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Equilibrium and kinetic studies on the removal of methylene blue dye from waste water using jumbo grass (*Sorghum Bicolour Sorghum Sudanefe)*

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ABSTRACT

The removal of methylene blue dye from waste water using Jumbo grass (Sorghum Bicolour Sorghum Sudanefe) has been studied experimentally by batch mode methods. The newly prepared bio-adsorbent was characterized and the adsorption capacity of the bio-sorbent was investigated by changing the parameters such as adsorbent dose, pH, contact time and initial dye concentrations. From the experimental data the Langmuir, Freundlich and Temkin adsorption isotherm models were arrived and the Pseudo second order, Elovich and Intra-particle diffusion kinetic models were also analyzed. Equilibrium data were well fitted to the Langmuir isotherm, Freundlich and Temkin model. Adsorption process was obeyed the Pseudo second order and Elovich kinetic models. The Langmuir adsorption capacity of adsorbent was found to be 12.99 mg/g. The results reveal that the raw Jumbo grass serves as low cost adsorbent for removal of methylene blue dye from waste water.

Keywords: Methylene blue dyes, Jumbo grass, adsorption, Isotherm, Kinetic model

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INTRODUCTION

Pollution of environment occurs due to both natural phenomena and man-made activities. The natural phenomena like El Nino and La Nina, powerful volcanic eruptions, earthquakes, etc, causing pollution in environment are beyond our control. On the other hand, pollution due to man-made activities (e.g. agricultural activity, industrial activity, etc.) may be controlled to a large extent [1]. Pollution in different segments like atmosphere, lithosphere (soil) and hydrosphere is shocking the living bodies in biosphere. Heavy metals and dyes are playing an important role for environmental pollution. Nowadays, water pollution is a very common problem. Generally, dyes are coloring agents which are having potential applications in textile, leathers, food coloring, printing, dyeing, cosmetics and paper making industries. About 10-15% of dyes is not binding during coloration in the textile industry and come out through effluent. The colored dye effluent affects the receiving water bodies as well as reduces sunlight penetration and photosynthesis [2]. Under anaerobic conditions, dyes are decomposed into carcinogenic aromatic compounds which cause some damage to aquatic life and human beings [3].

Methylene blue is a cationic dye which used in dyeing silk, wool, cotton and coloring paper. It is also used as reagent in microbiology, surgery and diagnostics and as a sensitizer in photo oxidation of organic pollutants [4]. The methylene blue (MB) dye is more responsible for some harmful effects such as heartbeat increase, vomiting, shock, cyanosis, jaundice and tissue necrosis in human being [5]. Therefore, removal of such dyes from effluents is an important task due to its harmful impacts on water sources. The removal of dyes is made by conventional methods such as coagulation and flocculation, adsorption, ozonation, electrochemical techniques and fungal decolorizaation [6]. The bio-sorption is a newer technology developed which has been found to be superior to other techniques for

removal of dyes from wastewater, because of its capability for adsorbing different types of adsorbates efficiently, and its simplicity of design. Plant waste is most abundant in nature which is inexpensive as they have very low economic value. Natural plant waste is widely used for water treatment process. The agricultural waste materials such as tea waste [7], wheat straw [8], grass waste [9], jackfruit peel, palm shell activated carbon [10], coir pith carbon, sugar cane stalks, neem leaf powder, saw dust activated carbon, mango seed shell [11] and carrot stem powder were used for the removal of methylene blue and other dyes from wastewater. The aim of the present investigation is to evaluate the use of Jumbo grass (*Sorghum Bicolour Sorghum Sudanefe)* as bio-adsorbent for removal of MB dye from waste water. A literature search reveals that no work has been studied on the removal of MB dye from waste water using Jumbo grass as adsorbent.

EXPERIMENTAL SECTION

Preparation of adsorbent

The adsorbent used in the present study was collected from Palar river bed near Vellore District, Tamil Nadu. The plants were washed with running water to remove the impurities. The washed plant materials were sun dried for seven days and cut into small pieces. The dried materials were ground well to fine powder and sieved. The produced biomass was dried in over at 55°C for 24 hours and stored in a desiccator. Here after Jumbo grass powder was called as Water washed Jumbo Grass (WJG) powder. The produced WJG adsorbent was characterized by Scanning electron microscope (SEM). The physical properties were also analyzed.

