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Adsorption Potential of Saccharum Bengalense Retz to Remove Malachite Green Dye from Aqueous Solution

Abdul Manan Pathan[a], Khan Muhammad Brohi[b], Rasool Bux Mahar[c], Rafi Zaman Brohi[b], Amanullah Mahar[a*]

[a] Centre for Environmental Science, University of Sindh, Jamshoro

[b] Institute of Environmental Engineering and Management, Mehran University of Engineering and Technology, Jamshoro

[c] U.S.-Pakistan Center for Advanced Studies in Water, Mehran University of Engineering and Technology, Jamshoro

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Abstract

The present research study aimed to assess the ability of *Saccharum Bengalense* Retz (SBR) for adsorption of carcinogenic dye malachite green (MG) from aqueous solution. The adsorbent was characterized by the techniques such as (SEM and FTIR). The analysis was conducted by different batch experiments in which effect of pH, dose, concentration of initial dye, and contact time were used as factors. The MG removal for equilibrium of adsorption reached up to 99% at 10ppm with 100mg dose of the adsorbent. The data of experimental work determined in respect of Langmuir adsorption isotherm and Freundlich isotherms was R^2 of 0.9892 and R^2 of 0.8313 respectively. The results suggested that *Saccharum Bengalense* Retz (SBR) could be used as an effective adsorbent in the industrial scale to remove the harmful carcinogenic dye MG.

Keywords: *Saccharum Bengalense* Retz; Malachite Green, Dye; Remove; Aqueous solution

1.INTRODUCTION

Water is referred to as a vital element of life and it's been polluted with multiple pollutants because of the industrialization and it is observed as the maximum trouble for the sustainability of healthful lifestyles on the earth. Disposal of artificial dyes into aquatic ecosystem without right remedy offers upward push to risky complications and disquiets. Further more than 10,000 dyes had been used as a coloring agent within side the formation of product in one-of-a-kind industries. Malachite Green (MG) is an N-methylated diamino triarylmethane artificial cationic dye, incredibly soluble in water and commonly utilized in fabric coloring, food and paper enterprises [1]. It is likewise applied as for a parasiticide, fungicide and antiprotozoal in aquaculture industries, clinical disinfectant and anthelmintic because of its efficacy and low cost, on the other hand, untreated malachite green dye effluent poses high quality hazard to marine ecosystem. Scientific proof shows that malachite green (MG) stays in the surroundings for a long period and may also harm carcinogenesis, mutagenesis, destruction of human respiratory system, nervous system liver, kidney, gut and gonads whilst ingested [2]; [3].

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Corresponding author
aman.mahar@usindh.edu.pk

The industry of aquaculture in Canada, United States, European Union and China forbids the use of MG, and the permissible environmental limit for the concentration of MG in water is set at 0.5–100 µg / L [4]. Therefore, the high concentration of MG must be removed from the water body. Hence, removing the dyes before discharging the wastewater into the environment presents a serious challenge for researchers. Thus, several studies have conducted to sort out an ecological solution to decrease its effect on water resources. Different biological or physico-chemical solutions have been used to eliminate distinct contaminants such as pesticides, dyes, heavy metals and other organic matters from water and wastewater as microbiological decolorization [5] chemical precipitation [6] ion-exchange, adsorption, coagulation-flocculation and photocatalytic degradation [7]. These methods have obvious shortcomings, especially the high cost. In recent years, among various technologies, the method of adsorption is one of the most effective and is generally preferred for wastewater treatment technologies, technically simple, sustainable, insensitive to harmful pollutants, and it is easy to control and cost-effective. Though, choosing the right adsorbent is always a thought-provoking task. [8]; [9]. Organic matter from various mineral products used in water treatment applications, such as walnut shell hybrids and arginine doped polyaniline [10], almond shell polyaniline bio composite [11] , biochar from Manihot esculenta Crantz [12] , activated carbon from Ziziphus lotus plant [13], Coconut pitch [14], walnut wood, rice straw [15], pomelo peel [16], mussel shell [17], sawdust [18], [19], orange peel [20], and cotton waste [21]. By using clay [22], carbonaceous and magnetic absorbents chitin and chitosan and lignocellulosic biomass for adsorption, MG is removed from the water system.

Therefore, in this study, we focus on the adsorption capacity of MG using the biomass of *Saccharum Bengalense* Retz. In the initial stage, the influence of parameters such as stirring time, adsorbent dose, pH and contact time were indomitable. And it is also, to acknowledge the mechanism of adsorption of the malachite green dye, an isothermal study was also carried out (Langmuir and Freundlich).

2. Materials and Methods

2.1 *Collection of adsorbents*

Saccharum Bengalense Retz was collected from agricultural land of District Kamber Shahdadkot, Sindh and Malachite green dye were purchased from Sigma-Aldrich Karachi Pakistan. For the batch experiment, all the glassware were used after washed with DI water and dried before used.

