

EXTRACTION, CHARACTERIZATION AND APPLICATION OF LIGNIN FROM CASHEW APPLE FIBER PRETREATED WITH ALKALINE HYDROGEN PEROXIDE

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ABSTRACT

The lignin resulting of pretreatment from cashew apple fiber with alkaline hydrogen peroxide in the process of bioethanol production was extracted, characterized and applied in the process of adsorption of the reactive blue dye Q-G125%. The effect of initial dye concentration, lignin load as adsorbent and temperature in adsorption were investigated. The lignin mass extracted was 12.69 g for each 100 g of in natura fiber. The extracted lignin showed characteristics similar to those mentioned in the literature. The maximum adsorption capacity (q_e) was 90 mg/g obtained in the process at 25 °C, with initial dye concentration of 1000 mg.L⁻¹ and adsorbent dosage of 5 g.L⁻¹.

1. INTRODUCTION

Lignin, which consists of 10-25% of the lignocellulosic biomass, is the second most abundant natural polymer. It is insoluble in water and stable in nature and acts as the "glue" that binds cellulose and hemicellulose. Its structure is three-dimensional and consists of three phenol groups which include: p-hydroxyphenyl (H), guaiacyl (G) and syringyl (S) (Fengel, 1989). Currently, a wide variety of chemicals can be produced in a sustainable way from the aromatic structures of lignin (Silva et al., 2013). Due to its high molecular weight, lignin can be used to produce carbon fibers, polymer modifiers, adhesives and resins (Frollini and Castellan, 2012,). In addition, lignin has antioxidant activity, because of the presence of phenolic groups and benzylic hydrogens. The lignin extracted during pretreatment has been a source of study in several literatures because it is a fibrous and quite resistant material (Li et al., 2015; Mohan et al. Al., 2015). Lignin has also been applied in dye adsorption processes (Guo et al., 2008).

In this context, this research aimed to extract and apply lignin from cashew apple fiber, an abundant agro-industrial residue in various regions of Brazil (Silva et al., 2013). The application of extracted lignin was investigated in the adsorption of the reactive blue dye Q-G125%, from aqueous solution. The adsorption and kinetic studies were carried out by varying the initial dye concentration, load lignin (adsorbent) and temperature.

2. MATERIAL AND METHODS

2.1. Lignocellulosic material and pretreatment

The raw material (cashew apple fiber from *Anacardim occidentale* L.) used in this study was kindly donated by the Jandaia Industry of Juice (Ceará, Brasil). The cashew apple fiber (CAF) was washed,

dried at 60 °C for 24 h and it milled, in order to obtain particles with size between 0.25 and 0.84 mm. The milled CAF was pretreated by alkaline hydrogen peroxide according to the best conditions obtained in the study of Correia *et al.* (2013). A solids concentration of 5% (w/v) CAF, was slurred in hydrogen peroxide H₂O₂ (4.3% v/v) with the H₂O₂ solution adjusted to pH 11.5 using 6 mol.L⁻¹ NaOH. The pretreatment was conducted in an orbital shaker (Tecnal – TE 422, SP, Brazil) at 35 °C for 6 h and 250 rpm. After the pretreatment step, the liquor was separated from the solid fraction by filtration. They were then reserved for the precipitation and recovery of lignin.

2.2. Lignin recovery

Lignin present in the liquor obtained of the pretreatment was recovered by precipitation with acidification at pH 2 using 50% v/v H₂SO₄. The mass of precipitated lignin was calculated in dry mass basis.

2.3. Lignin characterization

Elemental composition for carbon, hydrogen and nitrogen (CHN) of extracted lignin was performed on a CHNS/O Perkin Elmer PE2400 instrument. Proximate analysis (moisture, volatile matter, fixed carbon and ash) were carried out using an immediate analyser LECO TGA701. The analysis of Fourier transform infrared spectroscopy were conducted with aliquots of 2.7 mg of lignin mixed with 80 mg of KBr and grounded, until achieving a homogeneous powder. The samples were placed in a press with 8.5 tons for 15 min. The spectra were recorded in a FTIR Varian 660 spectrometer. The FTIR spectra were acquired in the 4000–400 cm⁻¹ region, with a total of 32 scans and a resolution of 4 cm⁻¹. Thermogravimetric analyzes were also performed using the STA 409 Netzsch Jupiter equipment subjected to the temperature range of 30 °C - 900 °C with heating rate of 10 K.min⁻¹ under N₂ atmosphere.

