need to recover the costly material, further broadened the role of adsorption technique in industrial effluent treatment processes [6].

Various conventional and non-conventional adsorbents were used to treat dyes present in the industrial effluent and researchers searching for adsorbents such that it is cost effective, abundantly available and easy to operate [1].

Dyes are largely divided into anionic (acid dyes), cationic (basic dyes) and non-ionic (disperse dyes) [7]. Malachite green (MG) is highly water soluble basic dye that appears as green crystalline powder [8]. It was revealed that large scale utilization because of its low cost.

Conventional activated carbon is normally used for removal of dye because of its high surface area, porosity and excessive capacity of adsorption. The main drawback of commercial activated carbon is high cost and regeneration problem. Activated carbons have been indigenously prepared by the various raw materials like bagasse, straw, fruit nuts, shells, hulls, agricultural byproducts [9].

Waste byproducts generated from agricultural activities have minute or no materialistic value and create a problem of waste disposal. Factors considered for selecting a raw material for the preparation of activated carbon are its abundance, storage life, low cost of procurement, high carbon content of raw materials and physico-chemical properties.

The usage of agricultural waste is of great importance since adds commercial value and reduces the cost of waste disposal by that it may play crucial part in the national economy.

Banana (Musaceae) stem is considered as agricultural waste after harvesting of banana, it is to be dumped or burned. However, it can be converted into a potential adsorbent [10].

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The diffusion of malachite green dye between liquid and solid phase adsorption system at equilibrium condition is explained by adsorption isotherms and on the basis of isotherms parameters values it is possible to decide the type of adsorption process [11].

In the design of industrial dye wastewater treatment process, prediction of adsorption kinetics is very important and also models of kinetic studies help in finding the rate of the process and its controlling step[12]. In the present work pseudo first order and pseudo second order kinetic models were used to check the well fitted model for the experimental data obtained from the banana stem malachite green batch adsorption processes.

Some of the research work carried out on various low cost agricultural by products for removal of dye from aqueous solution including Banana Leaves [10], Sugarcane Bagasse [13] and Pumpkin Seed Hull [14].

The main purpose of this research work is to find the adsorption capacity of banana stem carbon which is derived from agricultural by product for the removal of malachite green dye from aqueous solution in batch adsorption system at different working conditions.

II. MATERIALS AND METHODOLOGY

A Preparation of adsorbent: banana stem activated carbon was established by mixing 4 parts by weight of banana stem thoroughly with 3 parts of concentrated sulfuric acid by weight 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 after that 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.

B Adsorbate preparation: Malachite green dye stock solution was prepared by dissolving appropriate quantity (1mg/L) of malachite green, a coloring reagent in distilled water. Standard solution was prepared by diluting the stock solution as per the requirement. The same was used throughout the experiment.

C.Specification of dye used:

- Dye – Malachite green
- Color – Bluish green
- Type – Basic dye
- Chemical formula – C₂₃H₂₄CLN₂
- Molecular weight – 364.9
- Wave length (λ) – 616nm

The batch adsorption investigations were conducted by utilizing standard solution of malachite green in the concentration range of 1 – 5 mg/l, the other variable parameters were adsorbent dose (0.25 - 0.875 gm/l), contact time (0 - 60minutes) and pH of the medium (2 –10) and agitation speed of 100 rpm. The concentrations were determined with the help of carefully prepared calibration curve with standard malachite green dye solution.

D Equilibrium studies:

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

$$q_e = (C_0 - C_e)(V / W)$$

Percentage of dye removal is calculated by

$$= (C_0 - C_e) \times 100 / (C_0)$$

Where, C₀ = initial dye concentration in mg/L, C_e = concentration of dye solution at equilibrium condition in mg/L, V= volume of the solution in liter and W = mass of adsorbent used in gm. The kinetic studies were also carried out using the same procedure.

Sorption amount at any time t i.e, q_t (mg/g) was find out by

$$q_t = (C_0 - C_t) \cdot (V / W)$$

Where, C_t = concentration of dye at any time in mg/L.

