

The removal mechanism for methylene blue dye onto mango biosorbents

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Abstract: In this paper, the new sorbents for wastewater treatment were examined. The mango biosorbents were prepared from three types of mango trees and then were tested for the removal of methylene blue dye from wastewater through an adsorption process. The effects of various parameters e.g. methylene blue dye concentration, solution temperature, and contact time were studied. The kinetics, isotherms, and thermodynamics models were tested for methylene blue adsorption data. The mango biosorbents were found highly efficient for the removal of methylene blue dye (100%) at pH 7 within a period of 3–5 min.

Index Terms: Methylene blue; Mango biosorbents; Wastewater, Removal mechanism.

Introduction

Methylene blue (MB) is widely used in textile, paper, rubber, plastics, leather, cosmetics, and pharmaceutical industries. The effluents of these industries were discharged into natural water. The presence of low concentrations of this dye in the effluent was highly visible [1, 2]. The discharge of MB wastewater without treatment causes numerous problems e.g. chemical oxygen demand by the water body, and an increase in toxicity. Major problems associated with colored effluent are lowering light penetration, photosynthesis, and damages the aesthetic nature of the water surface [3-6]. Moreover, their degradation products may be mutagenic and carcinogenic [7-9]. Methylene blue dye may cause allergic dermatitis, skin irritation, dysfunction of the kidney, liver, brain, reproductive, and central nervous system [10]. Methylene blue dye is harmful to human beings, the need to remove the color from wastewater Effluents become environmentally important. It is rather difficult to treat dye effluents because of their synthetic origins and mainly aromatic structures, which are biologically non-degradable. There are currently numerous treatment processes for effluent discharged from industrial processes containing [11-17]. Among several chemical and physical methods, the adsorption process is one of the effective techniques that have been successfully employed for color removal from wastewater [11].

Mango trees grow to 30–40 m tall, with a crown radius of 10–15 m. The trees are long-lived, as some specimens still fruit after 300 years. Over 500 varieties of mangoes are known, many of which ripen in summer, while some give a double-crop The fruit takes four to five months from flowering to ripen. Mangoes grow in areas with high humidity, like coastal areas, such as the Nile

Delta. They grow best in tropical regions. In Egypt, the governorate of Ismailia is the main mango-growing area, known for producing the finest mangoes.

The aim of the study was to evaluate the adsorption activity of mango biosorbents for the removal of methylene blue from wastewater. The removal behavior of methylene blue onto mango biosorbents was studied to optimize the conditions for the removal of methylene blue. Also, the kinetic, thermodynamic, and isotherm models were examined.

2. Experimental

2.1. Preparation of Mango biosorbent

Mango biosorbents were prepared from three types of mango e.g. Golo, Zebd, and Awas. There are cleaned then dried at the oven temperature at 250 °C.

2.2. Recommended procedures

The removal of MB onto mango biosorbents was tested using batch experiments. A 0.1 g of mango biosorbents was shaken with 25 mL of the MB solution then the remaining MB concentration in the solution was analyzed at $\lambda_{max} = 460$ nm. The percentages of MB removal (%E) and the mango biosorbents capacity (qe) were calculated from the following equations:

$$\%E = ((C_0 - C_e)/C_0) \times 100 \quad (1)$$

$$q_e = (C_0 - C_e) V/m \quad (2)$$

Where C_0 is the initial MB concentration, C_e is the concentration of MB in solution at equilibrium, V is the volume of MB solutions and m is the mass of mango biosorbents.

3. RESULTS AND DISCUSSION

3.1 Optimum conditions for removing of Methylene blue using mango biosorbents

3.1.1 Contact time

The effect of contact time on MB (100 mg/L) removal using mango biosorbent was tested at pH=7 (Fig. 1). The removal rates of MB were initially rapid, where 85% of the total amount

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of MB was removed within the first 30 sec. Then the rates become slower with the increase in time until reaching 100% at 3-5 minutes.