Adsorption studies

Analytical grade chemicals and reagents were used in samples preparation. A stock solution of 1000 mg/L dye prepared by dissolving 1 g of MB dye in doubly distilled water and the pH of the solution is adjusted using 0.1N H_2SO_4 and 0.1N NaOH. From the stock solution, working solutions of 2 to 12 mg/L concentration of the dye were obtained by dilutions.

Batch mode equilibrium method

All experiments were carried out at 30°C temperature in the batch mode methods. The batch experiments were done in different Erlenmeyer glass flasks of 250 ml capacity. A known amount of adsorbent was added to the each flask. The mixture is agitated using rotary shaker at constant 150rpm for experiment to better mixing. Each flask was filled with a known volume (100ml) of dye solution with initial concentration of 2 to 12 mg/L. The flask containing the sample was withdrawn from the shaker at the predetermined time interval, separated and the equilibrium concentration of the dye was measured by UV-Visible Spectrophotometer using 661nm. The adsorption capacity Q_e (mg/g) and percentage removal were calculated from equation-1 and 2 respectively.

$$Q_e = [C_o - C_e] \times V/M \quad (1)$$

$$\% \text{ Removal} = [C_o - C_e] \times 100/C_o \quad (2)$$

Where, C_o is the initial dye concentration in solution (mg/L), C_e is the final equilibrium concentration in solution (mg/L), V is the volume of the solution (L), and M is the mass of the adsorbent used (g). The effect of different parameters such as dosage of the adsorbent dose, initial concentration, contact time and pH were studied on the removal of the MB dye. All the experiments were duplicated and the mean values are presented in this paper.

RESULTS AND DISCUSSION

The physico-chemical characteristics of the adsorbent WJG powder were determined by standard methods and the results are given in Table-1. The microstructure and surface morphology of the fresh WJG powder and dye loaded WJG powder were investigated by scanning electron microscope (SEM) and the images are given in Figure- 1 and 2. The SEM image of unloaded WJG powder reveals the nature of biomaterials which is fibrous and heterogeneous with lot of micro pores which are responsible for binding sites for dye molecules. The uptake of MB dye by WJG was demonstrated by the change in morphology of the adsorbent's surface. Based on the surface morphology result of WJG, it is suggested that the produced WJG can be used as adsorbent for liquid-solid system due to the importance of fibrous materials.

Table- 1: Characteristics of the adsorbent

Adsorbent	pH	Moisture content (%)	Ash content (%)	Bulk density (%)	Water soluble content (%)	Acid insoluble content (%)
WJG	6.75	9.9	11.00	0.325	7.13	3.6

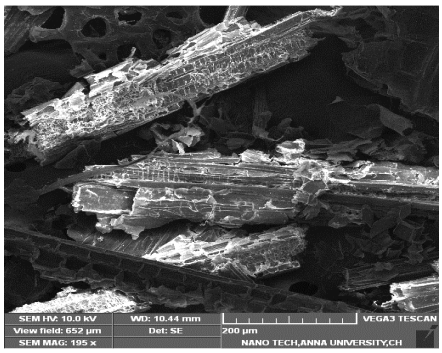

Figure 1: SEM image of unloaded WJG adsorbent

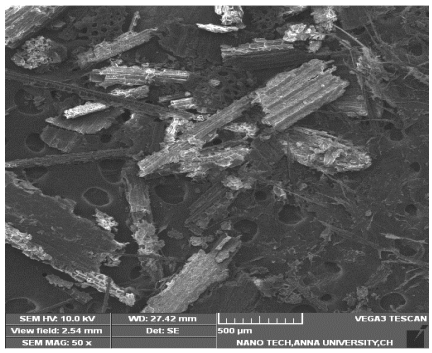

Figure 2: SEM image of dye loaded WJG adsorbent

Adsorption studies

Effect of pH

The effect of pH on MB dye removal by WJG was carried out in the range of pH from 2.5 to 9.5 at 4mg/L initial dye concentration with 100mg/100ml adsorbent dose at room temperature for 3 hr equilibrium time and the plot was given in Figure- 3. The pH affects the charge density on adsorbent's surface and degree of ionization of pollutants [12]. The maximum percentage removal of MB dye was 85.00% at 7.5pH. The H^+ ions are competed effectively at lower pH with MB dye to occupy sorption sites on bio-sorbent surface and at higher pH (> 7.5) an increase of –OH ions also causes decreases the adsorption of MB dye [13]. As the pH of the system increases from 2.5 to 7.5, the number of negatively charged sites on biomass surface increased and the number of positively charged sites decreases. This indicates that greater electrostatic attraction of the MB dye molecules by the WJG sorbent surface.

