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Utilization of Sugarcane Baggase, an Agricultural Waste to Remove Malachite Green Dye from Aqueous Solutions

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Abstract

In this work, the adsorption potential of agricultural waste material sugarcane baggase to remove malachite green dye from aqueous solution was investigated. The adsorbent was characterized by BET surface area measurement and FTIR analysis. Various parameters such as initial dye concentration, contact time, adsorbent dose and temperature were studied to observe their effects on the dye adsorption process. At optimum values of the above mentioned parameters, more than 95% removal efficiency was obtained within 120 min at adsorbent dose of 1 g/L for initial dye concentration of 50 mg/L. The adsorption of dye was found to follow a pseudo-second-order rate equation. Various thermodynamic parameters (ΔG_o, ΔH_o, ΔS_o) were also estimated. Adsorption mechanisms were investigated with intra-particle diffusion model, Furusawa and Smith model and Boyd's model to get deep insight of adsorption process. Langmuir isotherm model was fitted the best for the adsorption system with an adsorption capacity of 190 mg/g of adsorbent. The present adsorbent may be considered as an alternative adsorbent for the better performance of the malachite green dye removal from its aqueous medium.

Keywords: Biosorption; Malachite green; Sugarcane baggase; Agricultural waste; Wastewater

1. Introduction

In 21st century, numerous numbers of synthetic dyes are being used in various industries such as textile, leather, paper, printing, food, cosmetics, paint, pigments, petroleum, rubber, plastic, pesticide and pharmaceutical industry for different purpose. Among different types of dyes, malachite green dye (MG dye) is extensively used in the aquaculture industry world-wide due to its high effectiveness against parasitic treatment, and fungal and bacterial infections in fish and fish eggs [1]. It is extensively used in textile industries for dyeing, in food industry as a food coloring agent, food additive, and a medical disinfectant and anthelmintic [2]. Approximately 12% of synthetic dyes are lost during manufacturing and processing operations and 20% of these lost dyes enter the industrial wastewaters [3]. Textile industries consume two thirds of the dyes manufactured. During textile processing, up to 50% of the dyes are lost after the dyeing process due to poor interaction between dye molecules and fiber of fabrics and about 10–15% of them are discharged in the effluents [3]. Hence, considerable amounts of dyes come to effluent stream and pollute the waters. The discharge of MG dye into the aquatic system has generated much concern due to its reported genotoxic, mutagenic, teratogenic and carcinogenic effects [1, 2]. Discharge of MG into the hydrosphere can cause environmental degradation as it gives the undesirable color of water and reduces sunlight penetration. However, wastewater containing dyes are very difficult to treat, since the dyes are recalcitrant organic molecules, resistant to aerobic digestion and are stable to light, heat and oxidizing agents.

Therefore, removal of MG from effluents is essential not only to protect human health but also for the protection of water resources.

Among the various conventional methods for removal of dye molecules from effluents, Biosorption, the adsorption of pollutants by inactive, non-living biomass (materials of biological origin) has been strongly recommended by researchers worldwide as an efficient and economically sustainable technology for the removal of synthetic dyes from industrial effluents. Biosorption is a well established technique for the removal of textile dyes [2-11] from aqueous solutions. Numerous number of inexpensive and abundant biosorbents especially agro waste materials as well as industrial and municipal wastes have been proposed by several researchers for the removal of MG dyes [2-9] from their aqueous solutions. However for industrial application, the selection of adsorbent material is mostly done by availability of waste material and applicability of the adsorption method considering space, cost, the amount of wastewater etc. Utilization of agricultural solid wastes for the treatment of wastewater could be helpful not only to the environment in solving the solid waste disposal problem to farmers and agroindustries, but also to the economy. In the state of Madhya Pradesh (India) a lot of bagasse are available as waste material which can be used as efficient adsorbent material for removing dyes. Therefore, a study could also be carried out on the possibility of using these sugarcane baggase as alternative adsorbents for removal of hazardous MG dye from aqueous solutions; which formed the motivation of this present study.

In this paper, we report the adsorption properties of sugarcane baggase particles (SBP) for removal of MG dye from aqueous solution in batch system. Characterizations of SBP were done by BET and FTIR analysis. The experimental study includes evaluation of the effects of initial dye concentration, adsorbent dosage, contact time and temperature on the dye removal. The adsorption kinetic models, equilibrium isotherm models, and thermodynamic parameters related with the process were also performed and reported. Efforts have been given to find the most probable adsorption mechanism of dyes on SBP. This fundamental study will be helpful for further designing an adsorber for the treatment of effluents containing MG dye coming out from dying industries using SBP.

2. Experimental

2.1 Preparation of Adsorbents

Sugarcane bagasse were collected from sugar mill. It was washed thoroughly with water to remove any dirt, dust, sugar traces and any unwanted particles. Then the washed bagasse were sun dried and subsequently oven dried at 373±2K, until all the moistures are removed. Then it was grounded in a ball mill (Ball diameter: 2.54 cm, Ball mill diameter: 30 cm, No of ball: 25 and Rotation speed: 60 rpm) for 2 hours and was sieved in a sieve shaker. The sugarcane baggase particles (SBP) that passed the 150 µm size screen (Yield: 60 %) were chosen as adsorbent without any pretreatment for experimental work. Finally they were stored in an airtight container.

2.2 Preparation of dye solutions

Analytical grade MG dye [C.I.:42000; MW: 365, MF: $C_{23}H_{25}N_2Cl$, λ_{max}: 617 nm] purchased from *Central Drug House, New Delhi, India,* was used in this study. A stock solution of dye of concentration 200 mg/L was prepared by dissolving 0.2 g of solid dye in 1 L of distilled water. Experimental solutions of desired concentrations were obtained by successive dilution of the stock solution.

2.3 Characterization of Adsorbent

Pore volume and pore volume distribution of adsorbent plays an important role in adsorption. To find the pore volume and its distribution, BET surface area measurement technique was used. Figure 1 shows the pore size distribution curve of the adsorbent based on the nitrogen equilibrium adsorption isotherm at 77 K [12]. The specific surface area of the SBP determined from BET surface area analyzer was 10.2 m^2/g. It may be observed from the figure that, the SBP exhibited a multimodel distribution in both the micropore and mesopore domains. Three different zones of pores observed in the figure were in between 3.5 to 20 nm, 20 to 70 nm and 70 to 100 nm. About 78.48 % of total pores were in the range of 3.5 to 20 nm pore diameter. This indicates that adsorbent contains a very high mesopore volume.

