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Study of Methylene Blue Adsorption in Aqueous Solution Using Pineapple Crow as Adsorbent

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Abstract

Currently, contamination of drinking water from a wide range of pollutants is increasing, necessitating the development and characterization of low-cost adsorbents for their application in water pollutant adsorption to purify these effluents. This study employed pineapple crown treated with sodium and potassium hydroxides for the adsorption of methylene blue dye in aqueous medium, and characterized this adsorbent to understand how the adsorbate interacts with the adsorbent. Adsorption capacities were found to be 104.24 mg g^{-1}, 130.26 mg g^{-1}, and 138.99 mg g^{-1} for untreated, NaOH-treated, and KOH-treated adsorbents, respectively. The results underscore the effectiveness of alkali-treated pineapple crown as a promising adsorbent for pollutant removal from water, highlighting its potential application in water purification processes. This research contributes to addressing the critical need for sustainable and efficient methods to mitigate water pollution and ensure the availability of clean drinking water. The highest B/A ratio resulted in the best adsorption capacity in the material treated with KOH.

Keywords: adsorption; methylene blue; pinneaple

1. Introduction

Aquatic pollution is a serious environmental problem that affects water quality and ecosystem health. Among the pollutants, industrial dyes are particularly harmful because they are resistant to degradation, accumulate in water bodies, and are toxic to aquatic life. These dyes alter the transparency of the water, interfering with the photosynthesis of aquatic plants and negatively impacting the entire food chain. Additionally, they can pose health risks to humans through the contamination of drinking water and the consumption of contaminated aquatic organisms[1][2].

Among these dyes, methylene blue can cause serious harm to aquatic bodies and human health. In aquatic ecosystems, it is highly toxic to fish, invertebrates, phytoplankton, and algae, potentially altering water quality and affecting the food chain. For human health, exposure to methylene blue can result in intoxication, methemoglobinemia, dermatological irritation, allergic reactions, and neurological effects. Due to these risks, it is crucial to rigorously monitor and control the use of this compound to prevent environmental contamination and health impacts[3][4].

The adsorption of dyes using biomass waste is a promising technique for removing pollutants from water bodies. Materials such as fruit peels, sugarcane bagasse, sawdust, and other agro-industrial wastes can be converted into effective adsorbents due to their high availability and adsorption capacity. These biomaterials are sustainable, low-cost, and exhibit good adsorption properties due to their porous structure and the presence of functional groups on their surface. Using biomass waste not only helps mitigate aquatic pollution by removing toxic dyes but also promotes sustainable waste management, contributing to an

ecological and economical approach to wastewater treatment[2][4]. Based on this, the present work aims to study the adsorption of methylene blue using pineapple crowns, which are an agricultural waste produced on a large scale in Brazil.

2. Materials and Methods

2.1 Preparation and pre-treatment of the samples and Characterization of the Adsorbent Material

The pineapple crown used in this work was obtained from open-air markets in Feira de Santana - BA. After collection, the material underwent the following steps: I- cut into small slices; II- pre-dried in the sun to remove excess moisture; III- dried in a Nova Ética 330D oven at 80°C to constant weight; IV- ground in a Willye knife mill; V- washed with deionized water using a Quimis® automatic mixer and dried again in an oven at 105°C to constant weight. The biomass was then treated with sodium and potassium hydroxides for 10 minutes at room temperature, using 5 grams of biomass for 80mL of 0.1mol L^{-1} activating solution. The resulting material was filtered, washed with deionized water, and dried at 105°C for 24 hours in an air-circulating oven.

Morphological analysis was performed using a Hitachi S-3400N scanning electron microscope. TG analysis was done with a Shimadzu TGA-60H from 25 to 1000°C at a heating rate of 10°C min^{-1} under a nitrogen flow of 50 mL min^{-1}. The pH at the point of zero charge (pHPZC) was determined by the solid addition method. The difference between the final pH and initial pH (ΔpH) was plotted against the initial pH, with the point where ΔpH = 0 taken as pHPZC[2][4]. Surface acidity and basicity studies were conducted as described by [5]. Surface acidity was determined using a 0.1mol L^{-1} sodium hydroxide solution, and surface basicity was determined similarly using a 0.1mol L^{-1} HCl solution. Results were expressed in mmol of H^+ or OH^- per gram of adsorbent.