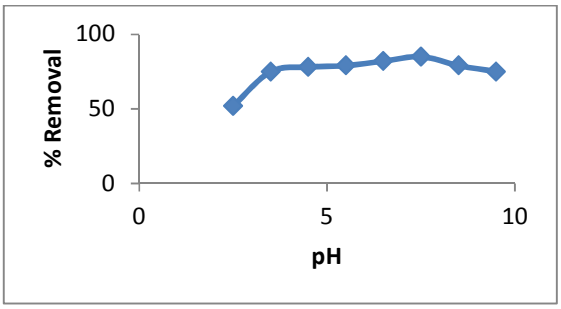

Figure 3: Effect of pH on dye removal by WJG

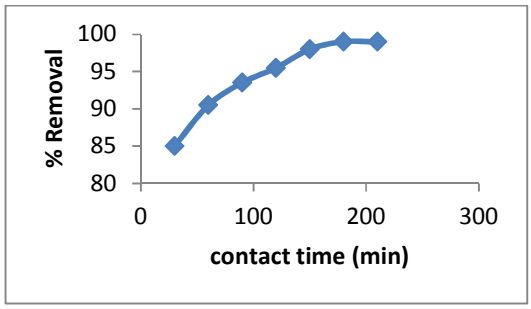

Figure 4: Effect of contact time on dye removal by WJG

Effect of Dose

The adsorption of MB dye on WJG powder was studied by varying the adsorbent dosages from 0.05 to 0.5g/100ml into series of 250ml Erlenmeyer flasks which contain 100ml dye solution of 4mg/L concentration with contact time 180mins. The percentage removal plot is shown in Figure- 5. It shows that the percentage adsorption increased with an increase in the WJG adsorbent dosage. This may be due to the increased WJG surface area and availability of more adsorption sites. Similar results are reported in the literatures [14].

Effect of Contact Time

It reveals that the percentage removal of dye increases with increase with contact time till equilibrium has been reached. After the equilibrium time there is no significant adsorption taking place. The equilibrium time for dye adsorption on WJG powder was found to be 180 minutes and highest removal of MB dye from waste water was 99.00% which is shown in Figure- 4. The water washed Jumbo grass have regular nature, as well as formation of overlapping fiber layers and cracks (porous) which allow for adsorption. In the process of dye adsorption, initially

dye molecules have to encounter the boundary layer effect before diffusing from boundary layer film onto adsorbent surface. This is followed by diffusion of dye into the porous structure of the adsorbent. This phenomenon will take relatively longer contact time [15]. This equilibrium time is one of important parameters for an economical wastewater treatment system.

Effect of Initial Ion concentration with Adsorbent doses

The effect of initial concentration was investigated with different initial concentrations of MB dye (2, 4, 6, 8, 10 and 12 mg/L) using different adsorbent dosages (0.05, 0.1, 0.2 and 0.5mg/100ml) at 180 minutes equilibrium time. The results show that WJG have good potential of dye removal. The percentage removal of MB dye by WJG was shown in Figure- 5. It reveals that the percentage removal decreases gradually with the increase in initial concentration, the removal is highly effective on 4 mg/L initial concentration after which removal decrease gradually. The same trend was followed for all the different adsorbent dosages. At lower concentrations, sufficient adsorption sites are available for adsorption of the dye molecules. However, at higher concentration the numbers of dye molecules are relatively higher compared to availability of adsorption sites [16]. The maximum removal of MB dye was 98.75% occurred with 4mg/L dye concentration at 0.5g dose.

