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Adsorbents obtained from black liquor residues: synthesis, characterization, and evaluation in the removal of textile dyes

Adsorventes obtidos de resíduos de licor negro: síntese, caracterização e avaliação na remoção de corantes têxteis

M. Oliveira[1]; V. G. Santos[1]; L. S. Carvalho[2]; D. Ruiz[3]; I. A. S. Barbosa[4]; C. F. Virgens[4]; A. R. Martins[1]*

[1]*Instituto Federal da Bahia, Campus Porto Seguro, 45810-000, Porto Seguro, Bahia, Brazil*

[2]*Instituto Federal da Bahia, Campus Camaçari, 42800-605, Camaçari, Bahia, Brazil*

[3]*Departamento de Físico-Química, Facultad de Ciencias Químicas, Universidad de Concepción, Chile*

[4]*Universidade do Estado da Bahia, 41195-001 Salvador, Bahia, Brazil*

* *andremartins@ifba.edu.br*

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In this work, charcoal-type adsorbents were prepared from black liquor, a cellulose and paper industry residue rich in lignin and containing inorganic salts. During the preparation of adsorbent materials, black liquor was dried at 120 °C and then pyrolyzed at different temperatures (600 °C, 700 °C, and 800 °C) under a nitrogen atmosphere. The samples were characterized by X-ray diffraction (XRD), thermogravimetric analysis (TG), scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDS), measurement of specific surface area (BET), point of zero charges (PZC) determination, and evaluating of removal capacity of methylene blue dye. DRX results indicated the presence of crystalline phases of different salts, mainly sodium carbonate, on the surface of the produced carbonaceous materials from black liquor waste. Besides, a significant effect of the pyrolysis temperature on the charcoal crystallinity was observed. Materials presented low values of porosity and specific surface area, and similar morphologies. Solids' surface character was predominantly alkaline, according to PZC curves. All solids were efficient in removing 70 to 85% of the methylene blue's color.
Keywords: industrial waste, adsorbents, black liquor

Neste trabalho, adsorventes do tipo carvão foram preparados a partir do licor negro, resíduo da indústria de celulose e papel rico em lignina e contendo sais inorgânicos. Durante a preparação dos materiais adsorventes, o licor negro foi seco a 120 °C e depois pirolisado a diferentes temperaturas (600 °C, 700 °C e 800 °C) sob uma atmosfera de nitrogênio. As amostras foram caracterizadas por difração de raios X (DRX), análise termogravimétrica (TG), microscopia eletrônica de varredura (MEV), espectroscopia de energia dispersiva de raios X (EDX), medição de área superficial específica (BET), determinação do ponto de carga zero (PZC), e avaliação da capacidade de remoção do corante azul de metileno. Os resultados de DRX indicaram a presença de fases cristalinas de diferentes sais, principalmente carbonato de sódio, na superfície dos materiais carbonosos produzidos a partir de resíduos de licor negro. Além disso, foi observado um efeito significativo da temperatura de pirólise na cristalinidade do carvão. Os materiais apresentaram baixos valores de porosidade e área superficial específica, e morfologias semelhantes. O caráter superficial dos sólidos foi predominantemente alcalino, de acordo com as curvas PZC. Todos os sólidos foram eficientes na remoção de 70 a 85% da cor do azul de metileno.
Palavras-chave: resíduos industriais, adsorventes, licor preto

1. INTRODUCTION

Anthropogenic activities for the exploitation of natural resources have been increasingly damaging the environment, so that it is necessary to develop research in the environmental area. The industry is responsible for a large part of water consumption and to produce highly contaminated effluents. It led to the development of various wastewater treatment technologies. Among these, could highlight the advanced oxidation processes (AOP), which consist of degrading stable toxic organic compounds, such as phenols and some dyes [1, 2].

A carbonaceous material adsorbent widely used in effluent treatment processes is activated carbon due to its properties such as high adsorption efficiency, high specific area, high porosity, and functional groups capable of acting in different systems, in addition to the relatively low cost. Besides, with modern preparation techniques, it has been possible to obtain charcoal with resistance to wear, abrasive destruction, and suitable for use in the most varied materials technology fields [3].

