Characterizing activated carbon synthesized from corn straw aiming water treatment

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Abstract
The emerging agenda for sustainable development and global warming control searches urgent researches to reduce environmental impacts. In this sense, activated carbons from agroindustrial wastes are widely used as adsorbents in food and pharmaceuticals industries, mainly for the separation and purification of biomolecules, due to their complex pore structure and high surface area. This research evaluates the corn straw activated carbon obtained from the chemical impregnating with phosphoric acid under stirring for 30 min, being sequentially drying at 50 °C and characterized looking for water treatment application. The adsorption of methylene blue from aqueous solutions was investigated by batch experiments carried out at 30 °C and 100 rpm, obtaining 99 mg g^{-1} as the maximum adsorption capacity. The activated carbon had different functional groups when compared to its precursor material, an iodine value of 405.83 mg I_2 g^{-1} and pH_{PZC} of 5.75, characterizing it as slightly acidic, with a surface area of 409.314 m^2 g^{-1}, presenting potential as a biosorbent for technological application.
Keywords: corn straw, adsorption, methylene blue, activated carbon

1. Introduction

According to Yagub et al. (2012), Saini et al. (2018) and Lima et al. (2019), approximately 100 tonnes of dyes are discharged per year in watercourses, interrupting the photosynthetic activity in aquatic system and retarding the growth of the biotic community, turning water unsuitable for consumption and raising concerns about its adverse effects on the human health and ecosystem.

The methylene blue (MB) dye is used in the production of paper and other materials (polyesters and nylons), in the pigmentation of cotton, wool, silk and leather, as well as in cosmetics, pharmaceuticals, tannery and food processing industries (Saini et al. 2018). Due to this high reactivity and ability to react with any substrate, it is considered a difficult residue to treat, being widely applied as a “model” compound to represent the adsorption behavior of toxic chemicals, particularly organic dyes, onto carbon materials (Wang et al. 2017, Saini et al. 2018).

The adsorption method is been considered as an environment-friendly alternative to the traditional methods of effluent treatment to remove dyes from wastewater due to this high efficiency, easy operation, environment friendliness and inertness to substances. Researches have attracted attention to the activated carbon in function of its porous structure, high specific area, high adsorption capacity, and the presence of several functional groups on its surface (Lima et al. 2019).

In this work, the corn straw residue was used for preparing activated carbon obtained from chemical impregnation with phosphoric acid investigating their physicochemical and surface properties aiming water treatment.

2. Materials and Methods

The corn straw was washed with water and sanitized with 100 ppm of sodium hypochlorite for 15 min. After being rinsed, the material was placed in an air-circulation furnace at 50 °C under constant weight and the dry material was crushed with a Wylle (30 mesh) cutting mill and packed in hermetically closed plastic flasks at room temperature.

For chemical activation and carbonization, the residue was impregnated with phosphoric acid under stirring on magnetic stirrer for 30 min and dried in an oven for 24 h. The carbonization was carried out in a muffle furnace, heated to 500 °C and remaining at that temperature for 30 min. The material was then immersed in a 0.1 M hydrochloric acid solution and boiled under reflux for a period of 60 min. Subsequently, it was washed in running water until neutral pH was reached (7.0) and dried at 100 ºC for 24 h.

The physicochemical properties of the adsorbent were characterised using the following techniques: Fourier transform infrared spectroscopy (FT-IR), for identifying the functional groups present in the adsorbent in the band of 400-3500 cm^{-1}; iodine number, performed according to ABNT standards (ABNT, MB-3410), used as a representative index of the amount of micropores present in the coal sample (Brandão and Silva 2006); the Brunauer, Emmett and Teller (BET) method to determine specific surface area (Brunauer et al. 1938); as well as the pH at the point of zero charge (pH_{PZC}), according to the methodology described by Silva et al. (2016), with a glass-electrode digital pH meter (Tecnal TEC-5) previously set with buffer solutions at a pH of 4 and 7.

