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Treatment of vinasse by adsorption on activated carbon from sugarcane bagasse agglomerated with Al_2O_3

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ABSTRACT. The objective of this work was to produce and characterize activated carbon from sugarcane bagasse agglomerated with Alumina (Al_2O_3) and apply it in treatment of vinasse pretreated by coagulation-flocculation to reduce the toxics parameters of vinasse. The adsorbent was characterized from textural analysis, XRD, pH_{ZPC}, SEM and EDS. Adsorption isotherms, adsorption kinetics and thermodynamic parameters of the process were obtained. The Langmuir isotherm model fitted the experimental data better and the pseudo-first-order model best represented the adsorption kinetics. The process was spontaneous, exothermic and with increased entropy. The combined coagulation-flocculation/adsorption process was efficient in reducing the parameters of color, turbidity, COD, TOC and toxicity of the vinasse with removal rates of 73.50, 96.06, 72.65, 76.08, 78% respectively.

Keywords: Eco friendly; industrial effluent; pyrolysis; chemical activation; toxicity.

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Introduction

The sugar and ethanol industries are among the most important industries in the world. In addition to having a great economic relevance, the sugar and ethanol sector is also responsible for the production of bioethanol which is a sustainable fuel source. The world production of ethanol is estimated at around 40 billion liters with 70% produced in Brazil and the USA. Brazil is the world's largest producer of ethanol from sugarcane averaging 400,000 liters per day. In the 2020/21 harvest, according to official data from the Brazilian National Supply Company (CONAB), ethanol production reached 29,8 billion liters. Ethanol is used as a raw material for the production of various products, such as paints, solvents, aerosols, etc. In addition, ethanol stands out as an important source of clean, renewable energy.

In contrast to this large production and market relevance, ethanol production also generates large amounts of by-products, such as sugarcane bagasse and also an effluent with a high toxic load, known as vinasse (Janke et al., 2015). Sugar cane vinasse is a brown-colored waste product with an acidic pH (3.5-5.0) composed of a mixture of water, salts, and high content of organic compounds. Typically, vinasse has a chemical oxygen demand (COD) ranging from 50-150 g L^{-1}, while biological oxygen demand (BOD) can account for up to 70% of the COD (Rulli, Villegas, & Colin, 2020; Naspolini, Machado, Cravo Junior, Freire, & Cammarota, 2017; Colin, Juárez-Cortes, Aparicio, & Amoroso, 2016). The main destination given to vinasse is its use in fertigation of sugarcane fields, due to the presence of macro and micronutrients, especially potassium. However, continuous and prolonged disposal of vinasse into the soil can cause a number of environmental effects, such as loss of microbial activity, permanent acidification of soil and water resources, and leaching of metals from the soil into the groundwater. It can also cause salinization, nutrient imbalance, reduced alkalinity, crop losses, increased phytotoxicity, and unpleasant odor (Fuess, Garcia, & Zaiat, 2018; Moraes, Zaiat, & Bonomi, 2015; Christofoletti, Escher, Correia, Marinho, & Fontanetti, 2013). Therefore, it becomes necessary to treat this effluent before its final disposal and thus ensure the long-term sustainability of the sugarcane sector.

Considering the negative environmental impact caused by fertigation, some processes have been evaluated to treat vinasse in order to reduce this impact, such as the photocatalysis process (Santana & Fernandes-Machado, 2008), vinasse concentration (Cortes-Rodriguez, Fukushima, Palacios-Bereche,

Ensinas, & Nebra, 2018), biological treatments (Rulli et al., 2020; Cabello, Scognamiglio, & Terán, 2009) and adsorption (Seixas, Gimenes, & Fernandes-Machado, 2016). Among these techniques, adsorption has stood out as an interesting, economical, simple, easy to operate technique with the possibility of regeneration of the adsorbent (Wang, Pan, Cai, Guo, & Xiao, 2017). In this context, the study to develop low-cost and efficient adsorbents, such as activated carbon produced from renewable raw materials and/or waste and by-products, is extremely necessary (Pallarés, González-Cencerrado, & Arauzo, 2018).