For a long time, activated carbon has been obtained mainly from oil residues, coal, or wood. Currently, various precursors had investigated, especially biomass and industrial waste [4]. An essential step in preparing the charcoals is activation, which can occur by chemical or physical treatments, or a combination of them. The activation process to high temperatures commonly involves pre-treatments at water vapor or carbon dioxide atmospheres. On the other hand, during chemical treatment, acids [5], bases [6], compounds based on potassium or calcium salts, or chlorides, for example, are used as chemical agents to promote the charcoal activation [7, 8]. In both cases, activation results in a significant increase in the production cost or tailings generation [9]. Therefore, it is highly relevant to research sources of activated carbon that do not need starting chemicals and cause less harm to the environment [7].

Black liquor is a by-product of cooking wood in the cellulose pulping process. It consists of a complex aqueous solution, composed of organic and inorganic matter, formed by salts' ions derived from chemical agents used in the carbonization [10]. The organic mixture consists mainly of lignin and alkaline residual salts containing sodium, sulfur, and potassium, which can age in the charcoal activation [5]. Thus, using black liquor as a precursor to produce activated carbon type adsorbent can generate environmental and economic benefits related to the use of waste and reduce operational costs in the stage of charcoal activation. Recent research has shown relative success in obtaining adsorbents with high area and porosity from black liquor. However, the authors generally employ high-cost treatment processes, with several stages, or not environmentally friendly, due to the disposal of solvents used for the activation step [11-13].

Based on these aspects, this work's main goal was to synthesize, characterize and evaluate charcoal-type adsorbents obtained by a simple process, based directly from black liquor pyrolysis, without pre-treatment using chemical agents, in the removal of the dye of water. Thus, it had intended to contribute with technologies around wastewater treatment using tailings from the pulp and paper industry.

2. MATERIAL AND METHODS

The black liquor sample collected from a pulp and paper mill was kiln-dried at 120 °C for 24 h. The material was then pyrolyzed under a nitrogen atmosphere for 2 h at different temperatures, producing LN samples at 600, 700, and 800 °C (LN600, LN700, and LN800, respectively).

The following techniques had used to characterize the solids: X-ray diffraction (XRD); thermogravimetric analysis (TG); Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), energy-dispersive spectroscopy (EDS), specific area measurements (BET method), point of zero charge measurement (PZC), and evaluated in the removal of methylene blue.

The samples' XRD measurements had performed using an XRD600 brand diffractometer from Shimadzu with a nickel filter. The solid was exposed to CuKα radiation ($\lambda = 1.5406$), produced at 30 kV and 20 mA, doing scanning in the range of 2θ from 10° to 80°. The samples' structural characterization had carried out by identifying the crystalline phases present, with automatic search in the crystallographic database Inorganic Crystal Structure Database (ICSD), through the Match 3 software.

The thermogravimetric analysis had carried out in a nitrogen atmosphere, with a flow of 50 mLmin-1 heating bulb 15 $^{o}C\ min^{-1}$. The curves had obtained in a SHIMADZU thermal balance, model DTG 60.

The Fourier transform infrared spectroscopy (FTIR) was conducted in a PERKIN ELMER model Spectrum100-FT-IR, in the region from 4000 to 400 cm^{-1}. Before analyses, samples were compressed on tablets by dilution with potassium bromide (200:1). Experiments had conducted using a resolution of 4 cm^{-1} and an accumulation of 32 sweeps.

Scanning electron microscopy (SEM) images had obtained through Tescan Vega-3 LMU equipment at 15 kV and 7000x magnification. Energy-dispersive X-ray Spectroscopy (EDS) experiments had performed in an X-act Oxford Instruments apparatus coupled with the electron microscope. The textural properties were determined from nitrogen sorption experiments, carried out at 77 K, in a Micromeritcs equipment, model ASAP 2020. The specific area (Sg) had calculated using the Brunauer - Emmett - Teller (BET) model.

Specific area values were determined by physical nitrogen adsorption isotherms, at -196 °C, in a Micromeritics TriStar II 3020 equipment. Before the experiment, the samples were pre-treated at 10 μmHg for 30 min and then heated at 200 °C for 60 min under nitrogen flow for surface cleaning. After pre-treatment, the dead volume and the saturation pressure, P°, were determined using 99.999% of pure helium gas. Before analyses, samples had heated at 200 °C (2 h) under a 10^{-6} Torr vacuum.

