EVALUATION OF CUMBARU (*Dipterys Alata*) ENDOCARP IN THE ADSORPTION OF CONGO RED

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ABSTRACT

Textile industry effluent plays a significant role in environmental degradation, due to dye rejects, which impact physicochemical properties of water. To mitigate the pollution, adsorption techniques can be used in tertiary effluent treatment, and agro-industrial waste is a sustainable option to adsorb organic compounds. The objective of this work is to evaluate the cumbaru (*Dipteryx alata*) endocarp as adsorbent for Congo Red dye. Composite Central Design (CCD) was used to analyse the effects of pH, temperature and mass of adsorbent on the responses amount adsorbed and efficiency of removal and the adsorption experiments were carried in a shaker at 200 rpm for three hours. The characterization of the structure of the adsorbent was done by FTIR, TGA and point of zero charge, whose results were coherent with the literature. The CCD analysis identified, with α = 95%, statistical relevance of mass, temperature, pH and temperature-pH interaction for both responses. The response surface model had R^2 of 0,91 and 0,98 for efficiency and amount adsorbed, respectively. The method determined optimal conditions of operation at 40 ºC, pH 5,24 and 0,3 g of adsorbent. The cumbaru proved to be a sustainable and effective option to remove Congo Red dye from aqueous solution.

Keywords: Adsorption. *Dipteryx alata*. Central Composite Design. Congo Red dye. Effluent treatment.

1 INTRODUCTION

Current social and environmental context reveals that the impact of human activity is complex, both qualitatively and quantitatively, Pollution is one of the many problems associated with industrial production and consumption, with accidental occurrences and environmental contamination, especially in areas with low prevention index[1]. In Brazil, even though there is significant availability of water resources, there are gaps in their distribution, with regions suffering from water shortage and textile industries degrading the water that is available[2].
In order to treat these effluents, there are many options, however, they demand significant long-term investments. Among these techniques, adsorption with activated charcoal is commonly used, but there is crescent interest in alternative, more sustainable options, such as biomass and agro-industrial waste[3]. One of said waste is the endocarp of the cumbaru (*Dipteryx alata*), a fruit from the Brazilian savannah.

In this context, this work had as main goal evaluate the use of cumbaru (*Dipteryx alata*) endocarp as adsorbent to remove Congo Red dye from aqueous solution and analyse, by central composite design, the influence of process variables in the adsorption.

2 MATERIAL & METHODS

The preparation of the cumbaru endocarp was done by washing the raw material with deionized water, followed by drying in a stove at 70 ºC for 24 hours and grinding in an industrial blender. The particles obtained were classified into different sizes of sieves as given by ABNT regulation.

The point of zero charge (PZC) was determined by adjusting the pH of eleven solutions to values equally spaced between 2 and 12[4], then adding 0,5 g of the previously prepared adsorbent and measuring, after 24 hours in a shaker orbiting at 200 rpm, the final pH.
The thermogravimetric analysis was done in a STA 449 F3 Jupiter model (Netzsch), with nitrogen atmosphere, gas flow of 20 mL/min, from 25 to 900 ºC with 10 ºC/min step.
The vibrational spectroscopy in medium infrared with Fourier transform (FTIR) was obtained from a BOMEN Hartmann & Braun - The Michelson series MB-100 spectrometer, with spectral window 4000 – 500 cm-1 of resolution of 4 cm-1, 6 cycle accumulation and scanning velocity of 0,2 cm/s.

Central Composite Design (CCD) of experiments was implemented to evaluate the impact of the independent variables pH, temperature and mass of adsorbent (factors) on the dependent variables amount adsorbed and removal efficiency (responses). The values of the factors are exposed on Table 1.

Table 1 Factors of the CCD, their levels and values

Factor	Symbol	Codified values				
		-1,68	-1	0	1	1,68
pH (-)	X1	4	5	6,5	8	9
Temperature (ºC)	X2	26	28,8	33	37,2	40
Mass of adsorbent (g)	X3	0,1	0,18	0,3	0,42	0,5

The initial concentration of Congo Red dye was 40 g/L and the experiment was conducted in an orbital shaker for three hours at 200 rpm with 15 mL of solution. After that, the samples were centrifuged at 4000 rpm for 20 minutes and the supernatant was analysed in a spectrophotometer to quantify the final concentration. The statistical analysis were carried out in the software Statistica® 12.

3 RESULTS & DISCUSSION

The determination of the point of zero charge (PZC) was done by adjusting a linear equation to the interval between the pH values 4 and 7, which have shown buffer effect as exposed on Figure 1.a. The Equation 1 is the linear equation adjusted. To determine the PZC, the equation was matched to zero and the pH determined was the PZC with a value of 4,45, denoting acid character.

$$\Delta pH = 4{,}12 - 0{,}925 \cdot pH \quad (1)$$

The result from the thermogravimetric analysis is on Figure 1.b, where the main losses of mass are highlighted. The degradation of hemicellulose, cellulose and lignin were pinpointed[6]. The FTIR spectrum revealed characteristic regions for C-H bonds in alkanes and alkenes in 2890 cm^{-1}, common in lignin molecules[7]; for C=O bonds around 1750 cm^{-1}, characteristic of aldehydes, ketones, carboxylic acids and esters.

