MACEIÓ - ALAGOAS
EBA15
15° ENCONTRO BRASILEIRO SOBRE ADSORÇÃO
15th Brazilian Meeting about Adsorption

Adsorption of methylene blue onto eucalyptus-based biochar: fixed-bed study

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Abstract

Over the years, activated carbons produced from solid (agro)industrial waste have been promising as adsorbents of synthetic dyes mainly due to the availability and relatively low cost of the raw materials. In this view, the present work aims to synthesize and characterize a biochar produced from eucalyptus sawdust for the removal of the methylene blue dye from an aqueous solution, in a fixed-bed operation. The biochar was characterized by XRD, DLS and 11 points assay, to evaluate the crystallinity, zeta potential (ZP) and zero-charge point (pH_{ZCP}), respectively. XRD identified a typical amorphous carbonaceous material similar to activated carbons. The biochar showed ZP = -22 ± 7.45 mV, indicating physio-chemical stability in aqueous solution. 11 points assay revealed pH_{ZCP} at pH 2.65 and 5.78, suggesting that at pH (7.10) of the fixed-bed adsorption, the biochar surface was deprotonated, hence increasing the electrostatic interaction between the methylene blue and the biochar surface. The fixed-bed operation reported 10% and 50% breakthrough time at t = 29.99 min and t = 54 min, respectively, with 55% of bed length used for adsorption. The experimental data was well fitted to Thomas (R^2 = 0.9503) and Yoon-Nelson (R^2 = 0.9499) models, suggesting high occupation of the adsorbent sites in a short time. The maximum adsorption capacity according to the Thomas model was 98.75 mg g^{-1}. Therefore, this work provided information about the adsorption performance of eucalyptus-based biochar in fixed-bed operation, which can be useful as a starting point for scale-up studies.

Keywords: Persistent organic pollutants; Synthetic dyes; Solid waste; Water treatment; Sustainability

1. Introduction

The adsorption process of persistent and toxic pollutants is a good solution to solve environmental problems, such as water, soil and air contamination. Activated carbon is well known for its high efficiency in removing heavy metals and persistent organic pollutants such as synthetic dyes, drugs, and pesticides from aqueous solutions [1]. However, the costs for the production of activated carbon can be high and require high quality/availability of raw materials [2]. Thus, the production of activated carbon from solid waste can be a promising solution to reduce costs and to obtain high-quality activation carbons, which is commonly labeled in this case biochars [3]. This strategy not only aims to improve the conditions of water bodies affected by leachate from domestic waste dumps but also proposes an alternative for the disposal of wood waste, which can pose fire and soil contamination risks [4].

In this view, the present work aims to synthesize and characterize a biochar produced from eucalyptus sawdust for the removal of the methylene blue dye from an aqueous solution, in a fixed-bed operation.

2. Materials and Methods

2.1. Synthesis of biochar

The biochar was produced from eucalyptus sawdust (*Eucalyptus grandis*) obtained from a lumber mill located in the Rivera region, Uruguay. Thus, 1.0 g of eucalyptus sawdust was sieved to obtain a material with a particle diameter of 0.5 mm. Afterwards, this material was heated to 800 ± 2 °C °C for 30 min in a tubular reactor (Parr Instrument, coupled with temperature controller, model NOVUS N480D) at 10 °C min^{-1} and under an inert atmosphere (N_2, flow rate = 80 mL min^{-1}). Then, the eucalyptus sawdust was activated physically with 100 mL min^{-1} of water vapor at 800 ± 2 °C for 30 minutes. The material obtained was labeled as biochar.

2.2. Characterization of the biochar

The prepared biochar was characterized by X-ray Diffraction (XRD) in a Bruker diffractometer (model D2 Advance) using a copper tube ($\lambda_{Cu\text{-}\alpha}$) with a wavelength of 0.1532 nm, Bragg angle ranging from 5° to 70°, and accelerating voltage and current of 30 kV and 30 mA, respectively. Moreover, Dynamic Light Scattering (DLS, Malvern-Zetasizer® equipment, model nano ZS, ZEN3600) was carried out to evaluate Zeta Potential (ZP) of the bichar. The zero-charge point (pH_{ZCP}) of the samples was determined using the 11-point test calculating the ΔpH [10].