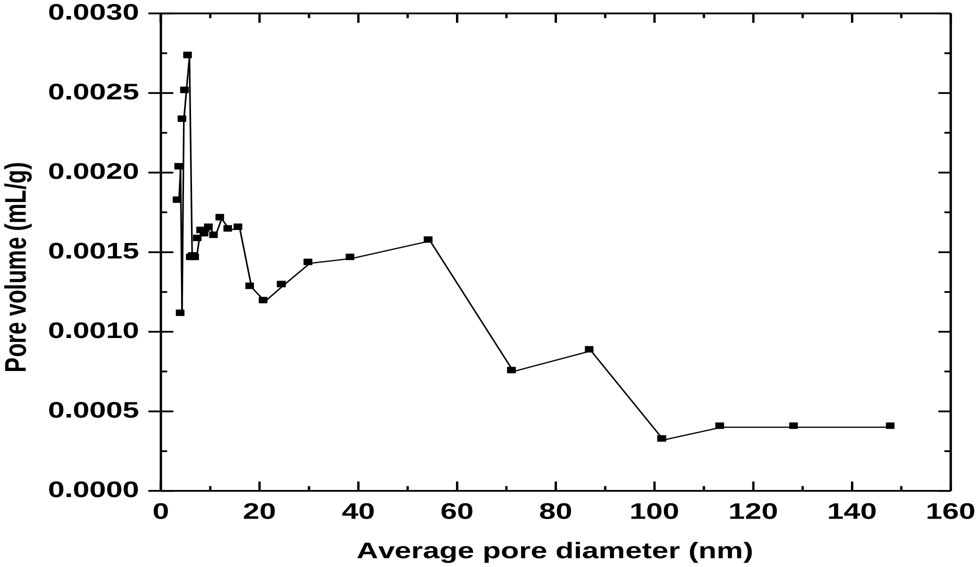

Figure 1: Pore size distribution of SBP obtained from BET analysis.

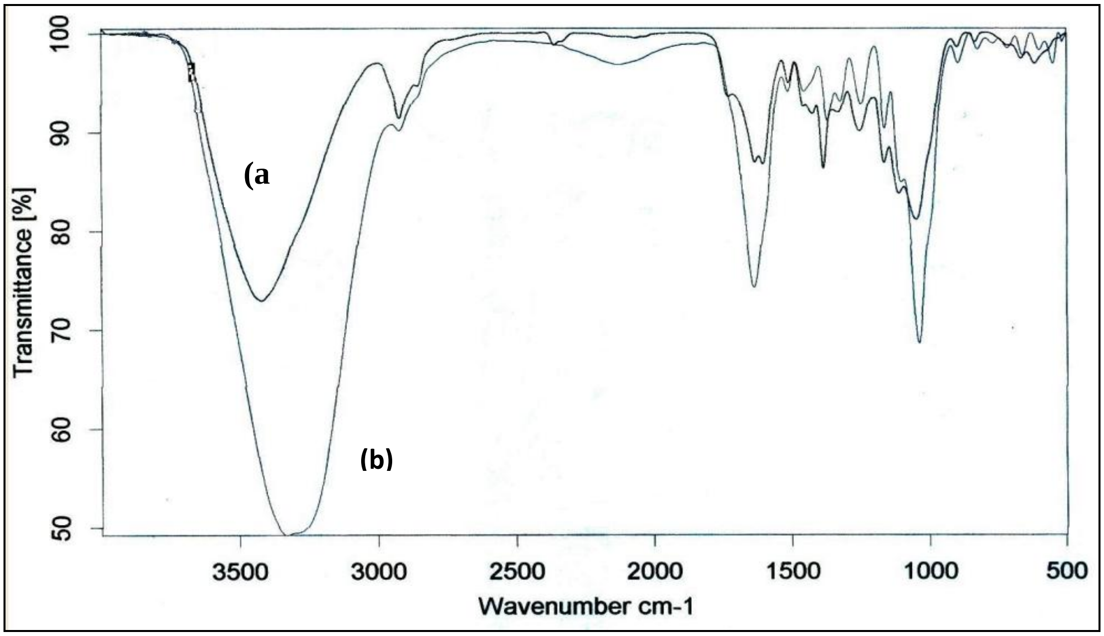

Figure 2: FTIR spectra of SBP (a) before and (b) after adsorption.

SBP is a lignocellulosic compound and is generally considered as structures built by cellulose molecules, organized in microfibrils and surrounded by hemicellulosic materials, lignin and pectin along with small amounts of protein [13]. The FTIR spectra of SBP before and after sorption of MG dye were analyzed to determine the vibration frequency changes in their functional groups within the range of 3500–500 cm^{-1} and are shown in Figure 2. From the figure it was observed that many broad and minor peaks are present in the spectra. For SBP before adsorption, various peaks are at 3420 cm^{-1} (presence of free and intermolecular bonded hydroxyl (-OH) bond), 2921 cm^{-1} (C-H bond), 1631 cm^{-1} (C=C bond), 1423 cm^{-1} (CH_3), 1160 cm^{-1} (C- N bond), 1048 cm^{-1} (C- O bond due to alcohols and carboxylic acids) and 1704.8 cm^{-1} (carboxylic groups of galactouronic acid) [14]. After adsorption of dye molecules it was found that, oxygen containing functional groups like, methoxy –OCH3, carboxy –COOH and phenolic –OH groups are affected after uptake process. This is judged from shifts in their position to lower frequency, shape or band intensity from 1048, 1704.8 and 3420 cm^{-1} to 1046.2, 1682.6 and 3406.6 cm^{-1} of m(–O–C), m(–COOH) and m(–OH) for SBP before and after MG adsorption, respectively. The results indicate that the participation of these groups via oxygen for MG binding to SBP in agreement with Person principal for hard-soft acids and bases [15].

