Elimination of Methylene Blue by low-cost Biomaterial prepared from Local Natural Residue

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ABSTRACT

This study aims to assess the use of natural waste (fruit kernels) for the preparation of a bimaterial in order to use it as a natural support for the elimination of a dye (methylene blue) from aqueous solutions for environmental protection. The biomaterial was characterized physicochemically and the determination of methylene blue concentration was carried out by a UV-Visible spectrophotometer. In order to clarify the adsorption process, experiments in a batch system were carried out to study the effect of operating parameters such as the initial concentration of methylene blue (2-10 $mg \cdot L^{-1}$), biomaterial (0.1-1 g) and the contact time (10-120 min). To describe the adsorption equilibrium, the experimental data were analyzed by the Langmuir isotherm and the Freundlich isotherm. The equilibrium is perfectly described by the Freundlich model (R^2>0.99) and the adsorption process is multilayer. The results of the present study suggest that washingtonia seed (WS) can be advantageously used as a low-cost biosorbent for water discoloration.

I. Introduction

Water pollution from industrial waste is a serious problem in many countries. This pollution may cause adverse effects on the environment and on human health [1]. Textile industries are the responsible for the discharge of large quantities of dyes into natural waterways [2]. Color is a visible pollutant and presence of even very minite amount of coloring substance it undesirable due to its apparence [3]. The presence of synthetic dyesin aquatic environments is the cause of color, whichis the first impact to recognize in an effeluent because very small amounts in water are very vesible. Dyes interfere also with the penetration of sunlights and thus delay photosynthesis, ibhibit the growth of aquatic biotics and interfere with the solubility of gases in water bodies [4]. Several organic dyes are hurmful to humans, methylene blue (MB) is not considered to be extremely toxic, but it can have various hurmful effects. Methylene blue has wider applications, which include coloring paper, dyeing cottons, wools and hair colorant [3]. It can cause short period of fast or rapid breathing, while oral ingestion produces a burning sensation and can cause nausea, vomiting and diarrhea [5]. The most technique used for the removal for dyes are adsorption, precipitation,

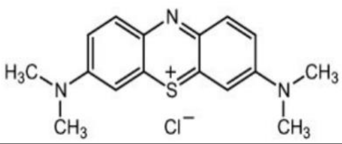
ion-exchange, membrane filtration, photocatalysis, flocculation and electrochemical treatment [4]. Among these methods, adsorption is preferred due to its simplicity, lower cost and high efficiency [6]. During the last years, many researchers have focused on the preparation of some biosorbents from natural wastes from natural waste of Paspalum notatum [3], weeds [4], potato peel [5], chicken eggshells [7], date stones [8], mango seed kernels [9], rices hulls [10], cocoa shells [11], banana peel [12], bagasse fly ash [13] and rice husk [14]. These biosorbents from agricultural waste materials being economic and eco-friendly due to their unique chemical composition, availability in abundance, renewablity, low cost and more efficiency seem to be a viable option for heavy metal remediation [9].
In the present study, methylene blue is selected as a model compound to evaluate the adsorptive capacity of fruit stones for the removal of dyes from aqueous solutions. The effect of some operating parameters such as: initial concentration of methylene blue, biosorbent dose and contact time have been investigated. Then, the equilibrium study was carried out and analyzed to describe the adsorption process.

II. Research Method

II.1. Sorbate

Methylene blue (MB) was used as adsorbate to evaluate the effectiveness of the prepared biosorbent. Some properties of MB are presented in Table 1. Stock solution of MB was prepared by dissolving an appropriate quantity of dehydrated MB (analytical quality, Sigma-Aldrich®). The experimental solutions of the desired initial concentration were obtained by diluting the MB stock solution with distilled water.

Table 1. Some properties of methylene blue.

Common nomenclature	Methylene Blue
Generic nomenclature	Basic Blue 9
Index color	52015
CAS N°	61-73-4
Chemical formula	$C_{16}H_{18}N_3SCl$
Molecular mass	319.85 $g\cdot mol^{-1}$
Wavelenght (λ_{max})	665 nm
Chemical structure	

II.2. Biosorbent

The raw material (WS) for preparation of biosorbent were obtained from the university of Ahmed Draia Adrar, Algerie.WS were collected and washed with tap water and afterwards with distilled water for three times. Then, they were dried in oven at 105 °C for 24 h to achieve constant weight, and then were crushed and milled. Thereafter, they were sieved into a uniform size. Some physico-chemical properties of prepared biosorbent are presented in Table 2.

