ADSORPTION OF METHYLENE BLUE DYE FROM AQUEOUS SOLUTION USING BIO-WASTE POPLAR FIBER

USTA, CANAN*; SEYHAN, AYBENIZ AND GÜRARSLAN, ALPER

Istanbul Technical University, Textile Engineering Department, Istanbul, Turkey

ABSTRACT

Poplar fiber corresponds to the seed hairs of the Populus genus trees and is a naturally abundant lignocellulosic fiber with the features of thin-walled large lumen, lightweight and hydrophobic properties. Based on the structure and properties exhibited by poplar fiber nominate it as a highly favored adsorbent material for cationic dyes. This study aims to determine the adsorption efficiency for methylene blue (MB) dye with chemically enhanced poplar fibers and compare its capacity with milkweed fibers. Prior to adsorption experiments, the fibers were treated with NaOH solution to remove the wax coating attached on the fiber surface. Adsorption studies were performed in a batch system using dye solution with initial dye concentration of 50 mg L^{-1}. The adsorbent dosage was evaluated at 10 g L^{-1} amount, with contact time of 3 h and without pH adjustment. After the experiments, the remaining dye concentration in liquid was quantified in UV-Vis spectrophotometry. The results revealed that poplar fiber exhibited higher adsorption capacity compared with milkweed fiber. Poplar fibers were efficient to decolorize MB dye solution, reaching a higher color removal percentage than milkweed fibers. It can be concluded that poplar fibers were alternative adsorbents for removing cationic dyes due to their hollow structure.

KEYWORDS

Poplar fiber; Dyeing; Adsorption; Cationic dye; Methylene blue.

INTRODUCTION

Waste generation during industrial processes significantly contributes to various environmental pollution problems. Particularly, textile processes consume large amounts of water and synthetic dyes, leading to the generation of colored effluents. The presence of dye contaminants in wastewater is a major concern for both human health and the environment, as even trace amounts of dye are noticeable in water [1]. Among the common dyes, methylene blue (MB), the structure shown in Figure 1, is widely used in textile processing due to its water solubility. While not highly toxic to humans, MB can cause eye and skin irritation and has systemic effects. Hence, the removal of the dye from wastewater is critical in addressing water pollution.

Several methods are widely used for the removal of dye from wastewater, including membrane filtration, ion exchange, reverse osmosis, coagulation and adsorption [2] [3]. Among these, adsorption stands out as one of the simplest and most cost-effective physico-chemical treatment process for removing dye molecules from aqueous solutions. This study focuses on adsorption due to its practicality and efficiency.

There is an increasing demand for cost-effective alternative technologies or adsorbents for dye removal. Natural agricultural materials, which are readily available in large quantities, may serve as low-cost and effective adsorbents.

Poplar fibers are a type of trichome fiber and grow as seed hair fibers on the branches of poplar trees. The variation in poplar species over time can be attributed to factors such as human activities, biological processes and genetic pollution from hybrid poplars [4]. Each poplar tree is capable of generating approximately 25 kg of poplar seed fibers [5]. The length of these fibers depends on the specific tree and the region where they are harvested, and lengths ranging from 3 to 16 mm have been reported in the literature [6] [7]. Poplar fibers typically have a diameter between 5 and 10 µm. These fibers have large hollow lumen, allowing them to float in the air and facilitating their dispersal. The internal diameter of the fibers accounts for approximately 90% of the total fiber diameter, resulting in an extremely low density of around 0.3 g/cm³ [7]. Poplar fibers have similar properties to milkweed and kapok fibers due to their hollow structure. While extensive studies were conducted on these fibers, the potential of poplar fibers have not been thoroughly investigated about

* **Corresponding author:** Usta C., e-mail: cananusta@itu.edu.tr

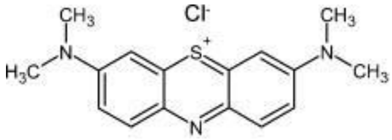

Figure 1. Chemical structure of Methylene Blue.

water treatment capacity. Therefore, this study aims to investigate the potential of poplar fiber as a viable solution for the adsorption of cationic dye from wastewater and provide an environmentally friendly and efficient approach to water purification.

