Removal of Basic Dyes from Aqueous Solutions by Sugar Can Stalks

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ABSTRACT

The adsorption removal of a basic dyes, methylene blue (MB) and crystal violet (CV) on sugar can stalks were investigated using batch adsorption technique. Different variables such as solution pH, dye concentration and temperature were examined to optimize the methods. Removal of both dyes was observed to be most effective at higher pH. Freundlich and Langmuir isotherm models were applied to the equilibrium data. The results showed that Langmuir equation fits better than the Freundlich equation. It was observed that the sugar can stalks adsorbent showed higher adsorption capacity for CV (18.7 mg/g) than MB (9.8 mg/g). The studies show that sugar can stalks, a waste inexpensive material, can be an alternative to other expensive adsorbents used for dye removal in wastewater treatment.

Key words: sugar can stalks, methylene blue, crystal violet, adsorption isotherm.

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INTRODUCTION

Decolorization of dye contaminated effluents generated from various industrial sources is of serious concern from environmental point of view because of their toxic effects and high biological and chemical oxygen demands. Due to their chemical structure, most of the dyes are resistant to fading on exposure to light, water and many chemicals [1]. There are many structural varieties of dyes that fall into cationic, anionic or nonionic type. Several methods for removing dyes from wastewater include flocculation, electroflotation, precipitation, electrokinetic coagulation, ion exchange, membrane filtration, electrochemical destruction, irradiation and ozonation have been used for the removal of dyes. All these methods have different color removal capability, capital costs, and operating rates. Among these methods, adsorption process is potential alternative to conventional treatment techniques for the elimination of dye contaminated effluents [2]. This process is based on the interactions between organic or inorganic pollutants and functional groups present on the biosorbent structure [3]. The efficiency of this process depends on several factors as the type of pollutant being studied to type of biosorbent used as well as other environmental parameters. Different kinds of adsorbents were used for basic dye removal from aqueous solutions such as biodegradable polymer [4], tree leaves [5], wood shells [6], palm kernel fiber [7], chitosan derivatives [8], natural clay [9], agricultural waste [10] and activated carbon [11].

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This study aimed to examine the use of sugar can stalks as an agricultural waste, for the efficient removal of basic dyes from aqueous solution. Methylene blue was used as a model for the study. Batch adsorption experiments were carried out systematically in terms of process parameters such as agitation time, initial dye concentration, adsorbent dose and pH.

MATERIALS AND METHODS

1. Preparation of adsorbent and dye solutions
Sugar can stalks used in this study were obtained from a local field near Benha city, Egypt. The raw stalks were washed several times with distilled water and then dried in an oven at 80 ℃ for 24 h, grounded in a laboratory mill and screened through a set of sieves to obtain fine powder of size 0.1-0.2 mm. The dried powder was stored in an air-tight container till use.

Methylene blue (MB) and crystal violet (CV) were selected as models of basic dyes for this study. The chemical structures of the two dyes are given in Fig. 1. A stock solution of dye (250 mg L^{-1}) was prepared by dissolving an accurate quantity of the dye in deionized water. Other concentrations varied between 10 and 50 mg L^{-1} were prepared from stock solution by appropriate dilution. Fresh dilutions were used for each experiment. The pH of the working solutions was adjusted to the desired values with 0.1N HCl or 0.1N NaOH. The pH values were measured by using a pH-meter model HI 8014, Hanna Instruments (Italy).
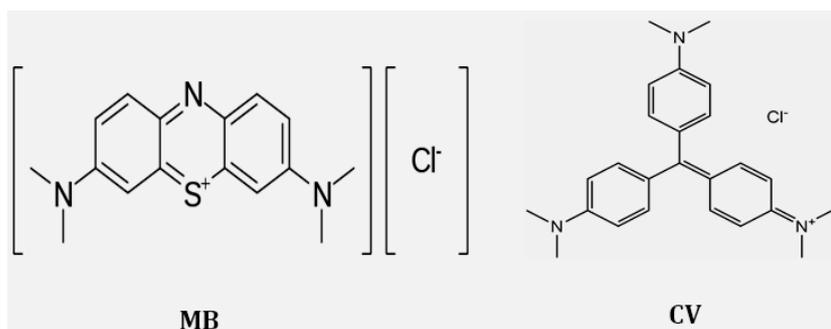

Fig. 1. Chemical structure of methylene blue (MB) and crystal violet (CV).