To determine the point of zero charges (PZC), the pH value of the solution containing the samples had controlled with the addition of sodium hydroxide or hydrochloric acid solutions before and after a specific time interval [14].

For the dye removal test, 100 mg of each solid and 50 mL of the methylene blue dye solution, with 10 mg L^{-1} concentration, were placed in a 100 mL beaker, kept under constant agitation, on a stirring plate, at room temperature (25 °C ± 2 °C). It took aliquots of 5 mL in the first 5 min; after in two intervals of 15 min; and at following intervals of 30 min, until the total time of two and a half hours. The adsorbent material was separated from the solution by centrifugation (3500 rpm) for 10 min, being the procedure repeated in case of solid particles remaining. The centrifugation step was repeated, washing the material with 0.1 mL of hydrogen peroxide (30%). The methylene blue' color removal percentual had calculated from the equations described by Castro et al. (2009) [15]. Moreover, tests with determined pH values (3, 7, and 9) of the reaction medium had carried out, using sodium hydroxide or hydrochloric acid solutions (0.1 mol L^{-1}) for pH control. Before this procedure, solids were washed and filtered until the residual liquid had a pH value equal to 7.0.

3. RESULTS AND DISCUSSION

X-ray diffractograms (Figure 1) indicated that various phases had formed. This behavior had expected, considering the heterogeneous chemical environment from the precursor residue. Also, depending on the pyrolysis temperature, structural changes had observed in the solids. Considering that solids had prepared from the same sample of black liquor and, therefore, have the same elemental composition, the distinguished profiles observed can be related to phase changes. Thus, based on chemical composition, determined by EDS (Table 1), knowledge of black liquor nominal composition, and search carried out in the Match software database, it was possible to identify the presence of the following phases: sodium carbonate (ICSD 96-101-1296), sodium sulfate (ICSD 96-210-2307), potassium carbonate (ICSD 96-900-9645), calcium oxide (ICSD 96-900-6708), and orthorhombic calcium carbonate (ICSD 96- 721-0492) and trigonal (ICSD 96-900-0971).

XRD profile of the solid prepared at 800 °C showed a smaller number of crystalline phases and a higher number of amorphous halos, indicating that the increase in temperature caused a decrease in the particles' size of the salts or favored the solubilization of the solid. In both cases, this can be due to the interaction of the inorganic phase with charcoal. Thus, the results indicate that the structure of inorganic material from black liquor and charcoal can undergo significant changes in the studied temperature range. In general, the diffractograms did not point to the presence of amorphous carbon halos characteristic of the activated carbon structure (peaks near 25 °C-45 °C) [16, 17], which, for example, may be related to the high content of crystalline inorganic phases.

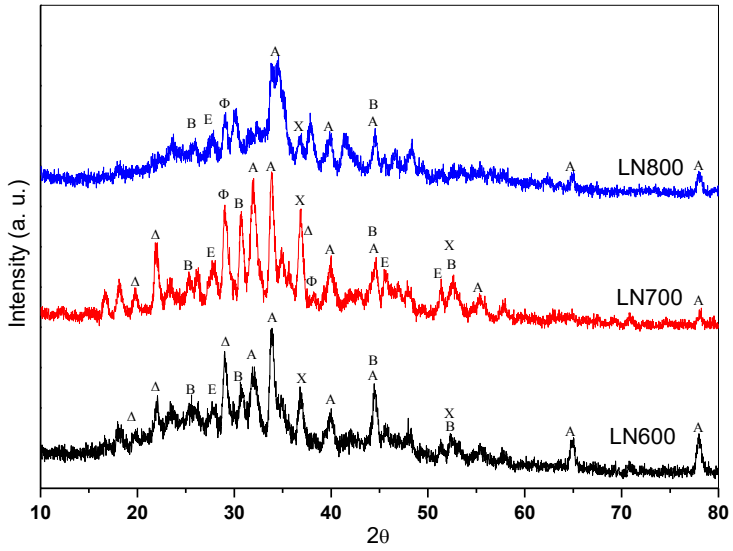

Figure 1: DRX profiles of the samples. Phases were identified as: A – orthorhombic sodium carbonate; Δ – monoclinic sodium sulfate; E – monoclinic potassium carbonate; X – cubic calcium oxide; B – orthorhombic calcium carbonate and Φ – trigonal calcium carbonate.