EXPERIMENTAL

Materials

Poplar fibers were directly collected during the blooming period in mid-May in the Kırklareli region of Türkiye. Milkweed fibers were obtained in partnership with Pangai Materials Science, Italy. Both of the fibers were mechanically cleaned to remove contaminants such as seeds, leaves, dust etc. Sodium hydroxide, 99% (Merck) and methylene blue were used as received without further purification.

Methods

Pretreatment of poplar and milkweed fibers

Aqueous NaOH solution was prepared and cooled to room temperature in a glass bottle. Then, 1.0 g of fiber was added immediately into this solution. Subsequently, the generated fiber/solution mixture was placed into the Gyrowash vessels to be processed at 70 °C for 1 hour. Then, fiber sample was washed with distilled water at ambient room temperature until no residual chemicals could be detected on the fiber surface. The wet pretreated fibers were dried at 40 °C for 24 h.

Measurement of the adsorption capacity

The adsorption capacity was measured by calculation of methylene blue dye concentration in the aqueous solution after adsorption. The adsorption process was conducted in 50 mg L^{-1} of methylene blue solution. A glass flask containing 1 g of the modified fibers and 50 ml of the MB solution was shaken for 3 h at room temperature. Then, fibers were filtered and the residual solution was analyzed at λ_{max} of 660 nm using UV-Vis Spectrophotometer.

Scanning electron microscopy (SEM)

The morphology of milkweed and poplar fibers was examined by scanning electron microscopy using TESCAN VEGA3 instrument with 10 kV accelerated voltage and 2.08-6.92 mm working distance. Surface images were taken at 5 kX magnification. Before analysis, fiber samples were coated with Au/Pd under vacuum conditions for 3 min.

RESULTS AND DISCUSSION

Hollow fibers have become widely adopted across numerous industries, with wastewater treatment being one of the primary applications. Their unique structure, featuring a high surface area-to-volume ratio, enables efficient separation and filtration processes, making them ideal for removing contaminants from wastewater [8]. Characterizing the structural morphologies of hollow milkweed and poplar fibers is essential for advancing adsorption technologies.

Scanning electron microscope (SEM) analysis of the fibers revealed a smooth surface, free from rough structures. This smoothness is likely due to a natural wax coating adhered to the fiber surface, as previously reported [9]. Structurally, each fiber resembles a cylindrical microtube with nano-scale surface wrinkles, as seen in Figure 2. Poplar and milkweed fibers exhibit a hollow tubular shape, with diameters around 10 µm and 25 µm, respectively. The presence of a large air-filled lumen in both fibers makes them highly suitable for applications requiring lightweight materials with high absorbency [10].

Chemical treatment, particularly using NaOH, effectively removed the waxy surface of poplar and milkweed fibers. This treatment also facilitated deesterification, breaking down the ester bonds attached to the aromatic rings of lignin [11]. Delignification resulted in an increased proportion of amorphous cellulose, which reduced the hydrophobicity of the fiber (as evidenced by the decrease in the static water contact angle) as reported in the literature [12] [13]. NaOH treatment altered the naturally smooth surface of both fibers, causing the surface to become rougher and increasing the overall surface area [14]. Hence, the adsorption capacity of treated fibers is affected by their chemical reactivity and the porosity of the functional groups present on their surfaces. The structural changes after treatment improved the adhesion of the dye to the outer surface of the fiber and improved its penetration into the inner lumen, thus increasing the dye removal in the chemically treated fiber compared to the untreated fiber.