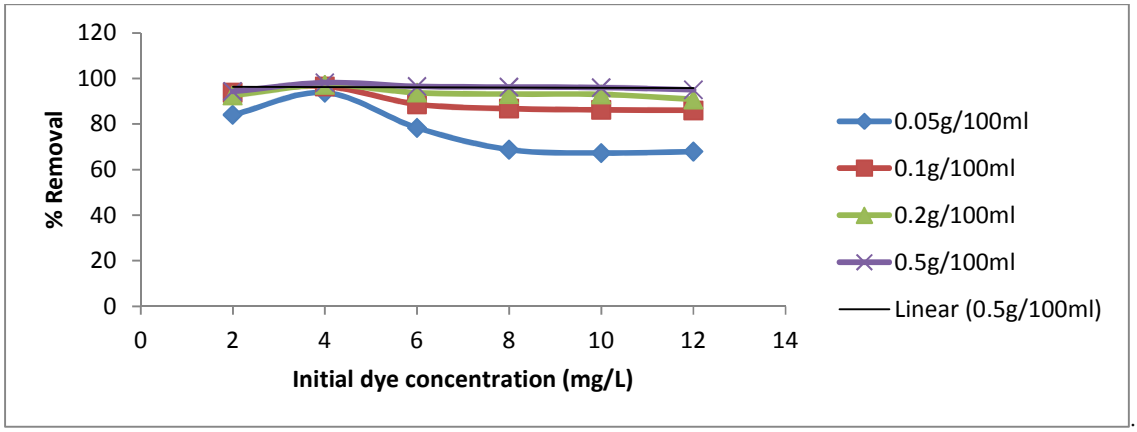

Figure 5: Effect of initial concentration with adsorbent dose on dye removal by WJG

Adsorption isotherm

Langmuir Isotherm model

Langmuir isotherm is based on the adsorption takes place at specific homogeneous sites within the adsorbent. Once a dye molecule occupied a site, no further adsorption can take place at the sites. The following Langmuir isotherm equation-3 was used in this study

$$1/Q_e = 1/bQ_mC_e + 1/Q_m \quad (3)$$

Where, C_e is the equilibrium concentration of the dye (mg/L), Q_e is the amount of dye molecules adsorbed at equilibrium (mg/g), b is the adsorption energy of the sorbent surface, Q_m is the maximum sorption capacity (mg/g). The Langmuir constants b and Q_m are calculated from the slope and intercept of the linear plot of $1/Q_e$ against $1/C_e$ are given in Table- 2. The Langmuir isotherm plot for the removal of MB dye was shown in Figure- 6. The data reveals that the Langmuir model is best fit for the adsorption of MB dye onto WJG. The Dimensionless separation constant R_L is an important characteristic for the Langmuir isotherm model which is defined as $R_L = l/ (l+bC_o)$, where b is the Langmuir constant and C_o is the initial concentration of the dye. The values of R_L indicate the shape of the isotherm as follows [17]. The calculated R_L values are given in Table- 2. The values of R_L were less than one (0.0143-0.0799) indicates that the isotherm is favorable.

R_L value	**Types of isotherm**
$R_L>1$	Unfavorable
$R_L= 1$	Linear
$0<R_L < 1$	Favorable
$R_L = 0$	Irreversible

Table- 2: Isotherm constants for adsorption of MB dye on WJG

Langmuir isotherm				Freundlich isotherm			Temkin isotherm		
Q_m	b	R_L	R^2	n	K_F	R^2	A	b	R^2
12.99	5.753	0.0143-0.0799	0.860	1.957	7.295	0.869	1.77	188.30	0.873

Freunlich Isotherm model

The Freundlich isotherm is derived by assuming a heterogeneous surface, with non-ideal and reversible multilayer adsorption, with non-uniform distribution of adsorption heat and affinities over surface of the adsorbent. The linear form of the Freundlich isotherm can be represented as follows:

$$\log Q_e = \log K_F + 1/n \log C_e \quad (4)$$

Freundlich isotherm constants 1/n and K_F of the adsorbent are calculated from the slope and intercept of the linear plot of log Q_e aginst log C_e as shown in Figure- 7. The values of adsorption intensity (n= 1.957) was more than one indicates the favorable adsorption on heterogeneous surface and K_F gives the capacity of the adsorbent/adsorbate system. The data are given Table- 2. The data reveals that the Freundlich isotherm is applicable and the correlation is statistically significant.

Tempkin Isotherm model

Temkin isotherm model provides the effect of interaction between adsorbate and adsorbent which explains the heat of adsorption of all the molecules on the adsorbent surface layer. The linear form of isotherm can be expressed as follows:

$$q_e = B\ln A + B\ln C_e \quad (5)$$

Where B = RT/b, b is the Temkin constant related to heat of sorption (J/mol), A is the equilibrium binding constant (L/g), R is the gas constant (8.314J/mol/L) and T is the absolute temperature (^oK), C_e is the concentration of adsorbate in solution at equilibrium (mg/L). A linear plot of q_e versus ln C_e (Figure- 8) helps for calculation of the isotherm constants A and b from the slope and the intercept. The data were listed in Table- 2. The Temkin isotherm fits the equilibrium data well implying that the MB dye adsorption on WJG was a chemisorptions process.