2.2 *Preparation of Saccharum Bengalense Retz powder*

Saccharum Bengalense Retz was initially washed with distilled water to remove the impurities. Secondly, the mass of (SBR) was grind into powder and put at 95^{0}C for overnight in electric oven. Finally, the obtained powder of (SBR) was used for further experimental study.

2.3 *Preparation of stock solution preparation of MG*

The stock solution of MG was prepared every day to obtain the experiment result through the study. Initially 100mg of malachite green dye powder was dissolved in 100ml of DI water (1000ppm). Than the solution was transferred into 200ml of volumetric flask and distilled water was added.

2.4 *Determination of absorbance and calibration curve of malachite green*

In this study, UV-Vis spectrophotometer (PE lambda 365) was used to obtain the absorbance of the dye solution (MG). The maximum absorbance wavelength (λ max) of MG was found at 617nm by prepared solution of a 10mgL^{-1}.
The 1000 ppm stock solution was prepared by dissolving 100 mg of dye (MG) in 100 ml of DI water. For determination the linear range of MG, a series of different concentration of MG was prepared. A graph of absorbance against concentration has been plotted to obtain the linearity range which was 0-15mg L^{-1} for malachite green dye.

2.5 *Batch adsorption experiment*

The batch adsorption experiment was carried out to analysis the efficiency of adsorbent dosage (SBR), pH, dye concentration and contact time throughout the study. Different amount of SBR adsorbent (5 to 50 mg) was carried in a 100 ml conical flask possessing aqueous solution of malachite green dye

(20 ppm) and the pH (2, 4, 6, 8 and 10) solution was regulated with 0.1 M NaOH and HCl. Thermodynamic study was done at two temperatures 280 and 303 K. The UV-vis spectrophotometer was used to measure before and after adsorption of MG concentration (λ max = 617nm). The dye removal efficiency and adsorption equilibrium can be achieved by using following equations:

$$R=\frac{(C_0-Ce)}{C_0}\times 100 \qquad (1)$$

$$qe=\frac{(C_0-Ce)}{m}\times V \quad (2)$$

Wherever C0 and Ce (mg/L) are the first and equilibrium concentration of dye (MG). R means (%) removal of MG. qe means the adsorption capacity (mg/g) of adsorbed amount of MG per unit weight of (SBR) adsorbent at equilibrium stage. V is the volume of solution (L) and m indicates the amount of adsorbent (mg) accordingly.

3. Result and discussion

3.1 *SEM analysis*

SEM technique is used to identify the surface morphology of the material *Saccharum Bengalense* Retz (SBR) before and after adoption of the malachite green (MG) dye as illustrated in (Fig.1. a and b). It is very clear that the surface morphology of the material (Fig.1 a) appears the pore like (60-90 µm) structure. However, number of micro pores have been formed after the adsorption. It is due to adsorption of MG dye.

Developing of micro pores on the large number of the surface of adsorbent and provided huge surface area for dye molecules to trap as shown in Fig.1b.

3.2 *FTIR analysis*

The FTIR spectra of SBR adsorbent and malachite green dye before and after adsorption are shown in Fig.1 (a and b) accordingly. The functional groups for dye removal were recognized by the FTIR technique at 4000 to 400cm-1. The strong bands at 3404-3357 cm-1 were matches to characteristics bands of O-H in Fig.2 (a and b) respectively. This indicates that group O-H has efficiency to remove the dye (MG).The 2882-2899cm-1 starching bands were indicates the (CH2) groups respectively, which show that CH2 groups have no roll in removal of malachite green dye and the similar wave number were reported. The short band at 1734 in Fig.2 (b) as before and after MG removal process were corresponds to C=O of the COOH. Response of malachite green dye with the SBR adsorbent may occur via the π- π interaction of dye (MG) with the aromatic rings of carbon nanotube, furthermore, reaction with OH and COOH functional groups. The dynamic groups at (1162 and 1033) cm-1 at Fig.2 (b) as before and after dye removal by the adsorbent, accordingly, verified the availability of a C-C bond that enhance the reaction of the MG dye with carboxylate groups. With respect to result, it can be significance that (MG) dye removal by SBR adsorbent happened mostly by the aromatic rings as well as OH and COOH groups.