2. Equilibrium studies
Adsorption experiments were carried out by adding a fixed amount of sorbent (0.05 g) into 250-ml Erlenmeyer flasks containing 50 ml of different initial concentrations (10–50 mg L^{-1}) of dye solution. The temperature was controlled at 25 ℃. Agitation was provided at 200 rpm 90 min. The initial and equilibrium dye concentrations were determined by absorbance measurement using double beam UV–vis spectrophotometer (Jasco V-530, Japan) at 664 nm and 586 nm for MB and CV, respectively. It was then computed to dye concentration using standard calibration curve. All the experiments were carried out in duplicate. The percentage removal of dye at equilibrium, C_e (mg L^1), was calculated by:

$$ \text{—} \qquad\qquad (1) $$

where C_i and C_e are the initial and final (equilibrium) concentrations of dye (mg/L), respectively. The amount of dye adsorbed q_e (mg/g), onto sugar can stalks was calculated from the mass balance equation as follows:

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$$q_e = \frac{(C_i - C_e)V}{W} \qquad (2)$$

where *V* is the volume of dye solution (L), and *W* is the mass of the adsorbent used (g).

RESULTS AND DISCUSSION

1. Effect of solution pH

One of the main variables affecting the adsorption process is pH [12]. The effect of initial solution pH was determined by agitating 0.05 g of sugar can stalks sorbent and 50 mL of dye solution of initial basic dye concentration of 50 mg L^{-1} using water-bath shaker (30 ºC) at different solution pH ranging from 2.0 to 11.8. Agitation was provided for 90 min contact time which is sufficient to reach equilibrium with a constant agitation speed of 200 rpm. The pH was adjusted by adding a few drops of diluted NaOH or HCl. As shown in Fig. 2, the solution pH will have a significant influence on dye adsorption. Adsorption of the two dyes increase with increasing solution pH. At low pH values, a remarkable decrease in the two dyes uptake was observed whereas in the range 6.5–9.0, the uptake efficiency was significantly increased. The decrease in the dye uptake at lower pH values may be due to the protons competition with the dye molecules for the available adsorption sites [13]. As the pH is increased, the surface charge density on the sugar can stalks changes and the adsorbent becomes negatively charged resulting in an enhanced attraction between the positively charged dye molecule and the adsorbent surface. This behavior is expected for basic dye removal [14,15].
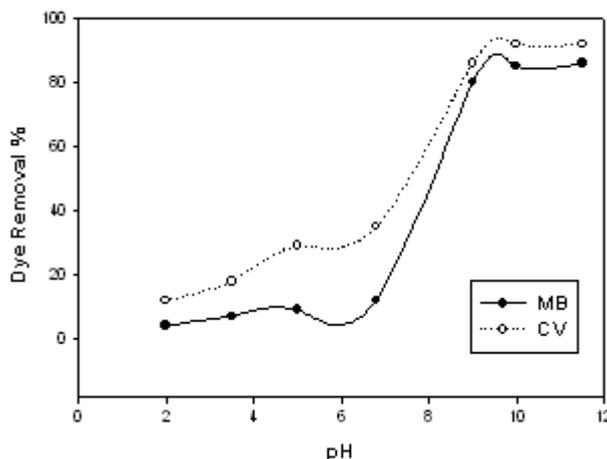

Fig. 2. Effect of pH on percent dye removal by sugar can stalks.