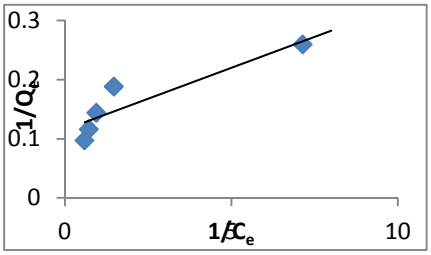

Figure 6: Langmuir isotherm for the removal of MB

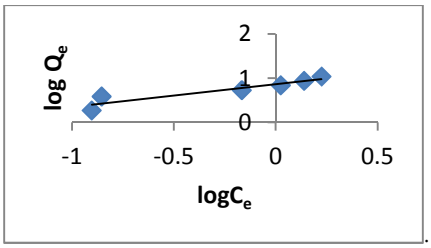

Figure 7: Freundlich isotherm for the removal of MB

Adsorption kinetic studies

For determining the kinetics of adsorption of MB dye onto WJG powder was studied by three kinetic models such as the pseudo-second order, Elovich and intra particle diffusion model.

Pseudo- second-order model

For the analysis of adsorption mechanism Ho and McKay proposed a pseudo- second order kinetic model and its linear form as follows;

$$t/ q_t = 1/k_2 q_e^2 + t/q_e \quad (6)$$

Where q_e (mg/g) and q_t (mg/g) are the amounts of adsorbate adsorbed on the surface of the adsorbent at equilibrium and at a given time t (min) and k_2 (g/mg/min) is the pseudo-second order rate constant. The parameters k_2 and q_e can be calculated from linear plot of t/q_t versus which shown in Figure- 9. The initial adsorption rate (h) can be calculated from k_2 and q_e values using equation- 7

$h = k_2 q_e^2$ (7)

h (mg/g/min) represents the amount of dye adsorbed per unit mass of adsorbent and unit time. This value (h) can be used to compare the initial sorption rate of dyes on various adsorbents at similar conditions. The data are given in Table-3. This suggests that the rate controlling step in adsorption of MB dye is chemisorptions involving valance forces through the exchange of electrons between sorbent and sorbate through chelation [18].

