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Removal of Carcinogenic Direct Azo Dyes from Aqueous Solution Using a Functional Biopolymer

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Abstract: In this study, a batch system was used to investigate the adsorption methyl violet from aqueous solution onto a β-cyclodextrin polymer synthesized with citric acid as a crosslinking agent. Several operational variables were tested. The results showed that increasing the amount of adsorbent improved the removal efficiency. Higher temperatures also enhanced dye adsorption, while ionic strength had no significant effect on the process. A slight decrease in removal efficiency was observed as pH values increased. FTIR spectra revealed the formation of a complex inclusion, which was identified as the dominant adsorption mechanism; this was further confirmed by the absence of the characteristic peaks of methyl violet in β-cyclodextrin polymer after adsorption.

Keywords: Cyclodextrin polymer, Textile dyes, Adsorption.

Introduction

The textile dyeing industry, in particular, is one of the largest polluters worldwide. It is estimated that this industry uses over five trillion liters of water annually, with effluents from textile processing and dyeing contributing to 20% of global water pollution. The toxic effects of dyes and their metabolites on living organisms, including humans, are well-documented. Azo dyes, such as methyl violet, eriochrom black T, and helianthin, are known for their harmful, long-lasting impact on ecosystems due to their persistence and xenobiotic properties. Although natural processes can remediate these contaminants, they do not always produce by-products that are non-toxic or less toxic, some environmental processes can even transform hazardous dyes into more toxic metabolites, including aromatic amines, diazonium ions, and hydrolyzed products. Moreover, microflora in the skin or intestinal ecosystems of mammals can convert certain non-toxic dyes into carcinogenic substances, which can have various toxic effects across different biological compartments.

The removal of dyes from wastewater has been a long-standing challenge. Several methods have been developed to address this issue, including membrane filtration (Raval et al., 2022). Photodegradation (Saeed et al., 2022). and adsorption (Salih et al., 2022). Among these, adsorption has proven to be the most effective and economically viable method for dye removal. Understanding adsorption equilibrium is crucial, as these data inform the selection of suitable adsorbents and the design of effective separation processes. There is a wide range of adsorbents available, with non-conventional materials such as (Oughlis-Hammache et al., 2010). Agricultural waste (Dubey et al., 2010; Ofomajas et al., 2011), and biomass receiving increasing attention. Biopolymers and natural molecules, such as cellulose (Musyoka et al., 2014). Chitosan (Huang et al., 2011). Starch, and cyclodextrins (Moulahcene et al., 2015). Have become popular for removing toxic

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pollutants from water. While adsorbents like activated carbon are highly effective, they can be difficult to regenerate. In contrast, cyclodextrin-based polymers are promising due to their ability to undergo multiple regeneration cycles, making them a more sustainable option (Oughlis-Hammache et al., 2024).

β-Cyclodextrin (β-CD) materials, which are natural, non-toxic, and inexpensive cyclic oligosaccharides derived from starch through enzymatic conversion, have shown significant potential for removing organic micropollutants from wastewater. Traditional β-CD-based polymers are chemically crosslinked with toxic agents like epichlorohydrin to improve their properties. However, these polymers tend to have limited nanoporous structures, which can restrict the adsorption capacity and efficiency. Recently, β-CD-based polymers crosslinked with citric acid have been developed, offering a larger surface area and mesoporous structure that enhances their ability to remove organic micropollutants. Insoluble cyclodextrin polymers are unconventional adsorbents, synthesized by using cyclodextrin (CD) as a complex molecule and a biopolyfunctional substance as a cross-linking agent. These adsorbents have been shown to be highly effective in removing dyes from wastewater, yielding excellent results.

This study investigates the use of cyclodextrin polymer; synthesized by combining β-cyclodextrin with citric acid as a cross-linking agent, for adsorbing methyl violet, in water treatment. The influence of several parameters, including contact time, adsorbent amount, initial pH, ionic strength and temperature, was evaluated.

Materials and Methods

Reagents

Methyl violet, was obtained from Sigma (Figure 1). The insoluble β-cyclodextrin polymer (P-β-CD) was sourced from In-Cyclo, a start-up company at the University of Rouen, France. Hydrochloric acid, sodium chloride, and sodium hydroxide were purchased from Chemi-nova, Labosi, and Merck KGaA, respectively.

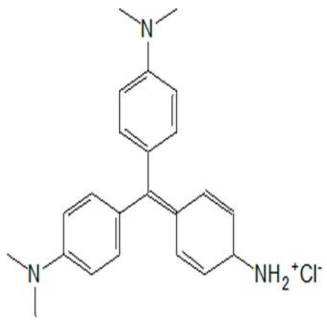


Figure 1. Chemical structure of methylviolet.