In the literature, some studies have used renewable and economically competitive alternatives, including the use of biomass, agricultural residues, and industrial by-products (Ahmed, Zhou, Ngo, Guo, & Chen, 2016; Tan et al., 2016). Among the byproducts used, sugarcane bagasse is a very interesting feedstock due to its low cost and wide availability. Some works aim to produce activated carbon from sugarcane bagasse (Jaguaribe, Medeiros, Barreto, & Araujo, 2005; Kalderis et al., 2008; Qureshi, Bhatti, Kazi, & Ansari, 2008; Foo, Lee, & Hameed, 2013; Sutrisno, Rizka, Hidayat, & Hidayat, 2016; Gonçalves, Pereira, & Veit, 2016; Giusto, Pissetti, Castro, & Magalhães, 2017; Seixas et al., 2016). However, the activated carbon obtained from sugarcane bagasse is formed by very fine particles and makes the separation, regeneration and subsequent application in fixed bed columns difficult. One of the alternatives to circumvent this difficulty is the application of binders and the manufacture of pellets before pyrolysis and activation (Gonçalves et al., 2016). Some binders have already been evaluated, such as sugarcane molasses, beet molasses, corn syrup or tar (Gonçalves et al., 2016), mostly organic compounds. Our proposal is to evaluate the use of an inorganic binder that enables the production of a granular activated carbon efficient in the adsorption of compounds present in vinasse.

One material with potential to perform this function is alumina, a chemical compound of great importance for engineering, being one of the most interesting existing ceramic materials, both for its numerous applications and for its varied physical properties, such as: extraordinary thermal stability at high temperature, high chemical inertia and satisfactory mechanical performance (Jia, Liu, Mao, & Wang, 2020; Kobayashi, Goto, Aoba, & Miura, 2019, Chen et al., 2019; Zahir et al., 2017). In addition, the material from burning sugarcane bagasse presents as its main chemical compound, silica, which together with Al_2O_3 form a material called silica-alumina, which represent a family of chemicals very useful in the field of adsorption and catalysis. They are substantially stable materials at relatively high temperatures (up to 500-700°C) and also have adjustable morphology and porosity, as well as mechanical strength (Busca, 2020).

The aim of this study was to prepare and characterize an activated carbon from sugarcane bagasse agglomerated with alumina and apply it to reduce the toxic parameters of vinasse, such as color, turbidity, chemical oxygen demand (COD), total organic carbon (TOC) and toxicity to a bioindicator. The intention is to add value to sugarcane bagasse and develop an efficient, low-cost and environmentally friendly treatment for vinasse, thus contributing to a more sustainable society.

Material and methods

Material

The sugar cane bagasse and vinasse were donated by Santa Terezinha Ltda. Sugar and Ethanol Industry, located in the district of Iguatemi-PR. The sugar cane bagasse was collected right after the sugar cane crushing stage. The bagasse was dried in an oven with air circulation at 65°C for 24 hours and stored in polyethylene bags. The dry bagasse was used without any pretreatment. The vinasse was collected in plastic gallons and stored under refrigeration at 4°C until the moment of use. To obtain the alumina, a solution of 1 M of $AlCl_3.6H_2O$ (SYNTH), 1 M of NH_4OH (NUCLEAR) and deionized water was used.

Methods

Synthesis of Alumina

The synthesis of the alumina precursor consisted of preparing the solution of $AlCl_3.6H_2O$ (1 M), keeping it under magnetic stirring on a stirrer/heater at a temperature of 60°C, and then a solution of NH_4OH (1 M) was added until the precipitation of the boehmite gel was completed. The precipitate was then filtered and washed first with NH_4OH at approximately 60°C for precipitation of the remaining boehmite and finally with deionized water for complete removal of the residual ammonium hydroxide.

Production of activated carbon

The activated carbon was produced in an experimental unit, presented in Figure 1, composed of a (1) nitrogen cylinder with (2) a flow meter to control the flow of inert gas, (3) a temperature controller N1100, (4) bipartite tubular furnace (Sanchis, power 3 kW, 220 V, maximum temperature 1200°C), (5) a fixed-bed reactor developed in stainless steel parts with gas inlet and outlet (6) a thermostatic bath to provide chilled water (3.5°C) to a (7) glass serpentine condenser responsible for collecting the pyrolysis liquid and (8) a glass flask for depositing the bio-oil.