2.4. Lignin application

The application of extracted lignin was investigated in the adsorption processes. Those experiments were carried out using required amount of adsorbate and adsorbent in 250 mL -flask Erlenmeyer, under agitation and temperature controlled in an orbital shaker. Samples were collected and centrifuged at 6000 rpm for 10 min and the remaining dye concentrations in supernatants were analysed at 623 nm in Biochrom LIBRA S22 UV-vis spectrophotometer. The amount of dye adsorbed was calculated as given in the Equation 1.

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

where C₀ and C are the initial and liquid phase concentration of dye (mg.L⁻¹), respectively. V is the volume of the dye solution (L) and m is the amount of lignin (g).

Five initial dye concentration were analysed (50 – 1000 mg.L⁻¹) on adsorption at 25 °C, pH 2 and the adsorbent dosage was fixed to 5 g.L⁻¹. After, the effect of adsorbent dosages (2 to 10 g.L⁻¹) was studied and the experiments were conducted at 25 °C, pH 2 and 200 mg.L⁻¹ initial dye concentration. The effect of temperature on adsorption was analysed from 25 °C to 50 °C, pH 2.0 and the initial dye concentration and the adsorbent dosage were fixed to 200 mg.L⁻¹ and 5 g.L⁻¹, respectively.

3. Results and discussion

3.1. Characterization of extracted lignin

From the liquid fraction obtained after pretreatment of the cashew apple fiber with alkaline hydrogen peroxide was extracted a lignin mass of 12.69 g for each 100 g of CAF with 6.65% moisture. Immediate analysis of the extracted lignin was 6.93% of fixed carbon, 78.34% of volatiles and 8.88% of ash. Contents of carbon, hydrogen and nitrogen in the samples were 47.57%, 6.86% and 5.60%, respectively. Konduri, *et al.* (2015) studied the characterization of hardwood lignin and obtained the following contents: carbon 64.76%, hydrogen 5.78% and nitrogen 0.03%.

In the TGA analysis, mass loss occurs at 115 °C mainly by the evaporation of water and low molecular weight substances, such as monoxide and carbon dioxide. The mass loss around 200 °C is due to the start of the lignin pyrolysis reaction. And above 300 °C usually occurs to the degradation of the lignin, occurring ruptures of the bonds between units that results in the loss of phenols. Above 400 °C occurs the degradation of the aromatic rings. The FTIR spectrum of lignin exhibited a strong vibration in the wavelength band at 1127 cm^{-1} , which is characteristic of the vibrational contribution of three types of groups named CH in a flat deformation, C= in the stretching of the syringyl units, as well as the secondary alcohols present in the lignin. The small band at 1158 cm^{-1} is attributed to asymmetric stretching of C-O in ester linkages. A band may be noted at 1654 cm^{-1} which is associated with the carbon double bond (C=); length ratio related to aryl ketone, present in the lignin structure. Bands at absorption intensities at 2852 and 2920 cm^{-1} were observed and characterize CH, CH₂ and CH₃ present in hydrocarbon molecules (Lopes *et al.*, 2013).

3.2. Application of extracted lignin

The effect of temperature, adsorbent dosage and initial dye concentration in the dye removal from aqueous solution using lignin as an adsorbent is shown in Figure 1A, 1B and 1C, respectively.

Removal of dye from the medium is rapid in the first few hours of the experiment and with increasing contact time the adsorption gradually decreased until reaching equilibrium in all studies. According to the data presented in the FTIR analysis of lignin and of structure of dye, possibly the removal of the reactive blue dye is a combination of mechanisms of adsorption of the dye on the surface of the lignin, with ionic exchanges or covalent bonds. Also, dye bonds of the neighborhood with the dye molecules already adsorbed on the surface of the lignin. Similar conclusions were obtained in the studies of Vimonses *et al.* (2009) and Silva *et al.*, (2013).