3.3 *Effect of pH on the adsorption capacity*

pH is one of the most important parameters which can affect the process of adsorption and the capacity of adsorbent. In this study, pH effect on adsorption of malachite green dye by *Saccharum Bengalense* Retz was adjusted in the pH range 2.0, 4.0, 5.0 and 6.0. It is very clear that the lower pH 2.0 was not favorable to development of adsorption. The removal adsorption efficiency of MG dye was 88% at the range of 2.0 pH as shown in Fig.3 (a). The pH value of the system increases from 2.0 the removal efficiency and adsorption capacity of the dye increases. Initially, due to high acidic pH, adsorption of MG is lower because the solution possess the excess number of H+ ions whereas the MG is positively charge carrier cationic dye, hence there is a viable adsorption performance among the molecule of dye and (H+). Furthermore, as the pH of the system is lower than 4.0, the –NH2 groups that surrounds at SBR surface are protonated, hence the electrostatic repulsion takes place between -NH3+ groups on the adsorbent (SBR) and the –N+ (CH3)2 groups of dye (MG) molecules.

Thus, decreased in number of negatively charged on the absorbent site is not favor for the adsorption. When the pH of MG dye solution increases from 5.0, the charge functional groups in the dye solution low, and the site of adsorption with an adverse potential on the surface of adsorbent projects which stimulates adsorption with molecules of dye through electrostatic attraction. Finally, when the pH was more than 6.0, the color gradually disappears of solution of the dye, due to modifying the dye molecule structure. Hence, the optimum condition (pH-5.0) was selected for the next adsorption experiments.

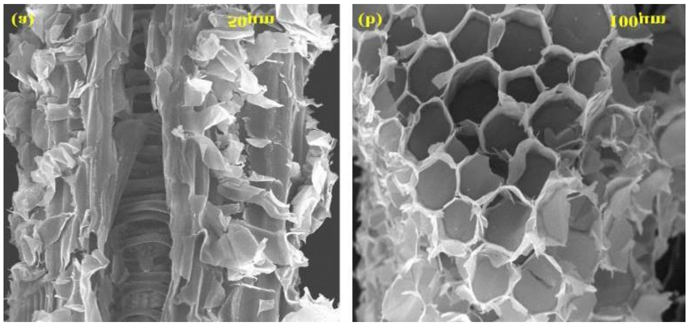


Fig.1 SEM images of *Sacchrum bengalense* retz
(a) Before (b) after adsorption of malachite green dye.

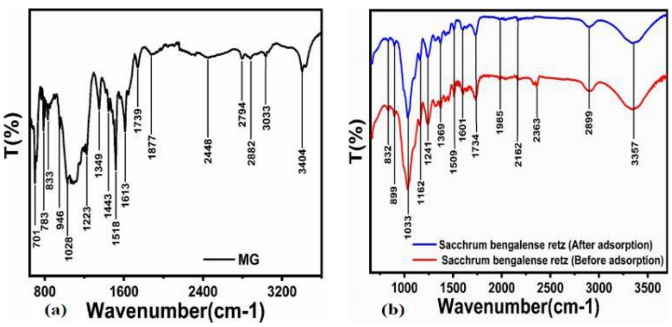


Fig.2 Infrared spectrum of the absorber:
(a) MG dye and (b) *Sacchrum bengalense* Retz
(b) before and after adsorption

3.4 *Effect of dose of SBR on the adsorption capacity*

The adsorbent dose is a key factor as it standardizes the adsorption capability and removal competency of an adsorbent for a specific concentration of initial dye under the given experimental conditions.

The amount of dose effect of SBR on the adsorption capacity was studied and the achieved results shown in Fig.2.

It is obvious from Fig.3 (b) that the adsorbent dose increased from 5mg to 50mg, the percentage removal of malachite green increased from 65% to 99%, it can be credited to further adsorption gaps provided by the dose of adsorbent increased.

3.5 *Effect of initial dye concentration (MG) on the absorption capacity*

The adsorption process is carried out to determine the concentration of initial dye through the adsorption capacity of SBR for malachite dye solution. The initial concentration of malachite dye (10, 20, 30, 40, 50, 60, 80 and 100) ppm, was Fig.3 (c) illustrate that the initial concentration of MG dye increases with respect to increasing the adsorption capacity of dye. This could be attributed due to increasing amount of MG offer an active force for MG, which will overcome whole bulk transfer resistance among liquid and solid phases. In contrary, the removal percentage of MG dye plummeted from 99% - 63%. This marvel can be recognized due to partial adsorption sites of SBR and capacity at a definite concentration.

3.6 *Effect of Contact time on adsorption capacity*

In the adsorption process, one of the important parameters is contact time.Fig.3 (d) shows the effect contact time on adsorption of MG dye. It very clear form the figure that the efficiency of the material increased rapidly in the initial stage of adsorption and indicate that there is no change in the later stage. It takes place as of at the initial stage of the reaction, the SBR absorbent surface has empty space and the concentration of MG dye is vast. After some period of time, the adsorption reduces by the absorbent due to decrease in empty sites. Consequently, 10 min optimum time was selected for the malachite green dye adsorption on the surface of SBR.