Similar to observed by DRX results, TG and DTG curves of black liquor (Figure 2), used as a precursor to charcoal, indicated that the material did not present a typical biomass profile [18]. It had identified three main events: the first, in the range of 27 to 160 °C, which is associated with water elimination; the second, from 160 to 630 °C is, commonly attributed to cellulose and residual hemicellulose degradation; and the third, from 630 to 812 °C, can be related to the lignin rupture [11]. These stages showed 8.6%, 20.2%, and 24.4% of mass loss, respectively.

On the other hand, the DTG peak at 800 °C had commonly attributed to the structural carbon partial decomposition [5]. For black liquor, the steps attributed to cellulose and hemicellulose degradation can also have related to partial lignin degradation, which occurs during the Kraft process. It is also possible that the thermal degradation profile of these materials is influenced by their chemical composition, which is rich in inorganic salts and base species. At the end of the experiment (at 1000 °C), there was still 53.2% of the mass, while the yield at 800 °C was only 12% (attributed to inorganic residues). These results indicate a high production of charcoal from black liquor, even at high temperatures.

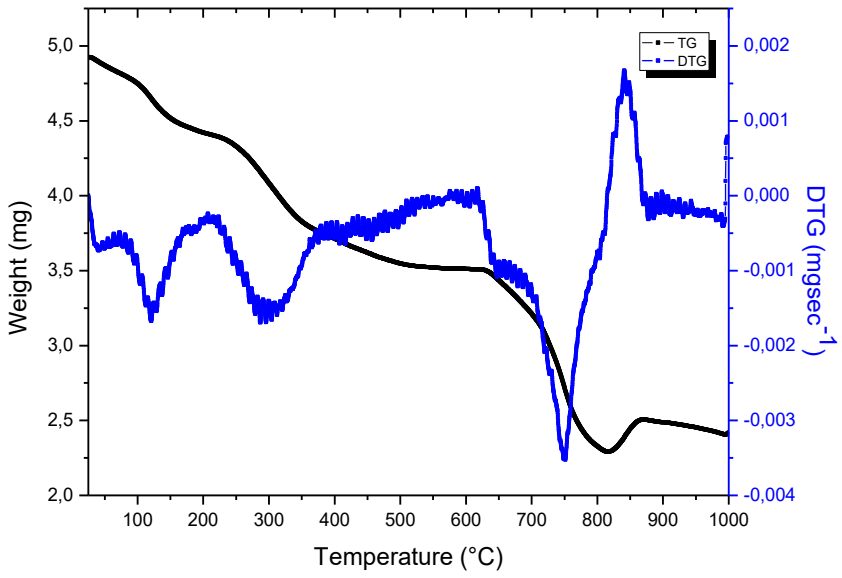

Figure 2: TG and DTG curves of the black liquor.

FTIR spectra (Figure 3) showed characteristic bands of functional groups present in activated carbon, such as hydroxide, carbonyl, and carboxyl [19]. Additionally, the solids showed similar spectra but with slight differences in wavelength values and bandwidth. It indicates that the functional groups present in the solids are the same, but the pyrolysis temperature affects their concentration and bond strength. It is important to note that even after thermal treatment at 800 °C, the material still maintains many functional groups, providing it essential applications in catalysis and adsorption [13].

A broadband centralized about 3450 cm^{-1} was observed, attributed to OH^- groups and adsorbed water. Due to OH^- related to different types of compounds, some authors consider this extended profile of the band inherent to activated carbon [16, 20]. Various species can be found on the obtained adsorbents' surface because of the precursor's heterogeneous chemical environment and basicity. Consequently, it can make it challenging to identify the bands in the region between 300 and 2700 cm^{-1}, which are characteristic of CH bond vibration, as reported by searchers who prepared charcoal from black liquor, using a thermal treatment with a mixture of CO_2 and N_2 [13]. Comparing the FTIR curves in Figure 3, a narrowing of the mentioned band was noted, with the increase in the pyrolysis temperature, probably due to water loss.