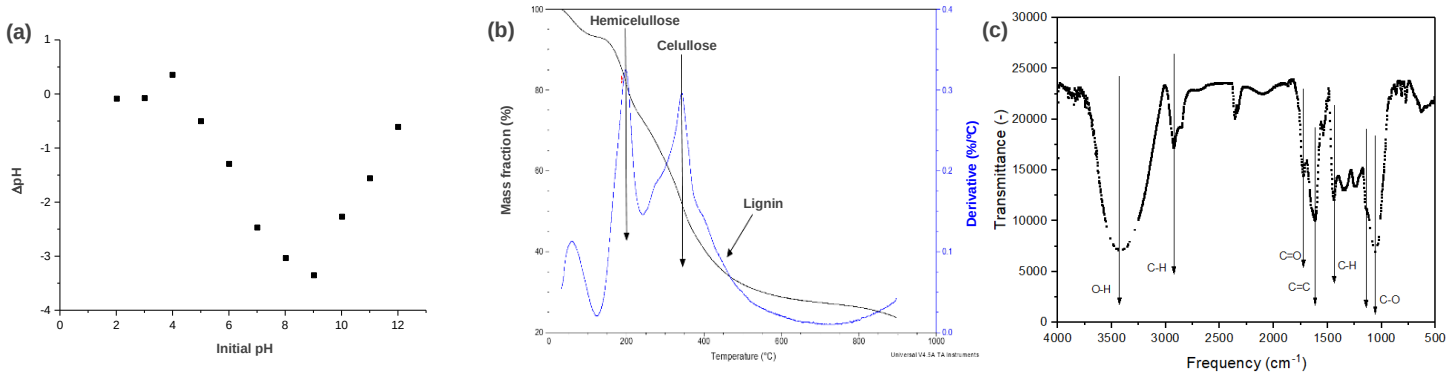

Figure 1 (a) Variation of pH in relation to the initial pH in the PZC experiment, (b) TGA and DTGA curves and (c) FTIR spectrum

The Pareto charts of effects for the removal efficiency and amount adsorbed are in Figure 2a and 2b, respectively. For both responses, the mass of adsorbent was the most influential variable, followed by temperature and pH and, lastly, the interaction term between temperature and pH. The confidence level used was 95%.

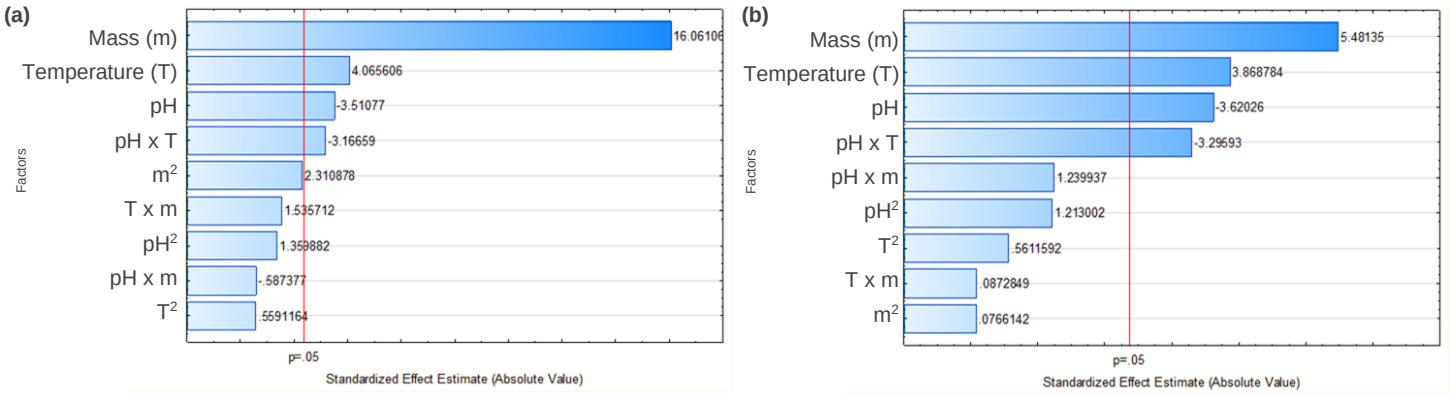

Figure 2 Pareto Charts for (a) removal efficiency and (b) amount adsorbed

Figures 3 and 4 shows the response surfaces for the removal efficiency and amount adsorbed, respectively. There is a non-linear relation between temperature and pH that is negligible in the remaining surfaces. Higher responses are correlated to higher mass, higher temperatures, and lower pH values. The optimum conditions of operation determined by the software Statistica were pH 5,24, 40 ºC and 0,3 g of adsorbent.

