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Eco-Friendly Adsorption of Cationic (Methylene Blue) and Anionic (Congo Red) Dyes from Aqueous Solutions Using Sawdust †

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Abstract: In this study, sawdust (SWS) was employed as an eco-friendly and low-cost adsorbent for the removal of anionic (Congo red, CR) and cationic (methylene blue, MB) dyes from aqueous solutions at 25 °C. The investigation encompasses various parameters affecting the adsorption process, including weight of sawdust adsorbent, pH, initial dye concentration, and equilibrium time. Characterization techniques such as Transmission Electron Microscopy (TEM) and Scanning Electron Microscopy (SEM) were conducted for an in-depth understanding of the adsorption mechanism. Optimal conditions were found to be SWS weight of 0.1 g/L, dye concentration of 15 mg/L, and equilibrium time of 1 h. Under these conditions, removal percentages of 95.88% for MB and 67.78% for CR were achieved, with adsorption capacities of 14.35 mg/g and 10.22 mg/g, respectively. The results demonstrate that SWS, though considered waste, has significant potential as a low-cost adsorbent for dye removal from aqueous solutions. Removal efficiency increased with SWS weight, ranging from 75.54% to 98.50% for MB, and 50.86% to 80.012% for CR, while adsorption capacity (Qe) inversely correlated with surface weight, ranging from 45.55 to 9.12 mg/g for MB, and 15.23 to 8.076 mg/g for CR.

Keywords: sawdust; adsorption; aqueous solutions; cationic dye; anionic dye

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1. Introduction

Adsorption is one of the pivotal techniques created by researchers for the removal of harmful chemicals from the environment. This method is widely used due to its effectiveness in selectively eliminating pollutants such as industrial dyes, medications, and heavy metals. Among these, dyes are particularly concerning as they are detrimental to both animal and human health, and their release into aquatic solutions can have severe environmental effects [1–6]. A common substance used in adsorption technology is activated carbon, prepared from readily available and inexpensive agricultural waste. This includes the peels of coconuts, pomegranates, watermelons, oranges, and palm fronds. Sawdust, a byproduct of various wood processing industries, constitutes over 40% of the lignocellulosic residues produced globally, totaling more than 180 million m^3. However, sawdust is often undervalued and underutilized, leading to the need to transform this low-value waste into valuable products through sustainable industrial processing [6–10].

Congo red (CR) is a non-biodegradable dye that is harmful to both human health and aquatic life. Its persistent aromatic structure necessitates extensive treatment before release into the environment. Several physical, chemical, and biological treatments for CR have been studied, each with its unique challenges, advantages, disadvantages, applications, and costs [11–13].

Methylene blue (MB), widely used in various industries, also poses serious environmental and health threats when released into water bodies. Despite its therapeutic benefits in controlled doses, wastewater containing MB dye can lead to diseases in humans such as cyanosis, tissue necrosis, and an increased heart rate. Moreover, MB affects plant life, inhibiting growth and reducing pigment and protein content in certain microalgae species. Therefore, the thorough treatment of wastewater containing MB dye is essential before industrial discharge [14–16].

2. Materials and Methods

2.1. Chemicals

Methylene blue or Methylthioninium chloride (molecular mass: 319.85 g/mol, chemical formula: $C_{16}H_{18}ClN_3S$) and Congo red (molecular mass: 696.665 g/mol, chemical formula: $C_{32}H_{22}N_6Na_2O_6S_2$) were purchased from Sigma-Aldrich (St. Louis, MO, USA). Standard solutions of the dyes (500 mg/L) were prepared by dissolving 0.5 g in 500 mL of distilled water (DW).

2.2. Preparation of Adsorbent

Sawdust (SWS) was collected from a sawdust factory in Hill-Iraq. The untreated SWS was washed several times in distilled water and filtered to obtain clean untreated sawdust. The cleaned material was oven-dried for 24 h at 60 °C, ground, and sieved to a particle size range of 0.5 to 1.0 mm. The prepared SWS was stored in a glass bottle for further use, with no additional physical or chemical treatments applied prior to experiments.

2.3. Equilibrium Studies

Adsorption experiments were performed by adding varying weights of SWS (0.01 to 0.1 g) into 100 mL conical flasks containing different initial dye concentrations (5 to 25 mg/L) and pH solutions (3 to 10) at 25 °C. The flasks were placed in a water-bath shaker at 130 rpm for 60 min until equilibrium was reached. The concentrations of MB and CR dyes were measured using a double beam UV–vis spectrophotometer at 630 nm and 590 nm wavelengths, respectively. The adsorption capacity, q_e (mg/g) and removal percentage % were calculated using Equations (1) and (2)