A shoulder centered at 1638 cm^{-1} had attributed to the presence of C=O groups, generally related to the presence of carbonyl groups of ketones and aldehydes, and carboxyl groups [5, 6, 13].

Another shoulder at 1450 cm^{-1} had attributed to the C = C bond in aromatic rings [19] present in activated carbon [5]. The latter also decreased with increasing temperature. Furthermore, a broad and intense band, centered on 1130 cm^{-1}, was assigned to groups such as C = C, C-O, C-C, related to the presence of phenols, ether, acids, and alcohols [16]. An intense band, centered on 615 cm^{-1}, can indicate vibrations of the metal-oxygen bonds [21] from inorganic waste.

The images obtained by SEM (Figure 4) show a well-defined and regular shaped surface. In general, the solids had smooth, little porous surfaces, differently from what was observed in other work, in which charcoal had prepared from the lignin extracted from the liquor [22]. It cannot observe significant differences in the solid's morphology as a function of the pyrolysis temperature.

EDS results (Table 1) confirmed sodium, sulfur, potassium, and calcium in the materials. The first two are from the Kraft process, which uses sodium hydroxide and sodium sulfide for the wood treatment. The last two come from the composition of the wood or possible contamination, respectively [22]. At least three analyses of each sample had carried out, which showed distinct element content values. On average, the element presents in the highest concentration in the samples was sodium, which justifies the base behavior identified from the measurements of PZC. Moreover, adversely to the had observed in other studies, which used black liquor from other sources to produce activated charcoal, did not have detected silicon, magnesium, and aluminum in the solids obtained in this work [8].

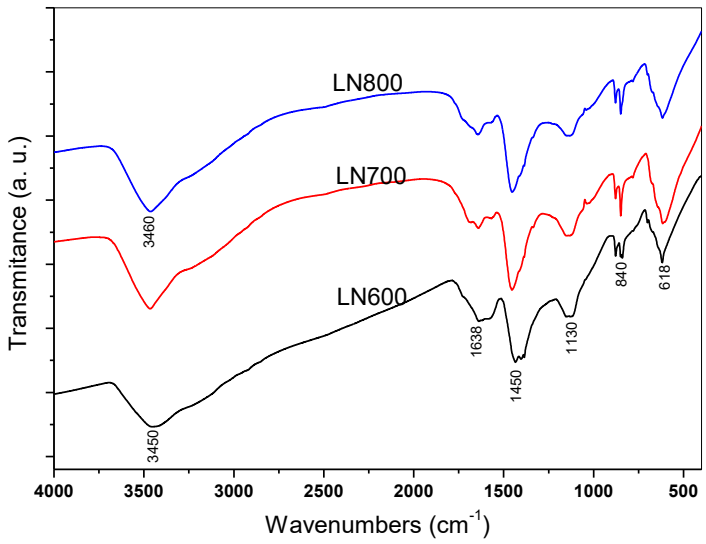

Figure 3: FTIR curves of the solids after pyrolysis.

