Novel Green Sorbents Derived from *Mesembryanthemum*-Based Biomass for Wastewater Treatment Applications

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ABSTRACT

A great challenge has been done for utilization of natural gas (NG) Biomass-based materials have received much attention recently in both academia and industry. Biomaterials have been widely applied for development of porous solids for wastewater treatment applications due to their low-cost, non-toxic, and containing of various chelating groups such as amino and hydroxyl moieties. This study reports for the first time, development of novel sorbent from *Mesembryanthemum*-based biomass for water purification applications. The obtained sorbent has been characterized using Fourier Transform Infrared spectroscopy (FTIR). The performance for removal of various water pollutants was investigated in batch mode. The effects of adsorption factors including, contact time, sorbent dose, pH and initial concentration. The results revealed that the obtained sorbent exhibited an extreme high potential for adsorbing water pollutants.

Keywords: Biomass; Wastewater treatment; Methylene blue dye; Adsorption; Adsorption isotherm models.

1. Introduction

Wastewater treatment have been received a significant attention due to the increase of pollution of water sources. Water pollutants are different in nature and have diverse sources. Among of them, dyes, organic synthetic materials, are mainly found in effluents of various industrial discharges, including dyeing and textile factories. Dyes are considered to be toxic and hazardous materials to human health and environment even at low concentrations [1]. Therefore, plenty of research work was conducted by many researchers to develop methods for removal of pollutants from the industrial effluents, such as chemical oxidation, incineration, wet oxidation, air stripping, adsorbents, electrolyte decomposition, ion exchange method, biological methods. Adsorption technique has been considered a powerful alternative method for the removal of dyes and other pollutants from industrial wastewaters. Therefore, it becomes the most popular water purification method due to its advantages, including the effectiveness, working at wide range of operating conditions, and the simplicity of removing a broad range of pollutants, even from the gaseous environment [2–4]. Adsorption process is a surface phenomenon in which the pollutants attachment to the adsorbent surface via physical or chemical interactions [5].

The adsorption efficiency is affected by the nature and type of adsorbent surface. Since the dyes have different structures and different functional groups, the researchers tried for long time to develop adsorbents that are both efficient and economical for dye removal. Early, activated carbon has been considered as an effective absorbent due to its high porosity and large surface area. But due to its high production cost, researchers tried to use several inexpensive materials as sorbents for the removal of pollutants from wastewaters [6-13]. Agricultural-based biomasses have been considered as low cost effective absorbents since they contain polysaccharides and proteins that have various functional groups like carboxyl, hydroxyl and phosphates, which are the most attractive sites for many pollutants. Among of these biosorbents, almond shell, maize cob waste, wood sawdust, and sunflower seed hull have been evaluated for wastewater treatment applications [14]. *Mesembryanthemum crystallinum (Cryophytum crystallinum)* is ice plant that belongs to the family Aizoaceae, which is a creeping plant with succulent leaves (see Figure 1). *Mesembryanthemum crystallinum* (MC) is flat succulent plant native to Africa, Sinai and southern Europe, and naturalized in North America, South America and Australia. *.Mesembryanth-emum crystallinum* is a halophyte plant widely used in the traditional medicine [15]. In the present study, the performance of *Mesembryanthemum crystallinum* (MC), collected from Libya biotope, for wastewater treatment applications has been investigated. In order to evaluate their potential of use, adsorption of methylene blue dye at various conditions has been studied.

Figure 1: *Image of Mesembryanthemum crystallinum.*

2. Materials and Methods

2.1 Materials

Methylene blue (MB) dye, H_2SO_4, and NaOH were the chemicals that have been used in this research work. The leaves and branches of the *Mesembryanthemum crystallinum* (MC) plant were collected from their native biotope in Libya during May 2018.