III. RESULT AND DISCUSSIONS

A Initial dye concentration effect on adsorption

The initial dye concentration effect on adsorption of Malachite Green dye onto banana stem carbon was investigated in the range of 1- 5 mg/L of initial dye concentration while adsorbent dose, agitation speed and contact time were kept at 0.75 g/L, 100 rpm and 60 minutes respectively for Malachite Green dye at natural pH and room temperature (27±2°C). From the Figure 1 it is evident that the maximum dye removal of 95 % at an initial dye concentration of 2 mg/L and decreased to 90 % for further increase in initial dye concentration for Malachite Green dye.

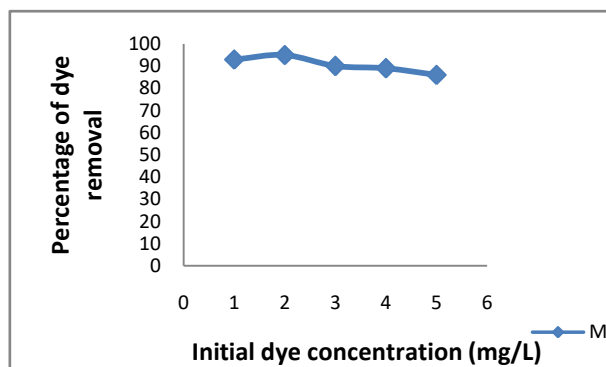


Figure 1: Initial dye concentration effect on 0.75 g/L of banana stem carbon

From the Figure 1 it is observed that, at lower concentration percentage of dye removal is high and it is goes on decrease with increase of dye concentration, and then reaches equilibrium condition after long time.

B Adsorbent dosage variation effect on adsorption

The Adsorbent dosage variation effect on Malachite Green dye uptake capacity on banana stem carbon was investigated at 2 mg/L of Initial dye concentration, agitation speed of 100 rpm, contact time of 60 minute, natural pH and room temperature (27±2°C) by varying adsorbent dosage from 0.25 – 0.875 g/L. The influence of adsorbent dosage variation on the removal of dye by banana stem carbon is presented in Figure 2. The percent of dye removal increases to 95 % with increase in adsorbent dose up to 0.75 g/L for Malachite Green dye and afterwards it remains constant with increase in banana stem dose.



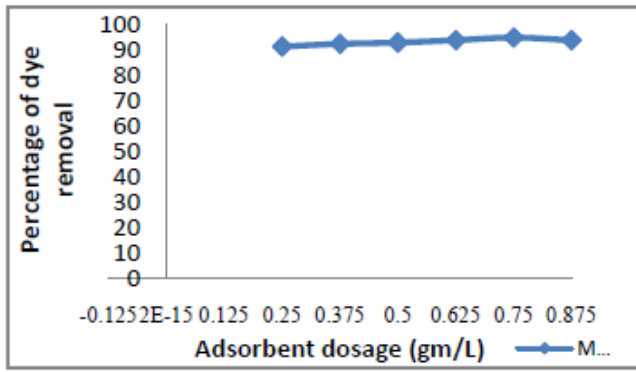


Figure 2: Banana stem carbon dosage variation effect on dye concentration of 2 mg/L

From the above figure it is noticed that, as the dosage of banana stem carbon increases the dye removal efficiency also increases, at the same time adsorption capacity per unit mass of banana stem carbon decreases. This is because, banana stem dose increases than number of sites available for adsorption increase by that dye removal efficiency increases.

C Contact time effect on dye removal

The contact time effect on adsorption of Malachite Green dye onto banana stem carbon was investigated in the range of 0 - 60 minutes while keeping adsorbent dose, initial dye concentration and agitation speed at 0.75 g/L, 2 mg/l and 100 rpm respectively at natural pH and room temperature (27±2°C). The contact time effect on uptake of dye is shown in Figure 3. The dye removal amount increased with increase in contact time up to 45 minutes and removal efficiency is 99 % for Malachite Green dye, and then becomes almost constant for further increase in contact time.