2.4 Batch Experiments

Adsorption experiments were carried out using a Jar Test Apparatus" (*Make: Scientific System, New Delhi*). For the present system diameter of agitator (D) was 7.5 cm, viscosity of water at 20 ^{0}C was taken as 1.002 mPa.s=1.002 × 100 g/cm.s, density of water at 20 ^{0}C=1.001 g/cm^{3}and agitation speeds of 300 rpm. Calculated value of N_{Re} was 28096. Maximum of four experiments were carried out simultaneously with initial time difference of 15 minutes. PHZPC of the adsorbent were determined as pH 7. Hence to achieve maximum dye removal [12], adsorption experiments were carried out at pH 7. All the experiments were carried out at ambient temperature in winter (293± 2 K) in batch mode using a 2 L beaker. In the present study, effects of contact time (varied from 0.5 to 120 minutes), initial dye concentration (25, 50, 75 and 100 mg/L), dry solid SBP dosage (0.25, 0.5, 0.75 and 1.0 gm/L for different initial dye concentrations of 25, 50, 75 and 100 mg/L.) and temperature (293, 303, 313 and 323 K) was evaluated. In order to study the adsorption isotherm, 0.1 g of SBP were kept in contact with 100 ml dye solution of different concentrations (20, 40, 60, 80, 100, 150 and 250 mg/L) at pH 7 for 24 hours (to confirm that the equilibrium has been reached) with constant stirring at temperature of 293 ± 2 K . After 24 hours the solution attains equilibrium and the amount of dye adsorbed (mg/g) on the surface of the adsorbent is determined by the difference of the two concentrations. Triplicate experiments were carried out for all the operating variables studied and only the average values are taken into consideration. The average deviation of triplicate results in the units of concentration is found to vary as ± 2 %. Blank experiments were carried out with dye solution and without adsorbent to ensure that no dye is adsorbed onto the walls of the beakers, agitator and baffles. Dye concentrations in the aqueous solutions were estimated using absorbance data obtained from UV-VIS spectrophotometer (*Make: Elico Instruments Ltd, India, Model: SL 159*). Concentrations of dye were estimated from the calibration curve and equations. The amount of dye adsorbed per unit weight of SBP at time (q_t) and dye removal efficiency were calculated as:

$$q_t = \frac{(C_0 - C_t)}{m} \times V \tag{1}$$

$$\%\,\mathrm{Dye\ Removal} = \frac{(C_0 - C_t)}{C_0} \times 100 \tag{2}$$

where, C_0 is the initial MG concentration (mg/L), C_t is the concentration of dye at any time t, V is the volume of solution (L) and m is the mass of SBP (g).

3. Results and discussions

3.1 Effect of contact time and initial dye concentration on dye removal

The variation in dye adsorption (dye uptake) per unit weight of SBP with contact time at different initial concentrations of 25, 50, 75 and 100 mg/L is presented in Figure 3. From the figure it can be observed that the rapid adsorption of dye takes place within the contact time of 5 minutes and thereafter adsorption process becomes slow. Further experiments were conducted with the contact time of 120 minutes duration. From the figure it can be observed that dye uptake increases with increase in dye concentration. Dye uptake varied from 24.66 mg/g to 90.157 mg/g for initial dye concentration of 25 to 100 mg/L dye concentration respectively. Increase in dye uptake was due to the availability of higher amount of dye molecules in the solution. However, at the same time percent removal of dye was decreased. For the initial concentration of upto 50 mg/L, more than 95 % adsorption has been observed, whereas for 100 mg/L, the percent removal of dye is 82 %. From the above observation, it is evident that for higher initial concentration of dye, the adsorption is very fast. The percentage removal of dye decreases with increase in initial concentration and takes longer time to reach equilibrium because of the fact that with increase in dye concentration, there will be increased competition for the active adsorption sites and the adsorption process will increasingly slow down. This explains the more adsorption time for higher concentration.

From the figure it can be observed that, that adsorption of MG dye are very fast in initial 5 minutes and become slower for all the four concentrations studied in this work. Experiments were carried out upto 180 minutes and it was observed that after 120 minutes, further increase in contact time did not enhance the adsorption. The fast adsorption rate at the initial stage (first 5 minutes) may be explained by an increased availability in the number of active binding sites on the adsorbent surface. The sorption rapidly occurs and normally controlled by the diffusion process from the bulk to the surface. In the later stage, the sorption is likely an attachment-controlled process due to less available sorption sites. Similar results have been reported in literature for adsorption of MG dye over sea shell powder [2].

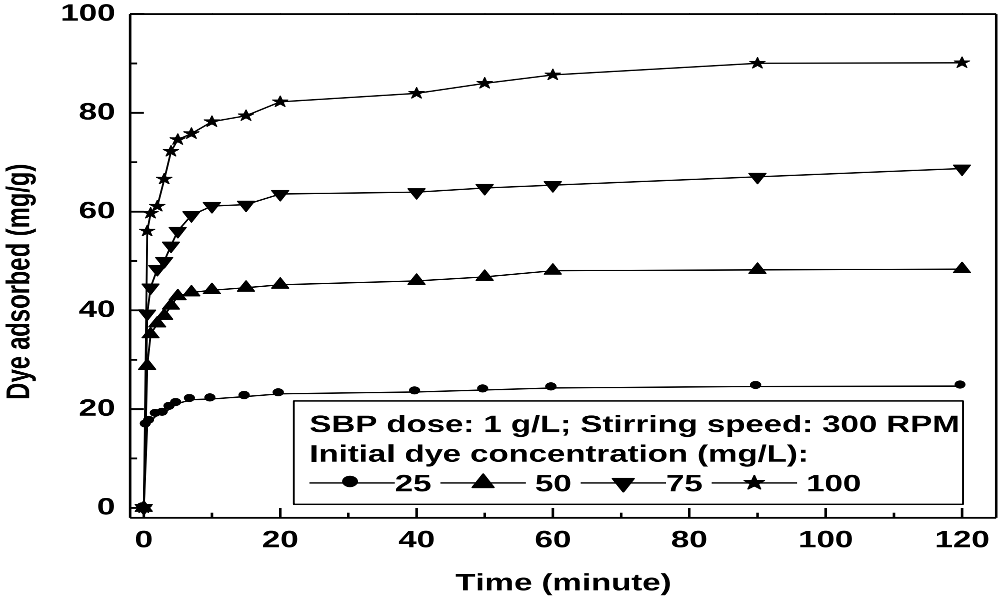

Figure 3: Effect of contact time and initial dye concentrations of MG dye.