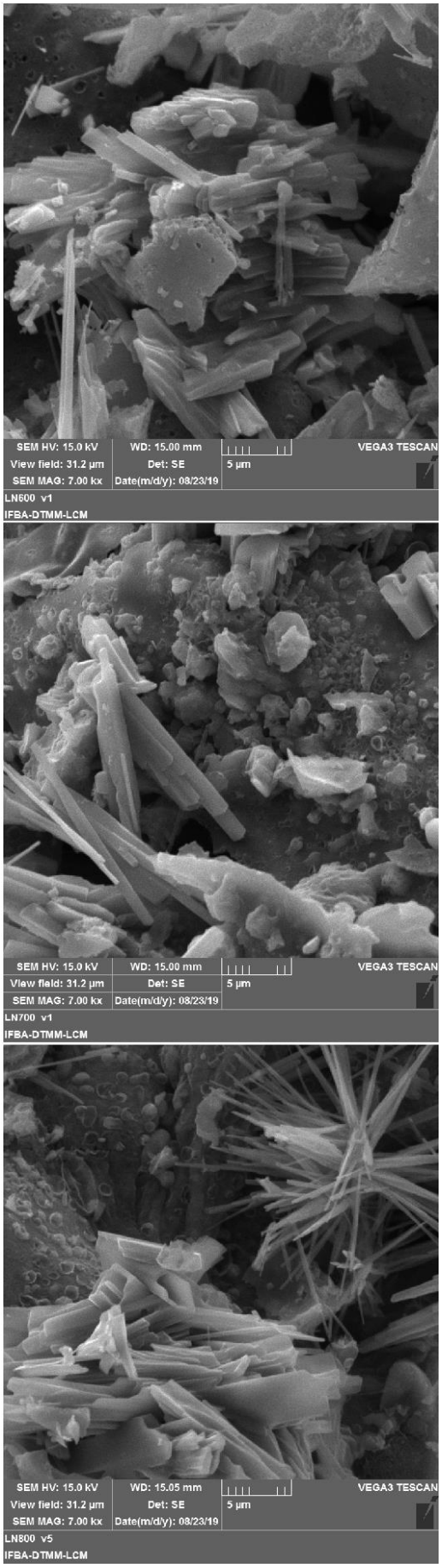

Figure 4: SEM images of the samples.

All solids showed low values of the specific area (Table 1), which was attributed to the high concentration of unwanted inorganic material or because the amount of sodium and potassium present on the surface was insufficient to guarantee the charcoal activation. According to the centesimal composition, it was possible to notice that the samples were exempt from the calcium element, and LN700 sample was the richest in sodium and potassium. These data agree with XRD results and indicate the need to develop more efficient washing methods after the pyrolysis step, to eliminate those inorganic residues unwanted.

Table 1: Specific area values (Sg) and chemical composition of the samples, determined by EDS.

Sample	Sg (m^2g^{-1})	Composition (%)				
		Na	S	K	Ca	Cl
LN600	6.2	0.8 - 53.0	19.0 -24.0	8.0 - 25.0	0.0 - 0.9	0.0
LN700	6.6	63.0 - 81.0	15.0 - 30.0	19.0 - 81.0	0.0	2.0 - 6.0
LN800	6.1	57.0 - 99.0	0 - 31.0	1.0 - 9.0	0.0	0.0 - 6.0

Figure 5 shows the ΔpH (pH variation or PZC) curves as a function of pH° (initial pH) of a solution containing the analyzed solid. All materials presented PZC above pH 10. This value is higher than those commonly found for charcoals produced from cellulose residues [5]. It can have related to the charcoal's most base characteristics obtained from the black liquor, which means that the solids can act as good adsorbents for anionic species when the solution's pH is lower than the PZC. In this case, the surface becomes positively charged [23], and the material can be promising for the adsorption of anionic dyes [24]. It was also possible to notice a slight increase in the PZC with the solids' preparation temperature.

All produced materials were active in removing methylene blue, with adsorption values between 70 and 80%. The samples showed similar behavior to each other, as observed by the curves for removal percentual of the color of methylene blue as a function of time (Figure 6). It is according to PZC results. It could have noted that all solids showed similar behavior, and the methylene blue removed amount became significant after 30 min of contact with evaluated solids (Figure 6a). It appeared that the LN700 sample showed good removal stability in the time interval of 60 to 90 min, indicating that it is the most promising sample compared to the others, and the removal increased with the contact time. This behavior had also observed when 0.1 mL of hydrogen peroxide (30%) was incorporated into the sample solution, as seen in Figure 6b, except to the LN600 sample, in which hydrogen peroxide addition promoted a slight increase in the adsorption activity, compared to the others solids. LN 700 had the lowest percentage of removal but showed a pseudo phase of stability over a long period. These results indicate a promising potential of black liquor in producing adsorbents for advanced dye oxidation processes, deserving a more detailed study about preparation variables and evaluation conditions of adsorbents performance [1, 2].