2.2 Adsorption Tests

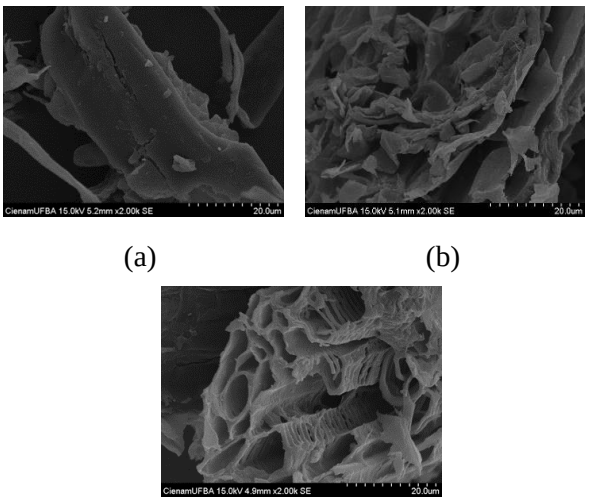
Equilibrium studies were conducted by placing approximately 100 mg of the samples in individual 100 mL flasks, to which 15 mL of solutions at concentrations of 100, 200, 400, 600, 800, and 1000 mg L^{-1} were added. The mixtures were agitated for 24 hours at 25ºC. After agitation, the samples were filtered and the final concentration was determined using a Femto Plus UV/VIS spectrophotometer at 660 nm for methylene blue. The adsorption capacity was determined using equation 1

$$qe = \frac{(Co - Ce)v}{m} \quad (1)$$

Where qe is the adsorption capacity (mg g^{-1}); Co is initial adsorbate concentration (mg L^{-1}); Ce is adsorbate concentration at equilibrium (mg L^{-1}); V is solution volume (L) and m is adsorbent mass (g)

3 Results and Discussion

Figures 1 (a), (b) and (c) show the results of electronic microscopy analysis of the samples taken.



(a) (b)

(c)

Fig. 1. Micrography of (a) *In natura* sample (b) Treated with KOH sample and (c) Treated with NaOH sample

The untreated material exhibited a dense and slightly rough surface. Upon alkaline treatments, an open structure with large cavities was observed, indicating a significant difference between the base-treated materials and those without any chemical treatment. This could be attributed to alkaline treatments partially or completely removing certain biomass macromolecules such as pectin, hemicellulose, and lignin [6]. To confirm the removal of these macromolecules, thermogravimetric analysis was conducted, and

their respective deconvolutions are shown in Figure 2. Table 1 presents the percentage relationship of the macromolecules analyzed by thermogravimetry.

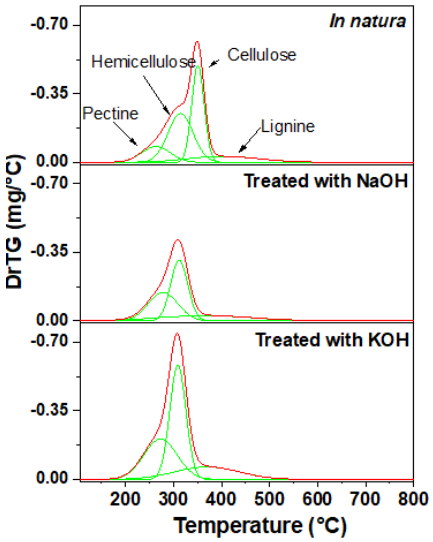


Fig. 2. Deconvolutions of Thermogravimetric Analysis

Table 1. Percentage relationship of macrocomponents analyzed by thermogravimetry

Macro (%)	Pectine	Hemicellulose	Cellulose	Lignine
In natura	13,75	36,96	36,37	12,92
Treated with NaOH	0	35,39	44	20,61
Treated with KOH	0	33,62	45,27	20,11

The decomposition of pectin occurs up to 200°C, hemicellulose decomposes between 200-300°C, cellulose between 350-400°C, and lignin between 250-500°C [7]. From the deconvolution analysis, it was observed that alkaline treatments completely removed pectin and partially removed hemicellulose, relatively increasing the proportion of cellulose and lignin. Considering that the hydroxyl groups, primarily in cellulose, mainly correspond to alcoholic hydroxyls, i.e., weak acids, they were neutralized by activating agents suggesting the formation of the (C-O-M^+) group on the surface [7]. The removal of these macromolecules generated a surface property that maximized the adsorption of methylene blue dye. This maximization can be understood because alkaline treatments make the hydroxyl groups of cellulose more accessible, thereby increasing the adsorption capacity. Table 2 presents the results obtained for the surface acidity and basicity of the studied adsorbents.