Apparatus

IR spectra were recorded using a Perkin-Elmer 4000 FTIR spectrometer, with a scanning range from 4000 cm^{-1} to 400 cm^{-1}. UV-Visible analysis was performed using a JASCO V-R30 spectrophotometer (Japan). For these measurements, a glass tank was used, and methyl violet solutions were prepared in deionized water. The absorbance was measured at 550 nm, the morphology of the polymer was analyzed using scanning electron microscopy (SEM) on a Cambridge Steroscan 360, operating in the LFD mode.

Adsorption Study

Adsorption experiments were conducted in a batch system. A 100 mL dye solution was placed in a glass bottle, and a known amount of cyclodextrin polymer was added and stirred. At specified time intervals, 3 mL of the solution was sampled. The dye solution was then separated from the adsorbent by centrifugation at 2000 rpm for 5 minutes and analyzed using a UV-Visible spectrophotometer.Stock solution of the dye (2.5 10^{-5} mol·L^{-1}) was prepared in deionized water. Experimental solutions with the desired dye concentrations were obtained by successively diluting the stock solution with deionized water. Calibration curve for the dye was created by measuring the absorbance of samples with known concentrations at 550 nm, using a UV/VIS spectrophotometer (JASCO V-R30, Japan).

Results and Discussion

Characterization of Cyclodextrin Polymer by SEM

As reported by Moulahcene et al. (2015). The β-cyclodextrin polymer exhibits a high swelling capacity due to its porous morphology, as confirmed by the SEM image (Figure 2). Additionally, this polymer has a relatively small surface area, suggesting that its adsorption mechanism differs from those of conventional adsorbents. Similar findings have been reported in the literature (Skiba & Lahiani-Skiba, 2013). The polymer also contains a relatively high number of acidic groups, which enables significant physical interactions within the polymer network, facilitating the adsorption of dyes.

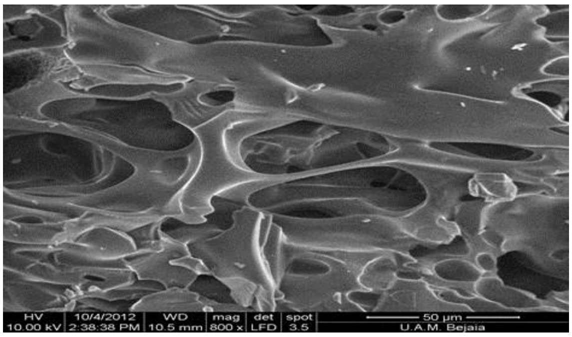
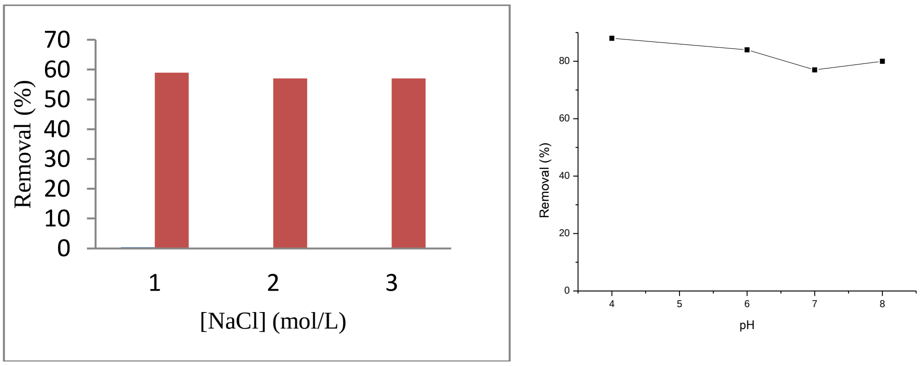


Figure 2. Feature (SEM) of ß-cyclodextrin polymer at 800×magnification.

Effect of Operators Variables on Methyl Violet Adsorption

Effect of pH and Ionic Strength

The effect of pH on methyl violet adsorption is illustrated in Figure 3b. Methyl violet does not remain undissociated under varying pH conditions. A slight decrease in adsorption is observed as pH increases. This behavior may be attributed to the substitution of chloride (Cl) by hydroxyl (-OH) groups, which reduces the ability of methyl violet to form inclusion complexes with cyclodextrins. Similar effects have been reported for other adsorbents, such as cellulose, where pH plays a significant role in methyl violet adsorption due to the positive charge on the dye (Musyoka et al., 2014). The effect of ionic strength was examined by varying the concentration of NaCl from 0 to 3 M. As shown in Figure 4a, ionic strength does not appear to influence methyl violet adsorption.