In this study, an oxidation pretreatment using sodium hydroxide (NaOH) was performed to remove wax, oil, pectin, lignin, and hemicellulose from poplar and milkweed fibers. Then, the increased hydrophilic properties of the treated fibers were used for organic pollutant removal application. Usage of natural milkweed and poplar fibers in removal of methylene blue from wastewater was studied and the decolorization effect was observed. Figure 3 shows the absorbance spectra of methylene blue (MB) at initial and post-adsorption concentrations. The maximum absorbance peak for all concentrations appears consistently at 660 nm in the visible light waveband, which is in agreement with other studies reporting that the absorbance peak of MB occurs at

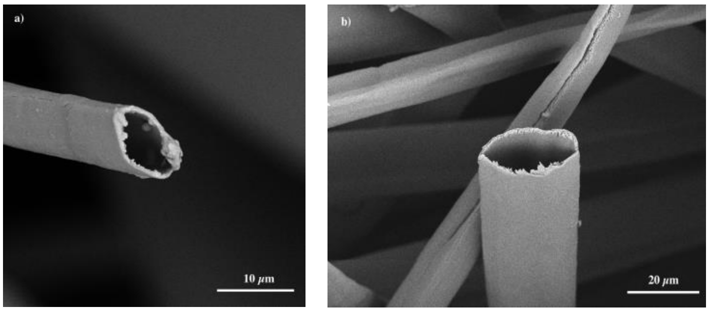

Figure 2. SEM images of raw (a) poplar and (b) milkweed fiber.

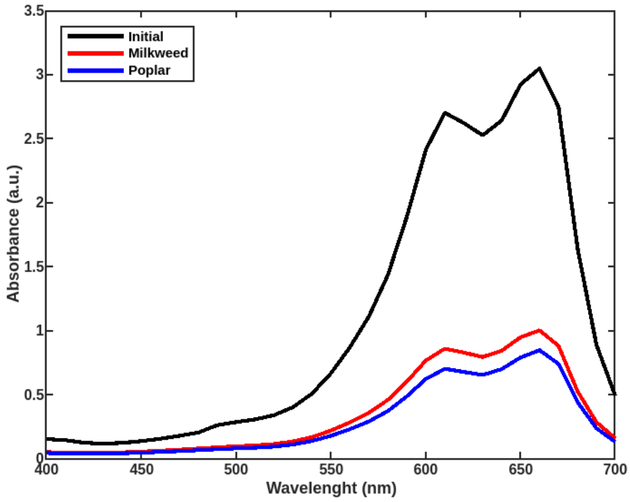

Figure 3. Absorbance curve of MB solution before and after the treatment with milkweed and poplar fibers.

Table 1. The percent value of MB concentration after the adsorption process.

	Milkweed Fiber	Poplar Fiber
MB Concentration (%)	~67%	~72%

660 nm in UV-Vis spectrophotometric analysis [15]. In our study, this peak was used to analyze the removal efficiency of methylene blue. As seen from Figure 3, it is clearly observed that the MB concentration decreases with adsorption by NaOH-treated milkweed and poplar fibers, leading to a corresponding decrease in the peak absorbance values. This behavior follows the Lambert-Beer law, which describes the quantitative analysis by UV-VIS spectrophotometry based on measuring the absorbance of MB solution at 660 nm due to equation (1) as follows [16]:

$$A = \varepsilon c l. \qquad (1)$$

where A represents absorbance, ε is the molar absorption coefficient, c is the concentration, and l is the optical path length. Thus, the absorbance peak trend in the MB solutions can be effectively used to determine MB concentrations based on this relationship.

In Figure 3, the changes in the absorbance curve of MB around 660 nm wavelength before and after treatment with milkweed and poplar fibers were presented. It is seen that the absorbance peak decreases when treated with both fibers and reaches a minimum value with poplar fiber. According to the Lambert-Beer law in Equation (1), this indicates that the MB concentration in the solution will decrease when treated with poplar fiber.

