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Adsorption studies of malachite green dye on activated carbon prepared from cocoa biomass

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Abstract

Synthetic dyes are organic compounds widely used in many industrial branches, such as textiles, pharmaceuticals, plastics, cosmetics, leather, photography, paper and food. When discarded into water resources without treatment, they can cause damage in aquatic life, reducing water reoxygenation and problems associated with photosynthetic activity reduction due to blocking the sunlight as well as causing alteration in metabolic processes of aquatic fauna and flora, resulting in microtoxicity for organisms. aquatic. The colorant malachite green (MG) is used in the textile industry to dye various materials and also act as an antiseptic to treat infections in fish. Despite its applications, MG has high toxicity, which causes allergies and skin irritation. This study explored the application of activated carbon prepared from cocoa biomass residues (ACC) for the removal of organic dyes. The ACC was characterized by Thermogravimetric Analysis and X-ray Diffraction. Adsorption isotherm studies were carried out using the MG dye as model compound. Dye removal was monitored spectrophotometrically. The Langmuir and Freundlich models were tested for equilibrium studies, and three kinetic models were evaluated: zero-order reaction, pseudo-first order and pseudo-second order. The experimental data fitted better in the pseudo-second order model, and the thermodynamic study indicated that the adsorption is endothermic and spontaneous process. The results showed that ACC was efficient in removing synthetic dyes, suggesting that cocoa shell residues can be used to produce activated carbon in a sustainable way, useful in the adsorption of pollutants.

Keywords: pollutants, adsorbent, kinetics, chemical equilibrium, thermodynamics.

1. Introduction

Textile dyes are complex organic substances that selectively absorb visible light, appearing colored due to chromophore groups in their structures [1]. Textile industries generate more than 92 million tons of waste and consume 1.5 trillion litre of water per year, contributing to 20% of water pollution [2].

The dye malachite green (MG) is used in the textile industry to dye cotton, jute, paper, silk, wool and leather products, in addition to serving as an antiseptic to treat parasites and infections in fish [3,4]. Despite its diverse applications, MG has high toxicity and can cause allergies and skin irritation, damage the liver, kidneys and heart, producing teratogenic effects on the nervous system and brain [4]. The use of biomass waste for the production of activated carbon can be considered a promising and sustainable approach in the decontamination of water contaminated by dyes. This process not only offers a possible solution for the removal of organic pollutants, but also enrich agro-industrial waste, such as coconut shells, sawdust, sugar cane bagasse and cocoa shells, which would otherwise be discarded [5,6]. Therefore, the objective of this work is to investigate the adsorption of malachite green dye using cocoa biomass, an agricultural residue abundant in Brazil.

2. Materials and Methods

2.1. Preparation and characterization of the adsorbent

The cocoa shells were obtained in a rural area in the city of Amargosa/BA, and were characterized according to the methods (American Society for Testing and Materials) ASTM E1757, D2867 and D5832, thermogravimetric analysis and X-ray diffraction.

The cocoa fruit shells were weighed and cut into small pieces and then dried in an oven for 24 hours at a temperature of 110 °C, sieved (80 –100 mesh) and then pyrolyzed under N_2 flow (150 $mL.min^{-1}$) in a stainless steel reactor (with ϕ = 5.0 cm) placed in a tubular furnace at a heating rate of 5 $°C.min^{-1}$ up to 800 °C, remaining at this temperature for two hours. The resulting charcoal was washed with a 1 $mol.dm^{-3}$ hydrochloric acid (HCl) solution, followed by washing with distilled water until reaching the neutral pH. Finally, the activated carbon was dried at 105 °C for 24 hours to remove moisture. After drying, the activated carbon was macerated and weighed.