(a) (b)

Figure 3. (a) ionic strength, (b) Effect of pH on methyl violet removal
by ß-cyclodextrin polymer, T= 30°C.

Effect of Adsorbent Amount

Effect of adsorbent amount on methyl violet adsorption is represented in the figure 4, the efficiently increases with increase of adsorbent amount and the equilibrium is attained at 1700 min.

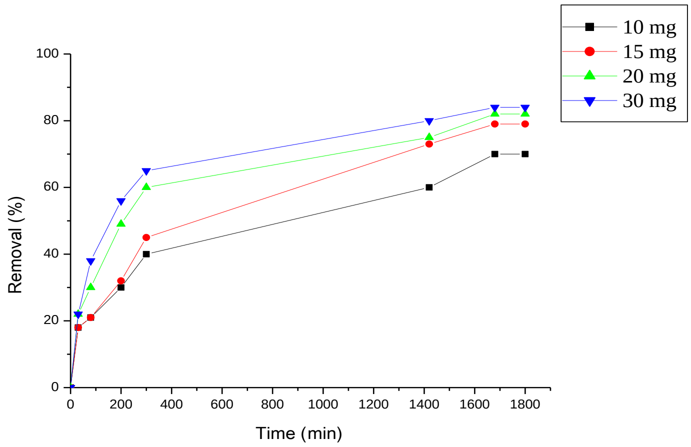


Figure 4. Effect of ß-cyclodextrin polymer amount on methyl violet removal, pH=4, T= 30 °C.

Effect of Temperature

Temperature plays a significant role in the adsorption of methyl violet onto ß-cyclodextrin polymer, as shown in Figure 5. The adsorption kinetics improve with an increase in temperature, which may be attributed to a higher rate of intraparticle diffusion or an expansion of the pore size (Moulahcene et al., 2015).

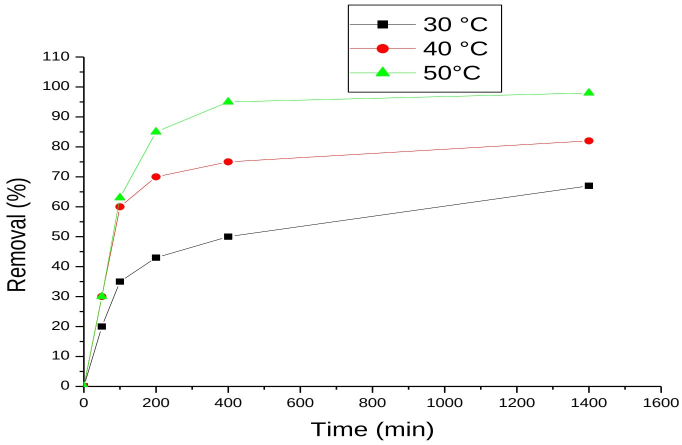


Figure 5. Effect of temperature (T) on methyl violet removal.

FTIR Characterization

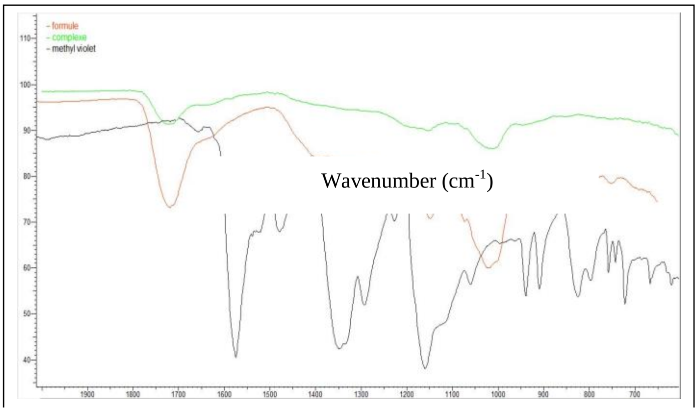


Figure 6. FTIR spectra of methyl violet and β-cyclodexrin polymers after and before adsorption, red (β-cyclodextrin polymer before adsorption), green (β-cyclodextrin polymer after adsorption) and black (methyl violet).

The FTIR spectra (400–4000 cm^{-1}) of methyl violet and β-cyclodextrin polymer, both before and after adsorption, are shown in Figure 6. The peaks at 1500 cm^{-1} and 1600 cm^{-1} correspond to the vibration of the aromatic C=C bond, while the peaks at 1200 cm^{-1} and 1300 cm^{-1} are attributed to the vibration of the aromatic amine bond in the methyl violet spectra. The absence of these characteristic peaks in the β-cyclodextrin polymer afteradsorption confirms the formation of an inclusion complex between β-cyclodextrin and methyl violet. This suggests that the adsorption process is governed by the formation of the inclusion complex rather than physical adsorption.

