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## Research Article

# STUDY OF ADSORPTION OF RHODAMINE B DYE USING THE RESIDUAL BIOMASS OF MDF AND PORONGO

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### ABSTRACT

The present work evaluated the use of residual biomasses of MDF (Medium Density Fiber) and porongo (*Langenatia siceraria*), as biosorbents, in the adsorption of Rhodamine B dye (RhB) in aqueous solution. The biosorbents were characterized by nitrogen porosimetry, zeta potential (ZP), adsorption kinetics tests and determination of experimental parameters, according to Langmuir and Freundlich models. Among the tested systems, the biomass of MDF showed the highest adsorption capacity (14 %) in relation to the porongo (7.6 %), after 120 minutes of reaction, due to its compatibility of surface charge with RhB, and the largest surface area (11.67 m<sup>2</sup> g<sup>-1</sup> of MDF and 7.33 m<sup>2</sup> g<sup>-1</sup>) and pore volume (0.030 cm<sup>3</sup> g<sup>-1</sup> for MDF and 0.020 cm<sup>3</sup> g<sup>-1</sup> for porongo).

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## INTRODUCTION

Pollution of water resources and their social and environmental impacts are of global preoccupation, due to the increasing scarcity of this resource, associated with the high energy and financial costs associated with its correct treatment. In addition, the agroindustrial materials stand out for the character of waste, which after processing their raw materials, present a lot of added value. The use of agroindustrial residues (residual biomasses) stands out in the production of renewable fuels, chemical products and energy, since their availability ends up solving the problem of accumulation of residues and avoids the contamination of soils and rivers (Ferreira-Leitão *et al.*, 2010). Moreover, the development of appropriate technologies for the treatment of wastes has been of great interest in recent times, in order to preserve natural resources and to comply with norms and legislation on effluent emission standards. Thus, the discharge of a given waste into a water receiver must be within parameters in order to reduce the impact of human activities on the aquatic environment (Zanoni and Carneiro, 2001).

Among these technologies, adsorption is one of the promising alternatives available for the removal of organic pollutants (Crini, 2005), since shows advantages such as simplicity of operation, application of low cost materials (such as

biosorbents), possibility of regeneration of adsorbents and do not generate toxic subproducts (Bhatnagar and Jain, 2005).

In this context, the work aims to evaluate the adsorption capacity of the residual biomass of MDF and porongo, as biosorbents, in the removal of Rhodamine B dye (RhB), through adsorption isotherms and correlating with their textural properties (surface area, diameter and volume of pores) and structural (zeta potential).

## MATERIALS AND METHODS

### Residual Biomass

Residual biomass of MDF (*Medium Density Fiberboard*) and porongo (*Lagenaria siceraria*) were used to evaluate the adsorption capacity acting as biosorbents. Thus, the biomass residuals were initially sampled, according to the Brazilian Association of Technical Standards (NBR 10,007:2004) (Brasil, 2004).

### Characterization of the biosorbents

The residual biomass were characterized according the structural and textural properties. Thus, for the determination of the specific surface ( $S_{BET}$ ), pore diameter ( $D_p$ ) and pore volume ( $V_p$ ) of the biosorbents was used the nitrogen porosimetry

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using in an equipment Gemini 2375 Micromeritics (Micromeritics Gemini VII 2375 Series, United States). The specific surface ( $S_{BET}$ ) were determined by the Brunauer-Emmett-Teller equation (BET method) in the range of  $P/P_0 = 0.05$  to  $0.35$ . The pore diameter and pore volume were determined using the Barret-Joyner-Halenda equation (BJH method). Moreover, the surface charge was determined by zeta potential (PZ) on a Malvern-Zetasizer® model nanoZS (ZEN3600, UK) with closed capillary cells (DTS 1060) (Malvern Instruments, UK) using a laser He-Ne of 4 mW (633 nm).