Using the relationship between the absorbance value at 660 nm and the concentration of MB as given in Equation (1), the degree of decolorization (% decolorization) can be calculated using the formula:

$$\%Decolorization = \frac{c_{initial(MB)} - c_{treated(MB)}}{c_{initial(MB)}} \times 100 \qquad (2)$$

where $c_{initial(MB)}$ is the initial absorbance value (before decolorization), and $c_{treated(MB)}$ is the absorbance value after treatment with poplar and milkweed fibers [17]. This calculation provides a quantitative measure of the effectiveness of the decolorization process with different fiber types.

The results for MB concentration percentages in this study are presented in Table 1, demonstrating that both treated fibers enhanced adsorption capacity effectively, showcasing the efficiency of these fibers for color removal. Particularly, poplar fiber presented slightly better performance compared to milkweed fiber. This improvement can be attributed to the structural differences between the fibers; specifically, poplar fiber's shorter length and smaller diameter increase its surface area, a critical factor since adsorption occurs on the fiber surface [18]. This increased surface area of poplar fiber facilitates greater adsorption capacity, emphasizing its suitability for efficient color removal.

CONCLUSIONS

This study investigated the potential of poplar fiber as an adsorbent for the decolorization of methylene blue (MB) dye in wastewater. The base modified milkweed and poplar fibers can be used as an effective alternative low-cost adsorbent for the removal of MB from its aqueous solutions. The amount of MB dye uptake on modified poplar fiber was found to be higher than milkweed fiber. Experimental results indicated that NaOH-treated poplar fiber facilitates a higher percentage of MB removal, showing its effectiveness as a decolorizing agent. It was found that the absorbance value of 0.8435 occurred for the initial dye concentration of 50 g L^{-1} by modified poplar fiber, whereas for modified milkweed fiber it was 0.9985 for the same experiment conditions. When compared to milkweed fiber, poplar fiber demonstrates slightly better performance due to its structural characteristics, such as fine short length and fiber diameter which enhance its adsorption capabilities. The successful application of poplar fiber in this process suggests it as a promising, eco-friendly alternative for treating dye-contaminated wastewater, providing a sustainable solution for water purification.

Acknowledgement: *This work was supported by the Scientific and Technological Research Council of Türkiye (TÜBİTAK) under Grants No. 124N407. Besides, the authors gratefully acknowledge the financial support by ITU Scientific Research Projects (Grant no: MGA-2024-45727).*