The amount of dye adsorbed per minute or rate of adsorption of MG dye for initial rapid phase, r_{rapid} (mg/g min) (first 5 minute) and slower phase r_{slower} (mg/g min) (remaining time upto 120 min) is shown in Figure 4. From the figure it can be observed that the rate of adsorption increases with initial dye concentration. The rate of adsorption in the initial rapid phase is found to be 4.23, 8.57, 11.22 and 14.91 mg/g min for initial dye concentration of 25, 50, 75 and 100 mg/L, respectively. Similar trend is observed for the slower phase where the rate of adsorption is 0.031, 0.078, 0.110 and 0.136 mg/g min for initial dye concentration of 25, 50, 75 and 100 mg/L, respectively. The rate of dye adsorption corresponding to Figure 4 fits the Eq. (3) for initial rapid phase and Eq. (4) for later slower phase, respectively.

$$r_{rapid} = 0.1389C_o + 1.052 \qquad R^2 = 0.992 \tag{3}$$

$$r_{slower} = 0.0749\ln C_0 - 0.2122 \qquad R^2 = 0.996 \tag{4}$$

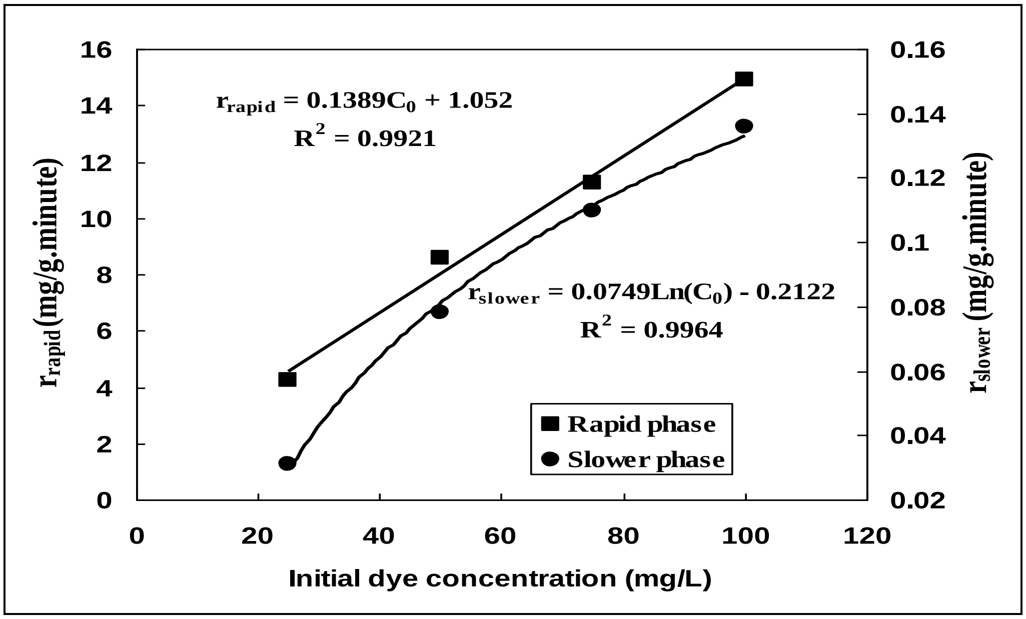

Figure 4: Effect of initial MG dye concentration on the adsorption rate.

3.2 Effect of SBP dose on dye removal

The effect of SBP dose (varying from 0.25 to 1.0 g/L) on the dye uptake and percentage removal of dye at four different initial dye concentrations 25, 50, 75 and 100 mg/L is shown in Figure 5. It can be observed from the figure that the overall dye removal from the solution increases with increase in adsorbent dose. It was due to the availability of higher surface area (more adsorption sites) at higher amount of adsorbent dose.

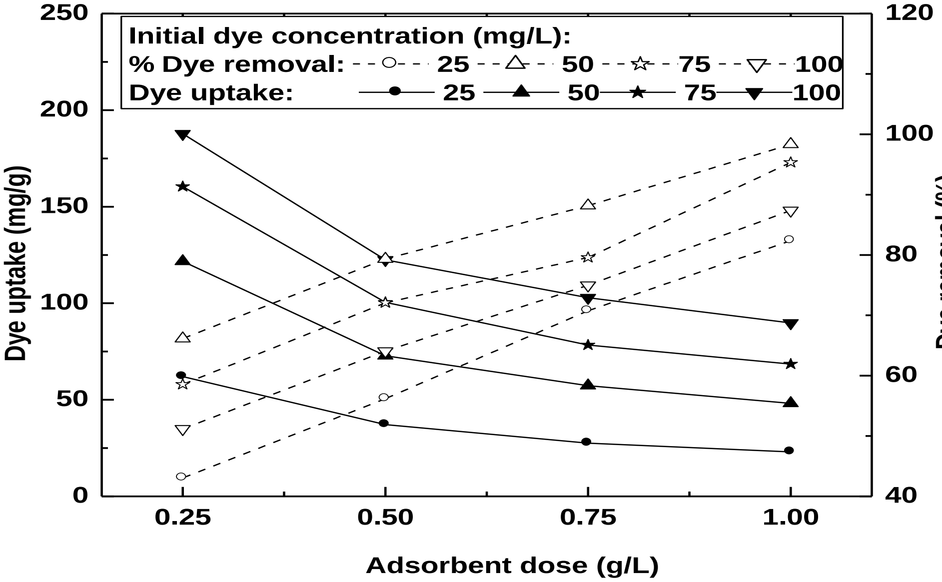

Figure 5: Variation of dye adsorption and dye removal with adsorbent dose. Time of adsorption: 120 min.

From the figure it also can be observed that dye uptake decreases with increases in SBP dose. But at the same time the overall removal efficiency increases. The decrease in dye uptake value (mg dye/g of SBP) is due to the splitting effect of flux (concentration gradient) between adsorbate and adsorbent. The increase in percentage color removal is because at higher SBP there is a very fast superficial adsorption onto the SBP surface that produces a lower solute concentration in the solution than when SBP dose is lower. However, dye uptake increases with the increase in initial dye concentration for constant SBP dose. This is due to the presence of more number of dye molecules in the solution.