**Adsorption kinetics**

The kinetic study was performed in batch reactor and in duplicate (with error less than 5%). Thus, the target solution for the test was rhodamine B dye with a concentration of  $20 \text{ mg L}^{-1}$ , where 50 mL of the solution was maintained in contact with residual biomass (biosorbent) at the concentration of  $0.7 \text{ g L}^{-1}$ , under magnetic stirring (150 rpm) for 120 minutes. During the process, 1 mL samples were collected and stored in Eppendorfs® at predetermined times (0, 5, 15, 30, 45, 60, 90 and 120 minutes) and centrifuged (Cientec refrigerated centrifuge, CT-5000R, Brazil), at 5.000 rpm for 20 minutes.

Finally, the variation of the RhB dye concentration over time was determined by reading the absorbance in a spectrophotometer (Cary 100Scan, UV-Vis Spectrophotometers, United States) fitted with a halogen lamp at 553 nm wavelength. Two quartz cuvettes were used to determine the absorbance, one filled with distilled and deionized water (reference cubete) and the other filled with the sample to be analyzed (sample cubete).

Therefore, the absorbance was related to the concentration of RhB through a calibration curve, according to Equation (1):

$$\text{Abs} = 0.2053C(\text{mg L}^{-1}) \text{ with } R^2 = 0.9911 (N=7) \tag{1}$$

**Adsorption Isotherms**

In the study of adsorption, the use of adsorption models is essential to try to propose how the adsorbate can interact with the adsorbent, highlighting the Langmuir and Freundlich isotherm models.

**Langmuir Isotherm**

The Langmuir isotherm states that adsorption occurs at specific adsorbent sites, these being homogeneous and that each site is responsible for the adsorption of a single molecule of adsorbate, and there are no interactions between the molecules adsorbed at neighboring sites (Langmuir, 1918). Thus, to determine the maximum adsorption capacity of the rhodamine B dye in the residual biomass of MDF and porongo, the adsorption isotherm was conducted by analyzing the data through the Langmuir model by Equation (2) (Ozacar and Sengil, 2003).

$$Q_{eq} = \frac{Q_{max} \cdot K_L \cdot C_{eq}}{1 + K_L \cdot C_{eq}} \tag{2}$$

where:

- $Q_{eq}$ : amount of RhB per gram of residual biomass ( $\text{mg g}^{-1}$ );
- $Q_{max}$ : maximum adsorption capacity ( $\text{mg g}^{-1}$ );

$K_L$ : constant of adsorption equilibrium or constant of Langmuir ( $\text{L g}^{-1}$ );

$C_{eq}$ : concentration of RhB in adsorption equilibrium ( $\text{mg L}^{-1}$ ).

Linearizing the Equation (2), the constant  $K_L$  and  $Q_{max}$  can be determined, according to Equation (3):

$$\frac{1}{Q_{eq}} = \frac{1}{Q_{max} \cdot K_L \cdot C_{eq}} + \frac{1}{Q_{max}} \tag{3}$$

**Freundlich Isotherm**

The Freundlich Isotherm admits a logarithmic distribution of active sites, which is a valid treatment when there is no appreciable interaction between the adsorbate molecules. Thus, this model is very applied in heterogeneous adsorption systems, not admitting the existence of a monolayer (Chen and Wang, 2007). The Freundlich equation is described by Equation (4):

$$Q_{eq} = K_F \cdot C_{eq}^{\frac{1}{n}} \tag{4}$$

where:

- $K_F$ : constant of Freundlich, referring to the adsorption capacity;
- $n$ : constant related to the adsorption intensity (dimensionless).