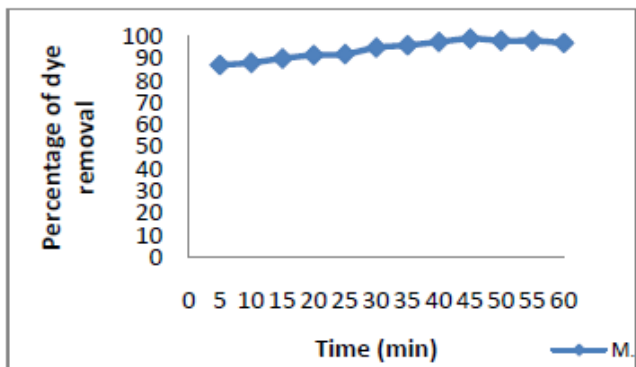


Figure 2: Contact time effect on percentage of dye removal

This may be due to the fact that banana stem carbon has pores media. In the beginning, malachite green molecules affected by boundary layer and after that diffused onto banana stem carbon surface, after some time ultimately entered into the pores media of banana stem carbon.

D pH variation effect on dye removal

The effect of pH varies in the range of 2 - 10 on adsorption of Malachite Green dye onto banana stem 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 0.75 g/L, 2 mg/ L and 100 rpm respectively at room temperature (27±2°C). The removal percentage of basic Malachite Green dye by banana stem 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 banana stem carbon increased from 91 % to 99 % for an increase in pH from 2 to 10 and at contact time of 45 minutes and the optimum pH is found to be 8.

Removal of malachite green dye at acidic pH is low, since excess of hydrogen ions present in the system takes part with the malachite green dye ion for adsorption.

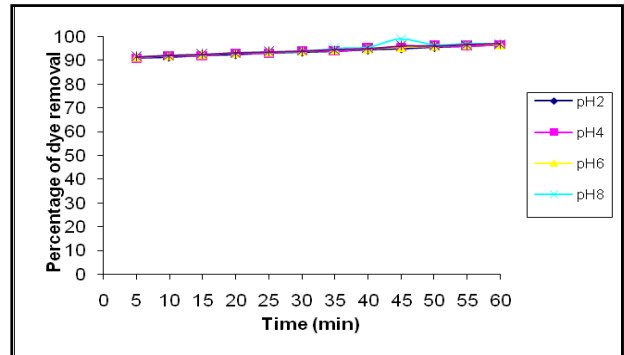


Figure 3: pH variation effect on dye removal on to banana stem carbon

E Adsorption Isotherms

For assessing the efficiency of the banana stem absorbent for MG dye removal Freundlich and Langmuir isotherms are considered.

The Freundlich isotherm presented in the form of:

$$\log (q_e) = \log (k_F) + (1/n) \log (C_e) \quad (1)$$

Where k_F = adsorption capacity and n = intensity of adsorption and were computed from the slope and intercept of the Freundlich graph of $\log Q_e$ versus $\log C_e$ (Fig.5). Where q_e is the amount of dye adsorbed at equilibrium (mg/g), C_e is the malachite green dye concentration at equilibrium in mg/L. The value of n between 0 - 10 indicating that adsorption is efficient for this adsorption system ($n = 1.707$ for this study from Table 1).

Table 1; Parameters of Freundlich for Malachite Green (MG) dye on banana stem carbon

$k_F(\text{mg/g})(\text{L/g})^{1/n}$	n	R^2
2.39	1.707	0.909

The Langmuir isotherm is presented in the form:

$$(C_e/q_e) = (1/Q_0b) + (C_e/Q_0) \quad (2)$$

Where C_e is the equilibrium concentration of malachite green dye in mg/L, q_e the amount of malachite green dye adsorbed at equilibrium condition in mg/g, Q_0 is the adsorption capacity of banana stem in mg/g and b is the energy of adsorption in L/mg. The values of adsorption capacity of banana stem and energy of adsorption were found out from the slope and intercept of the chart C_e/q_e versus C_e (Fig.6). The value of dimensionless factor $R_L = 1/(1+bC_0)$, where C_0 = initial dye concentration. The value of R_L lies between 0 - 1 ($R_L = 0.062$ for this study from Table 2), showing favorable absorption of dye on the banana stem carbon.