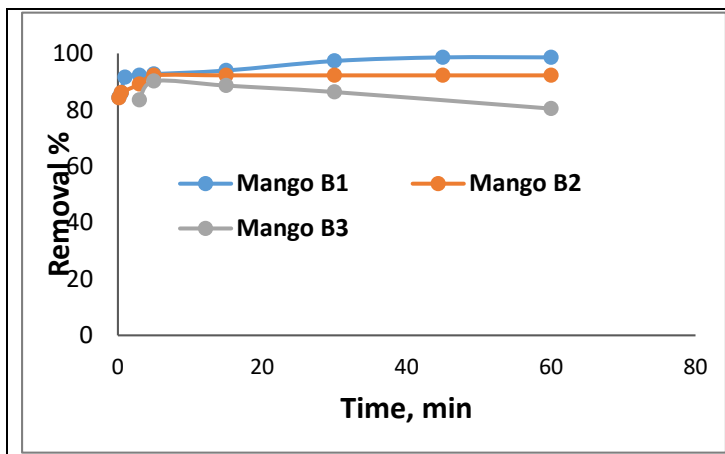


Fig. 1. Effect of contact time on the removal of MB using Mango biosorbents.

3.1.2 Initial MB concentration

The effect of initial MB concentration was studied for different MB concentrations at pH= 7 (Fig. 2). The removal rates of MB using mango biosorbent were increased with increasing MB concentrations. The maximum sorption capacity of the mango biosorbent was found to be 30 mg/g.

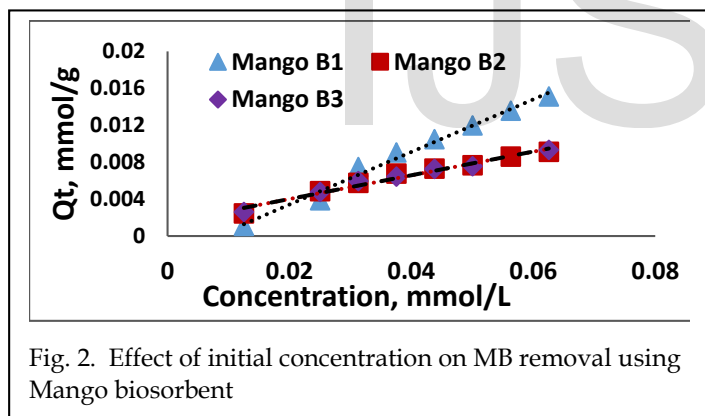


Fig. 2. Effect of initial concentration on MB removal using Mango biosorbent

3.1.3 Temperature

The effects of temperature (40-65 °C) on the sorption of MB using a Mango biosorbent were studied. The sorption percentages of MB were plotted against temperature. The obtained results revealed that the sorption of MB ions was slightly increased with increasing temperature.

3.2 Kinetic studies

The pseudo first-order (3) and pseudo second-order (4) were used to investigate the mechanism of adsorption and the rate controlling steps involved in the sorption.

$$\log(q_e - q_t) = \log q_e - (K_1 t / 2.303) \quad (3)$$

$$t/q_t = (1/K_2 q_e^2) + t/q_e \quad (4)$$

Where q_e and q_t is the sorption capacity at equilibrium and at time t . K_1 and K_2 is the pseudo first rate constant and the pseudo

second order rate constant. The half-life times ($t^{1/2}$) of Pseudo first order are calculated by $t_{1/2} = 0.693/K_1$, while that of second order are calculated by $t^{1/2} = 1/q_e K_2$.

The data showed that the average values of R^2 obtained for the pseudo-second-order sorption model (0.999) are higher than that obtained for the pseudo-first-order kinetic first-order kinetic (0.88), which indicates that the pseudo-second-order sorption is predominant (Fig. 3).

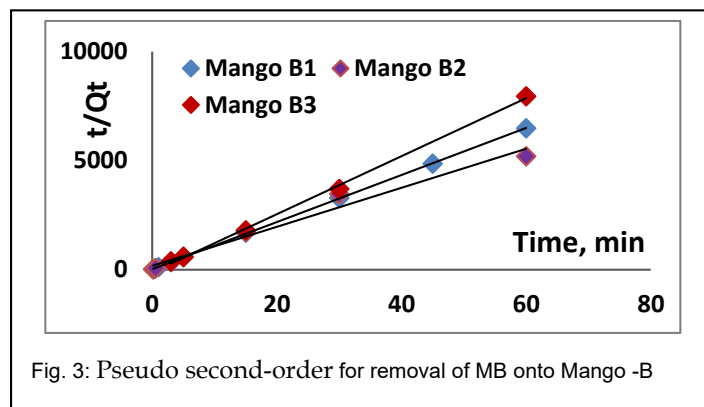


Fig. 3: Pseudo second-order for removal of MB onto Mango -B

The diffusion mechanism was investigated using the Morris-Weber (1), Reichenberg (2) and Bangham (3) equations.

$$Q_t = K_M \sqrt{t} \quad (1)$$

$$B_t = -0.4977 - \ln(1 - F) \quad (2)$$

$$\log \log(C_o / C_o - Q_m) = \log(K_o m / 2.33V) + \alpha \log(t) \quad (3)$$

Where Q_t is the amount of MB sorbed at time t . K_M is the intraparticle diffusion rate constant ($\text{mmol/g min}^{1/2}$). The B_t value is a mathematical function of [$F = Q_t / Q_e$]. D_i is the effective diffusion coefficient, and α , K_o is constant.