3.3 Adsorption isotherm study

An isotherm describes the equilibrium relationship between the adsorbate concentration in the liquid phase and that on the adsorbent's surface at a given condition. There are several isotherm equations available for analyzing experimental sorption equilibrium parameters. However, the most common types of isotherms are Langmuir model [16] and Freundlich model [17], which are represented as

$$q_e = \frac{Q_0 b C_e}{1 + bC_e} \tag{5}$$

$$q_e = K_F C_e^{\ n} \tag{6}$$

where, C_e (mg/L) and q_e (mg/g) are the liquid phase concentration and solid phase concentration of dye at equilibrium, respectively, Q_0 (mg/g) and b (L/mg) are the Langmuir isotherm constants, K_F is the Freundlich constant K_F [mg/g(L/g)$^{1/n}$] related to the bonding energy, and n is the heterogeneity factor. n is a measure of the deviation from linearity of the adsorption. It indicates the degree of non-linearity between solution concentration and adsorption.

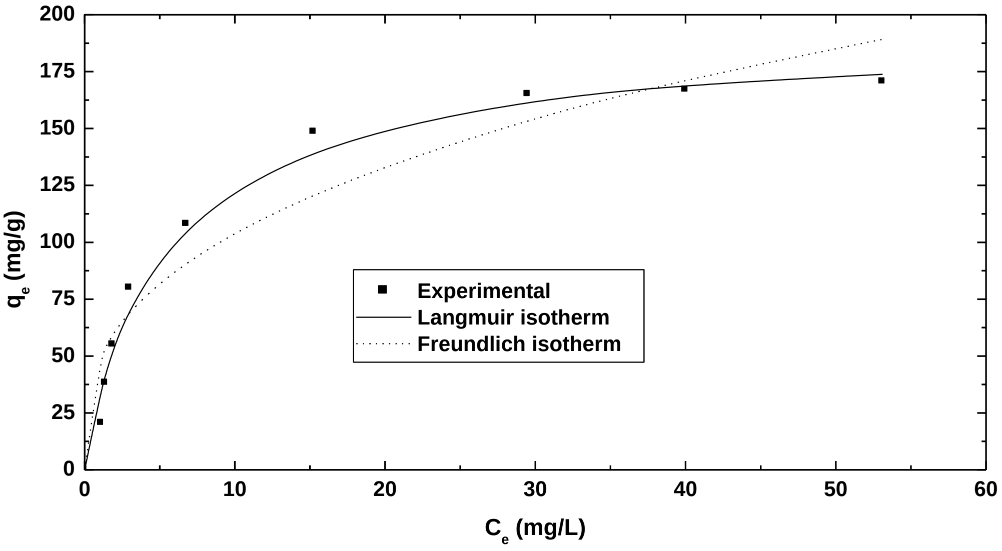

Figure 6: Langmuir and Freundlich adsorption isotherms for MG dye on SBP.

Various parameters obtained from Langmuir and Freundlich isotherm are shown in Table 1 and the modeled isotherms are plotted in Figure 6. From the figure 6, it was observed that Langmuir isotherm was best fitted with the experimental results. Regression coefficient for Langmuir isotherm was 0.9878 compared to 0.9096

Table 1: Langmuir and Freundlich isotherm constants for the adsorption of MG dye on bagasse.

Langmuir isotherm model			Freundlich isotherm model		
Q_0 (mg/g)	b (L/mg)	R^2	K_F [mg/g(L/g)$^{1/n}$	*n*	R^2
190	0.20	0.9878	47.95	0.35	0.9096

of Freundlich isotherm. This signifies that dye adsorption is taking place through monolayer adsorption. Calculated maximum adsorption capacity of SBP was 190 mg/g. The Langmuir isotherm is applicable when there is a strong specific interaction between the solute and the adsorbent. Ion exchange and affinity type adsorptions generally follow Langmuir isotherm. This isotherm predicts the saturation of the adsorption sites by solute molecules, indicating monolayer formation.

3.4 Adsorption kinetics

The kinetics of MG dye adsorption onto SBP was evaluated using different models such as pseudo-first-order [18] and pseudo-second-order models [19]. Details of mathematical expressions (Eqs. 7 and 8) are given in Table 2. In the Eqs 7 and 8, k_1 and k_2 are the rate constants for pseudo first order and pseudo second order model, respectively. Fitting the adsorption experimental data to these models, various parameters were calculated and reported in Table 2. Among these models the criterion for their applicability is based on judgment on the respective correlation coefficient (R^2) and agreement between experimental and calculated value of q_e. The high values of R^2 (~1) and good agreement between two qe values indicate that the adsorption system followed pseudo-second-order kinetic model (Table 2) and hence the process is chemisorptions controlled [12].

3.5 Effect of temperature on dye removal

To observe the effect of temperature on the adsorption capacity, experiments are carried out for three different dye concentrations of 25, 50 and 100 mg/L) and at four different temperatures (293K, 303K, 313K and 323K) using SBP dose of 1 g/L. It has been observed that with increase in temperature, adsorption capacity decreases as shown in Table 3. This implies that for the initial dye concentration of each solution, the adsorption is exothermic in nature.

Table 2: Pseudo-first-order and pseudo-second-order rate constants for different dye concentrations.

Initial dye concentration (mg/L)	$q_{e,expt}$ (mg/g)	Pseudo-first-order model $\ln(q_e - q_t) = \ln q_e - k_1 t$ (7)			Pseudo-second order model $\frac{t}{q_t} = \frac{1}{k_2 {q_e}^2} + \frac{t}{q_e}$ (8)		
		$q_{e,cal}$ (mg/g)	k_1(min^{-1})	R^2	$q_{e,cal}$ (mg/g)	k_2 (g/mg.min)	R^2
25	24.67	6.40	0.048	0.889	24.75	0.040	0.999
50	48.35	11.85	0.050	0.859	48.50	0.023	0.999
75	68.72	21.23	0.055	0.908	68.31	0.011	0.999
100	90.16	27.90	0.049	0.923	90.50	0.008	0.999

Table 3: Variation of percentage removal of MG dye at different temperatures.