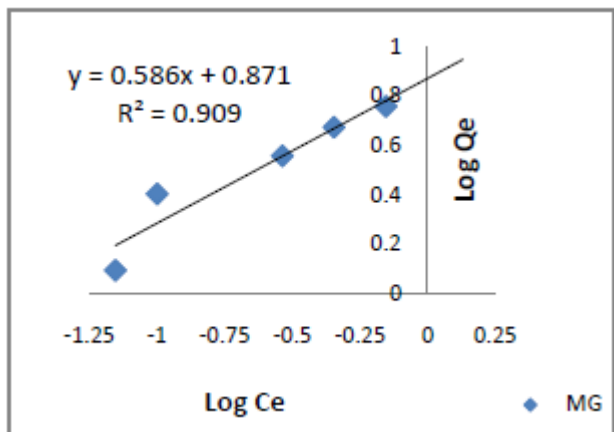


Figure 5: Freundlich isotherms for banana stem carbon

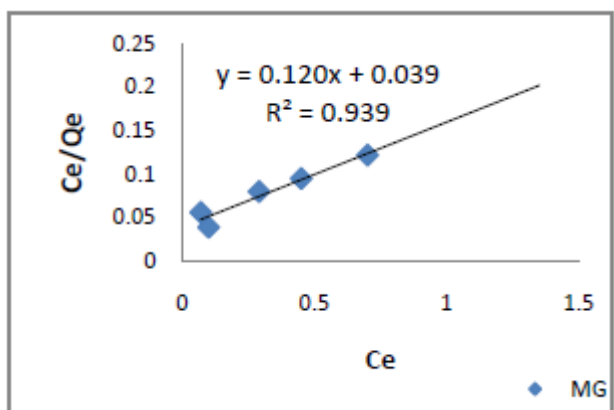


Figure 6: Langmuir isotherms for banana stem carbon

Table 2: Parameters of Langmuir isotherms for Malachite Green (MG) dye on banana stem carbon

Qo(mg/g)	b(L/mg)	R ²	R _L
8.29	3.04	0.939	0.062

Table 1 and 2 exhibit the parameters of the two isotherms and the related correlation coefficients. On the basis of R² values it is confirmed that the equilibrium data's fitted very well with both Freundlich and Langmuir isotherms. The adsorption capacity of banana stem carbon for the Malachite Green dye (8.29 mg/g).

F Kinetic studies

The expression for pseudo-first-order equation is:

$$\log (q_e - q_t) = \log (q_e) - (k_1 / 2.303) t \quad (3)$$

Where q_e = quantity of malachite green dye adsorbed at equilibrium in mg/g and q_t = quantity of malachite green dye adsorbed at any time t in minute, respectively, and k₁ is the rate constant of adsorption in 1/min. Values of k₁ were calculated from the graph of ln (q_e - q_t) versus time (Fig. 8).

From the table 3 it is found that q_e experimental reading is not same with the q_e calculated from the graph. Therefore, first order kinetic model is not favorable for the banana stem carbon – malachite green batch adsorption system.

The pseudo-second-order kinetic equation is as follows:

$$(t / q_t) = (1 / (k_2 q_e^2)) + (1 / q_e) t \quad (4)$$

Where k₂ (g mg⁻¹ min⁻¹) is the rate constant of second order adsorption. The parameters k₂ and q_e can be obtained from

the graph of (t/q_t) versus time (Fig. 9). This model is better to predict the behavior over the whole experimental values adsorption than pseudo-first order model. The correlation coefficient is close to 1.0 (Table 4). The calculated q_e values obtained from this model nearly same as that of the experimental values.