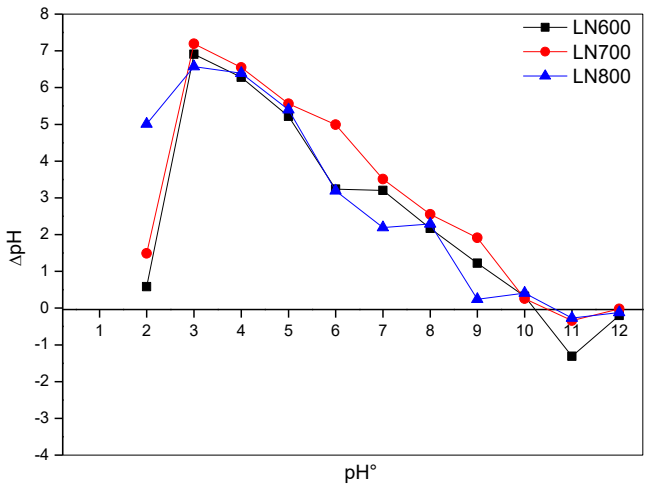

Figure 5: pH variation as a function of PZC (ΔpH).

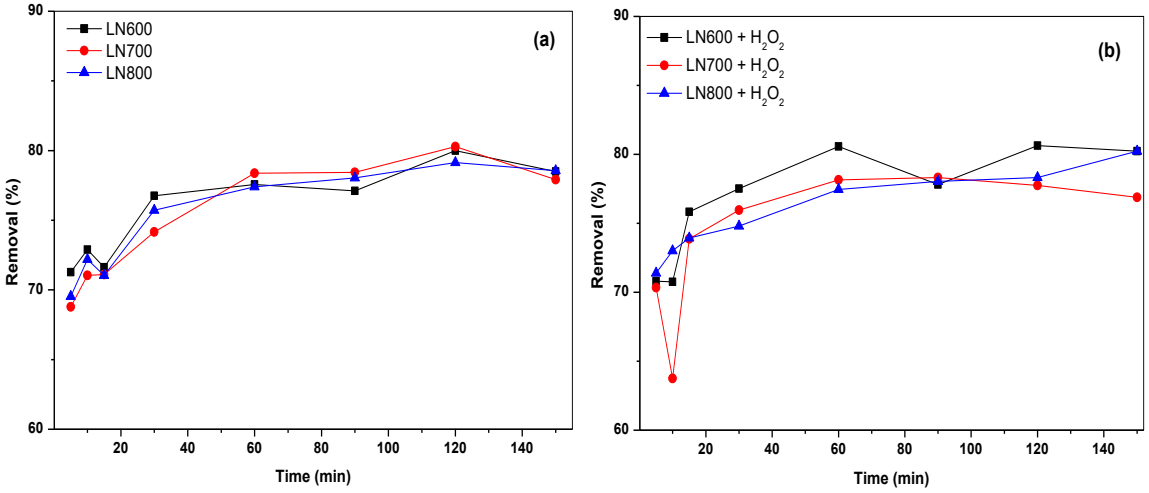

Figure 6. Percentage of methylene blue that was removed by the samples, as a time function, without the hydrogen peroxide presence (a) and after addition of hydrogen peroxide solution (b).

The Fenton type's advanced oxidative process occurs with the iron species, producing hydroxyl radicals capable of oxidizing even stable organic compounds [1, 15]. No significant amount of iron had found among the inorganic residues present in the black liquor used as precursor material of the solids prepared in this work. Fe absence, Fenton reaction catalyst, may explain the similar behavior observed in the methylene blue removal curves, with or without hydrogen peroxide addition.

The samples' methylene blue adsorption curves during tests carried out in pH-specific values (3, 7, and 9) of the reaction medium, after solids washing, are displayed in Figure 7. It had seen that the methylene blue removal was almost 100%, which indicates that the washing step significantly increased the adsorption capacity of these materials. On the other hand, there was no significant effect of the pyrolysis temperature on the solids' adsorption capacity, as they all showed practically the same behavior.

It is not uncommon for charcoal-type adsorbents obtained from residual biomass to show almost 100% adsorption of methylene blue dye when tested under optimized conditions. However, in general, these adsorbents are prepared using methods that require chemical or physical activation, often associated with waste generation [4, 9, 13]. Adversely, practically no chemical or physic treatment had used for the solids prepared in this work, reducing both production costs and reducing waste formation.