2. Effect of contact time

Preliminary tests were conducted to assess the contact time necessary for each adsorption system to reach equilibrium and, for experimental purposes, each system was given a contact time in excess of this period. To determine the equilibrium, 25 mL of dye solution containing 50 mg L^{-1} of MB or CV was separately mixed with 0.05 g of the adsorbent at room temperature. The resulting supernatants were analyzed at 10-min time intervals until equilibrium was attained. The equilibrium times for the adsorption of MB and CV onto the sugar can stalks were found to be about 90 min (Fig. 3).

Hence, relatively rapid equilibrium time was attained using all four adsorbents. As a consequence, subsequent adsorption experiments were all performed for 90 min, a period which was assumed to be largely ample for performing all the experiments.
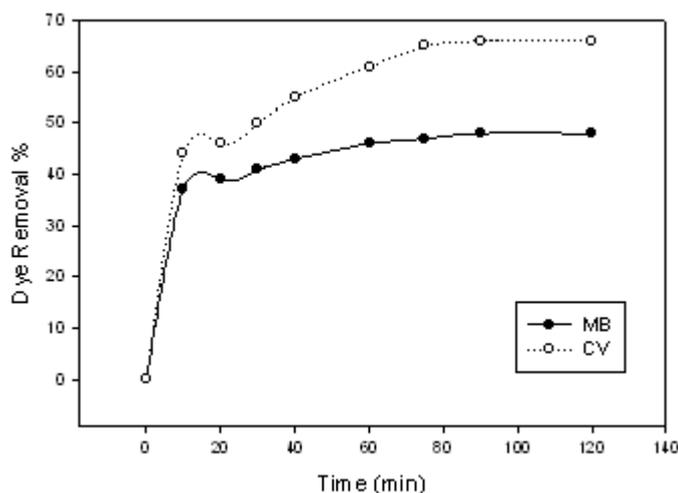
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Fig. 3. Effect of contact time on percent dye removal by sugar can stalks.

4. Effect of adsorbent dose

To study the effects of adsorbent dosage on dye removal, the pH of the dye solutions were left without any change. The initial concentrations of the two dye solutions were 50 mg L^{-1}. Fig. 4 shows the effect of Sugar can stalks dosage on percent dye removal. For MB and CV, the removal efficiency increases rapidly with increasing adsorbent dosage till reach 0.15 g/50 mL. At this dosage, the removal efficiencies were 54.2% and 66.5%, respectively. This increase in adsorption with adsorbent dose can be attributed to increased adsorbent surface area and availability of more adsorption sites. Equilibrium time was lesser at higher adsorbent doses [16].
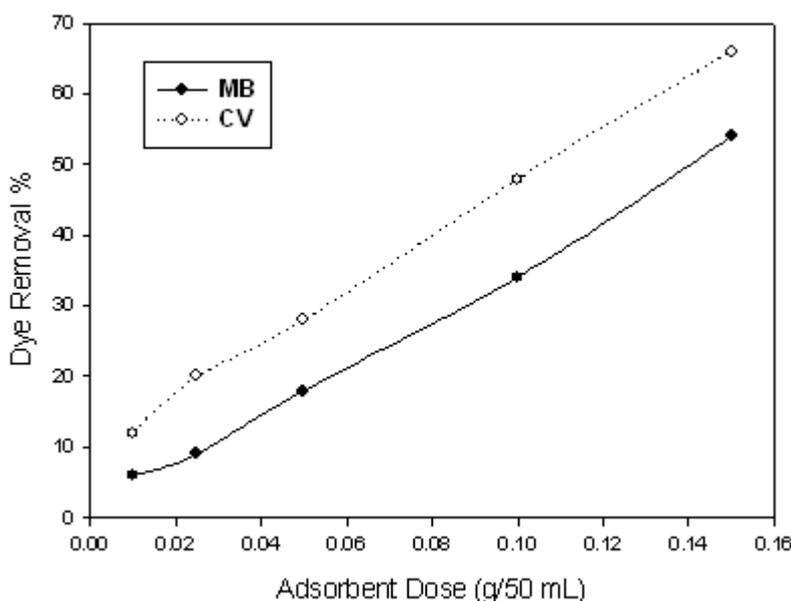

Fig. 4. Effect of adsorbent dose on percent dye removal by sugar can stalks.