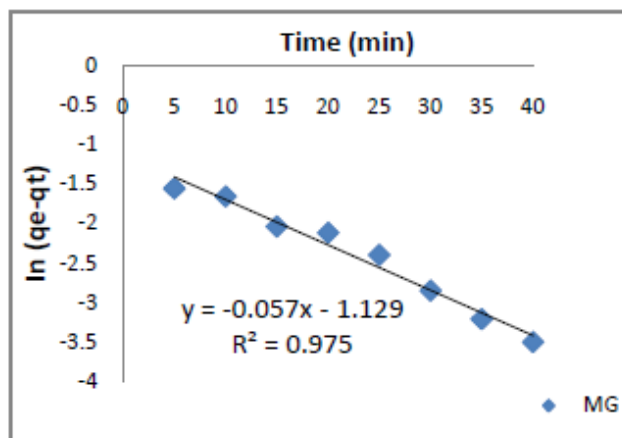


Figure 7: Pseudo-first order kinetic plot for the adsorption of malachite green on banana stem carbon

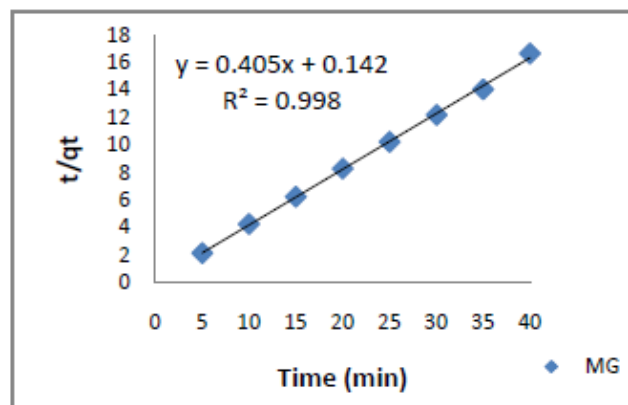


Figure 8: Pseudo-second order kinetic plot for the adsorption of malachite green on banana stem carbon

Table 3: Pseudo first order kinetic constants for the adsorption of Malachite Green dye onto banana stem carbon

q _e exp (mg/g)	k ₁ (min ⁻¹)	q _e cal (mg/g)	R ²
2.53	0.031	3.09	0.975

Table 4: Pseudo pseudo second order kinetic constants for the adsorption of Malachite Green dye onto banana stem carbon

q _e exp (mg/g)	k ₂ (g mg ⁻¹ min ⁻¹)	q _e cal (mg/g)	R ²
2.53	2.852	2.46	0.998

The adsorption results (Table 4) confirmed that the adsorption kinetics for malachite green dye onto banana stem carbon can be fit well with pseudo-second-order kinetic equation. Therefore in this adsorption system chemical adsorption is control the sorption rate.

G Intra particle diffusion

The intra particle diffusion model is written in the form:

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

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

The values of the K_p , C and regression coefficients R^2 are tabulated in Table 5.

Table 5: Intra particle model parameters for the adsorption of Malchite Green onto banana stem carbon

$K_p(\text{mg g}^{-1} \text{min}^{0.5})$	C	R^2
0.046	2.209	0.981

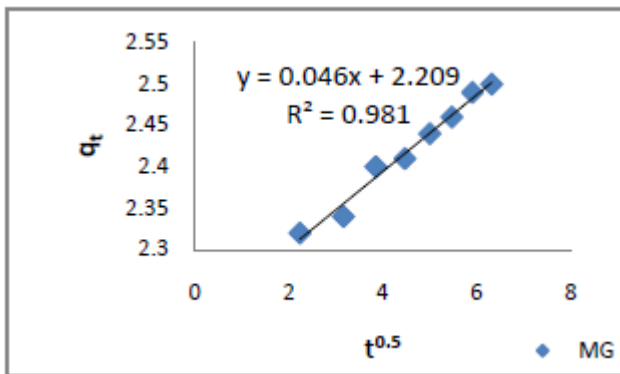


Figure.9: Intraparticle diffusion kinetic model for the adsorption of MG on banana stem carbon

From the results it is concluded that intra particle diffusion is not only the rate controlling step, since the straight line does not pass through the origin and value of C is not equal to zero. The thickness of boundary layer is indicated by the C intercept value. In the banana stem – malachite green batch adsorption system inter particle diffusion does not control the entire adsorption process.

