Investigation of removing Methylene Blue and Basic Violet 16 dyes from water solutions using *Silybum marianum* (milk thistle) seeds as an adsorbent

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Abstract

Water pollution control is becoming more critical. Even small traces of organic pollutants can cause visible color changes in the environment. Therefore, removing color and treating textile dyes are environmentally important tasks. Physical and chemical methods are commonly used to remove dyes, but dealing with the concentrated sludge they produce remains a major challenge. Moreover, these methods tend to be expensive. In this study, *Silybum marianum* (milk thistle) seeds, a natural plant, were used as adsorbents for wastewater treatment. The seeds of Silybum marianum (also known as sour thistle, Virgin Mary plant, or milk thistle) were ground into powder, and aqueous solutions were prepared. The cationic dyes Methylene Blue (MB) and Basic Violet 16 (BV16) were used to assess their effectiveness in wastewater treatment under UV light, with the goal of determining optimal conditions.

During the trials, the best operating parameters for each dye were determined. These included initial dye concentration, amount of adsorbent, temperature, and contact time. For Methylene Blue (MB), optimal conditions were 10 mg/L initial concentration, 0.3 g of adsorbent, 40°C, and 180 minutes of contact time. The same parameters for BV16 were 30 mg/L, 1.5 g, 50°C, and 60 minutes. By using these optimal conditions, removal efficiencies for MB and BV16 reached 88.49% and 92.06%, respectively. Therefore, utilizing a natural material, *Silybum marianum* (milk thistle) seeds, as an adsorbent, facilitated the effective removal of toxic dyes from aqueous solutions.

Keywords: Adsorption, *Silybum marianum* seed, Methylene Blue, Basic Violet 16, Wastewater

1. Introduction

Water is the most basic building block for life. However, rising populations and increasing wastewater are leading to environmental pollution and challenges in accessing clean water resources. The textile industry is one of the world's most vital industries. However, due to inefficient dye fixation on fabrics, it also ranks among the top contributors to ecosystem pollution [1].

Textile industries alone use about 1.6 million liters of water daily [2]. The textile industry ranks as the second most polluting sector globally in terms of liquid waste, residual gases, and solid waste, contributing 10% of carbon emissions [3]. It employs thousands of dyes and pigments worldwide [4]. Wastewater from textile dyeing industries (TDIW) contains persistent organic compounds and is therefore poorly biodegradable. Consequently, these toxic substances or pollutants pose serious risks when released untreated into natural water environments.

Adsorption is one of the most common methods for wastewater treatment in the textile industry. Literature data shows that the following adsorbent materials are used: chitosan (CS), which is one of the biopolymers [5]; plane tree fruits (Platanus orientalis L.) [6]; nanostructured adsorbents [7]; water hyacinth [8]; bamboo charcoal [9]; arjun sawdust [10]; lignocellulosic fiber [11]; tall fern [12]; dried seeds of Moringa oleifera [13]; rosemary [14]; tea waste [15]; eggshells [16]; bentonite clay [17]; and various natural substances that have been used.

Silybum marianum (L.) Gaernt, a member of the Asteraceae family (also known as milk thistle), grows in Europe, Asia, and North Africa [18]. Milk thistle is a plant from the daisy family that contains silymarin as the main component among six primary flavonolignans and minor polyphenolic substances [19]. Milk thistle seeds are rich in fatty acids, including linoleic (60%), oleic (21%), and palmitic (13%) acids [20]. The active ingredient in milk thistle (*Silybum marianum*, S. marianum) seeds is one of the chemotype-specific medicinal plants used in the production of drugs for liver diseases [21]. In previous studies, camel thorn seeds have been used as adsorbents for removing dye from water and for remediating metabolite- and heavy metal-contaminated soils [22], proving to be effective adsorbents.

This study investigated the removal of Methylene Blue (MB) and Basic Violet 16 (BV16) from aqueous solutions using a camel thorn seed adsorbent through an adsorption process. It also explored the effects of different parameters such as adsorbent amount, temperature, initial dye concentration, and contact time.