Dye concentration (mg/L)	Percentage removal of dye at temperature			
	293 K	303 K	313K	323 K
25	98.33	98.02	97.42	96.79
50	95.34	94.09	92.55	90.06
100	82.37	79.47	74.46	66.71

3.6 Adsorption thermodynamics

The thermodynamic parameters change in Gibb's free energy (ΔG^0), change in entropy (ΔS^0) and change in enthalpy ΔH^0 for the adsorption of MG over SBP has been determined by using the following equations

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \qquad (9)$$

The Gibb's free energy change of the process is related to the equilibrium constant by the following equation.

$$\Delta G^0 = -RT \ln\left(\frac{q_e m}{C_e}\right) \qquad (10)$$

So Eq. (9) can be rewritten as

$$\ln\left(\frac{q_e m}{C_e}\right) = \frac{\Delta S^0}{R} + \frac{-\Delta H^0}{RT} \qquad (11)$$

The values of Gibb's free energy (ΔG^0) have been calculated by knowing the enthalpy of adsorption (ΔH^0) and the entropy of adsorption (ΔS^0) and $\Delta \mathrm{H}^0$ are obtained from a plot of $\ln\left(\frac{q_e m}{C_e}\right)$ versus $\frac{1}{T}$ (Figure 7).Once these two parameters are obtained, ΔG^0 is determined from Eq. (9).

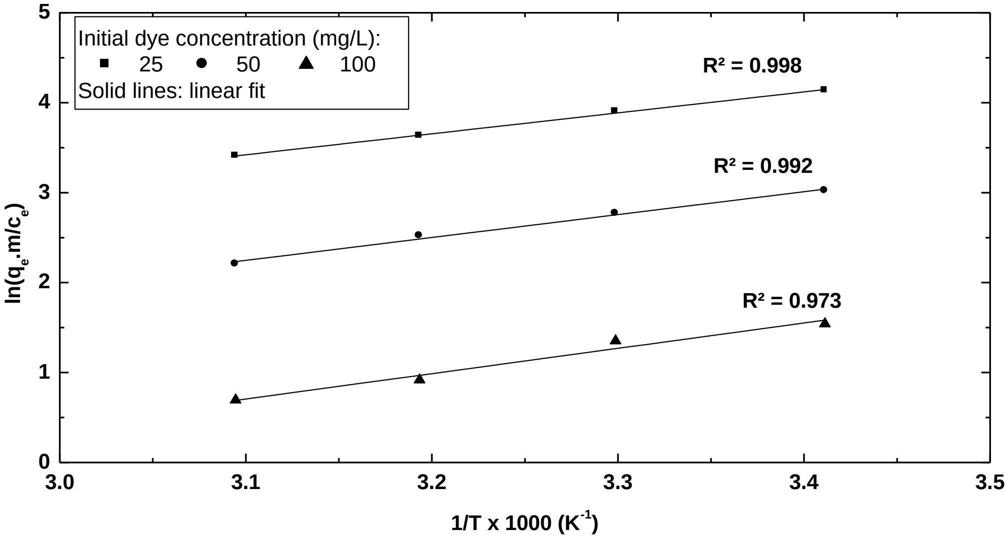

Figure 7: Effect of temperature on adsorption of MG dye on SBP.

The values of ΔH^0, ΔS^0 and ΔG^0 for the initial dye concentrations of 25, 50 and 100 mg/L are shown in Table 4. Negative ΔH^0 indicates that the adsorption is exothermic in nature. The exothermic nature is also indicated by the decrease in the amount of adsorption with temperature (Table 1). The adsorption is associated with a decrease in entropy of -31.57,-46.92 and -66.7 J/mol. K, respectively, which indicates that the adsorbed dye molecules on the bagasse surface are more organized compared to those in the aqueous phase. Similar observations have been reported in the literature [10]. The higher heat of adsorption obtained in this work indicates that chemisorptions rather than the physical adsorption are prevalent in this case. The negative values of

ΔH^0 and ΔG^0 indicate that the adsorption process is spontaneous and exothermic in nature. The negative value of ΔS^0 suggests decreased randomness during adsorption [10].

Table: 4: Thermodynamic parameters for the adsorption of MG dye on SBP.

Dye concentration (mg/L)	$-\Delta H^0$ (KJ/mol)	ΔS^o (KJ/mol.K)	$-\Delta G^0$ (KJ/mol) at temperature			
			293 K	303 K	313 K	323 K
25	19.36	-31.57	10.10	9.79	9.47	9.16
50	21.16	-46.92	7.41	6.94	6.47	6.00
100	23.41	-66.70	3.86	3.19	2.52	1.86

3.7 Adsorption mechanisms

3.7.1 Intraparticle diffusion model

In this model, it is assumed that the mechanism for dye removal by adsorption on a sorbent material is taking place through four steps:

a) Migration of dye molecules from bulk solution to the boundary layer film of the adsorbent through bulk diffusion.

b) Diffusion of dye molecules through the boundary layer to the surface of the adsorbent via film diffusion.

c) The transport of the dye molecules from the surface to the interior pores of the particle occur through intraparticle diffusion or pore diffusion mechanism.

d) Adsorption of dye at an active site on the surface of material by chemical reaction via ion-exchange, complexation and/or chelation.

In general, the dye sorption is governed by either the liquid phase mass transport rate or through the intraparticle mass transport rate. Pore-diffusion models should be formulated so as to consider not only the particle size but also particle shape. The adsorption process is a diffusive mass transfer process where the rate can be expressed in terms of the square root of time (*t*). The intra-particle-diffusion model is expressed as follows [20]

$$q_t = k_i t^{0.5} + I \tag{12}$$

The plot of q_t versus $t^{0.5}$ will give k_i as slope and I as intercept. The intercept I represents the effect of boundary layer thickness. Minimum is the intercept length, adsorption is less boundary layer controlled. Figure 8 represents the plot of q_t versus $t^{0.5}$ plot for the initial dye concentration of 25, 50, 75 and 100 mg/L. It seems that for all the four concentrations plots are non linear in nature but careful observation infers that data points can be better represented by double linear with different in slope (k_i) and intercept (I). The values of k_i and I are summarized in Table 5 along with regression constant (R^2) for different initial dye concentrations. In first straight line, the sudden increase (within a short time period) in slope signifies that the dye molecules are transported to the external surface of the SBP through film diffusion and its rate is very fast. After that, dye molecules are entered into the SBP by intraparticle diffusion through pore, which is represented in second straight line. Both the line does not pass through the origin that concludes that both film diffusion and intraparticle diffusion are simultaneously occurring during the adsorption. Similar result is found in the literature [12] for adsorption of cationic dye on kaolin.