H Regression analysis

The estimated linear model interrelating percentage of color removal with the controlling parameters is expressed in the following Equation (6) & (7) for Malachite Green dye.

$$Y = A_0 + A_1 X_1 + A_2 X_2 \quad (6)$$

$$Y = 90.2928 + 0.1034266 X_1 + 0.08958 X_2 \quad (7)$$

Where, X_1 = contact time in minutes, X_2 = pH of dye solution and Y = percentage of color removal.

From the model, for Malachite Green dye the most substantial controlling parameter is contact time affecting percentage of dyeremoval in the banana stem – malachite green adsorption system and the least significant parameter is the pH.

From correlation matrix correlation of percentage of color removal to pH is 0.08958 and for contact time is 0.1034266 for Malachite Green dye adsorption onto banana stem carbon.

From the figures the R^2 evaluated as 0.932 Malachite Green dye (Figure.10) adsorption onto banana stem. The results indicate that the linear regression model gives the best results (R^2 nearly equal to 1).

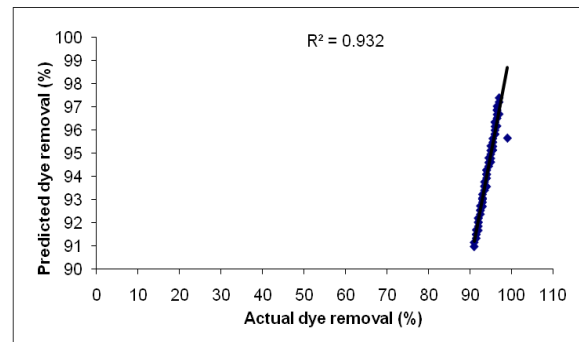


Figure 10: Linear regression plot showing observed and predicted percentage color removal of MG on banana stem carbon

The prime features of this research work is tabulated as in table 6.

Table 6: The main highlights of the Banana stem malachite green dye adsorption system

Parametre	Result
Maximum dye removal effeceny (99%) at initial dye concentration of	2 mg/L
Maximum dye removal effeceny (99%) at adsorption dosage of	0.75 gm/L
Maximum dye removal effeceny (99%) at contact time of	45 minutes
Maximum dye removal effeceny (99%) at optimum pH of	8
Value of n from Freundlich isotherm	1.707
Value of RL from Langmuir isotherms	0.062
Adsorption capacity of banana stems carbon for the Malachite Green dye.	8.29 mg/g
Correlation coefficients of Freundlich and Langmuir isotherms	0.909 and 0.939
Pseudo first order kinetic constant $q_{e,exp} = 2.53 \text{ mg/g}$	$q_{e,cal} = 3.09 \text{ mg/g}$
Pseudo second order kinetic constant $q_{e,exp} = 2.53 \text{ mg/g}$	$q_{e,cal} = 2.46 \text{ mg/g}$
Intra particle diffusion constant C	2.209
Correlation coefficients of Pseudo first order kinetic, Pseudo second order kinetic, Intra particle diffusion and Regression analysis.	0.975, 0.998, 0.981 and 0.932 respectively

IV. CONCLUSION

From the end results of this research work, it can be concluded that banana stem an agricultural waste be used as a novel material for removal of malachite green dye present in the wastewater even in the lesser concentration by that its possible come down the contamination level of water bodies.



The removal percentage of Malachite Green dye by banana stem carbon is 99% at pH8 for a contact time of 45 minutes at initial dye concentration of 2 mg/L at an adsorbent dosage of 0.75 gm/L. The experimental data of this study well fitted with both Freundlich and Langmuir isotherms. The kinetics of the adsorption system was favorable to the pseudo second-order kinetic model. The intra particle diffusion is not a stage controlling the rate of the entire adsorption process. The results suggested that the linear regression model gives the best results. The results of the present study reveal that the low cost adsorbent prepared from the banana stem waste removes the dye selected for this investigation very efficiently and effectively.

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