2. Materials and Methods

2.1. Materials and Reagents

The dyes used in the experiment, Methylene Blue (MB) (C16H18ClN3S, MW: 319.85 g/mol) and Basic Violet 16 (BV16) ($C_{23}H_{29}ClN_2$, MW: 368.9 g/mol), were supplied by Sigma-Aldrich. Stock solutions of 1000 mg/L were prepared with distilled water available in the laboratory. These solutions were diluted to desired concentrations using the stock solution. (Silybum marianum) Milk thistle seeds, as shown in Figure 1, used as adsorbents, were purchased from a herbalist.

(a) (b)

Figure 1. *Silybum marianum* plant (a) [23], seeds (b) [24].

Buffer solutions with pH 4, 7, and 10 for the experiments were obtained from Merck. Solutions with pH values of 4, 7, and 10 were used as citrate, phosphate, and carbonate buffers, respectively. Batch adsorption experiments were carried out in a Julabo SW 22 heated shaking water bath. Samples taken from the solution during the experiments were analyzed using UV-VIS spectrophotometry with an Agilent 8453 instrument. The distilled water was supplied by a Mikrotest MSD-08 purification system. Additionally, centrifugation was performed with the Elektromag device.

2.2. ADSORPTION STUDIES

To evaluate the adsorption of MB and BV16 dyes, 50 mL of each dye from their stock solutions was placed into a 100 mL glass beaker. Experiments were carried out under controlled laboratory conditions at room temperature (25 °C). A shaking water bath was used to investigate the effects of initial concentration (5-50 mg/L), adsorbent amount (0.1-1.5 g), temperature (25-40 °C), and contact time (5-180 minutes) on adsorption. The studies were conducted using the batch method. After the adsorption process, the absorbance at the maximum wavelength was measured and recorded with a UV-Vis spectrophotometer (which is 663 nm for MB and 545 nm for BV16). Equations 1 and 2 were utilized to calculate the percentage removal (%Removal) and adsorption capacity (Qe) of MB and BV16 dyes in the solution.

$$\%R = \frac{C_0 - C_e}{C_0} x\, 100 \quad (1)$$

$$Q_e = \frac{C_0 - C_e}{m} \, x\, V \quad (2)$$

3. Results and Discussion

3.1. Effect of initial dye concentration

Experiments were conducted within a specific concentration range (5-50 mg/L) to investigate how the initial dye concentration affects the MB and BV16 dyes used. In this experiment, 50 mL of each dye solution was transferred to a 100 mL glass beaker. As an adsorbent, 0.3 g of *Silybum marianum* seed was weighed and added to the beaker. Shaking was performed at 25 °C for 30 minutes at 150 rpm. Absorbance values were then measured.

Figures 2 and 3 display the %Removal values and adsorption capacity graphs, respectively. Analyzing the %Removal values indicates that the optimal concentrations are 10 mg/L for MB and 30 mg/L for BV16.

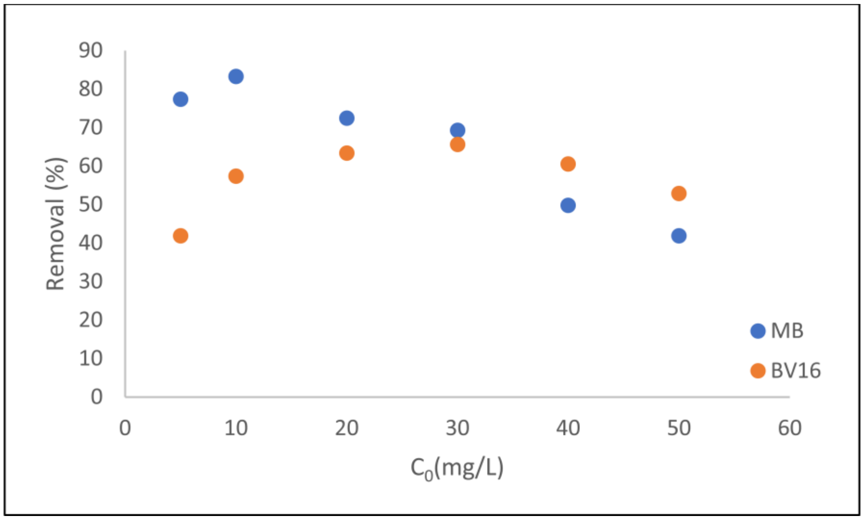

Figure 2. Effect of initial dye concentration on the removal efficiency of MB and BV16.