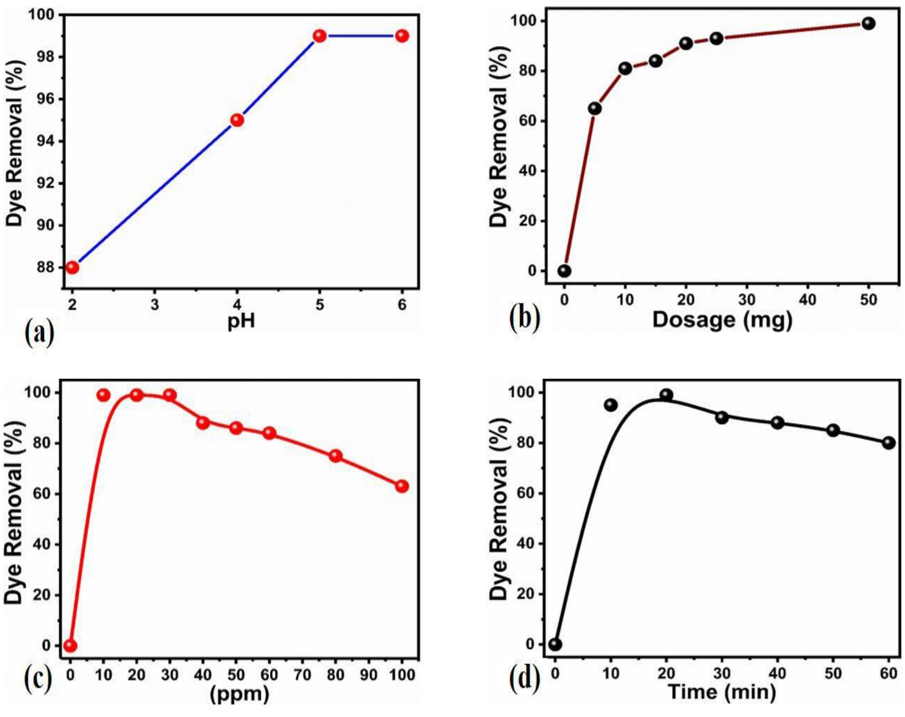
3.7 *Adsorption isotherm*

Data of equilibrium and how malachite green dye is adsorbed onto SBR as well as the adsorbed amounts and remaining dyes in the solution were fitted in both Freundlich isotherms and Langmuir were investigated too. Adsorption of monolayer onto a finite number of homogenous sites are represented by the Langmuir adsorption isotherm as described below, (Langmuir, 1918).

$$q_e = \frac{q_{max} \times K_L \times C_e}{1 + K_L \times C_e} \qquad (3)$$

adjusted respectively.

where qe = adsorbed MG at equilibrium (mg/g), q max = adsorption capacity (mg/g), KL = equilibrium adsorption constant (L/mg), and Ce = equilibrium MG concentration in the solution. Whereas, the adsorption of adsorbates onto a heterogenous surfaces with different functional groups can be described by the Freundlich adsorption isotherm and is expressed below, (Freundlich, 1907).



the color from textile industrial wastewater and malachite green dye was selected to study. The selection of bio-adsorbent was selected on the basis of its local availability and cost effectiveness. The adsorption process was carried out through batch experiments. The aqueous samples were characterized for SEM and FTIR. The analysis was conducted by different batch experiments (effect of pH, dose study, concentration of initial dye, and contact time).

The MG removal for equilibrium of adsorption reached up to 99% at 10ppm with 100mg dose of the adsorbent. The data of experimental work were

Fig.3 (a) The influence of pH on the adsorption capacity of (pH 2, 4, 5 and 6), (b) the influence of the 5-60 mg SBR dose, (c) the influence of the Initial MG dye concentration of 10, 20, 30, 40, 50, 60, 80 and 100 ppm, and (d) the effect of contact time on adsorption capacity at 10, 20, 30, 40, 50 and 60 minutes.

$$q_e = K_F \times C_e^{1/n} \quad (4)$$

Whereas, KF = Freundlich constant ((mg/g) (L/g) n) and n = heterogeneity factor.

The Langmuir plot of Ce/qe vs. Ce presented a linear regression curve with slope of 1/qmax and intercept of 1/(KL*qmax) (Fig. 4a) as well as a high R^2 of 0.98 representing good linear fitting. In distinction, the Freundlich isotherm (Fig. 4b) had a much lesser R2 of 0.8313, showing fit as poorer. Consequently, Langmuir isotherm, well-fit indicates MG adsorbed as a monolayer on SBR surfaces at an adsorption quantity maximum of 212.7 mg g−1.

4. Conclusion and recommendations

This study was aimed to use bio-adsorbent to remove determined for the respect of Langmuir adsorption isotherm and Freundlich isotherms which is R2 of 0.9892 and R2 of 0.8313. The bioadsorption is a cost effective and environment friendly approach to treat industrial wastewater.

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