Plots of Q_t versus $t^{1/2}$ for the diffusion of MB onto Mango biosorbent according to Morris-Weber Model give straight lines, where R^2 value is 0.81 which does not pass through the origin. The value of the diffusion rate constant is $0.0002 \text{ mmol/g min}^{1/2}$.

The double logarithmic plots of the Bangham equation with the time yield linear curve. The correlation coefficient R^2 for the sorption of MB onto the mango biosorbent is 0.66, this result shows that the diffusion of MB into pores of each sorbent is involved in the rate-controlling step. The values of α are 0.0009.

For Reichenberg diffusion model, relation between B_t and give correlation coefficient is 0.88 for removing of methylene blue using Lignin-biosorbent (Fig. 4).

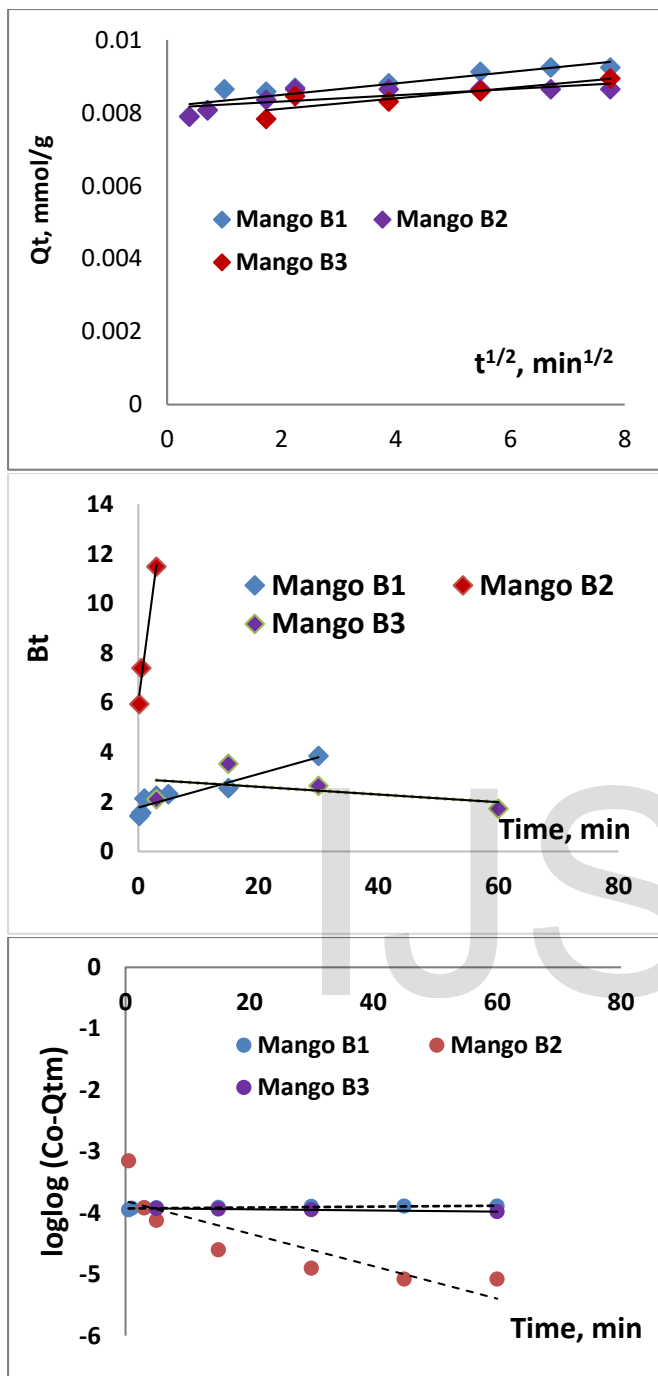


Fig. 4: Diffusion models for sorption of MB using Mango biosorbent

3.3 Equilibrium studies

Langmuir [$C_e/Q_c = (1/K_L b) + (C_e/K_L)$] and Freundlich [$\text{Log } Q_c = \text{Log } K_F + 1/n \text{ Log } C_e$] models are mainly used to describe sorption equilibrium of MB using mango biosorbents. Langmuir isotherm is based on an assumption of monolayer sorption, independent energy of sorption and initially free sites. The Freundlich equation assuming heterogeneous surface energy. The average values of R^2 obtained from Langmuir model (0.98) is higher