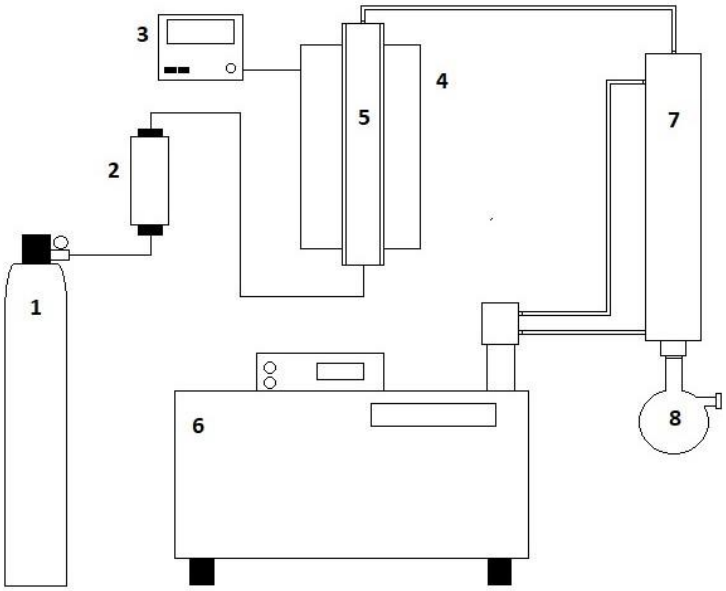

Figure 1. Experimental module for the production of cane bagasse activated carbon agglomerated with alumina.

Initially, the sugarcane bagasse was submitted to a pyrolysis process with N_2 (150 mL min^{-1}) at 450°C to eliminate the volatile products of the organic matter degradation, in order to maintain, besides the mineral elements, only a carbonized skeleton. After the heat treatment, the bagasse was mechanically mixed with the boehmite gel, in the proportion of 30 g of bagasse to 35 g of boehmite gel obtained in the previous step, and then the pellets were prepared. The mixture was placed in a manual pelletizer and then pressed in a mechanical press. The applied pressure was 3 tons for five seconds, resulting in a pellet with dimensions of 3 cm in diameter and 1 cm in height. The pellets were submitted to a pyrolysis treatment under nitrogen flow (150 mL min^{-1}) with a heating ramp of 10°C min^{-1} and plateau of 450°C, the temperature necessary for the bohemian gel to be transformed into alumina in its gamma phase, which has a high specific area (100-200 m^2 g^{-1}), for 1h and 30 min. (Goodboy & Downing, 1990).

After pyrolysis, the samples were chemically activated with NaOH at a ratio of 1 g carbon to 3 g reagent. The mixture was left to rest for 1h and was oven dried at 110°C for 18h, and then activated in a stainless-steel reactor with a heating ramp at 5°C min^{-1} at 400°C for 1 hour during dehydration and up to 450°C for an additional hour. After activation, the material was washed. Initially the activated carbon was immersed in distilled water and stirred for 20 min. The suspension was filtered on quantitative white paper with pores of 25 µm and washed with distilled water. In this washing step, the activation byproducts (carbonates, silicates, etc.), which are water soluble, were removed from the carbonaceous matrix, leaving the pores free, characteristic of activated carbon (Navarro, Sepúlveda, & Rubio, 2000; Seixas et al., 2016). After this procedure, the AC was oven dried at 110°C for 18h and then sieved with the retained fraction between 18 and 20 mesh (Tyler).

Characterization

After the production of activated carbon, the material was submitted to a characterization process based on textural analysis performed by N_2 adsorption/desorption isotherms at 77 K, using Micromeritics equipment, model: ASAP 2020. The specific area of the materials was estimated by the BET method. The meso and micropore areas were determined by BJH and t-plot methods, respectively, the average pore diameter was estimated by BJH method, the micropore size distribution was determined by Dubinin-Astakhov method.

The X-ray diffraction analysis was carried out with the objective of identifying the crystalline species present in the samples and was carried out in a Bruker diffractometer, with 40 kV and 30 mA copper ion source, angular velocity of 0.7° min^{-1} in the range of 5° to 65°2θ with a pitch of 0.01.