2.2. Adsorption studies of MG dye on activated carbon

Adsorption isotherm studies with the dye Malachite Green ($C_{23}H_{25}ClN_2$) on ACC were carried out for five systems (with concentrations: C_1=140.6 $mg.dm^{-3}$; C_2=175.8mg. dm^{-3}; C_3=281.2$mg.dm^{-3}$; C_4=316.4 $mg.dm^{-3}$; e C_5=351.6 $mg.dm^{-3}$) at 30ºC and under stirring at 750rpm for 48h. Monitoring the removal of the dye from the solution was carried out by reading a spectrophotometer. Spectrophotometer scans were performed at times t_0, t_1, t_2, t_3, t_4, t_5, t_6, t_7, t_8, t_{24} and t_{48}. The amount of dye adsorbed in equilibrium with the dye in solution was obtained using equation 1.

$$q_e = \frac{(C_0 - C_e) * V}{m} \quad (1)$$

where, q_e = amount of adsorbate retained in the adsorbent and in equilibrium with the solution; C_0 = Initial adsorbate concentration; C_e = Concentration of adsorbate in solution at equilibrium; V = volume of the solution; and m = mass of the adsorbent.

To describe the adsorption kinetics, zero-order, pseudo-first-order and pseudo-second-order reactions kinetic models were tested.

The temperature effect was studied on the adsorption experiments in a range between 30 ºC – 66 ºC using a solution with concentration 281.28 $mg.dm^{-3}$ and the measurement was carried out at different time using the spectrophotometer.

3. Results and Discussion

3.1. Preparation and characterization of the adsorbent

The high presence of potassium oxide in this biomass promotes the production of materials without the need for additional activating agents. Potassium acts as a natural activating agent, resulting in materials that exhibit good textural properties [7].

Therefore, the term activated carbon was considered due to the high mineral content, mainly potassium (79.53%) present in the biomass, which enabled a natural activation of the prepared coal.

The results of immediate analysis of cocoa biomass applying ASTM standards methods were 11.2% moisture, 6.7% ash, 79.6% volatiles and 2.3% fixed carbon. Cocoa biomass has a high volatile content and relatively low ash content, which favors the production of carbon.

The DTG curves in Figure 1 were deconvolved to quantify the biomass components using Gaussian curves and assuming correlation coefficient R^2= 0.9983. The analysis of the thermal decomposition of biomass residues presented thermogravimetric curves, Figure 1, with three regions of mass loss show one event related to hemicellulose (between 160-400°C), another event at 270-400°C attributed to cellulose and a third event referring to lignin at 160-600°C.

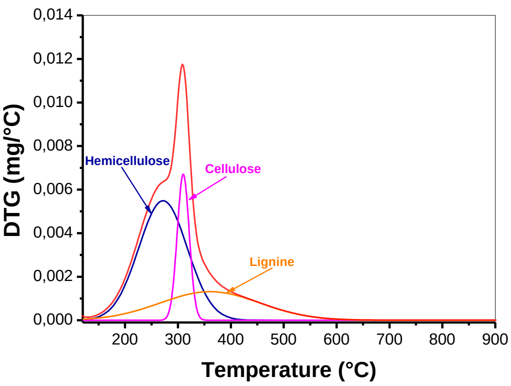

Fig. 1. Thermogravimetry and deconvolution of the derivative of the thermal analysis in N_2 atmosphere of cocoa biomass on a dry basis.

Table 1 presents the estimated composition of lignocellulosic components by volatilization obtained by the Gaussian area of the macrocomponents. Hemicellulose had a content of 44.75%, cellulose 13.46% and the total lignin was 22.02%.

Lignin content is an important factor as it influences the formation of fixed carbon, and the observed content is similar to the content normally found in biomasses for activated carbon production, ranging between 13%-40%.

Table 1. Macrocomponent composition of cocoa biomass.

macrocomponent	Peak region (°C)	%
Hemicellulose	160 - 400	44.75
Cellulose	270 - 400	13.46
Lignin	160 - 600	22.02

The powder X-ray diffraction patterns of the biomass waste sample and coal are shown in Figure 2. The samples are mainly made up of an amorphous carbon matrix [8].

For ACC, two characteristic halos of amorphous materials are observed at approximately 2θ = 29.28º and 43.10º. These halos indicate a small amount of crystalline material that can be related to the graphitic structure [8,9].