5. Effect of dye initial concentration

Kinetic experiments were carried out by agitating 50 ml of dye solution of concentration ranging from 10 to 50 mg L^{-1} with 0.05 g of sugar can stalks in a 250 ml beaker at 25 ºC at an optimum pH and at a constant agitation speed of 200 rpm for 90 min. Samples (3.0 ml) were pipette out at different time intervals, centrifuged and the concentration of dye analyzed by measuring its absorption spectra at λ_{max}. The removal of dye was rapid in the initial stages of contact time and gradually decreased with time until equilibrium. The rapid is probably due to the abundant

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availability of active sites on the sugar can stalks, and with the gradual occupancy of these sites, the sorption becomes less efficient. This is in accordance with the results obtained in dye adsorption experiments onto different types of adsorbents [17-20]. The adsorption data for the uptake of MB and CV versus dye initial concentration are presented in Fig. 5.
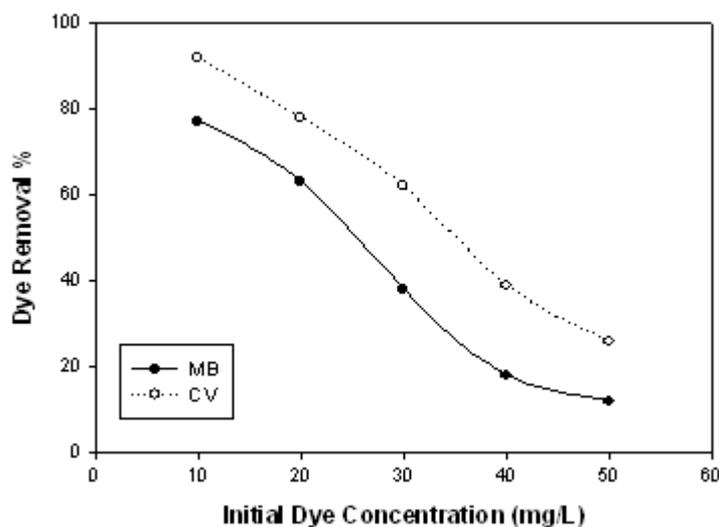
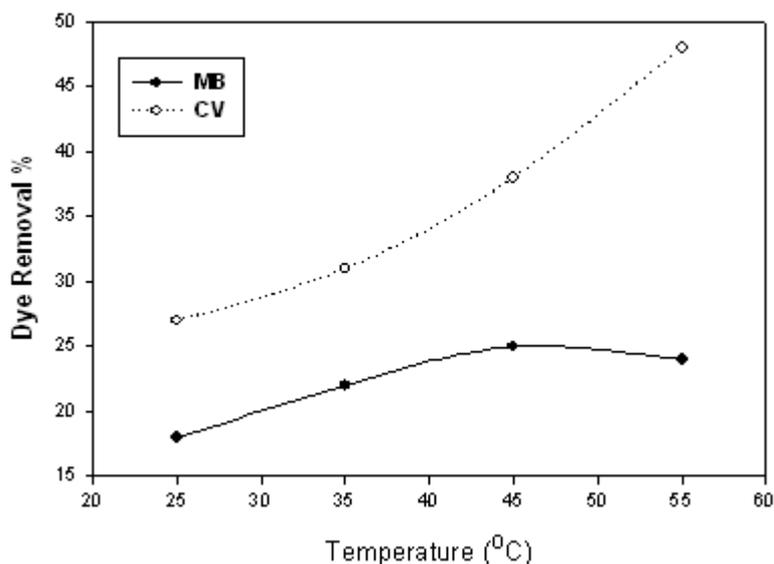**Fig. 5. Effect of initial dye concentration on percent dye removal by sugar can stalks.**

Fig. 6. Effect of temperature on dye removal by sugar can stalks.