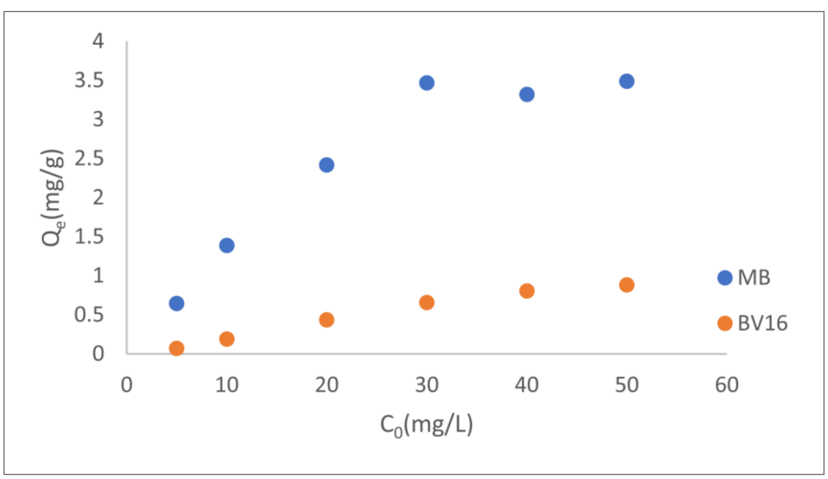

Figure 3. Effect of initial dye concentration on the adsorption capacity of MB and BV16.

In the study, the removal percentage of MB dye at the optimal concentration (10 mg/L) was 83.26%. The removal percentage of MB dye ranged from 41.85% to 83.26%. After reaching optimal conditions, increasing the concentration decreased the removal percentage. Similarly, the removal percentage of BV16 dye at its optimal concentration (30 mg/L) was 65.64%. The removal percentage of BV16 dye ranged from 41.86% to 65.64%.

4.2 Effect of adsorbent amount

To examine how the amount of adsorbent affects MB and BV16 dyes, specific quantities of adsorbent were weighed. The quantities ranged from 0.1 to 1.5 g. These were placed in separate glass beakers (five samples). Additionally, 50 ml of 10 mg/L MB and 30 mg/L BV16 solutions were measured and poured into 100 ml glass beakers. The solutions were stirred in a water bath shaker at 150 rpm for 30 minutes at 25°C. The absorbance values of the solutions were then measured using a UV-Vis spectrophotometer. The percent removal values and adsorption capacities are shown in Figures 4 and 5.

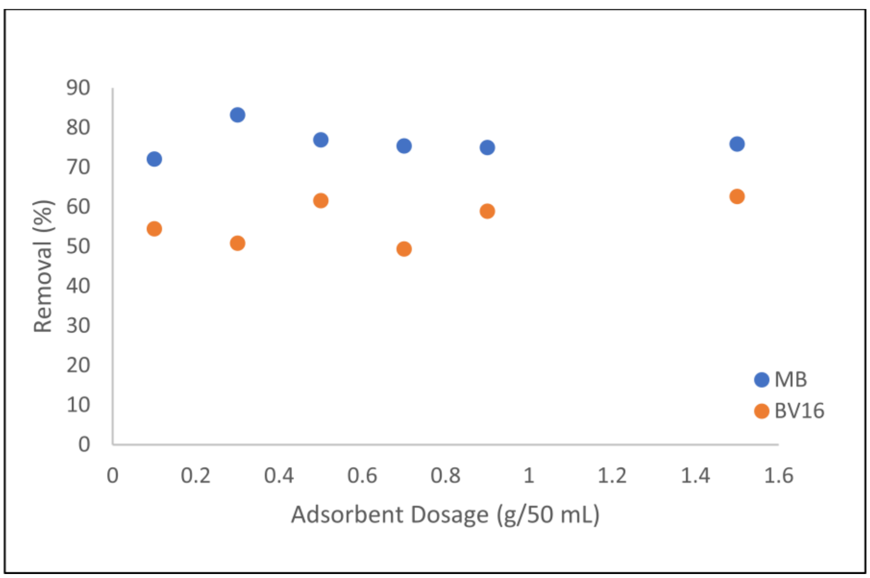

Figure 4. Effect of adsorbent amount on the removal efficiency of MB and BV16.