REFERENCES

1. Yu Z., Qi T., Qu J., et al.: Removal of Ca(II) and Mg(II) from potassium chromate solution on Amberlite IRC 748 synthetic resin by ion exchange. J Hazard Mater, 167, 2009, pp. 406–412. https://doi.org/10.1016/j.jhazmat.2008.12.140
2. Dawood S., Sen T.K.: Removal of anionic dye congo red from aqueous solution by raw pine and acid-treated pine cone powder as adsorbent: equilibrium, thermodynamic, kinetics, mechanism and process design. Water Res., 46, 2012, pp.1933–1946. https://doi.org/10.1016/j.watres.2012.01.009
3. Mohammod M., Sen T.K., Maitra S., et al.: Removal of Zn^{2+} from aqueous solution using castor seed hull. Water Air Soil Pollut, 179, 2011, pp. 363–372. https://doi.org/10.1007/s11270-010-0503-0
4. Ciftci A., Kaya Z.: Genetic diversity and structure of Populus nigra populations in two highly fragmented river ecosystems from Turkey. Tree Genetics & Genomes, 15(4), 2019, 66 p. https://doi.org/10.1007/s11295-019-1370-5
5. Liu Y., Lyu L., Xiong X., et al.: Structural characteristics and sound absorption properties of poplar seed fibers. Textile Research Journal, 90(21–22), 2020, pp. 2467–2477. https://doi.org/10.1177/0040517520921396
6. Gurarslan A., Narinç M.E.: Investigating the rose oil and toluene absorption of populus fiber. Textile Research Journal, 89(10), 2019, pp. 1952–1963. https://doi.org/10.1177/004051751878333
7. Chen H.L., Cluver B.: Assessment of Poplar Seed Hair Fibers as a Potential Bulk Textile Thermal Insulation Material. Clothing and Textiles Research Journal, 28(4), 2010, pp. 255–262. https://doi.org/10.1177/0887302X10375845
8. Huang J.H., Zhou C.F., Zeng, G.M., et al.: Micellar-enhanced ultrafiltration of methylene blue from dye wastewater via a polysulfone hollow fiber membrane, Journal of Membrane Science, 365 (1-2), 2010, pp. 138-144. https://doi.org/10.1016/j.memsci.2010.08.052
9. Sangalang R.H.: Kapok Fiber-Structure, Characteristics and Applications: (A Review), Oriental Journal Of Chemistry, 37(3), 2021, pp. 513-523. http://dx.doi.org/10.13005/ojc/370301
10. Usta C., Seyhan A., Gurarslan A.: Utilization of poplar fibers in needle punched nonwovens, Cellulose, 31, 2024, pp. 8351–8367. https://doi.org/10.1007/s10570-024-06062-w
11. Futalan C.M., Choi A.E.S., Soriano H.G.O., et al.: Modification Strategies of Kapok Fiber Composites and Its Application in the Adsorption of Heavy Metal Ions and Dyes from Aqueous Solutions: A Systematic Review. International Journal of Environmental Research and Public Health, 19(5), 2022, 2703 p. https://doi.org/10.3390/ijerph19052703
12. Wolok E., Lahay I.H., Machmoed B.R., et al.: Modification And Characterization Of Ceiba Pentandra (L.) Gaertn. (Kapok) Fiber: Physical Properties. International Journal of Research -GRANTHAALAYAH, 7(7), 2019, pp. 381-390. https://doi.org/10.5658/WOOD.2018.46.4.393
13. Liu Y., Wang J., Zheng Y., et al.: Adsorption of methylene blue by kapok fiber treated by sodium chlorite optimized with response surface methodology, Chemical Engineering Journal, 184, 2012, pp. 248–255. https://doi.org/10.1016/j.cej.2012.01.049
14. Mohamed M.A., W Salleh W.N., Jaafar J., et al.: Physicochemical characterization of cellulose nanocrystal and nanoporous self-assembled CNC membrane derived from Ceiba pentandra. Carbohydr Polym., 57, 2017, pp. 1892-1902. https://doi.org/10.1016/j.carbpol.2016.11.078
15. Shiffman D.: Chapter 7: Cellular automata. Nature of Code, 2012. 15. Tseng K.H., Chung M.Y., Chang C.Y., et al.: A Study of Photocatalysis of Methylene Blue of TiO_2 Fabricated by Electric Spark Discharge Method, Hindawi Journal of Nanomaterials, Volume 2017- 9346201. https://doi.org/10.1155/2017/9346201
16. Hołysz L., Rek P., Huber M., et al.: Evaluation and comparison of various methods used for aggregates investigations, Adsorption, 30, 2024, pp. 265–277. https://doi.org/10.1007/s10450-023-00393-z
17. Tiandho Y., Afriani F., Evi J., et al.: Kinetic evaluation of methylene blue decolorization by CuO as a Fenton-like catalyst. IOP Conf. Ser.: Earth Environ. Sci., 926, 2021, 012103 p. https://doi.org/10.1088/1755-1315/926/1/012103
18. Chatterjee S., Kumar A., Basu B., et al.: Application of Response Surface Methodology for Methylene Blue dye removal from aqueous solution using low cost adsorbent, Chemical Engineering Journal, 181–182, 2012, pp. 289-299. https://doi.org/10.1016/j.cej.2011.11.081