Table 2. Some physico-chemical properties of prepared biosorbent.

pH (23 °C)	5.25
Conductivity ($mS\cdot cm^{-1}$) (23 °C)	1.331
Dry matter (%)	5.462
Ash rate (%)	4.089
Organic matter (%)	95.98

II.3. Adsorption experiments

The effects of experimental parameters: initial MB concentration (2-10 mg·L^{-1}), bisorbent dose (0.1-1 g) and contact time (10-120 min) on the adsorptive removal of MB were studied in a batch mode using 25 mL of each MB solutions at a shaking speed of 300 rpm. After adsorption process, the biosorbent was separated by centrifugation. The solutions were centrifuged for 5min with 9000 rpm using centrifuge (SIGMA 2-16P, Germany). The supernatant was analyzed using a UV-Visible spectrophotometer (Cary 60, Malaysia) at a wavelength of 665 nm. The removal rate (R %) and equilibrium capacities of MB adsorbed (q_e mg/g) were calculated from the following equations [9] :

$$R = \frac{C_0 - C_e}{C_0} \times 100 \quad (1)$$

$$q_e = \frac{(C_0 - C_e)}{m} V \quad (2)$$

Where C_0 (mg·L^{-1}) is the initial MB concentration; C_e (mg·L^{-1}) is the equilibrium MB concentration; V (L) is the volume of the solution; and m (g) is the mass of the biosorbent.

III. Results and Discussion

III.1. Effect of MB initial concentration

The results of MB initial concentration effect of on the adsorption capacity are show in Figure 1. We note that this latter increases along with increase in initial acetic acid concentration. The equilibrium adsorption capacity from 0.028 to 0.145 mg·g^{-1} could be attributed to the ratio of the available adsorption active sites to the initial number of acetic acid moles [15].

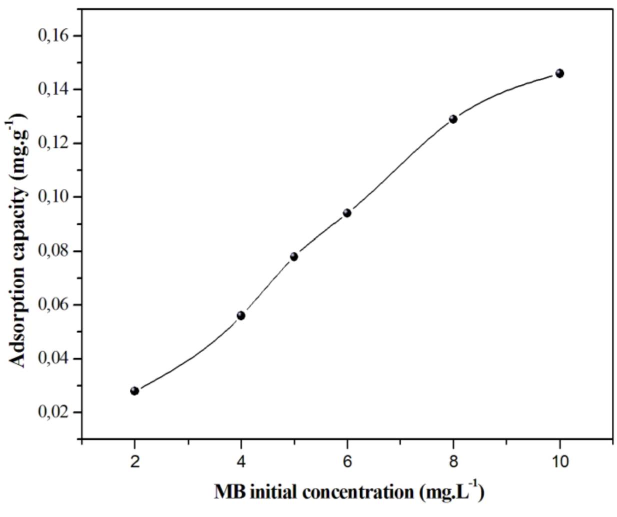


Figure 1. Effect of initial MB concentration on the adsorption capacity of prepared biosorbent.

III.2. Effect of biosorbent dose

The effect of biosorbent dose in the range of 0.1 to 1 g was used to the adsorption experiments and the results are given in Figure 2. The adsorption capacity decreases with increasing of the biosorbent dose. It decreases from 0.816 mg·g^{-1} to 0.041 mg·g^{-1}. This raise of the adsorption capacity due to the concentration gradient between solute concentrations in the solution and on the biosorbent surface [16].

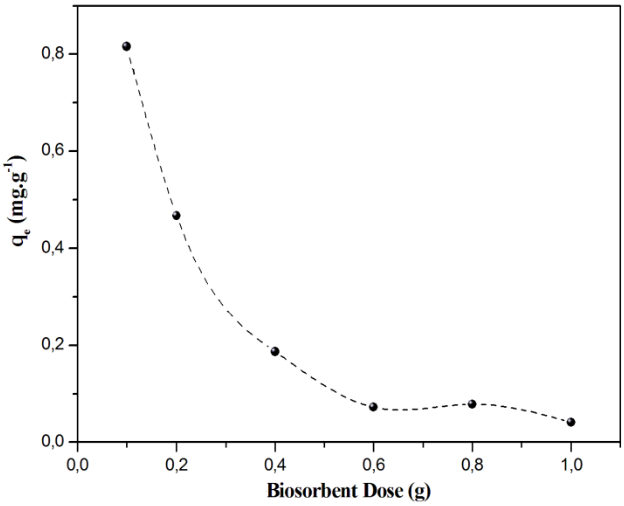


Figure 2. Effect of biosorbent dose on the adsorption capacity of MB.

III.3. Effect of contact time

The effect of contact time on the methylene blue adsorption was determined and the corresponding variation of removal rate is shown in Figure 3. The results indicate that the removal rate increase with increase of contacyt time. The removal rate increases from 22.7 to 72.37 %. This variation could be due to the abundance of active binding sites on the biosorbent, and with gradual occupancy of these sites, the adsorption becomes less efficient. According to results, the contact time of 90 min was selected as the optimum value of contact time.

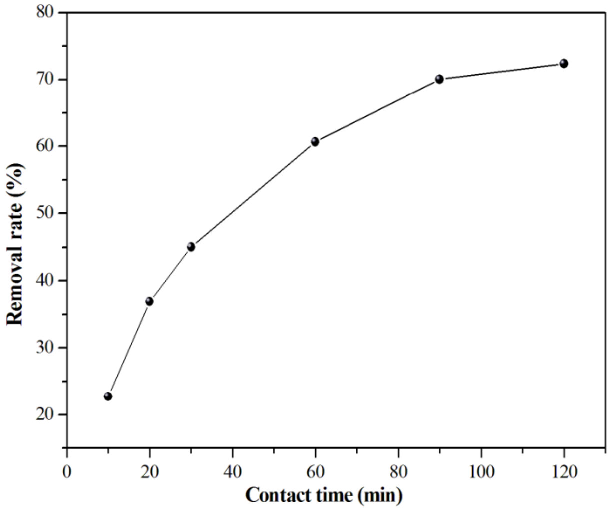


Figure 3. Effect of contact time on the adsorption of MB by prepared biosorbent.