2.3. Fixed-bed adsorption assay

The fixed-bed adsorption was carried out on a bench-scale system (18.0 L fed) operating at flow rate 20 mL min^{-1}, adsorbent mass 0.604 g and at natural pH(7.10) and 25 ± 2°C. A solution of 10 mL L^{-1} of MB dye was fed to the column, with the absorbance of the effluent measured in a UV-Vis Spectrophotometer (Shimadzu) at a wavelength λ = 665 nm. For this, the aliquots (3 mL) were collected at predetermined intervals (0, 3, 5, 10, 15, 30, 45, 60, 75, 90, and 120 min).

2.4 Kinetic studies

The experimental data of the adsorption of MB onto biochar were fitted to Thomas and Yoon-Nelson model, according to Eq. (1-2) [5].

$$\frac{C}{C_0} = \frac{1}{1 + \exp\left[\frac{K_{TH}(q_0 * m - C_0 * t)}{v}\right]} \qquad (1)$$

$$\frac{C}{C_0} = \frac{\exp[K_{YN} * t - K_{YN} * \tau]}{1 + \exp[K_{YN} * t - K_{YN} * \tau]} \qquad (2)$$

Where: C_0 = initial concentration of methylene blue (mg L^{-1}), C_t = concentration of methylene blue at time t (mg L^{-1}); t = time (min); K_{TH} = Thomas rate constant (L mg^{-1} min^{-1}); q_{max} = maximum adsorption capacity of the adsorbent (mg g^{-1}); m = adsorbent mass (g); v = volumetric flow rate (mL min^{-1}); K_{YN} = Yoon-Nelson rate constant (min^{-1}) and τ = time required for 50% fixed-bed breakthrough.

3. Results and Discussion

3.1. Characterization results

Figure 1(a) presents the XRD patterns of the samples, whereas Figure 1(b) shows the zero-charge point evaluated for the biochar.

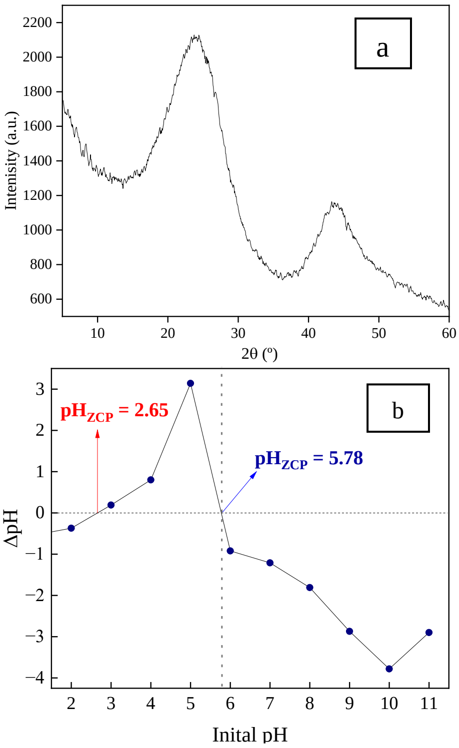

Figure 1. (a) Diffractograms; and (b) pH_{ZCP} of the biochar.

According to Figure 1(a), an amorphous carbonaceous diffractogram was reported, which is typical of activated carbon produced from solid (agro)industrial residues [6]. This result confirms the obtention of biochar. Moreover, biochar showed ZP equal to -22 ± 7.45 mV, indicating physio-chemical stability of the adsorbent in aqueous solution due to electrostatic factors.