$$q_e = \frac{(A_0 - A_e) \cdot V}{W} \quad (1)$$

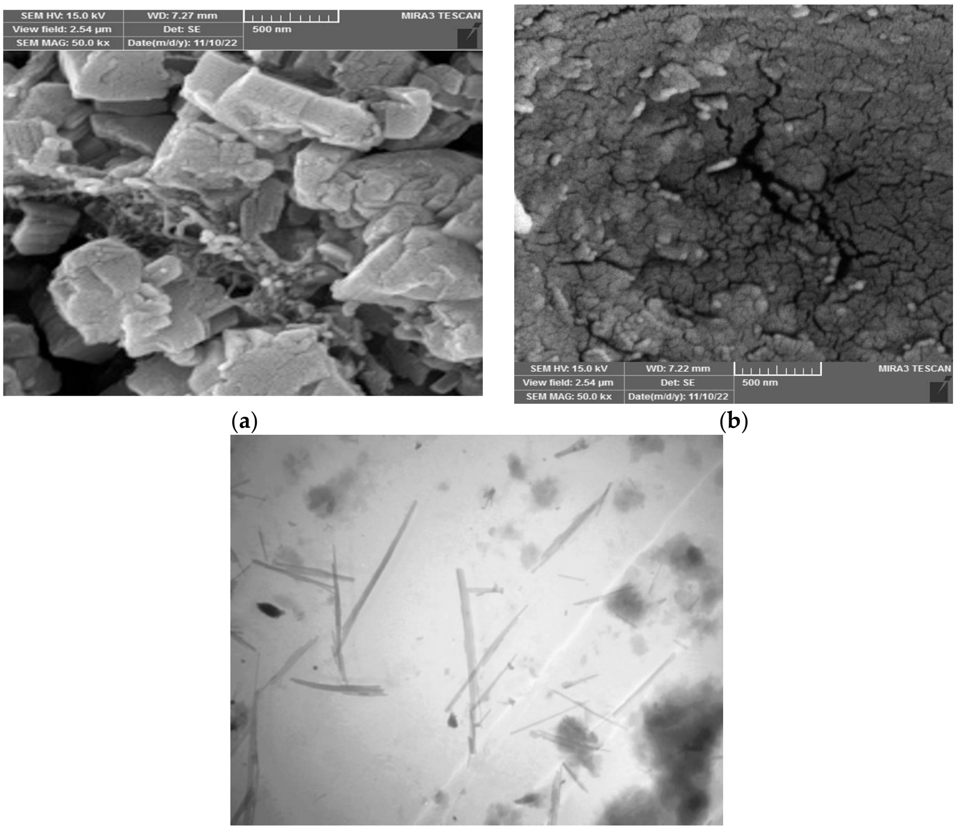
$$E\% = \frac{(A_0 - A_e)}{A_0} \times 100 \quad (2)$$

where A_0 and A_e are the initial and equilibrium concentrations of the dye, V is the volume in milliliters, and W is the weight in grams.

3. Results and Discussion

3.1. Characterization of Adsorbent

Figure 1 displays the Field Emission Scanning Electron Microscope (FESEM) and Transmission Electron Microscopy (TEM) images characterizing the sawdust (SWS) adsorbent. The FESEM image in Figure 1a reveals lamellar aggregates forming a porous and rough surface, enhancing the material's absorbance capability by facilitating water diffusion. After adsorption, Figure 1b illustrates a change in surface morphology, such as the disappearance of surface roughness, indicating the fullness of active sites [16,17]. Figure 1c showcases dark spots via TEM, evidencing active sites contributing to adsorption and increased surface efficiency [18].



(**a**) (**b**)

(**c**)

Figure 1. FESEM: (**a**) SWS before adsorption, (**b**) SWS after adsorption, and TEM (**c**) SWS adsorbent.

3.2. *Effect of Equilibrium Time*

Figure 2 demonstrates the effect of equilibrium time on the removal of MB and CR dyes by SWS. The removal percentage increased over time, reaching equilibrium within 60 min for concentrations studied (15 mg/L). The adsorption curve's steep initial increase indicates a high rate of adsorption, with optimum removal percentages of 97.77% for MB and 68.87% for CR dyes at 60 min. Hence, the best equilibrium time was selected as 60 min for all experiments [19–21].

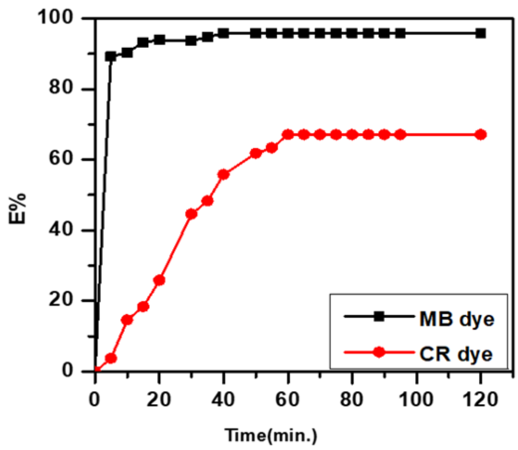


Figure 2. Effect of equilibrium time.

3.3. *Effect of Weight of SWS*

Figures 3 and 4 depict the impact of SWS weight on MB and CR dye adsorption. An increase in SWS weight from 0.05 to 0.15 g corresponded to removal percentage increases from 75.54% to 98.50% for MB dye and 50.86% to 80.012% for CR dye. Conversely, adsorption efficiency (Qe) decreased with increasing surface weight, as shown in the results [16,22–27].