2.2 Biosorbents Preparation and Adsorption Experiments

The Novel Leaves-MC and Branches-MC biosorbents were prepared as follows. After overnight drying at 60 ^{o}C, Leaves and branches of *Mesembryanthemum crystallinum* (MC) plant were ground separately using a manual mortar (size range 1-3 mm). The produced powders were used in adsorption experiments without any further modifications. The adsorption experiments were carried out in a flask and the aqueous solution was agitated with magnetic starrier at 150 rpm. To evaluate the adsorption study, 0.6 g of biosorbent were added into 100 mL of MB dye aqueous solution with a specific initial concentration and pH. Various samples were taken at different contact time for investigation of the removal percentage. After, removal of the sorbent sample, the concentration was obtained using UV-VIS spectrophotometer via measuring absorbency values at 664 nm. The adsorption percentage was calculated according to Eq.1.

$$R\% = \frac{(C_{Ao} - C_A)}{C_{Ao}} \times 100 \qquad (1)$$

where C_{Ao} and C_A are the initial and the concentration of MB dye in the solution at time (t), respectively.

2.3 Characterization

The structure of the *Mesembryanthemum crystallinum* (MC) was confirmed by Fourier a Bruker Vertex infrared spectroscopy (FTIR), resolution 3 cm^{-1}, in the range of 4000-500 cm^{-1} using the KBr pellet technique. Dry leaves of *Mesembryanthemum crystallinum* (MC) were crushed into powder in a mortar and an amount about 6-8 mg of sample was used in each pellet.

3. Results and Discussion

3.1 Analysis of FTIR

The FT-IR spectra of leaves powder of used *Mesembryanthemum crystallinum* (MC) for adsorption of MB dye is shown in Figure 2. The FTIR spectrum of the sample was obtained in the scanning range of 500∼4000 cm−1. The absorption bands for FT-IR show existence the characteristics of cellulosic nature. The absorption band at 3426 cm−1 was due to the banding of hydroxyl groups (−OH). In addition, the FT-IR results also show significant peaks at about 2935 and 2848 cm^{-1}, which can be assigned to the C-H symmetrical and C-H asymmetrical stretching vibration from the organic-moiety. The band at 1634 cm^{-1} is suggested to $-NH_2$ groups stretching vibrations and N−H for primary amine. Furthermore, appearance of bands at 1316 cm^{-1} and 1018 cm^{-1} assigned to the existence of the features of carbohydrate polymers nature. The apparent existence of amine and hydroxyl functional groups together with leaves of *Mesembryanthemum crystallinum* (MC) confirms the sample is in hydrophilic in nature, which helps to substantiate the effective removal of dyes through the photodegradation- adsorption process [20].

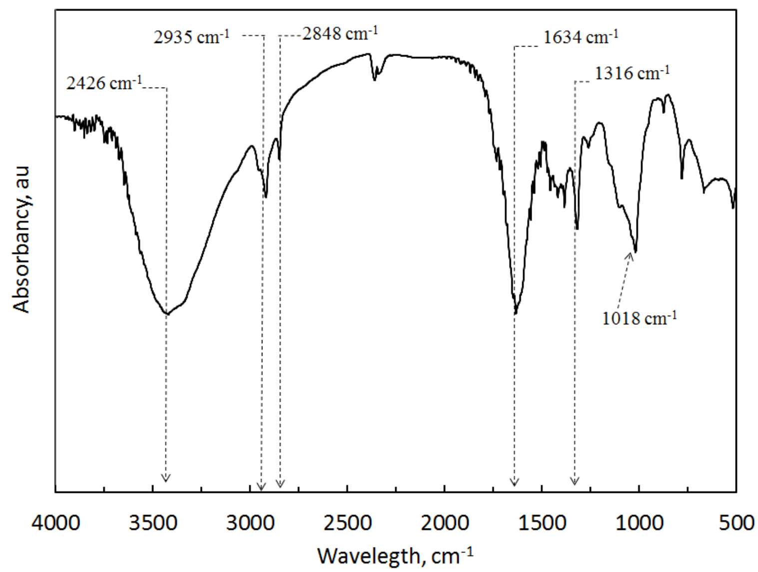

Figure 2: *FT-IR spectra of leaves powder of Mesembryanthemum crystallinum (MC)*.

3.2 Effect of Absorbent Type

Due to their abundance, biomaterials — organic materials derived from living substances — have attracted a lot of research attention as potential non-toxic, low-cost and environmentally friendly adsorbents [5,13,14]. In this study, both leaves and branches of *Mesembryanthemum crystallinum* (MC) in the form of powder were examined to remove methylene blue dye (MB dye) from aqueous solution over a wide range of time (0–100 min). The results showed that the prepared adsorbents exhibited high adsorption capacities for MB dye. For example, the maximum percentage removal (*R%*) of 95.3 % and 80.1% were achieved for Leaves-MC and Branches-MC, respectively (see Figure 3). This suggested that presence of active groups in both biomass particles has significant contribution for MB dye adsorption via ionic exchange mechanism interaction. In addition, higher adsorption efficiency of (Leaves-MC can be justified on the basis of availability of more adsorption sites and higher surface area for leaves than branches.