The cationic dye used in the adsorption trials was methylene blue (Sigma ®). A stock solution of 1000 mg L^{-1} of MB was initially prepared and subsequently diluted, preparing solutions of 100, 250, 500 and 750 mg L^{-1}, used in the adsorption studies, performed in batch mode. In all the experimental runs, a biomass load of 1%

(w v[-1]) was used and the system was agitated in an incubator shaker operating at 100 rpm and ambient temperature of 30 ºC.

For the equilibrium study, experiments were carried out in the time established in the kinetic study, being subsequently applied the adsorption isotherm models of Langmuir (Langmuir, 1918) and Freundlich (Freundlich, 1906) in order to evaluate the data of the process.

3. Results and Discussion

The comparison spectrum between the residue and the corn straw activated carbon, measured in the region from 400 to 4,000 cm^{-1}, is presented on Figure 1.

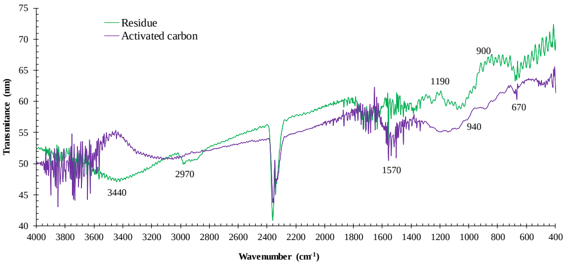

Figure 1. Fourier transform infrared spectra of corn straw

The band located around 3400 cm^{-1} is characteristic of the vibrational stretching of –OH. At wavelength close to 2400 cm^{-1} the band is related to the CO_2 contained in the ambient air and the band located at 1700 cm^{-1} is assigned to the carbonyl (–C=O) stretching from the carboxylic acid (COOH) while the spectra between 1100 and 990 cm^{-1} includes all the vibrations from the –C=O bonds in the primary and secondary hydroxyl and the carboxylic acid. These peaks indicate that the biomass can have ionizable functional groups (hydroxyl, carbonyl and carboxylic) that favors the sorption of cationic adsorbates such as MB (Lugo-Lugo et al. 2012).

The surface area of the corn straw residue increased from 156.89 to 409.31 m^2 g^{-1} after conversion to activated carbon, indicating a significant improvement in the physical properties of the residue.

The analysis of the point of zero charge (pH_{PZC}) in water evaluates the ideal pH range for the adsorption and indicated an acidic characteristic for the corn straw residue (pH_{PZC} 1.26). In the MB dye, the corn straw pH_{PZC} was close to neutrality (5.91). For the activated carbon, due to the need to wash it until reach neutrality, the value obtained was 5.75, characterizing it as slightly acidic. Wang et al. (2017) obtained a pH_{PZC} of 4.05 for corn straw biochar without chemical activation.

Iodine number, considered as a measure of activity level (higher number indicates higher degree of activation), has a typical range of 500-1,200 mg g^{-1} (Jadhav and Mohanraj 2016). The medium value of iodine number found for corn straw activated carbon was 405.83 mg g^{-1}, below the ideal range of activated carbons, suggesting that the chemical activation applied has not a potential to be developed to a commercial scale yet; however a good adsorptive capacity be reached and will be preented

Table 1 presents the parameters obtained from the adjustments of the Langmuir and Freundlich models for the removal of methylene blue. The results showed that the Langmuir model provided a better fit to the adsorption than the Freundlich model (R^2 0.998 versus 0.93-097). According to the results obtained, the separation factor (R_L) indicate a favourable adsorption.

Table 1. Parameters for the equilibrium models

Models	Parameters	Corn straw	
		Residue	Activated carbon
Langmuir	q_{max} (mg g^{-1})	55.56	88.50
	K_L (L mg^{-1})	0.117	0.119
	R_L	0.079	0.078
	R^2	0.9982	0.9987
Freundlich	K_F (L g^{-1})	8.351	19.379
	n	2.040	3.023
	R^2	0.9714	0.9344

4. Conclusions

Corn straw residues were considered good adsorbents of the MB dye, reaching a maximum removal above 95%. Langmuir model isotherm presents a better fit and favorable adsorption processes. The activated carbon produced presented an alternative to improve the adsorption properties of biomass, however a lower expected result for the iodine number (405.83 mg g^{-1}) and pH_{PZC} 5.75 but accepted for water treatment.

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