6. Effect of temperature

A range of reaction temperatures (25, 35, 45 and 55 ºC) were used and the flasks were agitated for 90 min. A 0.05 g sample of sugar can stalks was added to 50 ml volume of dye solution set at optimum pH and agitated at 200 rpm for all the experiments. The experiments were carried out at initial dye concentration 50 mg L^{-1} for all the studies. It has been believed that the temperature generally has two major effects on the adsorption process. Increasing the temperature will increase the rate of diffusion of the adsorbate molecules across the external boundary layer and in the internal pores of the adsorbent particle, owing to the decrease in the viscosity of the

solution. In addition, changing the temperature will change the equilibrium capacity of the adsorbent for a particular adsorbate [21]. The temperature dependence of MB adsorption kinetics is shown in Fig. 6. The experimental results indicate that the magnitude of adsorption is proportional to the solution temperature. Results show that the amount of MB adsorbed increased from 18% to 24% and that of CV increased from 27% to 48% when the temperature increased from 25 to 55 ℃. These results imply that adsorption process for MB and CV would be endothermic.

7. Adsorption Isotherms

The adsorption isotherm indicates how the adsorption molecules distribute between the liquid phase and the solid phase when the adsorption process reaches an equilibrium state. The analysis of the isotherm data by fitting them to different isotherm models is important to find the suitable model [22]. Several models have been published in the literature to describe the experimental data of adsorption isotherms. The Langmuir and Freundlich are the most frequently employed models. In this work, both models were used to describe the relationship between the amount of dye adsorbed and its equilibrium concentration.

7.1. Langmuir isotherm

Langmuir's isotherm model suggests that uptake occurs on homogeneous surface by monolayer sorption without interaction between sorbed molecules. The model assumes uniform energies of adsorption onto the surface and no transmigration of adsorbate in the plane of the surface. The linear form of Langmuir isotherm equation is represented by the following equation [23]:

$$\frac{C_e}{q_e} = \frac{1}{bQ_o} + \frac{C_e}{Q_o} \qquad (3)$$

where q_e is the amount adsorbed at equilibrium time (mg/g), C_e is the equilibrium concentration of the adsorbate ions (mg/L), Q_o and b are Langmuir constants related to maximum adsorption capacity (monolayer capacity) and energy of adsorption, respectively. When C_e/q_e is plotted against C_e, a straight line with slope $1/Q_o$ and intercept $1/bQ_o$ is obtained (Fig. 7a), which shows that the adsorption of MB and CV follow Langmuir isotherm model. Values of Q_o and *b* were calculated from the intercept and slope of the linear plot and are presented in Table 1. The essential characteristics of the Langmuir equation can be expressed in terms of a dimensionless separation factor, R_L, defined as [24]:

$$R_L = \frac{1}{(1+bC_o)} \qquad (4)$$

where C_o is the highest initial solute concentration, *b* is the Langmuir's adsorption constant (L mg^{-1}). The R_L value implies the adsorption to be unfavorable ($R_L > 1$), linear ($R_L=1$), favorable ($0 < R_L < 1$) or irreversible ($R_L= 0$). Values of R_L were found to be <1 (Table 1) which confirmed that sugar can stalks is favorable for adsorption of MB and CV under experimental conditions used in this study.

7.2. Freundlich isotherm

The Freundlich isotherm [25] is the earliest known relationship describing the sorption equation. This fairly satisfactory empirical isotherm can be used for non-ideal sorption that involves heterogeneous sorption and is expressed by the following equation:

$$q_e = K_F C_e^{1/n} \qquad (5)$$

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The equation may be linearized by taking the logarithm of both sides:

$$\tag{6}$$

where K_F and n are Freundlich constants, n giving an indication of how favorable the adsorption process is and K_F (mg/g)(L/mg)$1/n$ is the adsorption capacity of the adsorbent. K_F can be defined as the adsorption or distribution coefficient and represents the quantity of dye adsorbed onto activated carbon adsorbent for a unit equilibrium concentration. Fig. 7b, shows a straight line with a slope of $1/n$ and an intercept of ln K_F when ln q_e is plotted against ln C_e. The slope $1/n$ ranging between 0 and 1, is a measure of adsorption intensity or surface heterogeneity, becoming more heterogeneous as its value gets closer to zero [26]. Freundlich constants (K_F and n) were calculated and recorded, which are listed in Table 1.