III.4. Adsorption isotherm

For adsorption equilibrium, MB solutions with concentrations varying from 2 to 10 mg·L^{-1} were mixed with 0.6 g biosorbent dose into 25 mL beaker under stirring at 300 rpm for 30 min at room temperature.

The Langmuir and Freundlich adsorption isotherms, often used to describe the adsorption of solutes from a liquid phase, were applied to our experimental results.

The Langmuir isotherm is one of the models that describe monolayer coverage. It assumes a homogenous adsorption surface with binding sites having equal energies. Linear form of the Langmuir isotherm equation can be expressed as follows [17]:

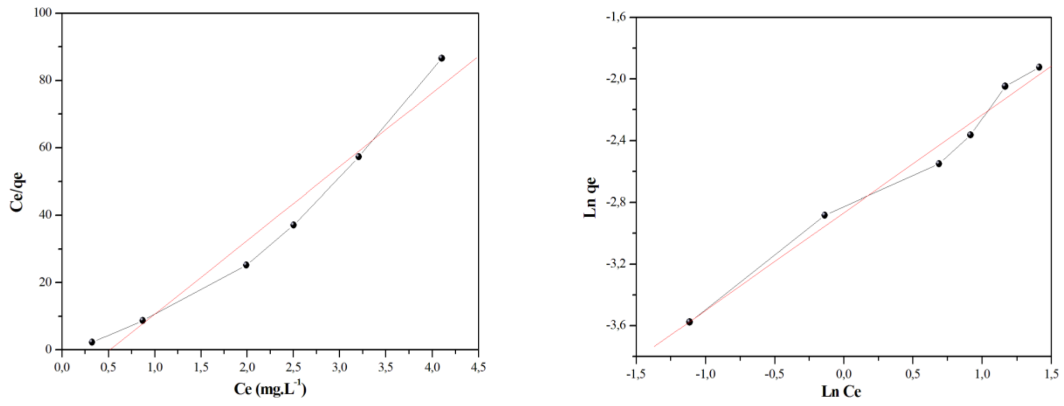
$$\frac{C_e}{q_e} = \frac{C_e}{Q_{\max}} + \frac{1}{K_L Q_{\max}} \tag{3}$$

Where K_L (L·mg^{-1}) is the Langmuir constant, Q_{max} (mg·g^{-1}) represents the maximum adsorption capacity under the experimental conditions. Q_{max} and K_L are determined from the slope and intercept of plotting C_e/q_e versus C_e, respectively (Figure 4 (a)).

Freundlich isotherm is an empirical equation based on an exponential distribution of adsorption sites and energies. The linearized Freundlich isotherm equation is represented by the following equation [18]:

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \tag{4}$$

Where K_F (mg·g^{-1})·(L·g^{-1})$^{1/n}$ is the Freundlich constant related to the bonding energy. n is the heterogeneity factor and n is a measure of the deviation from linearity of adsorption. K_F and n are, respectively, determined from the intercept and slope of plotting ln q_e versus ln C_e (Figure 4 (b)).



(a) (b)

Figure 4. Langmuir isotherm of MB on the prepared biosorbent (a), Freundlich isotherm of MB on the prepared biosorbent (b)

The Langmuir and Freundlich isotherm constants are listed in the table 3. From thr results, we show that the Freundlich model has the highest value of regression coefficient compared to the Langmuir model, which indicates that this model describes very well the experimental data of adsorption process and suggest that the adsorption of methylene blue on the surface of prepared biosorbent is a multilayer adsorption. According to the Langmuir model, the maximum monolayer adsorption capacity of MB on prepared biosorbent was 0.0457 mg·g^{-1} and the value of Freundlich constant (n) indicates the feasibility of adsorption process.

Table 3. Langmuir and Freundlich isotherm parameters for MB adsorption on prepared biosorbent.

Langmuir model		Freundlich model	
Q_{max} (mg·g^{-1})	0.0457	K_F (mg·g^{-1})·(L·g^{-1})$^{1/n}$	0.0568
K_L (L·mg^{-1})	3.8432	n	1.5790
R^2	0.9797	R^2	0.9905

III. Conclusion

Batch adsorption study of methylene blue (MB) from aqueous solutions has been carried out using biomaterial (biosorbent) prepared from washigtonia seed (WS). Equilibrium isotherm data were in good agreement with Freundlich than Langmuir model, which indicates that the adsorption is a multilayer process. The maximum monolayer adsorption capacity of MB was found to be 0.0457 $mg \cdot g^{-1}$ and the value of Freundlich constant (n= 1.58) indicates the feasibility of adsorption process. Based on the obtained results, it can be concluded that the agricultural waste can be used as low-cost biosorbent for basic dyes removal in water treatment.

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