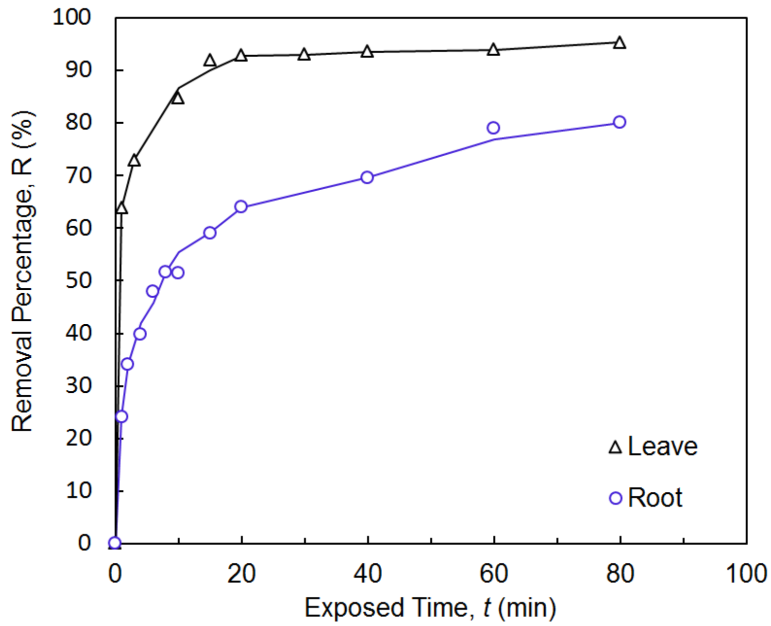

Figure 3: *Effect of sorbent type on the adsorption efficiency of MB dye*.

3.3 Effect of Contact Time

Figure 2 represents the effect of contact time on MB dye adsorption using Leaves *Mesembryanthemum crystallinum* (MC) Biomass (Leaves-MC) and Branche *Mesembryanthemum crystallinum* Biomass (Branches-MC). The adsorption experiments were evaluated for initial concentration of 25 mg MB dye/L using 0.6 g sample dosage at ambient conditions for 80 min. As seen in Figure 2, the adsorption efficiency was increased with contact time. For example, the removal percentage was increased from 63.8 % to 92.8 % with an increase in time from 1 min to 20 min, respectively. This increase is attributed to the mass transfer limitations of MB dye from the bulk concentration to the sorbent surface. These observations are in good agreement with the previously reported studies [13.].

In addition, it was observed that the MB dye adsorption was fast during the first 2 min, after which it became slower and finally reached equilibrium. The removal percentage of MB dye using Leaves-MC reached a constant rate after 20 min; however, Braches-MC showed an equilibrium adsorption after 1 h. The rapid MB dye adsorption was due to the large number of active sites available at sample surface for adsorption at the beginning of the contact time. However, the availability of these active sites decreased with contact time due to saturation with adsorbates. The remaining available active sites on sorbent surface become difficult to occupy by pollutants due to the repulsion between the solute molecules of the solid and bulk phases. Also, the surface energy of sorbents has a significant contribution for the interactions of pollutants with sorbents [14].

3.4 Effect of Sorbent Dosage

The amount of sorbent is an important parameter, which is proportionally affects the adsorption efficiency of the pollutants. Figure 4 shows the results of MB dye removal using Leaves-MC sample at initial pH value of 8 and initial MB dye concentration of 25 mg/L for a contact time of 80 min. The dosage of the Leaves-MC adsorbent varied from 0.3 to 1.2 g. The results showed that the removal percentage of MB dye increases with increasing the amount of sorbents, which ascribed to the increase in the number of active sites. For instance, the adsorption efficiency was increased from 63.95% to 92.83% with increasing the adsorbent dosage from 0.3 g to 0.6 g, respectively. Even though a sorbent dosage greater than 0.6 g led to a nonsignificant increase in MB dye removal (see figure 3), a dosage of 0.6 g of Leaves-MC was selected for all further experiments.

