EVALUATION OF MANGO LEAF(*Mangifera indica*) IN NATURE AS ADSORBENT FOR CRYSTAL VIOLET DYE

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ABSTRACT

Mango production in the Northeast region in Brazil results in a significant amount of residue, notably the leaves, which have potential for sustainable applications. This study focused on the adsorption capacity of crystal violet (VC) dye by mango leaves (ML). In addition to determining the point of zero charge (pHpcz), adsorption tests were carried out using in nature biomass, following a 2^2 composite factorial design. Variables included pH (5 and 9) and initial concentration of VC (100 and 300 mg/L), with the midpoint set at (7, 200 mg/L). The responses evaluated were the percentage of dye removal (R%) and the adsorption capacity (AC). The ideal range for %R was 240 to 300 mg.L^{-1} for concentration and 5.2 to 8.5 for pH, while the optimum point for AC was 300 mg.L^{-1} and pH 9.

Keywords: Adsorption. Mango Leaf. Crystal Violet. Environmental Contamination.

1 INTRODUCTION

The textile sector, considered one of the largest segments of the industry, presents a significant growth perspective with the increase in electronic sales platforms, expected to generate around 3 billion dollars by 2030. However, this growth also implies a considerable increase in consumption of potable water, especially in the washing, bleaching and, mainly, dyeing phases, where the dye is fixed to the fabric. According to the United States Environmental Protection Agency (USEPA), a minimum of 40 liters of clean water is needed to color 1kg of fabric, and this value may increase depending on the dyeing process and the raw material used[1].

Crystal violet, a synthetic base dye, is widely used in industry, including leather processing, fabric dyeing and veterinary drug, providing identity and visual appeal to goods. Annually, more than 10,000 tons of synthetic dyes are used globally, but around 10% to 15% of these dyes are released as effluents into water bodies, often without effective treatment[2]. Due to their aromatic structure, these dyes face significant biodegradation challenges, resulting in the adsorption and reflection of sunlight, hindering the photosynthesis of aquatic flora and negatively impacting the ecosystem, leading to a reduction in dissolved oxygen[3]. Crystal violet is dangerous to human health, because fish can easily absorb the compound, converting it into leucocrystal violet. This derivative is associated with harmful effects, such as teratogenic, carcinogenic, clastogenic changes and reproductive disorders in women. Furthermore, effluents containing crystal violet can cause dermatitis and skin irritation when they come into contact with the skin[4].

Adsorption with biomass is recognized as an effective treatment method, notable for its ease of operation, low cost and absence of inhibitory by-products. ML has gained global prominence due to its remarkable adsorption power. Tests with ML in nature for the adsorption of the cationic dye methylene blue showed significant results, achieving a removal of 95-98% in concentrations of 25-200mg.L-1[5]. Brazil, as the sixth largest mango producer in the world, stands out with a production of 1,546,375 tons in 2022, reaching a productivity of 19,817 kg/ha in an area of 78,033 hectares. The Northeast region leads this production, contributing 80.39% of the total, especially the states of Pernambuco and Bahia, which together produced 444,750 and 633,151 tons, respectively[6]. During cultivation, the natural fall or cutting of many mango leaves results in large amounts of biomass with high added value. Given this scenario, the objective of this study is to evaluate the removal percentage and adsorption capacity of the crystal violet dye, using mango leaves as an adsorbent. The work seeks to improve the understanding and effectiveness of this process, aiming to contribute to sustainable and efficient solutions in the treatment of dyes in the environment.

2 MATERIAL & METHODS

Sample Preparation: Initially, the LM samples were washed rigorously until the water reached transparency and no odor, ensuring the complete removal of impurities and residues. They were then subjected to drying in an oven at 100 ºC for 12 hours, aiming to reduce humidity to levels suitable for subsequent processing phases. The dehydrated leaves were crushed in a ball mill (PM 400 - Retsch), seeking to achieve a particle size of approximately 0.150 mm and sieved (BERTEL). Finally, the OHRUS humidity analyzer was used to determine the moisture content of the material to ensure a content of less than 10%.