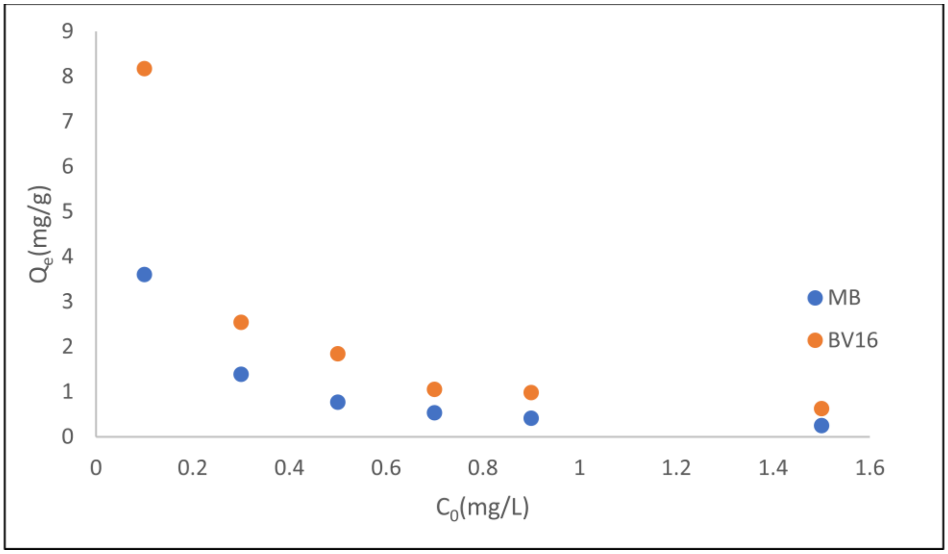

Figure 5. Effect of adsorbent amount on the adsorption capacity of MB and BV16.

The optimal amount of adsorbent for achieving 83.24% removal of MB is 0.3 grams, and for BV16, with a removal rate of 62.63%, it is 1.5 grams. The adsorbent amounts and removal percentages for MB are nearly identical. This indicates that the amount of adsorbent does not significantly affect this dye. The values for BV16 show both increases and decreases.

4.3 Temperature effect

The effect of temperature on the MB and BV16 dyes used in the experiment was examined. Fifty milliliters of each dye solution (MB; 10 mg/L and 0.3 grams, BV16; 30 mg/L and 1.5 grams) were prepared and stirred at 150 rpm at temperatures ranging from 25 to 50 °C. The mixtures were stirred for 30 minutes at each temperature using a water-bath shaker. Measurements were taken with a UV-Vis spectrophotometer.

The removal efficiency values in the experiment assessing the effect of temperature are shown in Figure 6. The optimal temperature for MB dye is 40°C, with a removal percentage of 88.47% at this temperature. The lowest removal percentage for MB dye is 74.41%, observed at 30°C. For BV16 dye, the optimal temperature is 50°C, with a removal percentage of 84.49% at that temperature. As the temperature increases from 25°C to 40°C for BV16 dye, the removal percentage increases by 6% and 10%, respectively.

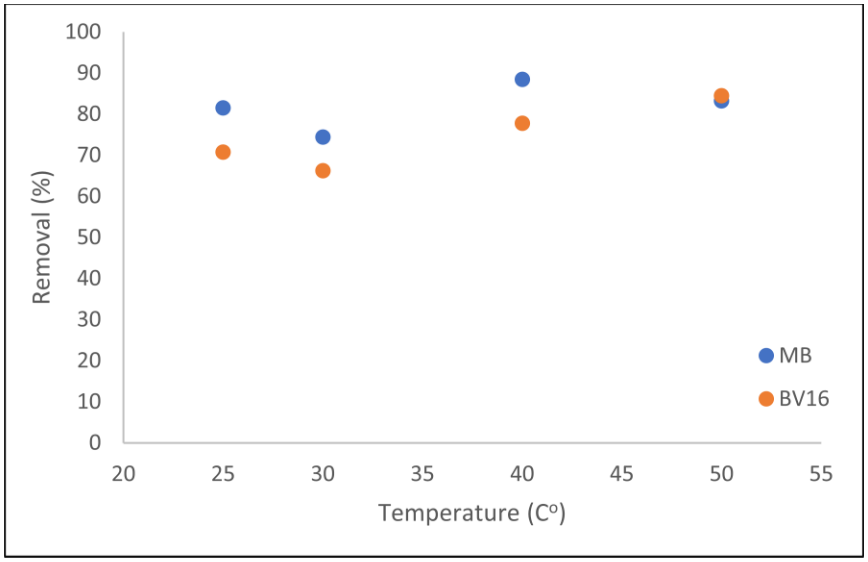

Figure 6. Effect of temperature on the removal efficiency of MB and BV16.