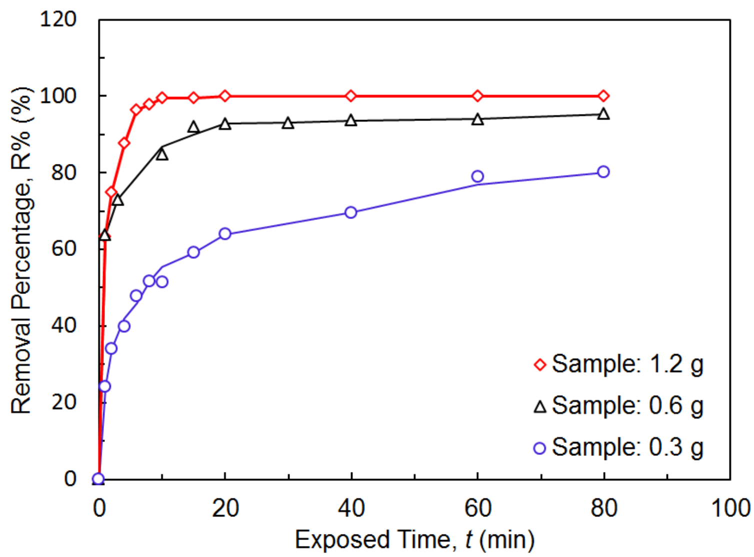

Figure 4: *Effect of sorbent dosage on the adsorption efficiency of MB dye*.

3.5 Effect of Initial MB Dye Concentration

The effects of the initial concentration of MB dye on the removal efficiency were also investigated using 0.6 g of Leaves-MC with a contact time of 1 h. The initial concentration of MB dye in the solution was varied between 12.5 to 50 ppm, while all the other parameters were kept constant during the experiments. Figure 5 demonstrated the removal percentage as a function in contact time for different initial MB dye concentration. For example, the percentage removal of MB dye decreased from 92.8 % to 69.1 % when increasing the initial concentration from 25 to 50 ppm, respectively. This decrease in adsorption of MB dye is due to the fact that the time required to attain equilibrium was expected to be longer at higher concentrations than at lower concentration. As seen in Figure 5, adsorption with initial concentration of 12.5 ppm showed approximately constant adsorption efficiency after only 6 min. Although 97.7% MB dye removal was obtained using an initial concentration of 12.5 ppm, increasing the initial concentration of MB dye in the solution leads to a decrease in the adsorption efficiency.

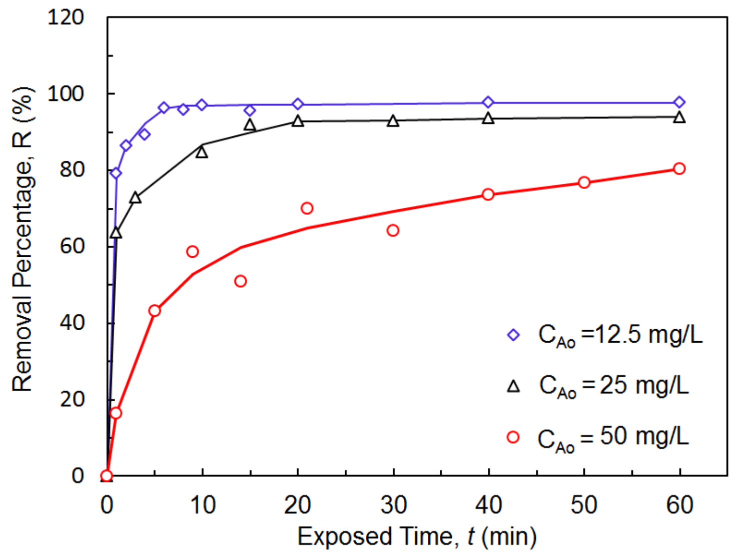

Figure 5: *Effect of initial concentration on the adsorption efficiency of MB dye.*