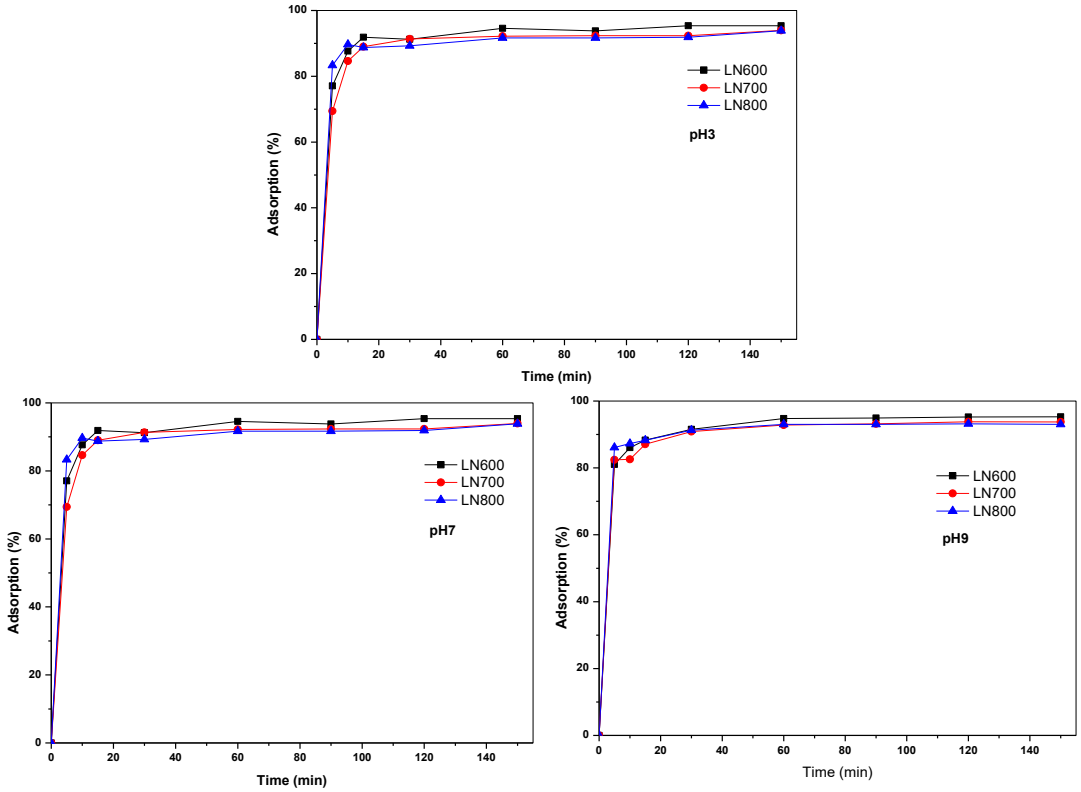

Figure 7. Methylene blue adsorption curves, as a time function, after samples washing, and at different pH values.

It had observed a significant effect of the pyrolysis temperature used in preparation on solids structure and crystallinity.

All the solids were efficient in removing the methylene blue color (70 to 85%), even with no treatment before or after pyrolysis. Furthermore, the pyrolysis temperature employed did not influence the activity of the solids. On the other hand, tests with hydrogen peroxide indicated no significant catalytic activity of solids in advanced oxidative processes. Adsorption experiments performed with prior washing of the material, post pyrolysis, and pH control suggested that the washing process favors the increase of adsorption capacity, which remains close to 100% at different pH values (3, 7, and 9). Thus, results indicated that black liquor has the potential for use in the adsorbents production to remove methylene blue dye of residual water, requiring a more detailed study about preparation and application conditions variables of the obtained adsorbents.

4. CONCLUSION

In this work, adsorbent charcoal solids were prepared from a waste of the paper and cellulose industry, called black liquor, pyrolyzed in different temperatures. Results appointed that:

i. Different phases in the charcoals were obtained due to the several salts present in the black liquor, mainly sodium carbonate.

ii. The solids showed low porosity and surfaces with similar morphologies.

iii. The charcoal's specific area values were lower than the activated charcoals prepared by other methods, attributed to high inorganic compounds concentration in black liquor. Still, despite that, they maintained good activity.

iv. The solids presented a liquid surface predominantly cationic.

5. ACKNOWLEDGMENT

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