POTENTIAL OF MALT BAGASSE AS AN ADSORBENT FOR CRYSTAL VIOLET DYE: A SUSTAINABLE APPROACH

Caíque S. dos Santos[1]*, Larissa S. Conceição[1], Rafael J. N. Gomes[1], Luciene S. Carvalho[2], Leila M. A. Campos[1,3]

[1] Chemical Engineering / CATAM / NQV, Universidade Salvador (UNIFACS), Salvador-BA, Brazil.
[2] Institute of Chemistry, Universidade Federal do Rio Grande do Norte (UFRN), Natal, Brazil
[3] Postgraduate Program in Chemical Engineering, Universidade Federal da Bahia (UFBA), Salvador, Brazil.
* Corresponding author's email address: caiquesantos.social@hotmail.com

ABSTRACT

In 2022, Brazil became the world's third largest beer producer. However, Malt Bagasse (BM), the main by-product of this industry, is often destined for animal feed or discarded. At the same time, the increase in the use of dyes, many of them harmful to the environment, by the textile industry raises environmental concerns. This study proposes a sustainable solution using Malt Bagasse (BM) to remove the dye Crystal Violet (VC) from textile industry effluents. Zero Point of Charge (pH_{PCZ}) studies and adsorption tests were carried out using Response Surface Methodology (RSM). The results indicated that the Initial Concentration (C_i) of the VC influenced adsorption, while the pH had a limited influence. UV-VIS and FTIR analyses were carried out on the liquid and solid phases, respectively. The percentage removal of VC (%R) and the Adsorption Capacity (CA) of the BM were evaluated, with the ideal conditions being pH 9 and an initial VC concentration of 300 mg.L^{-1}, demonstrating the potential of the BM as an adsorbent for cationic dyes.

Keywords: Adsorption. Response Surface. Malt Bagasse. Crystal violet. Adsorption capacity.

1 INTRODUCTION

The indiscriminate dumping of dyes into nature, without restrictions, has become a global concern due to the devastating environmental impacts. Approximately 20 to 30% of the waste resulting from the dyeing process is discharged into bodies of water, contributing to water pollution[1]. These dyes, when disposed of in wastewater, are responsible for serious environmental impacts due to their toxic, mutagenic nature, posing a significant threat to marine biodiversity and human health[2].

The cationic dye Crystal Violet (VC), commonly used in the textile industry, is harmful to aquatic ecosystems, causing a decrease in photosynthesis and the depletion of oxygen in the water, as well as being able to originate carcinogenic contaminants through chemical reactions[3]. Although techniques such as coagulation, ultrafiltration and adsorption have been suggested to treat this problem, they are expensive and have limited effectiveness. Therefore, it is necessary to explore sustainable alternatives, such as bioadsorbents, to remove dyes from textile industry wastewater and mitigate their environmental impacts.

Malt Bagasse (BM) has emerged as a promising bio adsorption solution for removing the dye Crystal Violet (VC). This predominant by-product of the brewing industry represents around 85% of the total waste generated, with each liter of beer resulting in 140 to 200 g of BM. This amount is significant, especially considering that Brazil was the third largest beer producer in the world in 2022[4,5]. However, the majority of BM is currently used as animal feed or is simply discarded, which shows that this valuable resource is being used inappropriately[6].

In this study, the aim was to evaluate the effectiveness of Malt Bagasse (BM) as a bioadsorbent in the removal of the dye Crystal Violet (VC), with the aim of reducing the environmental impacts of discharging this dye into water bodies. The analysis focused on investigating the effect of pH and initial concentration on adsorption, offering crucial insights for improving the treatment of textile effluents. This approach is fundamental to the development of sustainable strategies in industrial waste management, contributing significantly to the preservation of water resources and the environment.

2 MATERIAL & METHODS

Preparation of the BM sample: The brewery waste was washed thoroughly until the water became clear, odorless and without signs of fermentation. It was then dried in an oven at 60 ºC until it reached a moisture content of less than 10%, crushed and sieved to obtain a particle size equivalent to 0.150 mm.
Determination of the Zero Charge Point (pH_{PCZ}): the methodology known as the "11-Point Experiment"[7] was used, which consisted of mixing 50 mg of the BM sample in 50 mL of aqueous solution, with the initial pH being adjusted by varying the pH from 2 to 12. The pH_{PCZ} value was identified as the pH at which stability occurred after 24 hours, indicating the most favorable pH range for the adsorption process.
VC adsorption process: Initially, a 2^2 factorial design was carried out consisting of two factors, initial concentration of the VC dye (C_i) and pH, at two levels, with three repetitions of the central point, totaling 7 experiments, with the percentage removal of the crystal violet dye (%R) and the adsorption capacity of the biomass (CA) as the response surface, as shown in Table 1.