4.4 Effect of contact time

Experiments to examine the contact time effect on MB and BV16 dyes were conducted following these steps. The concentration, amount of adsorbent, and temperature were adjusted to determine the optimal conditions for both dyes. Solutions were prepared at 10 mg/L, 0.3 grams, and 40°C for MB dye; and 30 mg/L, 1.5 grams, and 50°C for BV16. 50 mL of these solutions was taken and placed in 100 mL glass beakers. The solutions were shaken in a water bath at 150 rpm for specific time intervals (5-180 minutes). Afterward, the concentrations were measured using a UV-Vis spectrophotometer.

The results of the optimal removal efficiency values influenced by contact time are shown in Figure 7. The optimal contact times for percentage removal of MB and BV16 sizes are 180 and 60 minutes, respectively.

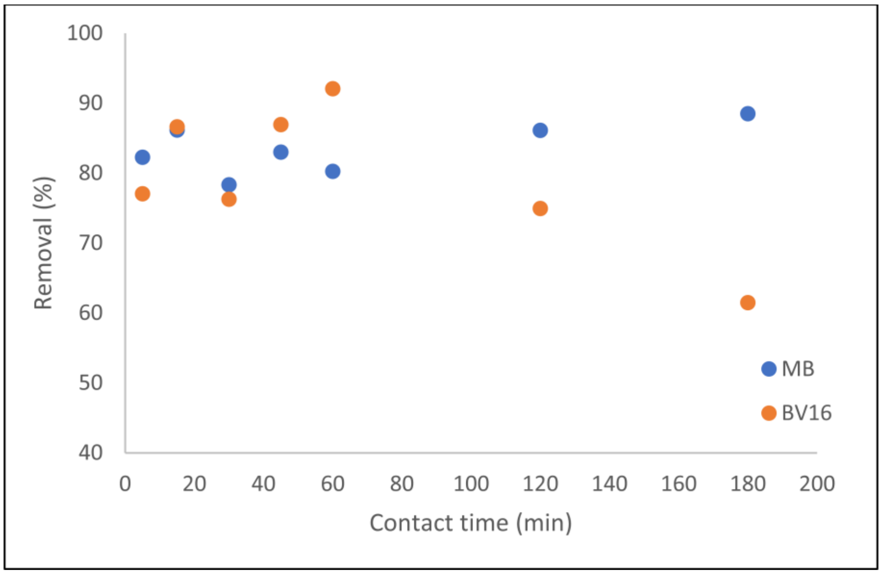

Figure 7. Effect of contact time on the removal efficiency of MB and BV16.

As a result of the experiments, the percentage removal of MB dye at the optimal contact time was found to be 88.49% at 180 minutes. The percentage removal of the other dye studied, BV16, at its optimal contact time was 92.06% at 60 minutes. The lowest removal percentage for BV16 was observed at 180 minutes of contact time, dropping to 61.47%.

Conclusion

Various methods are used to remove dyes from wastewater. Adsorption is one of these methods. It is commonly employed because it is effective and cost-efficient, and the search for different adsorbents for this method is expanding. Camel thorn seed is one of the adsorbents used. The study aimed to remove MB and BV16 dyes, which are harmful to the environment and human health, from wastewater using camel thorn seed. The effects of various parameters on adsorption performance were examined in the experiments. These parameters included initial dye concentration, adsorbent amount, temperature, and contact time. The optimal conditions for these parameters are as follows: For MB dye, the optimal values are 10 mg/L, 0.3 g, 40°C, and 180 minutes. For BV16 dye, the optimal values are 30 mg/L, 1.5 g, 50°C, and 60 minutes. When all conditions were optimized, the removal percentages increased to 88.49% for MB and 92.06% for BV16. Based on these results, it can be concluded that *Silybum marianum* (milk thistle) seeds are an effective adsorbent for removing dyes from wastewater.

Based on the experiments in this study, it is believed that Silybum marianum (milk thistle) seeds used as an adsorbent can help clean textile wastewater containing MB and BV16 because of their natural, abundant, and environmentally friendly properties.

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