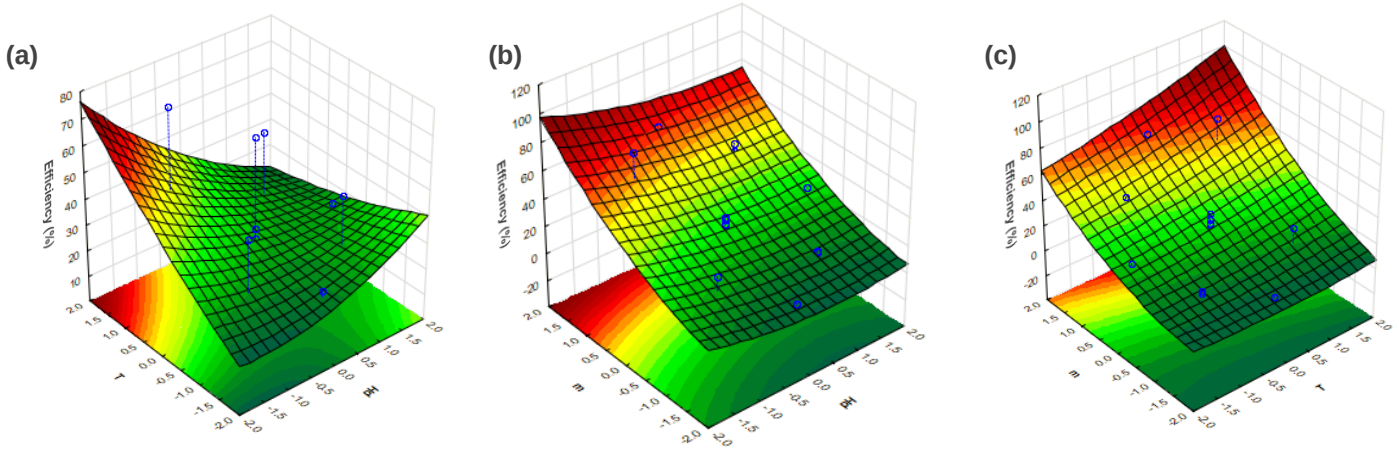

Figure 3 Response surfaces for the removal efficiency in relation to (a) temperature (T) and pH, (b) pH and mass (m) and (c) temperature (T) and mass (m), in codified values, with the third factor fixed in its central value.

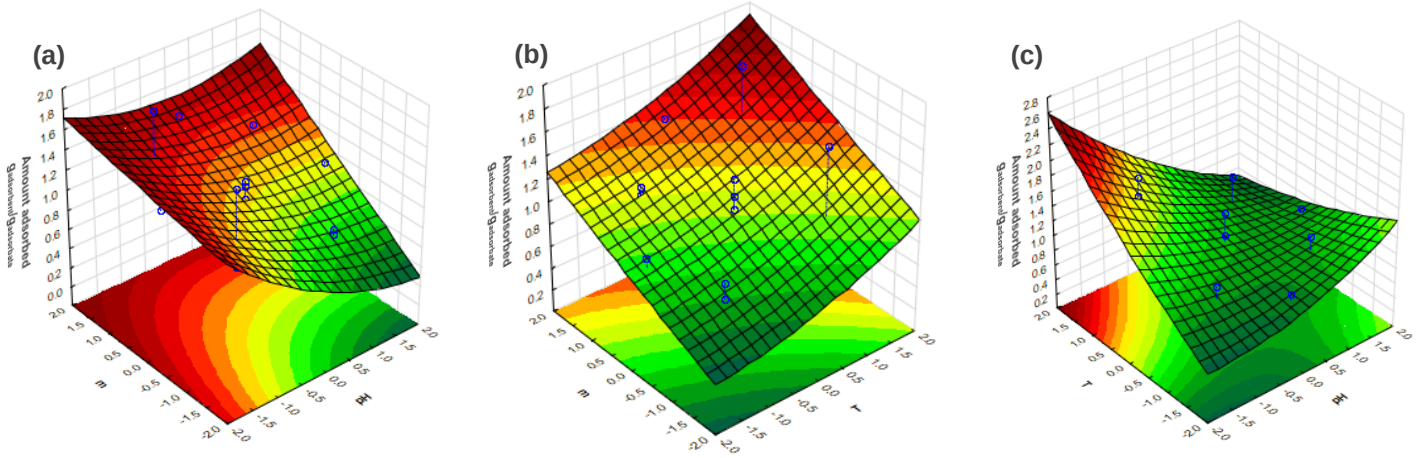

Figure 4 Response surfaces for the amount adsorbed in relation to (a) temperature (T) and pH, (b) pH and mass (m) and (c) temperature (T) and mass (m), in codified values, with the third factor fixed in its central value.

4 CONCLUSION

The cumbaru endocarp has proven to be an effective sustainable adsorbent to remove Congo Red dye from aqueous solution. The FTIR spectrum revealed a adsorbent rich in lignin compatible with literature, the thermogravimetric analysis showed the degradation of the hemicellulose, of the cellulose and of the lignin. The point of zero charge obtained was 4,45, denoting acid character of the material. The variables that influence the removal efficiency and amount adsorbed, determined by the CCD experiment, were, from higher to lower: mass, temperature, pH and pH *versus* temperature interaction. The optimal condition was at 40 ºC, pH 5,24 and 0,3 g of adsorbent.

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