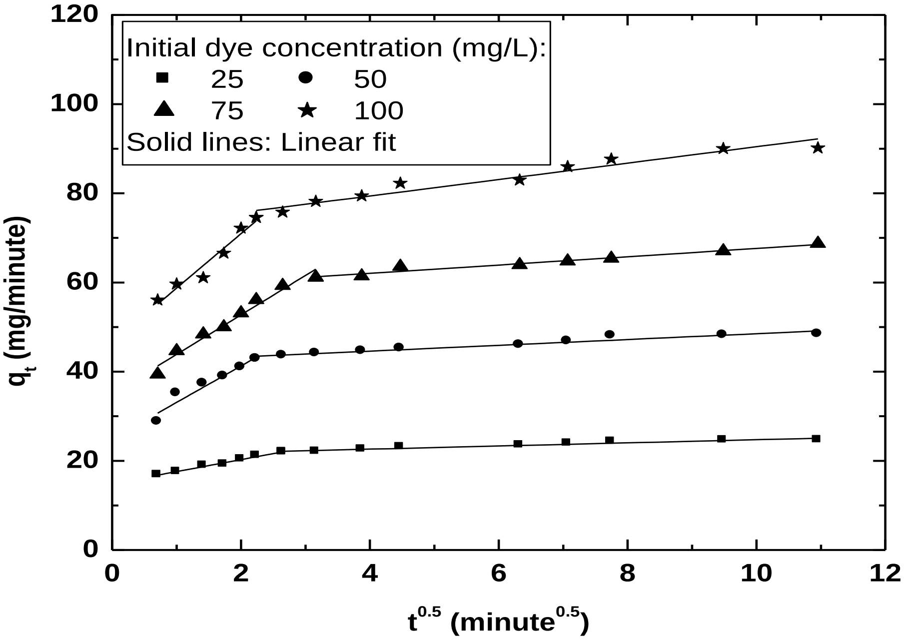

Figure 8: Intra-particle-diffusion model for adsorption of MG dye on SBP.

Table 5: Intra-particle-diffusion model parameter for adsorption of MG dye on SBP.

Initial dye concentration (mg/L)	1st straight line			2nd straight line			$K_S \times 10^6$ (m/s)
	k_i (mg/g.min$^{1/2}$)	I (mg/g)	R^2	k_i (mg/g.min$^{1/2}$)	I (mg/g)	R^2	
25	2.69	14.88	0.987	0.352	21.2	0.94	3.08
50	8.173	24.92	0.928	0.651	41.98	0.941	3.78
75	8.842	35.03	0.971	0.93	58.32	0.966	5.63
100	12.19	46.53	0.953	1.842	72.01	0.946	6.26

3.7.2 Furusawa and Smith model

The external mass transfers of MG dye onto SBP surface are analyzed using the external mass transfer model proposed by Furusawa and Smith [21]. The experimental data of dye adsorption are analyzed assuming a three step model:

(1) External mass transfer of dye ions from bulk solution to the SBP surface.
(2) Intraparticle diffusion.
(3) Adsorption at internal site.

However, in general step (3) is rapid compared to the first two steps. For fully turbulent mixing of solid/liquid adsorption system, as the mixing in the liquid is very high, intra-particle diffusion is also very high. Hence, it may be assumed that the step (1), external mass transfer of dye ions from bulk solution to the SBP surface is the rate determining step. The change in concentration of dye with respect to the time can be expressed by the equation:

$$-\frac{dC_t}{dt} = K_S S\left(C_t - C_e\right) \tag{13}$$

At time t=0, C_e = 0, thus Eq. (13) becomes:

$$\left[\frac{d\left(C_t/C_o\right)}{dt}\right]_{t=0} = -K_S S \tag{14}$$

where, K_S is the external mass transfer coefficient (m/s) and S is the surface area of adsorbent per unit volume of the particle slurry (m^2/m^3). In our case, S was experimentally determined by the BET surface area measurement. The external mass transfer coefficient K_S can be calculated from the slope of C_t/C_o versus time t using Eq. (14). In the present investigation, the K_S values are obtained using the experimental kinetic data for the first initial rapid phase of 5 min where the external mass was expected to be the dominant process. The calculated external mass transfer coefficient for different initial dye concentrations are summarized in Table 5.

3.7.3 Boyd's model

Present study showed the presence of both external and intraparticle diffusion in the actual process. However for the design aspect it is important to determine the actual rate limiting step involved in the process. Thus to determine the actual rate controlling step involved in the process, Boyd et al. [22] proposed the pore diffusion model based on the solid phase concentration and not based on the solute concentration which helps to apply this model to understand the mechanism or to predict the rate limiting step in any solid/liquid adsorption systems which are normally a pseudo process. The Boyd's kinetic expression was given by the Eqs. (15-17) as follows:

$$F = 1 - \frac{6}{\Pi^2}\exp(-B_b t) \tag{15}$$

$$B_b t = -0.4977 - \ln\left(1 - F\right) \tag{16}$$

$$F = \frac{q_t}{q_e} \tag{17}$$

Where, F is fraction of solute adsorbed at any time t, $B_b t$ is Boyd's function. The $B_b t$ values at different contact time can be calculated using Eq. 17. The calculated $B_b t$ values were plotted against time t as shown in Figure 9 which is used to identify whether external transport or intra-particle transport controls the rate of sorption [23].

From the figure, it was observed that the plots were linear but does not pass through the origin confirming that, for the studied initial dye concentration, external mass transport mainly governs the sorption process. The calculated B_b t values were used to calculate the effective diffusion coefficient, D_i using the relation [23]

$$B_b = \Pi^2 \frac{D_i}{r^2} \tag{18}$$

where, B_b is boyd's Constant (s^{-1}), r represents the radius of the particle calculated by sieve analysis and by assuming as spherical particles. Calculated values of effective diffusion coefficient are summarized in Table 6. From the table it was observed that calculated values of D_i are 29.89, 30.35, 32.01, 31.44, respectively.