3.6 Effect of Initial pH

The initial pH of aqueous solution is an important parameter affecting the adsorption efficiency [13]. Therefore, the effects of initial solution pH were studied in the pH range of 2.0 -12.0 using Leaves-MC sorbent at MB initial concentration of 25 mg/L, adsorbent dose of 0.6 g and room temperature, and the results were represented in Figure 6. As shown in the insert Figure, a maximum removal percentage of 94.9 % of MB dye was observed at initial pH of 12.0 after 1 h. In addition, the removal efficiencies of MB dye were slightly decreased to 93.6 85.2 % and 85.2 % with the decrease in initial pH to 8.0 and 2.0, respectively. The reduction in the MB dye removal percentage is attributed to the fact that the unfavorable adsorption of dye cations on the positively charged sorbent surface caused by the electrostatic repulsion. However, at higher initial pH value (pH = 12.0) the surface of Leaves-MC may gain a negative charges, which contribute to an increase in MB dye adsorption due to the electrostatic force of attraction with sorbent surface. It is well-known that for basic dye adsorption, negatively charged groups on the adsorbent are necessary. At lower pH values charge of the surface of Leaves-MB may get positively charged ions and thus the competitive effects of ions as well as the electrostatic repulsion between the dye molecules and the positively charged active adsorption sites on the surface of the Leaves-MC lead to a decrease in the uptake of dye molecules. Similar adsorption tendency of MB dye were reported by several studies [6,13].

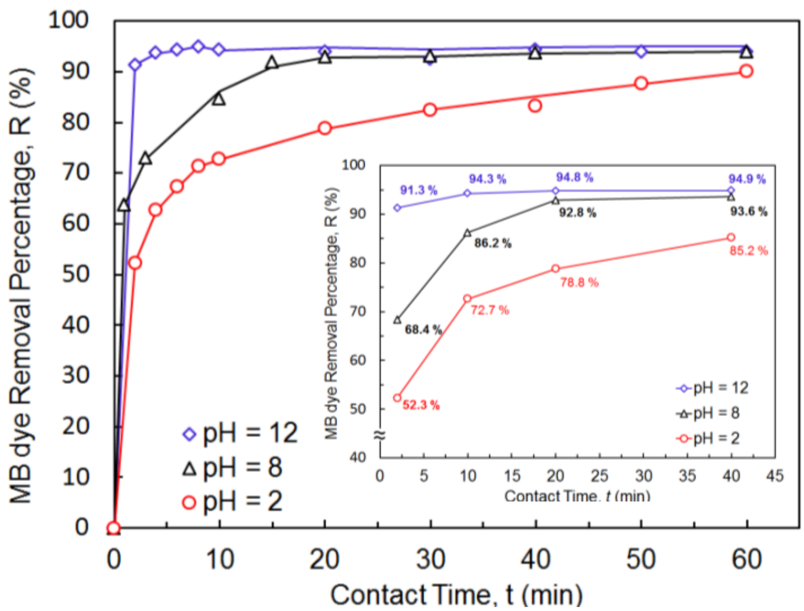

Figure 6: *Effect of initial pH of MB dye aqueous solution on the adsorption efficiency of MB dye*.

Early studies indicated that the adsorption of cationic dye molecules onto the sorbent surface is significantly dependent on initial pH since the functional groups, which are the key point for interaction between dye molecules and adsorbent, can be protonated or deprotonated to produce different surface charges in solution at different pH values [1,6,13,16]. Furthermore, after 4 minutes, the removal percentage was approximately constant in the pH of 12.0 for MB, whereas it increased gradually for pH 2.0 and 8.0.

4. Conclusions

In this paper, *Mesembryanthemum crystallinum* (MC)-based biosorbents for the removal of toxic MB dye from aqueous solution have been studied. The use of (MC)-based biosorbents offers many attractive features such as the outstanding adsorption efficiency for MB dye and the fact that these materials are low-cost, non-toxic and biocompatible. Several parameters such as adsorbent dosage, contact time, pH and initial concentration were found to significantly affect the MB dye removal efficiency. The optimum removal from the aqueous solution was achieved at pH 12.0, 0.6 g sample dosage, 4 min contact time, and 25 ppm initial MB dye concentration. In addition, these sorbents showed a fast kinetics for first 4 min, and then a gradual increase in adsorption efficiency was observed until reach equilibrium in a short time (10 – 20 min). A maximum 94.9 % removal percentage of MB dye from aqueous solution was achieved. This high adsorption capacity by Leaves-MC is mainly attributed to additional adsorption sites.

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