Point of Zero Charge (pHpcz): A mixture was prepared containing 50 mg of biomass in 50 mL of water, varying the pH from 2 to 12 with adjustments using NaOH 0.1 mol.L^{-1} and HCL 0,1 mol.L^{-1} solutions. After 24 hours in equilibrium, new pH measurements were carried out, the values obtained were used to construct the graph of final pH versus initial pH, aiming to identify the ideal pH for the adsorption process.

Adsorption Test: With the intention of optimizing the adsorption process, a 2^2 factorial design was carried out, consisting of two factors, initial concentration of the dye and pH, at two levels, with three repetitions of the central point, totaling 7 experiments, having as a response surface the percentage of removal of the crystal violet dye (%R) and the biomass adsorption capacity (AC), as represented in Table 1.

Table1. Adsorption test conditions

Levels	pH	Initial Conc. VC (mg.L^{-1})
-1	5	100
0	7	200
1	9	300

Initially, 250 mL of a 100 mg.L^{-1} CV solution were prepared and then 50 mL of this solution was transferred to two different beakers, one beaker adjusted to pH 5, while the other was adjusted to pH 9 using a pH meter (AZ-86505). The same procedure was performed for a VC 300 mg.L^{-1} solution. For the central point solution, 250 mL of VC 200 mg.L^{-1} was prepared, transferring 150 mL to a beaker to adjust pH 7.

After preparing the solutions, 0.2g of ML and 50 mL of VC 100 mg.L^{-1} were mixed in an Erlenmeyer flask, repeating the procedure for VC 100mg.L^{-1}-pH 9, 300mg.L^{-1}-pH 5 and 300 mg.L^{-1}-pH 9 solutions, in addition to 200 mg.L^{-1}-pH 7. Incubation occurred under shaking at 250 rpm for 160 minutes at room temperature. After this time, the samples were centrifuged at 3600 rpm for 15 minutes and subjected to UV-VIS analysis to determine absorbance, for subsequent construction of the calibration curve and, consequently, determination of the final concentration of the CV solution. The percentage of dye removal and the adsorption capacity of the adsorbent were calculated using Equations 1 and 2, respectively.

$$RD\ (\%) = \frac{Ci - Ce}{Ci} * 100 \qquad (1)$$

$$CA = \frac{Ci - Ce}{X} * V \qquad (2)$$

3 RESULTS & DISCUSSION

Point of Zero Charge(pHpcz): pHpcz is a characteristic that defines the pH at which a solid exhibits neutrality between positive and negative charges. This property is crucial to predict the surface charge of the adsorbent in relation to pH, because when the pH exceeds the pHpcz value, the surface acquires negative charges, and vice versa. This phenomenon has significant implications for the interaction between solid material and chemical species in solution[7]. Figure 1 shows the initial and final pH values for determining the FM pHpcz.

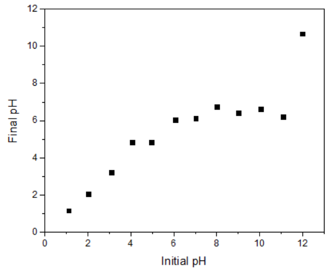

Figure 1. Determination of the pHpcz of the ML.

Based on the results obtained, the pHpcz of the FM sample was determined as 6.38, calculated from the arithmetic mean of the points on the curve that demonstrated stability. This value indicates that the adsorption of cationic compounds, such as crystal violet dye, is facilitated when the pH of the solution is higher than the pHpcz of the FM, due to the increase in anions on the surface of the biomass. A study in the literature found a pHpcz of the fresh mango leaf equivalent to 5.6[8], suggesting that the ideal pH for the adsorption of crystal violet dye should be neutral or alkaline. Variations in results can be attributed to different biomass planting regions, as well as variations in climate and soil conditions.

Figure 2 shows the response surfaces (A) and contour (B) of the optimal conditions for removing the VC dye by ML, whose initial concentrations are between 240 and 300 mg.L^{-1} and the pH is between 5.2 and 8.25.