Conclusion

The synthesis of insoluble polymer using β-cyclodextrin as the base material and citric acid as the cross-linking agent was found to be a viable approach, producing a product that can serve as an effective and promising sorbent in the liquid-solid sorption process for removing azo dyes from wastewater effluents. The adsorption of methyl violet, onto the β-cyclodextrin polymer was investigated,various operational parameters were tested for this dye. Adsorption of methyl violet onto the β-cyclodextrin polymer increased with a higher amount of adsorbent, while pH had a slight effect. In contrast, ionic strength did not influence the adsorption process. The adsorption mechanism was primarily governed by the formation of an inclusion complex between methyl violet and β-cyclodextrin, as evidenced by the absence of characteristic peaks in the FTIR spectra of methyl violet within the β-cyclodextrin polymer after adsorption. These results suggest that the β-CD polymer could be a promising alternative for methyl violet removal, offering a more cost-effective solution compared to other adsorbents. Its advantages include good adsorption properties, ease of preparation, and relatively low cost. This β-CD polymer could help mitigate the environmental impact of dye effluents released into aquatic systems, while also lowering the costs associated with wastewater treatment, whether for disposal or reuse in industrial processes.

Scientific Ethics Declaration

The author declares that the scientific ethical and legal responsibility of this article published in EPSTEM Journal belongs to me.

Notes

This article was presented as an oral presentation at International Conference on Technology, Engineering and Science (www.icontes.net) held in Antalya/Turkey on November 14-17, 2024.

References

Dubey, S. P., Dwivedi, A. D., Sillanpää, M., & Gopal, K. (2010). Artemisia vulgaris-derived mesoporous honeycomb-shaped activated carbon for ibuprofen adsorption. *Chemical Engineering Journal*, *165*(2), 537-544.

Huang, X.Y., Bin, J.P., Bu, H. T., & Jiang, G. B.(2011). Removal of anionic dye from aqueous solution using ethylenediamine modified chitosane. *Carbohydrate Polymer*, *84*(4), 1350-1356.

Moulahcene, L., Skiba, M., Senhadji, O., N. Milon, N., Benamor, M., &Lahiani-Skiba, M. (2015).Inclusion and removal of pharmaceutical residues from aqueous solution using water-insoluble cyclodextrin polymers. *Chemical Engineering Research.and Design*, *97*, 145–158.

Musyoka, S. M., Mittal, H., Mishra, S.B., & Ngila, J.C.(2014).Effect of functionalization on the adsorption capacity of cellulose for the removal of methyl violet. *International Journal of Biological Macromolecules*, *65*, 389–397.

Raval, A. R., Kohli, H. P., & Mahadwad, O. M.(2022). Application of emulsion liquid membrane for removal of malachite green dye from aqueous solution. Extraction and stability studies. *Chemical Engineering Journal Advances*, *12*, 100398.

Saeed, M., Alwadi, N., Ben Ferhat, L., Baig, A., Nabgan, W., & Iqbal, M.(2022). Co_3O_4-Bi_2O_3 heterojunction . An effective photocatalyst for rhodamine B dye. *Arabian Journal of Chemistry*, *15*(4), 103732.

Skiba, M., &Lahiani-Skiba, M.(2013) Novel method for preparation of cyclodextrin polymers physico-chemical characterization and cytotoxicity. *Journal of Inclusion Phenomena and Macrocyclic Chemistry*, *75*, 341–34.

Salih, S. J., Abdul Kareem, A. S., & Anwer, S. S.(2022). Adsorption of anionic dye from textile wastewater raw corncob. *Hellyone*, *8*(8), e10092.

Ofomaja, A. E. Ukpebor, E. E., & Uzoekwe, S. A.(2011). Biosorption of methyl violet onto palm kernel fiber. Diffusion studies and multistage process design to minimize biosorbent mass and contact time. *Biomass and Bioenergy*, *35*(10), 411, 2-4123.

Oughlis-Hammache, F., Moulahcene, L., Senhadji-Kebiche, O., Moussi, N., Meziani, H., Benamor, M., Skiba, M., &Lahiani-Skiba, M.(2024). Modeling and optimization of the adsorption process of pharmaceutical residues in aqueous solution by the experimental design method. *Materials*, *17,* 3594.

Oughlis-Hammache, F., Hamaidi-Maouche, N., Aissani-Benissad, F., & Bourouina-Bacha, S. (2010). Central composite design for the modeling of the phenol adsorption process in a fixed-bed reactor. *Journal of Chemical & Engineering Data*, *55*(7), 2489-2494.

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