Figure 1(b) shows the 11 points assay reporting that the adsorbent presented two points of zero charge (pH_{PCZ}), at pH 2.65 and 5.78, respectively. The point of zero charge indicates that at pH < pH_{PCZ} the surface of the adsorbent will be protonated, that is, with a positive surface charge, whereas at pH > pHPCZ, the surface will be deprotonated, and therefore, with a negative surface charge [7]. In this case, the presence of two pH_{PCZ} suggests that at pH < 2.65, the biochar surface will be protonated, whereas at pH > 5.78 it will be deprotonated. However, in the pH range between 2.65 and 5.78, the behavior may be more complex, with different surface charges due to the functional groups present in the structure or it may be in a state in which there is a combination of charges that partially cancel each other out (Zwitterion), resulting in a variable net charge. Based on this, it can be inferred that the pH of the solution during the test (pH 7.10) favors the adsorption of methylene blue by the biochar, since its surface is deprotonated, which increases the electrostatic interactions of attraction between the pollutant and the adsorbent material.

3.2. Adsorption Results

Figure 2 shows the breakthrough curve for the adsorption of MB in the fixed-bed operation.

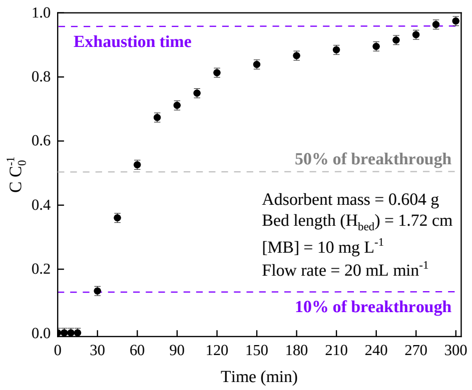

Figure 2. Breakthrough curve for the adsorption of MB onto eucalyptus-based biochar (pH 7.1).

According to Figure 2, the biochar showed 50% breakthrough at time t_b = 29.99 min and exhaustion time t_e = 270 min, with 58% of bed length used. Thus, from the total bed length (H_{bed} = 1.72 cm) 0.99 cm was used for adsorption, whereas 0.73 cm was used as mass transfer zone. Furthermore, the prepared biochar showed a high adsorption capacity (19.86 mg g^{-1}) for methylene blue dye in fixed-bed operation.

3.3 Kinetic studies

The curve fitting used for the experimental data is shown in Table 1.

Table 1. Curve fitting of experimental data

Thomas model	
k_{TH} (L mg^{-1} min^{-1})	0.9522
q_{max} (mg g^{-1})	98.75
C_0 (mg L^{-1})	0.9014
m (g)	0.610
v (mL min^{-1})	21.02
R^2	0.9503
Yoon-Nelson	
K_{YN} (min^{-1})	0.042
τ (min)	65.20
R^2	0.9499

* Flow rate = 20 $mLmin^{-1}$| adsorbent mass = 0.604 g | [MB] = 10 mg L^{-1} | pH 7.1

According to Table 1, the adsorption data can be explained by both Thomas and Yoon-Nelson kinetic models (R^2 ~ 0.95). Thus, Thomas model indicates that the adsorption process may be governed by a more balanced dynamic between adsorption and desorption, suggesting a more uniform distribution of active sites on the biochar surface [8]. According to Thomas model, the maximum adsorption capacity of the biochar for the MB dye was 98.75 mg g^{-1}, with Thomas rate constant K_{TH} = 0.95222 L mg^{-1} g^{-1}. However, this adsorption can be explained by the Yoon-Nelson model suggesting that the adsorption process is characterized by fast uptake of the adsorbate onto the biochar due to a high affinity between the adsorbate and adsorbent, resulting in the high occupation of adsorption sites [9]. According to Yoon-Nelson model, the time required to achieve 50% breakthrough ($C C_0^{-1}$ = 0.5) was 65.2 min, which is very close to experimental data ($t_{b,50\%}$ = 60 min).

4. Conclusion

A biochar was successfully synthesized from eucalyptus sawdust. Thus, the prepared biochar showed high adsorption capacity for methylene blue dye in fixed-bed operation. Furthermore, future studies should be carried out to address the effect of the fixed-bed diameter, bed height and flow rate to obtain more information on the process prior to scale-up studies.

Acknowledgements

The authors would like to thank the Applied Nanomaterials Research Group (GPNAp) and Franciscan University (UFN) for their support/assistance in carrying out the present work. This study was financed in part by the Coordenação de Aperfeiçoamento de Pessoal de Nível Superior Brasil (CAPES) - Finance Code 001.

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