It is observed in Figure 1-A that the adsorbed amount (rate of adsorption) increased with the increase of temperature. According to JIMENEZ; BOSCO and CARVALHO (2004) an increase in the temperature can cause the increase of kinetic energy, and also increase the rate of intraparticle diffusion of the adsorbate. This increase can also produce a pore clearing within the adsorbent structure, allowing the penetration of larger adsorbate molecules (DOGAN; ALKAN; DEMIRBAS, 2006). However, in this study did not have significant difference in adsorption capacity in the range temperature of 25-50 °C. Then, the selected temperature was 25 °C.

Figure 1-B represents the study of quantity of adsorbent in the dye removal. It was observed that a high load increased the adsorption capacity, but did not observe significant difference between 5, 7 and 10 g.L^{-1} and the selected was 5 g.L^{-1} of lignin. An increase in percentage of removal may be concluded due to the increase in the adsorbent surface areas and therefore more active functional groups resulting.

In the initial dye concentrations of 50 and 100 mg/L, the lignin was able to completely adsorb the dye (data not show). The maximum adsorption capacity (q_e) of the lignin was 90 mg/g. It can be proposed that an increase in the initial dye concentration leads to an increase in mass gradient, and thus acts as a driving force for the transfer of dye molecules from bulk solution to the surface of lignin (Silva et al., 2013), but the percentage removal (data not show) of dye decreased with an increase the initial dye concentration, probably due to the low amount of adsorbent.

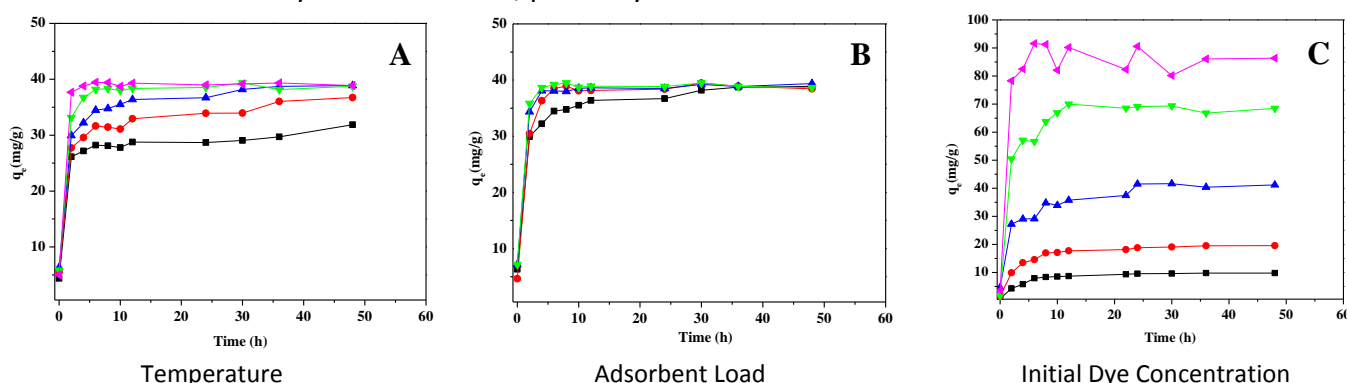


Figure 1. (A) Effect of temperature on adsorption capacity: (■) 25 °C, (●) 35 °C, (▲) 40 °C and (▼) 50 °C using 5 g.L⁻¹ of lignin and 200 mg.L⁻¹ initial dye concentration. (B) Effect of adsorbent load: (■) 2 g.L⁻¹, (●) 3.5 g.L⁻¹, (▲) 5 g.L⁻¹, (▼) 7 g.L⁻¹ and (◆) 10 g.L⁻¹ at 25 °C using 200 mg.L⁻¹ initial dye concentration; (C) Effect of initial dye concentration: (■) 50 mg.L⁻¹, (●) 100 mg.L⁻¹, (▲) 250 mg.L⁻¹, (▼) 500 mg.L⁻¹ and (◆) 1000 mg.L⁻¹ using 5 g.L⁻¹ of lignin at 25 °C.

4. CONCLUSIONS

The lignin extracted from cashew apple fiber pretreated with alkaline hydrogen peroxide show characteristics similar to those mentioned in the literature and it can be to apply in the adsorption of the reactive blue dye.

5. REFERENCES

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