To observe the morphology of the activated carbon, a scanning electron microscope (SEM) Quanta 250, XT software was used. The sample was fixed on a support by means of conductive double-sided carbon tape and then metallized with gold in a Bal-TEC metallizer model SCD 050 to ensure the electrical conductivity of its observation surface. The EDS was performed in an Oxford Instruments Detector, AZtec Energy EDS software coupled to the scanning electron microscope.

The analysis of pH_{ZPC} was carried out by adding 20 mg of the adsorbent in 20 mL of aqueous solution of NaCl 0.1 M, under 12 different conditions of initial pH (1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12), adjusted with HCl or NaCl 0.1 M solutions. The solutions remained in agitation (100 rpm) for 24h in a thermostatic bath, at 25ºC. At the end, the solutions are filtered and the final pH of the solution is measured. The pH_{ZPC} corresponds to the range in which the final pH remains constant, regardless of the initial pH, that is, the surface behaves like a buffer.

Adsorption tests

The activated carbon produced was tested for adsorption of vinasse. Before the adsorption test, the vinasse underwent a coagulation/flocculation process in order to reduce the large number of suspended solids and allow better performance of the activated carbon. Satyawali & Balakrishnan, 2008 used activated carbon as the sole decolorization process and found it to be inefficient in vinasse treatments. A better option is combined treatment such as coagulation-flocculation followed by adsorption that will result in more effective decolorization. The coagulation/flocculation process was performed with Tanac SG coagulant from Tanac. The clarification tests of the previously treated vinasse were performed in 125 mL conical flasks closed with plastic film, with slow stirring in a thermostatic bath. Solutions of 20 mL of vinasse diluted in water in the proportion of 4, 8, 12, 16 and 20 mL were used in contact with 3.0g of adsorbent and the temperature varied at 30, 40 and 50°C for 72h. For the kinetic study, 3 g of adsorbent and 20 mL of vinasse were also used with sample withdrawal every hour. At the end of the contact time, the adsorbent material was filtered in quantitative paper with pores of 25 µm.

Evaluation of the efficiency of vinasse treatment

The evaluation of the efficiency of the vinasse treatment was performed by analyzing the following parameters: color, turbidity, pH, chemical oxygen demand (COD), total organic carbon (TOC) and toxicity. We verified the ability to remove these parameters from the vinasse in natura measurements, compared to the measurements taken after the treatment processes, coagulation/flocculation and adsorption.

Color, turbidity and pH

Color and turbidity readings were determined according to the procedures described in Standard Methods for the Examination of Water and Wastewater. The analyses were performed in a Hach DR/2010 spectrophotometer, with the following wavelengths: color at 455 nm and turbidity at 860 nm. Color and turbidity readings were expressed in mg PtCo L^{-1} and FTU, respectively. The pH of the samples was determined using a Digimed digital pH meter at 27°C.

Chemical Oxygen Demand (COD)

The determination of COD was performed according to the American Public Health Association [APHA]. 1995) through digestion and photometric quantification at 600 nm. A HACH reactor and a HACH spectrophotometer, model DR/2010, were used.

Total organic carbon (TOC)

Total organic carbon of the samples was determined by the direct method and performed using and Hach HX0001-00846 high range test tubes (20 to 700 mg L^{-1} C).

Toxicity test

To evaluate the toxicity of the vinasse after treatment *Artemia salina* was used as a bioindicator organism of toxicity of chemical substances and pollutants. The guideline for hatching *Artemia salina* cysts consists of incubating the cysts in saline solution prepared with sea salt at a concentration of 35g L^{-1} for 48h at 28°C with continuous lighting and aeration. After hatching, the most active organisms were separated from cysts that

did not hatch using a light beam directed at these organisms for over 24h. For toxicity tests, ten larvae of *Artemia salina* were transferred with the aid of a dropper, to a multi-well plates containing 35g L^{-1} of saline solution and 1g L^{-1} of potassium dichromate at five different concentrations (0, 10, 20, 40 and 60 mL), which corresponded to the control plate (toxic reference) and ten more larvae were added to another multi-well plate containing 35g L^{-1} saline solutions prepared with a sample to be tested at six different concentrations (0, 0.1, 0.3, 0.7, 1 and 2 mL), which corresponds to the sample plate. The plates were maintained for 24 hours in the dark and the tests were performed in triplicate. Mortality of nauplii was assessed and, when the rate was greater than 50%, it was possible to determine the LC_{50} from the Reed–Muench graph. The test was considered valid if the mortality in the control did not exceed 10%.