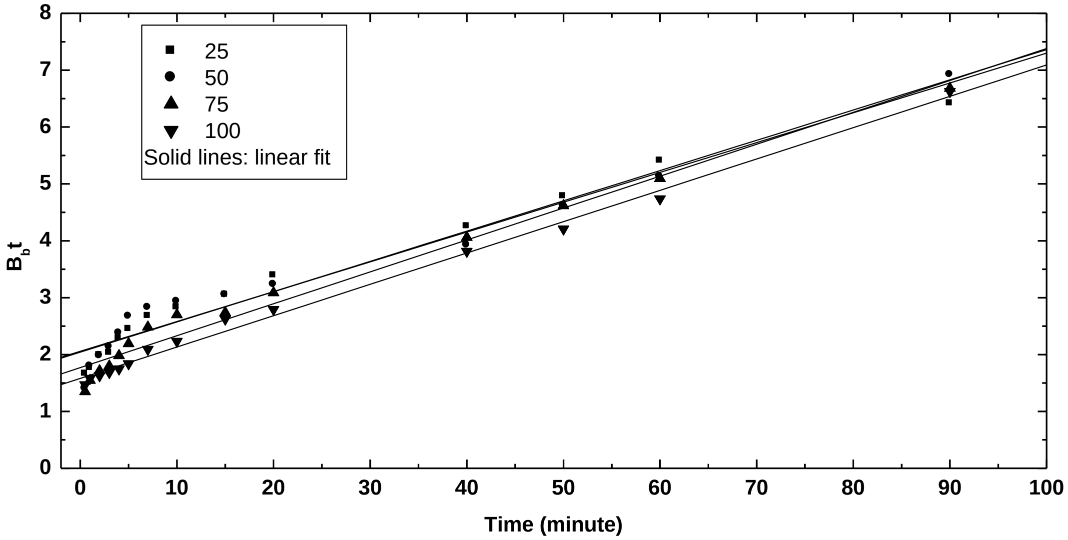

Figure 9: Boyd plot for MG dye on SBP.

Table 6: Effective diffusion coefficient of MG dye on SBP.

Initial dye concentration (mg/L)	Boyd's function, B_bt	D_i (cm^2/s)
25	0.0524	29.89
50	0.0532	30.35
75	0.0561	32.01
100	0.0551	31.44

3.8 Comparison of SBP with other sorbents

Table 7 summarizes the comparison of the maximum MG dye adsorption capacities of various sorbents including SBP. The comparison shows that SBP has higher adsorption capacity (190 mg/g) of MG dye than many of the other reported adsorbents. The easy availability and cost effectiveness of SBP are some of the additional advantages, reflecting a promising future for SBP utilization in MG dye removal from aqueous solutions.

Table 7: Comparison of MG dye adsorption capacity of SBP with some reported adsorbents.

Adsorbent	**Q_0(mg/g)**	**Reference**
Sea shell powder	42.33	[2]
Chemically modified rice husk	17.76	[3]
Lemon peel	51.73	[4]
Hen feathers	26.1	[5]
Rattan sawdust	62.7	[6]
Degreased coffee bean	55.3	[7]
Pineapple leaf powder	54.64	[8]
Waste apricot	116.27	[11]
SBP	190	[present study]

Conclusions

Bagasse has been identified to be an effective adsorbent for the removal of MG dye from aqueous medium. The amount of dye uptake (mg/g) was found to increase with increase in dye concentration, adsorption time and decrease with increase in SBP dosage. The equilibrium data are analyzed against Langmuir and Freundlich isotherm equations. The result shows that the experimental data are best correlated by Langmuir isotherm. The maximum adsorption capacity of SBP was calculated as 190 mg/g. The kinetics of dye removal is found to follow a pseudo second order kinetic expression. The dye uptake process was found to be controlled by external mass transfer at earlier stages and by intraparticle diffusion at later stages. The negative values of ΔH^0 and ΔG^0 indicate that the adsorption process is spontaneous and exothermic in nature. The negative value of ΔS^0 suggests decreased randomness during adsorption A Boyd plot confirms the external mass transfer as the slowest step involved in the sorption process. The present findings suggest that SBP may be used as an inexpensive and effective biosorbent without any treatment or any other modification for removal of MG dye from aqueous solutions.

References

1. Srivastava, S., Sinha, R., Roy. D., *Aquatic Toxicol.* 66 (2004) 319.
2. Chowdhury, S., Saha. P., *Chem. Eng. J.* 164 (2010) 168.
3. Chowdhury, S., Mishra, R., Saha, P., Kushw. P., *Desalination* 265(2011) 159.
4. Kumar, K.V. , *Dyes and Pigments.* 74 (2007) 595.
5. Mittal, A., *J. Hazard. Mat.* 133 (2006) 196.
6. Hameed, B.H., El-Khaiary. M.I., *J. Hazard. Mat.* 159 (2008) 574.
7. Baek, M.H., Ijagbemi, C.O., Se-Jin, O., Kim, D.S., *J. Hazard. Mat.* 176 (2010) 820.
8. Chowdhury, S., Chakraborty, S., Saha. P., *Colloids and Surfaces B: Biointerfaces* 84 (2011) 520.
9. Jin, B. Y., Jian, F. C., Liu., C. Z., *J. Hazard. Mat.* 137 (2006) 865.
10. Reddy, M.C.S., Sivaramakrishna, L., Reddy. A. V., *J. Hazard. Mat.* 203 (2012) 118.
11. Basar, C.A., *J. Hazard. Mat.* 135 (2006) 232.
12. Nandi, B.K., Goswami, A., Purkait., M.K., *J. Hazard. Mat.* 161 (2009) 387.
13. Asheh, S.A., Duvnjak, Z., *J. Hazard. Mat.* 56 (1997) 35.
14. Pehlivan, E., Yanik, B.H., Ahmetli, G., Pehlivan. M., *Bioresource Technol.*, 99 (2008) 3520.
15. Pearson, R.G., *J. Am. Chem. Soc.* 85(1963) 3533.
16. Langmuir, I., *J. Am. Chem. Soc.* 40 (1918) 1361.
17. Freundlich, H., *Z. Physik. Chem.* 57 (1907) 385.
18. Lagergren, S., *K. Sven. Vetenskapsakad. Handl.* 24 (1898)1-39.
19. Ho, Y.S., McKay. G., *Process Biochem.* 34 (1999) 451.
20. Weber, WJ., Morris. J.C., *J. Sanit. Eng. Div. Am. Soc. Civil Eng.* 89 (1963) 31.
21. Furusawa, T., Smith. J.M., *Ind. Eng. Chem. Funda.* 12 (1973) 197.
22. Boyd, G.E., Adamsom, A.W., Myers Jr., L.S., *J. Am. Chem. Soc.* 69 (1947) 2836.
23. Reichenberg D., *J. Am. Chem. Soc.* 75 (1953) 589.

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