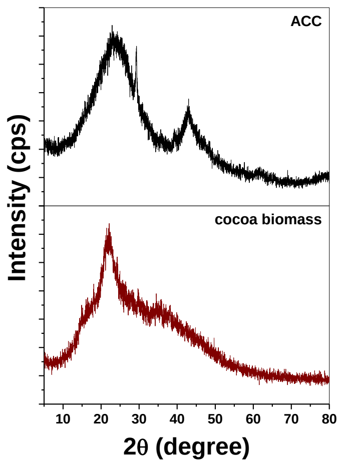

Fig. 2. Diffractogram of biomass (above) and ACC (below).

The yield obtained in the preparation of activated carbon from cocoa biomass was 25.95%. The yield observed herein is in accordance with the work developed by Coutinho (2018), where the yield was 38.87% using an activation temperature of 380 ºC and a yield of 38.76% was obtained by Gonçalves (2021) using an activation temperature of 500 ºC.

3.2. Adsorption studies of MG dye on activated carbon

Adsorption isotherm studies (figure 3) were carried out for five solutions with different concentrations over a period of 48h. Dye removal was relatively rapid in the initial stages of the process, until equilibrium was reached. The time required to establish equilibrium, using ACC as an adsorbent, was closely 4 hours.

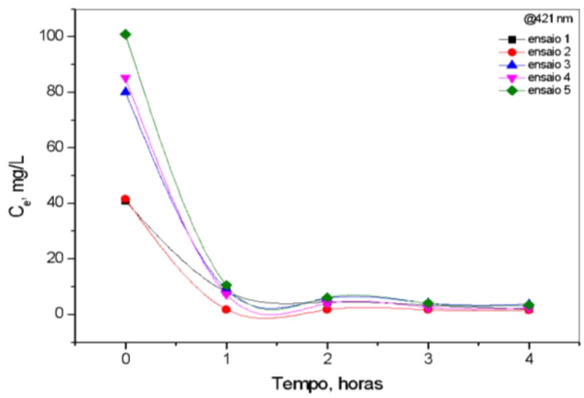

Fig. 3. Kinetic study of MG adsorption on activated carbon

The pseudo-second order kinetic model was that fitted better to the experimental data.

Linear adjustments were applied to the experimental data set using the Langmuir and Freundlich equations. The experimental data did not fit the tested models. Eventually, these adsorption isotherm models may not be the most suitable for this type of reaction scenario. However, it was not possible to perform modeling using other mathematical models.

Using the data obtained in the experiments, the thermodynamic parameters could be estimated. The $\Delta_{ads}H$ indicated that the reaction is endothermic and the $\Delta_{ads}S$ and $\Delta_{ads}G$ (in the temperature range) values indicated that the reaction occurs spontaneously. Also, increasing the temperature, the $\Delta_{ads}G$ became more negative.

Nascimento et al., (2014) p.82, highlight that "negative values for $\Delta_{ads}G$ accompanied by positive values for $\Delta_{ads}S$ indicate that the adsorption process is spontaneous and that the adsorbent has an affinity for the adsorbate" [10].

4. Conclusions

The prepared carbon derived from cocoa biomass showed good efficiency in removing the synthetic malachite green dye, leading to the conclusion that cocoa shell residue can be used as a potential precursor for the production of activated carbons, which can be used in adsorption of pollutants.

The fact that cocoa biomass residues are not used by the agroindustry, and are most often discarded in the trash, makes them a cheaper alternative for the production of activated carbon and also contributes to sustainability and adequate final disposal of waste solids. The experimental data for the kinetic studies were better adjusted to pseudo-second order reactions, and the equilibrium studies did not satisfactorily fitted the tested Langmuir and Freundlich models. However, it was not possible to perform modeling using other mathematical models. The thermodynamic study indicated that the adsorption process is endothermic and the ACC-MG interactions occurred spontaneously.

Acknowledgements

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