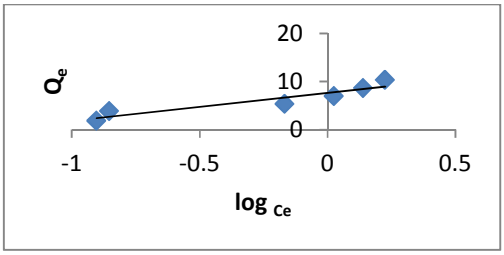

Figure 8: Temkin isotherm for the removal of MB

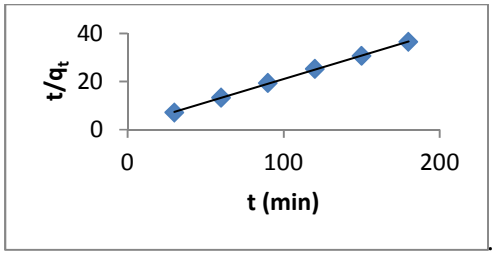

Figure 9: pseudo-second order for the removal of MB

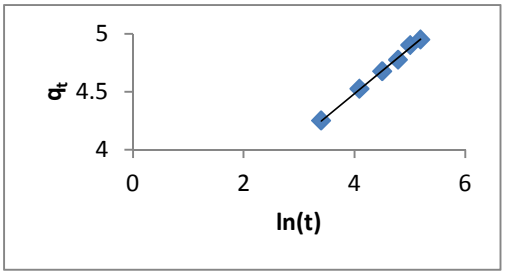

Figure 10: Elovich kinetic model for the removal of MB

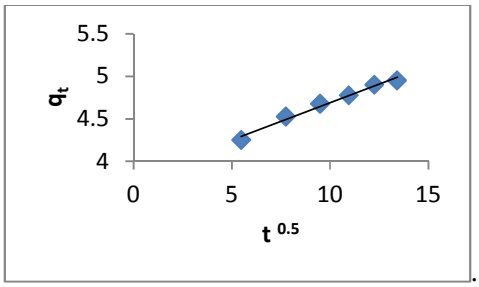

Figure 11: Intraparticle diffusion kinetic model for removal of MB

Elovich model

The Elovich equation was developed to explain the kinetics of chemisorptions of gas onto solids and its differential form is represented in eqn.8. The parameters α is the rate initial concentration (mg/g.min) which also represents the rate of chemisorptions at zero coverage, and Parameter β is the desorption constant (g/mg) and is related to the extent of surface coverage and the activation energy of chemisorptions [19].

$dq_t/ d_t = \alpha \exp(-\beta d_t)$ (8)

Where q_t is the amount adsorbed at time t, and α and β are constants during any one experiment. To simplify the Elovich equation-8 becomes

$q_t = \beta(\alpha\beta) + \ln(t)$ (9)

The α and β are Elovich constants are related to the initial adsorption rate (mg/g/min) and desorption constant (g/mg) can be obtained from the slope and intercept of the linear plot of q_t against ln(t) (Figure- 10). Equation -9 is used study the Elovich equation to the kinetics of MB dye sorption on WJG. The Elovich equation considers the rate-controlling step in the diffusion of the adsorbate molecules and describes chemisorptions on adsorbents and has been applied for the adsorption of solute from liquid solution. Correlation coefficient (R^2) of Elovich model for adsorption of dye onto WJG was found to be good and the adsorption is mainly controlled by diffusion and chemisorptions. The Elovich model parameters α, β and R^2 are summarized in Table-3.

Intra- particle diffusion model

The intra-particle diffusion theory was developed and assumes that intra- particle diffusion is the only rate controlling step of the adsorption process when the negligible diffusion of the liquid film surrounding the adsorbent. The intra-particle diffusion is investigated by its mathematical expression as follows:

$$Q_t = K_{id}\, t^{½} + C \quad (10)$$

Where q_t is the amount of dye adsorbed at time t, C is the intercept and K_{id} is the intra- particle diffusion rate constant (mg $min^{0.5}$ g^{-1}). If intra- particle diffusion was involved in the adsorption then a plot of q_t against $t^{1/2}$ (Figure- 11) would gives linear relationship. The slope was used to identify the intra- particle diffusion rate constant, K_{id} and the intercept C value give an idea of the boundary layer thickness; the larger the intercept, the greater the effect of the boundary layer. The values of K_{id} and C are shown in Table-3. The deviation of straight lines from the origin indicates that the pore diffusion is not the sole- rate determining step. Hence, the intra- particle diffusion kinetic model is not the rate- controlling step [20].

Table- 3: Kinetic parameters for adsorption of MB dye on WJG at 30 °C

Pseudo-first order model				Elovich model			Intraparticle diffusion model		
q_e	k_2	h	R^2	α	β	R^2	k_{id}	C	R^2
5.15	0.025	0.663	0.999	659.00	2.551	0.997	0.087	3.811	0.983

Thermodynamic parameter

Chemical changes occur spontaneously at given temperature if the Gibbs free energy is negative. The ΔG° was calculated from the equilibrium constant K_d corresponds to the ratio of Q_e to C_e [21],

$$\Delta G^0 = -RT \ln K_d \quad (11)$$

Where, ΔG^0 is the Gibbs free energy change (KJ/mol), T is the temperature (^oK), R is the gas constant (8.314 J mol/K). The calculated negative value of ΔG° (-8.36 KJ/mole) shows that the adsorption process is feasible and spontaneous nature.

CONCLUSION

The equilibrium and kinetic studies for the removal of MB dye from waste water solution by water washed Jumbo grass was analyzed. The study was concluded that the WJG was one of the potential adsorbent for removing dye from synthetic water solutions. The effects of dye adsorption on WJG by various factors such as pH, contact time, dosage and initial concentration were investigated. The equilibrium parameters have been evaluated and the data fitted well to Langmuir isotherm, Freundlich and Temkin isotherms. Kinetic studies reveal that the adsorption of MB dye on WJG obeyed very much for pseudo-second order and Elovich kinetic model than intra-particle diffusion model. The thermodynamic parameter was calculated which reveals that adsorption was spontaneous and exothermic in nature.

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