than that obtained from Freundlich model (0.71), indicated that the Langmuir model is a good fit to the adsorption experimental data and suggests monomolecular layer as well as a homogeneous distribution of active sites on Mango biosorbent surface (Fig. 5).

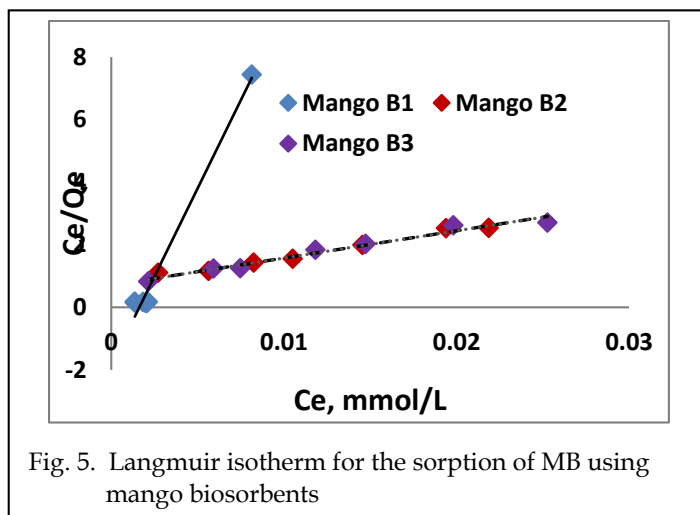


Fig. 5. Langmuir isotherm for the sorption of MB using mango biosorbents

3.4. Thermodynamic studies

Gibbs free energy (ΔG), enthalpy (ΔH), and entropy (ΔS) for the sorption of MB onto Mango biosorbent was evaluated. The enthalpy (ΔH) was -36.09 kJ/mol , the negative value of ΔH reveal to the sorption process of MB using Mango biosorbent is exothermic. The Gibbs free energy (ΔG) was -25.3 kJ/mol ; these values attributed to the sorption process are spontaneous. Finally, the entropy (ΔS) of sorption MB onto Mango biosorbent was -36 J/K mol (Fig. 6).

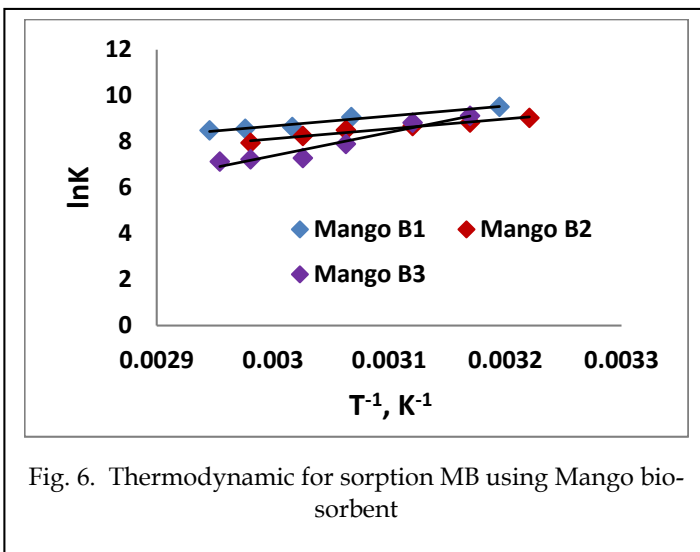


Fig. 6. Thermodynamic for sorption MB using Mango biosorbent

4. CONCLUSION

Mango biosorbents were tested for the sorption of MB. The maximum sorption capacity of the mango biosorbents was found 0.32 mmol/g within 60 sec. The kinetic studies were followed by a pseudo-second-order model. The equilibrium isotherms showed that the Langmuir model had a good fit for the experimental data. The negative value of ΔG indicated that the spontaneous nature of the sorption process. Mango biosorbents proved their efficiency in the removal of MB from water samples under optimum conditions.

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