Samples	Basicity (mmol g^{-1})	Acidity (mmol g^{-1})	Ratio B/A
In natura	9,08	2,32	3,91
Treated with NaOH	9,79	2,53	3,87
Treated with KOH	8,61	1,36	6,33

The ratio between the quantity of basic sites and acidic sites is an indicator of surface acid-base characteristics [8]. If B/A > 1, the surface has more basic sites, indicating a negative charge. If B/A = 1, the quantity of basic sites equals that of acidic sites, indicating a neutral surface. If B/A < 1, the surface has more acidic sites, indicating a positive charge [8]. All samples showed B/A > 1, confirming a predominance of basic sites, hence an adsorptive potential for cationic dyes such as methylene blue. Treatment with KOH resulted in the highest B/A value, suggesting this adsorbent will likely exhibit superior removal of methylene blue dye. Figure 3 shows the results for zero charge pH.

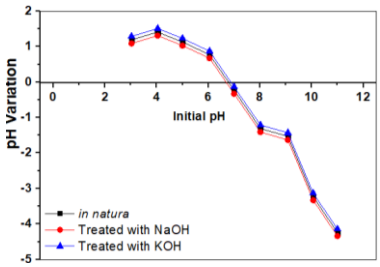


Fig. 3 The zero point charge (pHZPC) of the adsorbents.

Generally, the surface of the adsorbent becomes positively charged when it accepts protons from an acidic solution or negatively charged when it releases protons into a basic solution. A neutral surface is represented by pHpzc [2][4]. Analysis of the zero point charge pH (pHpzc) indicates that the studied adsorbents will interact better with anions at pH < 7, thus carrying a positive charge. At pH > 7, the surface will interact more favorably with cations, carrying a negative charge. Therefore, adsorption of methylene blue, which is a cationic and basic dye [2][4], will be favored at pH values above 7, as used in the studies with a pH of 6.8 for

methylene blue removal. Figure 4 displays the adsorption isotherms obtained in this study.

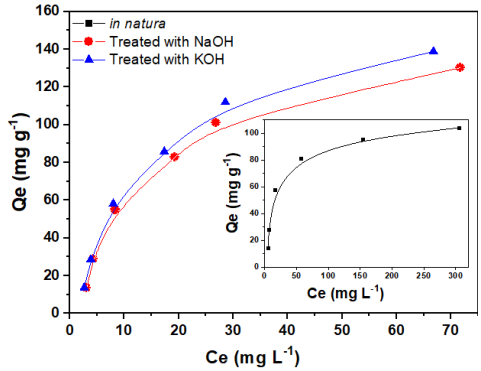


Fig. 4 Adsorption isotherms of methylene blue dye for the different studied adsorbents.

The untreated adsorbent exhibited a removal of 104.24 mg g^{-1} of methylene blue dye. Results for the base-treated adsorbents were more satisfactory. The amounts adsorbed by these adsorbents significantly increased compared to the untreated adsorbent, with removal capacities of 130.26 mg g^{-1} and 148.99 mg g^{-1} for NaOH and KOH treatments, respectively. These results can be directly attributed to the B/A ratio, indicating that higher ratios enhance removal efficiency. Additionally, it can be suggested that KOH treatment yielded superior results due to residual potassium remaining from the activation agent reacting with surface hydroxyl groups, even after successive washings. This induces local charge separation and polarization (C-O-K^+), thereby facilitating the adsorption process.

4 Conclusions

SEM analysis showed basic treatments altered pineapple crown morphology. Alkaline treatments partially removed hemicellulose and completely removed pectin, maximizing methylene blue dye adsorption. B/A ratio > 1 for all adsorbents indicates predominance of basic sites, effective for cationic pollutants. Zero point charge pH favored dye adsorption at pH > 7. Adsorption isotherms indicated alkaline treatments significantly increased adsorption compared to untreated, with KOH-treated adsorbent achieving 138.99 mg/g removal.

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