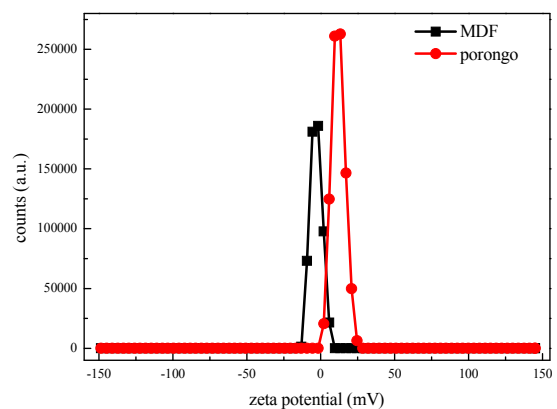
Linearizing the Equation (4), the constant  $K_F$  and  $n$  can be determined, according to Equation (5):

$$\log Q_{eq} = \log K_F + \frac{1}{n} \cdot \log C_{eq} \tag{5}$$

**RESULTS AND DISCUSSION**

**Characterization of Residual Biomass**

Figure 1 shows the zeta potential (PZ) curves of the residual biomass verify their stability and surface charge in order to determine their influence on the adsorption of Rhodamine B (RhB) dye. For the MDF biomass, a peak of  $-3.09 \pm 0.21 \text{ mV}$  and for the porongo of  $13.8 \pm 0.35 \text{ mV}$  was observed. For the adsorption process it is necessary to have a compatibility between this surface potential and the adsorbed molecule load (Toledo *et al.*, 2005). In addition, the RhB molecule is characterized by having a positive charge, that is, a cationic nature (Debrassi *et al.*, 2011; Salleh *et al.*, 2011). Thus, as the MDF biomass is negatively charged and the RhB dye is positively charged, the adsorption capacity tends to be higher on the MDF surface, relative to the porongo, due to attractive electrostatic forces, forming more stable suspensions, since the surface charge does not allow the formation of particle agglomeration (Mohanraj and Chen, 2006).

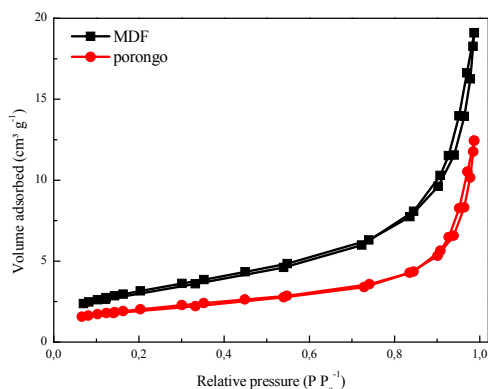


**Figure 1** Zeta potential of the residual biomass

The surface area ( $S_{BET}$ ), pore diameter ( $D_p$ ) and pore volume ( $V_p$ ) of the residual biomass were obtained by the BET/BJH methods, according to Table 1. The  $N_2$  adsorption / desorption isotherms of the residual biomass are presented in Figure 2. According to Table 1, the residual biomass of MDF showed higher surface area ( $11.67 \text{ m}^2 \text{ g}^{-1}$ ) and pore volume ( $0.030 \text{ cm}^3 \text{ g}^{-1}$ ), in relation to porongo biomass ( $7.33 \text{ m}^2 \text{ g}^{-1}$  and  $0.020 \text{ cm}^3 \text{ g}^{-1}$ , respectively). For the adsorption process, it is necessary that the biosorbent presents a considerable surface area in order to have a greater number of active sites and thus a greater capacity of adsorption of the pollutant (Cessa *et al.*, 2009). Moreover, the isotherms are type IV with H3 hysteresis curves, according to the Brunauer, Deming, Deming and Teller (BDDT) classification, and the pore diameter distribution suggests mesoporous structures (2-50 nm) (Iupac, 1985).

**Table 1** Surface area, pore diameter and pore volume of the residual biomass samples

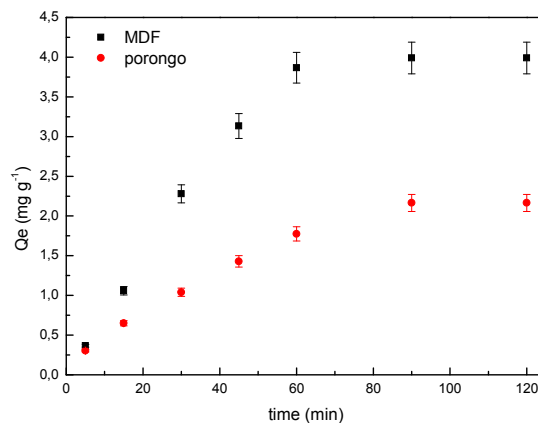
Sample	$S_{BET} (\text{m}^2 \text{ g}^{-1})$	$D_p (\text{nm})$	$V_p (\text{cm}^3 \text{ g}^{-1})$
MDF	11.67	9.47	0.030
porongo	7.33	10.96	0.020