The results suggest that Langmuir model could be applied to the adsorption of MB and CV, while Freundlich model is applied only to CV adsorption on sugar can stalks. The Langmuir isotherm fits quite well with the experimental data (correlation coefficient $R^2 > 0.99$) for the two dyes. A high correlation coefficient ($R^2 > 0.98$) indicated a high applicability of Freundlich model for CV, whereas the low correlation coefficient ($R^2 = 0.22$) shows poor agreement of Freundlich isotherm with the experimental data for MB.

Table 1. Langmuir and Freundlich adsorption isotherms parameters for MB and CV adsorption on sugar can stalks.

Dye	Langmuir Isotherm				Freundlich Isotherm		
	Q_o	b	R_L	R^2	K_F	$1/n$	R^2
MB	9.8	0.897	0.022-0.100	0.9903	8.44	0.067	0.2214
CV	18.7	0.325	0.058-0.235	0.9957	9.63	0.217	0.9867
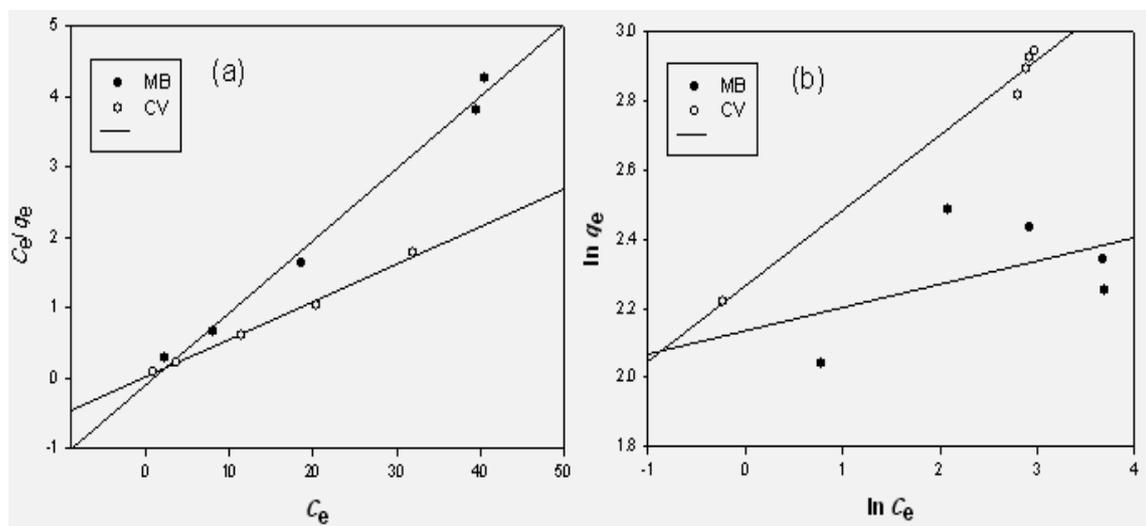
Fig. 7. Langmuir (a) and Freundlich (b) isotherm plots of MB and CV dyes adsorption on sugar can stalks.

CONCLUSION

The adsorption of MB and CV onto sugar can stalks is favored at high pH and higher temperature, specially for CV. The removal of MB and CV by adsorption was found to be rapid at the initial period of contact time and then slows down with increasing reaction time. The adsorption process was endothermic for the two dyes. The sorption capacities were 9.8 and 18.7 mg g^{-1} for MB and CV, respectively. Sugar can stalks which is an agricultural waste material can

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be used for industrial water treatment to eliminate low concentrations of basic dyes as methylene blue and crystal violet.

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