Results and discussion

Characterization of vinasse

The results of the analyzed parameters of the vinasse in natura are presented in Table 1. The vinasse showed an acid pH of approximately 4.6, a value that is in accordance with what is reported in the literature (Rulli et al., 2020; Seixas et al., 2016; Souza, Girardi, Santana, Fernandes-Machado, & Gimenes, 2012; Christofoletti et al., 2013). The acidic pH of the vinasse is due to the presence of sulfuric acid added to the mash during the fermentation process and the presence of organic matter that is basically in the form of organic acids (Seixas et al., 2016; Moraes, Santos, Delforno, Fuess, & Silva, 2019). The high value of chemical oxygen demand (COD) is a characteristic of vinasse independently of the raw material (sugarcane, sugar beet, tequila, mezcal) as stated by Moran-Salazar et al. (2016).

Table 1. Physical-chemical characteristics of fresh vinasse.

Parameter	Concentration
pH	4.6
Color (mg PtCo L^{-1})	40 600
Turbidity (FAU)	10 756
COD (mg O_2 L^{-1})	74 650
TOC (mg L^{-1})	20 250

Regarding the high value of turbidity, this is also a common characteristic of vinasse and is caused by the presence of particles in suspension and in a colloidal state, which can present various sizes and a wide variety of materials, including fine sand particles, clay and microorganisms (Robles-González, Galíndez-Mayer, Rinderknecht-Seijas, & Poggi-Varaldo, 2012). It is typical that vinasse contains suspended solids. All the values obtained from the characterization confirm the polluting potential of the vinasse effluent.

Characterization of the adsorbent

The N_2 adsorption/desorption isotherm for activated carbon showed characteristics of micro and mesopores with small hysteresis of type H3, associated with non-rigid aggregates of plate-shaped particles, originating pores in cracks as shown in Figure 2. Table 2 shows the values of specific area, volume, average pore size and the zero-point charge (pH_{ZPC}) of both activated carbon without binder and activated carbon agglomerated with alumina for comparison and evaluation of the effect of the binder on the parameters in question. The specific area of the activated carbon agglomerated with alumina suffered a small reduction when compared to the activated carbon without agglomerate, as well as the total volume of pores, this effect is expected, according to the literature this reduction is due to the addition of agglomerates produces more compacted samples, with a predominance of micropores, a consequence of the greater contact between the fibers of the bagasse provided by the presence of the binder (Gonçalves, Mendes, Pereira, & Sousa, 2006).

The pH_{ZPC} value obtained for the activated carbon from bagasse was 8.86, a value in agreement with that found by Seixas et al., 2006 who stated that the activated carbons with NaOH have a basic zero charge value when compared to non-activated ones, since the NaOH activation process promotes changes in the surface groups of the material. The increase in the pH_{ZPC} value for the activated carbon bagasse agglomerated with alumina is due to the presence of alumina which presents a basic surface (Gouvêa & Murad, 2001). The pH_{ZPC} of the alumina agglomerated activated carbon bagasse indicates that the adsorbent can interact with negative species present in the vinasse, which has a lower pH (pH = 4.6 table 1) than pH_{ZPC} (Fiol & Villaescusa, 2009).

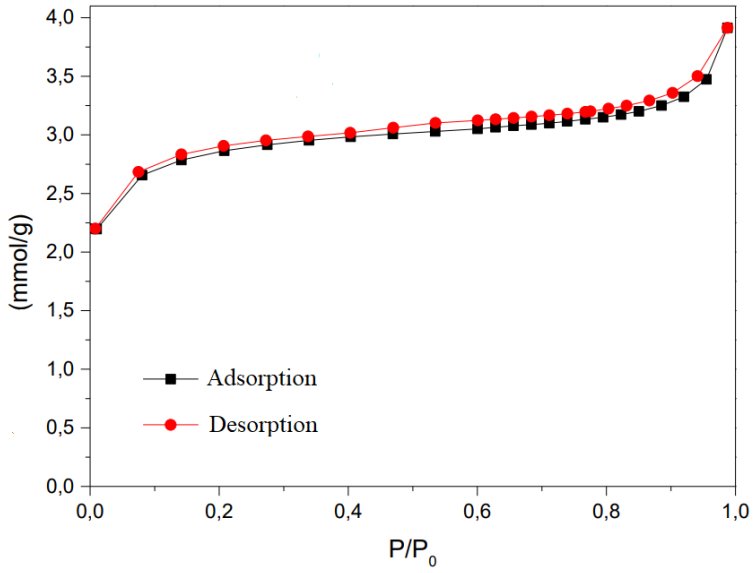

Figure 2. Adsorption/desorption isotherms from N_2 at 77K.