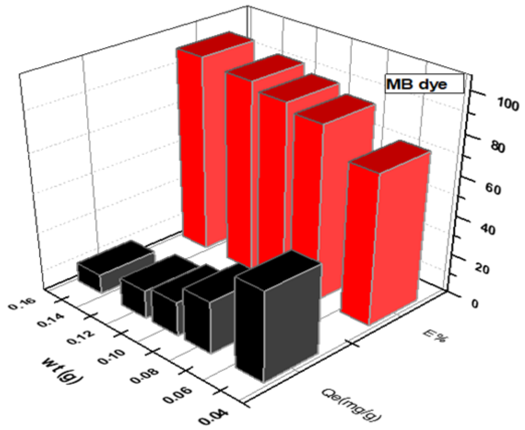


Figure 3. Effect of weight of SWS surface on removal of cationic MB dye.

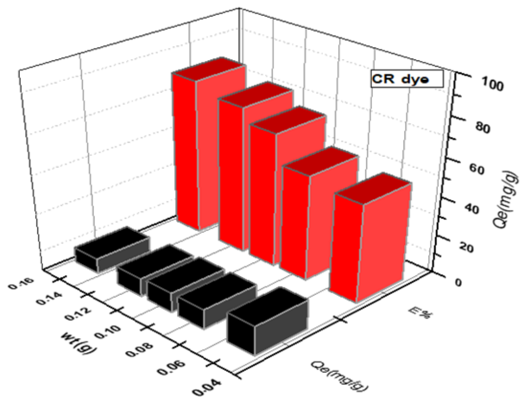


Figure 4. Effect of weight of SWS surface on removal of anionic CR dye.

3.4. Effect of pH Solution

Figure 5 displays the extraordinary influence of pH on the adsorbent surface and MB and CR dye ionization. MB dye sorption was almost constant at pH 6 to 10, but decreased at pH 3, whereas CR dye showed better removal in acidic media, depending on the surface charge [17,18,20,28,29].

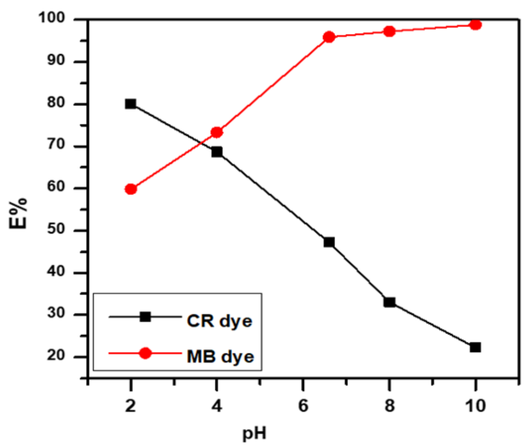


Figure 5. Effect of pH solution on anionic CR dye and cationic MB dye.

3.5. Effect of Initial Concentration of Anionic and Cationic Dyes

Figure 6 illustrates the influence of initial dye concentration on adsorption capacity (Qe mg/g) for dye concentrations between 5 and 25 mg L^{-1}. The results show the adsorption efficiency for SWS at 15 mg/L concentration of CR and MB dyes, revealing the impact of initial concentration on adsorption performance [30].

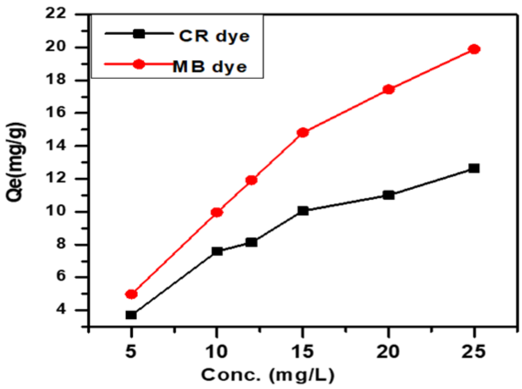


Figure 6. Effect of initial concentration of anionic CR dye and cationic MB dye.

3.6. Conclusions

In this study, an environmentally friendly and cost-effective approach of utilizing sawdust as an adsorbent surface was explored without relying on any chemical treatment. This process was characterized by a detailed examination of various factors influencing the adsorption of MB and CR dyes. The optimal removal percentages achieved were 97.77% for MB dye and 68.87% for CR dye within a 60 min equilibrium time. The pH had distinct effects on the adsorption of the two dyes, with the sorption of MB dye being optimal at pH levels of 6–10, and CR dye performing best at pH 3. Additionally, the removal percentage increased with the weight of SWS, with the range of 0.05–0.15 g yielding a significant improvement in removal efficiency from 75.54% to 98.50% for MB dye and from 50.86% to 80.012% for CR dye. These findings underscore the potential of sawdust (SWS) as an accessible and promising adsorbent for the removal of dyes from water. Its effectiveness in adsorbing different dyes at various conditions emphasizes its versatility, presenting it as an attractive option for broader applications in water treatment. Further optimization and exploration of this method could contribute to sustainable and economically viable solutions for water purification and dye removal.

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Conflicts of Interest: The authors declare no conflicts of interest.

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