**Figure 2**  $N_2$  adsorption / desorption isotherms of the residual biomass samples

**Kinetics and Adsorption Isotherms**

Figure 3 shows the amount of RhB per gram of residual biomass (MDF and porongo), indicating that the system reaches equilibrium for about 90 minutes. In addition, the kinetic adsorption study showed that after 120 minutes of reaction, the adsorption capacity was 13.96% and 7.58% of the rhodamine B dye on the biosorbents of MDF and porongo, respectively. It should be noted that this higher adsorption capacity of the MDF is related to the compatibility of the surface charge and with the greater surface area and volume of pores, providing a greater number of available active sites and greater intermolecular diffusion of the dye.



**Figure 3** Quantity adsorbed from the Rhodamine B dye as a function of time for the different residual biomasses

The values of the experimentally parameters for the adsorption of the rhodamine B dye using the residual biomass were obtained using the Langmuir (Equations 2 and 3) and Freundlich (Equations 4 and 5) models, according to Table 2. It can be seen that the  $R^2$  values obtained from the models indicate that the Freundlich isotherm model ( $R^2 = 0.89$  for the MDF biosorbent and  $R^2 = 0.91$  for the porongo biosorbent) showed the best fit in relation to the experimental results with the Langmuir isotherm model ( $R^2 = 0.63$  for the MDF biosorbent and  $R^2 = 0.67$  for the porongo biosorbent), indicating a logarithmic distribution of active sites and not admitting the existence of an ideal monolayer for heterogeneous adsorption systems (Dotto *et al.*, 2011). In addition, the maximum amount of adsorption of the rhodamine B dye in the MDF and porongo biosorbent, obtained by the Langmuir model, was  $0.07 \text{ mg g}^{-1}$  and  $0.03 \text{ mg g}^{-1}$  respectively, confirming the endothermic character of the adsorption process (Hema and Arivoli, 2009).

**Table 2** Parameters of isotherms obtained through the Langmuir and Freundlich models

Biomassa	Langmuir isotherm		
	$Q_{max} (\text{mg g}^{-1})$	$K_L (\text{L g}^{-1})$	$R^2$
MDF	0.07	14.14	0.63
	Freundlich isotherm		
	N	$K_F (\text{L g}^{-1})$	$R^2$
	0.06	3.30	0.89
Porongo	Langmuir isotherm		
	$Q_{max} (\text{mg g}^{-1})$	$K_L (\text{L g}^{-1})$	$R^2$
	0.03	18.40	0.67
	Freundlich isotherm		
	N	$K_F (\text{L g}^{-1})$	$R^2$
	0.04	2.48	0.91

**CONCLUSION**

It was possible to evaluate the adsorption capacity of the rhodamine B dye under the residual biomass of MDF and porongo as biosorbents, where the models employed by Langmuir and Freundlich were able to represent the experimental data well, being the Freundlich model the most efficient in this study, ideal for heterogeneous adsorption. The residual biomass of MDF presented better adsorbent in relation to the porongo, due to its compatibility of load (negative charge of  $-3,09 \pm 0,21 \text{ mV}$ ) with the adsorbate RhB, besides its greater surface area ( $11.67 \text{ m}^2 \text{ g}^{-1}$ ) and pore volume ( $0.030 \text{ cm}^3 \text{ g}^{-1}$ ). Therefore, it is emphasized that further modifications are

required on the surface of these biomasses in order to increase adsorption capacity and promote greater removal of RhB dye, such as the activated carbon preparation for surface area increase and porosity.

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