Table 1. Adsorption test conditions.

Factors	Levels		
	-1	0	+1
C_i (mg.L^{-1})	100	200	300
pH	5	7	9

Five different solutions were prepared with VC concentrations: 100 mg.L^{-1} at pH 5 and 9, 200 mg.L^{-1} at pH 7 and 300 mg.L^{-1} at pH 5 and 9. The pH was adjusted with HCl 0.1 mol.L^{-1} or NaOH 0.1 mol.L^{-1} and measured with a pH meter (AZ-86505). During adsorption, the mass of the BM (5 g), volume of the VC solutions (50 mL), agitation (250 rpm), temperature (25 ºC) and time (9600 s) were kept constant. After adsorption, the sample was centrifuged at 3600 rpm for 30 minutes. The liquid and solid fractions were respectively analyzed by UV-VIS (590 nm) and FTIR (4000 to 400 cm^{-1}). A standard curve was constructed to obtain the final concentrations. The percentage removal (%R) and adsorption capacity (CA) were calculated using Equations 1 and 2, respectively, where C_i and C_f correspond to the initial and final concentrations of the dye, in mg.L^{-1}, V is the volume of the solution, in liters, and X refers to the dry mass of the adsorbent, in grams.

$$\% R = \frac{Ci - Cf}{Ci} * 100 \quad (1)$$

$$CA = \frac{Ci - Cf}{X} * V \quad (2)$$

3 RESULTS & DISCUSSION

Zero Charge Point (pH_{PCZ}): The zero charge point (pH_{PCZ}) indicates the neutrality of the adsorbent's surface charges in relation to the pH of the solution, and is fundamental for understanding and optimizing adsorption and contaminant removal processes. When the pH exceeds the pH_{PCZ}, the surface becomes negatively charged, while the opposite occurs at pH below the pH_{PCZ}. These dynamic influences the interaction between the solid and the chemical species in the solution, directly impacting the processes of adsorption and removal of contaminants. Figure 1 shows the relationship between initial and final pH, which is essential for determining the optimum pH for adsorption.

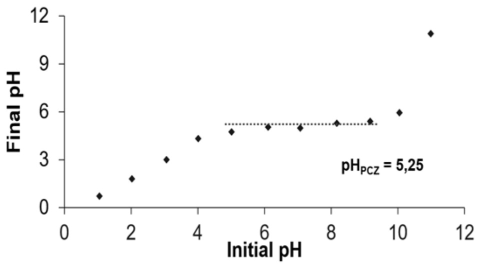

Figure 1. Determination of pHPCZ for BM.

Analysis of the results revealed that the pH_{PCZ} of malt bagasse (BM) was equivalent to 5.25, indicating its buffering nature, which implies that efficient adsorption of the cationic dye occurs at a pH higher than the isoelectric point of BM. In a study evaluating BM as an adsorbent[8], pH_{PCZ} values equivalent to 6.00 were found when dried in an oven and 7.00 when dried in a microwave oven.

Adsorption of VC: Figure 2 shows the calibration curve for the VC dye (R^2 = 0.998), which allows the variation in the concentration of the dye in contact with the malt residue to be monitored.

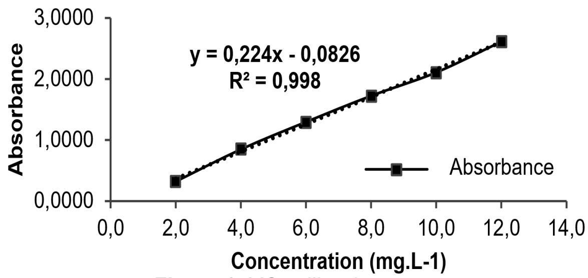

Figure 2. VC calibration curve.

Figures 3 and 4 show the response surface graphs for %R and CA, respectively, which show that the best conditions for removing VC and adsorption capacity are in the range between 250 and 300 mg.L^{-1}.

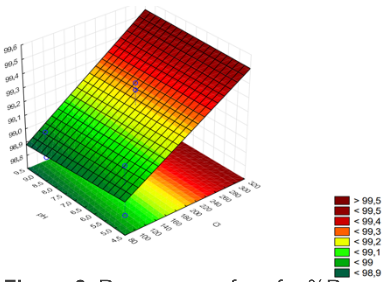

Figure 3. Response surface for %R.

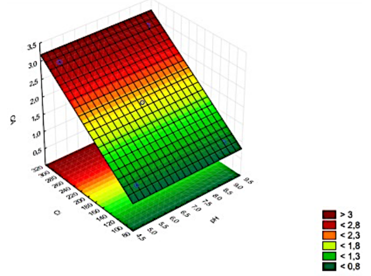

Figure 4. Response surface for CA.