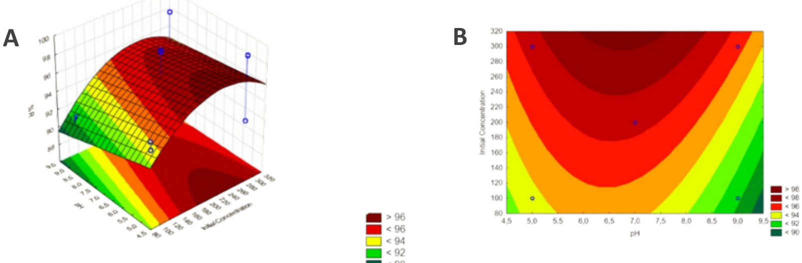

Figure 2. Response surface (A) and contour (B) for the percentage of VC dye removal

Figure 3 shows the response surfaces (A) and contour (B) of the optimal conditions of FM adsorption capacity, whose concentrations are between 240 and 300 mg.L^{-1} and the pH, between 5.2 and 8, 25.

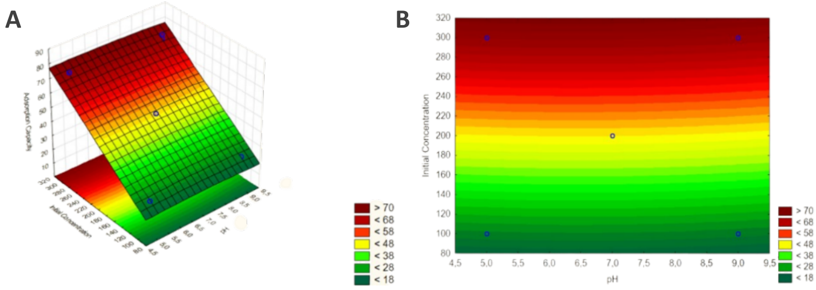

Figure 3. Response surface (A) and contour (B) for adsorbent removal capacity

When analyzing the Pareto Diagram regarding the percentage of VC removal (Figure 4A), it was found that the variables initial concentration (1L), (Q), pH (2L) and initial concentration versus pH (1L*2L) do not match were statistically significant, at a 95% confidence interval, and were therefore eliminated from the model. In relation to the Pareto Diagram (Figure 4B), it was found that only the initial concentration of VC (2L) had a significant influence on the adsorption capacity of the ML.

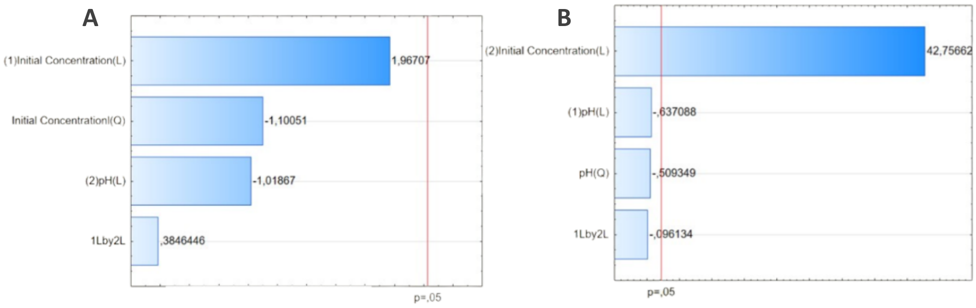

Figure 4. Pareto diagram percentage of VC removal (A) and FM adsorption capacity (B).

4 CONCLUSION

Statistical analysis of the results indicated that none of the variables studied had a significant influence on the adsorption of the Crystal Violet (CV) dye by the ML adsorbent. However, it was observed that the initial dye concentration had a significant impact on the adsorption capacity of ML, which highlights the adsorbing power of ML and suggests its potential to adsorb effectively at higher concentrations. To optimize adsorption conditions, future studies should explore other variables. Furthermore, it is crucial to perform isothermal studies to understand the equilibrium relationship between the dye concentration in the liquid phase and the amount adsorbed on the ML. Likewise, kinetic studies are essential to elucidate the dynamics of adsorption over time.

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