With regard to the Pareto Diagram, both %R (Figure 5) and CA (Figure 6) show that only the C_i variable significantly affected the adsorption process.

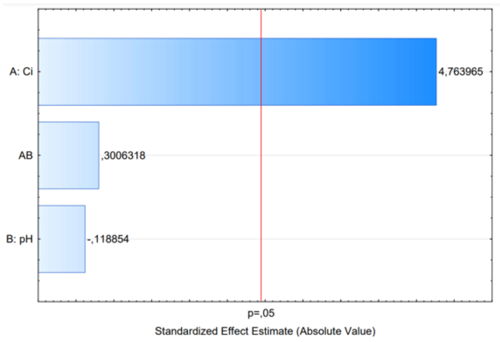

Figure 5. Pareto diagram for %R.

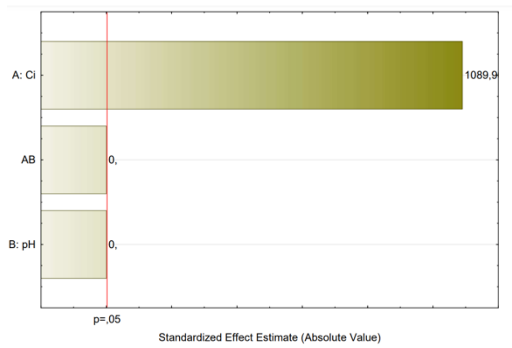

Figure 6. Pareto diagram for CA.

Figure 7 shows the spectrogram obtained for BM before and after the VC. adsorption process in the 200 mg.L^{-1} concentration solution at pH 7.

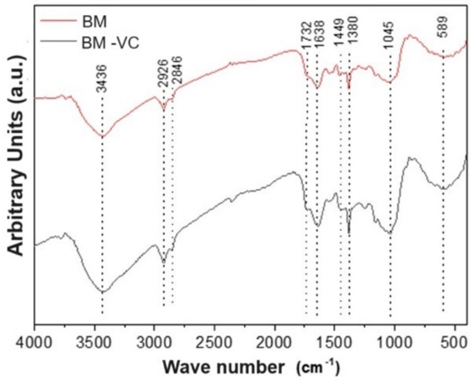

Figure 7. FTIR spectrum of BM before adsorption and after VC adsorption.

The spectrograms obtained before and after the adsorption process showed that there was no change in the presence of the functional groups present in the biomass, which shows that the adsorbed dye did not alter the molecular structure of BM.

4 CONCLUSIONS

Statistical analysis revealed that variations in pH did not affect the adsorption efficiency of the VC dye by BM. However, the initial concentration showed a significant impact on the Adsorption Capacity (CA) between less and more concentrated solutions. This highlights the potential of BM as a dye adsorbent. The optimum conditions for maximum VC removal were identified at pH 9 and a concentration of 300 mg.L^{-1}, achieving 99.43% removal. Future research should address other factors, such as kinetic and thermodynamic studies, to strengthen the effectiveness of BM as a dye adsorbent and better understand the dynamics of adsorption over time.

REFERENCES

1 ALMEIDA, E. J. R. 2018. Avaliação da remoção de cor e toxicidade de azo corantes pelo emprego de tratamentos microbiológicos, adsortivos e processos oxidativos avançados. Rio Claro.
2 NACHIYAR, C. V., RAKSHI A. D., SANDHYA, S., JEBASTA N. B. D., NELLORE, J. 2023. C. S C. Environmental Engineering, p. 100339.
3 OLOO, C.M., ONYARI, J.M., WANYONNI, W.C., WABOMBA, J.N., MUINDE, V.M. 2020. E. Chemistry and Ecotoxicology. v.10, 64-72.
4 MASSARDI, M. M; MASSINI, R. M .M; SILVA, D. J. 2020. The Journal of Engineering and Exact Sciences. v. 6, 1-9.
5 MAPA. 2023. Anuário da Cerveja 2022.
6 CORREIA, L. F., BARROS, J. M. H. F., MARINHO, A. F; CLERICUZI, G, Z; SOUZA, K. 2020. R.S Development. v. 9, p. 730997781.
7 ZANELLA, O. 2012. Sorção de Nitrato em Carvão Ativado Tratado com CaCl2. Porto Alegre. UFRGS.
8 TIZZIANI, I. M. Avaliação da secagem do bagaço de malte para aplicação como biossorvente. 2021. UTFPR, Francisco Beltrão.

ACKNOWLEDGEMENTS

Dedicated thanks to ÂNIMA, UFBA, UFRN, CNPQ, FAPESB, IBTR and UNIFACS who made the research possible.