Table 2. Specific area, volume, average pore size and zero charge point for bagasse activated carbon without alumina and bagasse activated carbon agglomerated with alumina.

Adsorbent	Specific area ($m^2\ g^{-1}$)	Total pore volume ($cm^3\ g^{-1}$)	Medium Size (Å)	pH_{ZCP}
Sugarcane bagasse carbon with aluminum	913	0.2004	17.22	10.06
Sugarcane bagasse carbon	1287	0.456	15.34	8.86

From the diffractogram of the sample of activated carbon of sugarcane bagasse agglomerated with alumina, it was possible to verify the existence of a crystalline structure with well-defined peaks and high intensity as shown in Figure 3. The crystallinity presented by the adsorbent is characteristic of cellulose, which among the three main components of biomass is the only one with a partially crystalline structure. At 2Θ = (36.3103) a diffraction peak characteristic of the crystallographic plane (11-1) with an interplanar distance of 2.562 Å characteristic of alumina (#35-0121) was identified. At 2Θ = (42.8252); (45.0972); (53.0083) also refer to alumina peaks in a monoclinic arrangement (#11-0517). In addition, the presence of other diffraction peaks was observed that can be attributed to the inorganic components present in the bagasse.

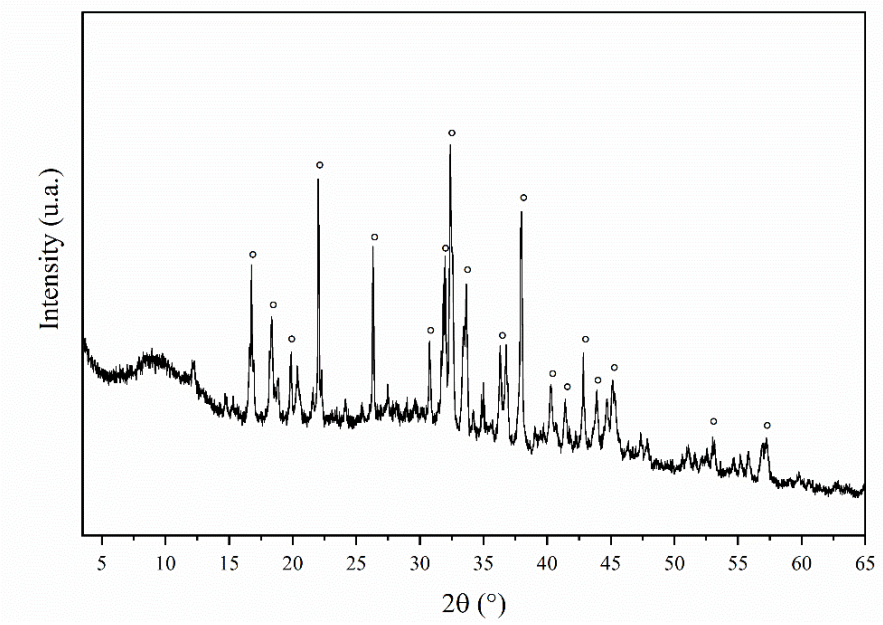

Figure 3. Diffractogram of the activated carbon sample of sugarcane bagasse agglomerated with alumina.

According to the activated carbon micrographs, shown in Figures 4a, 4b and 4c, it was possible to observe an irregular structure of the sample with a large number of pores and cavities of different sizes and also the presence of a fibrous structure, characteristic of the sugar from sugarcane bagasse used as raw material. From the EDS analysis (Figure 4d), a heterogeneous composition was observed, with peaks referring to carbon and oxygen, common in activated carbon from vegetable material. The presence of sodium is a consequence of chemical activation and aluminum comes from the alumina used as binder.

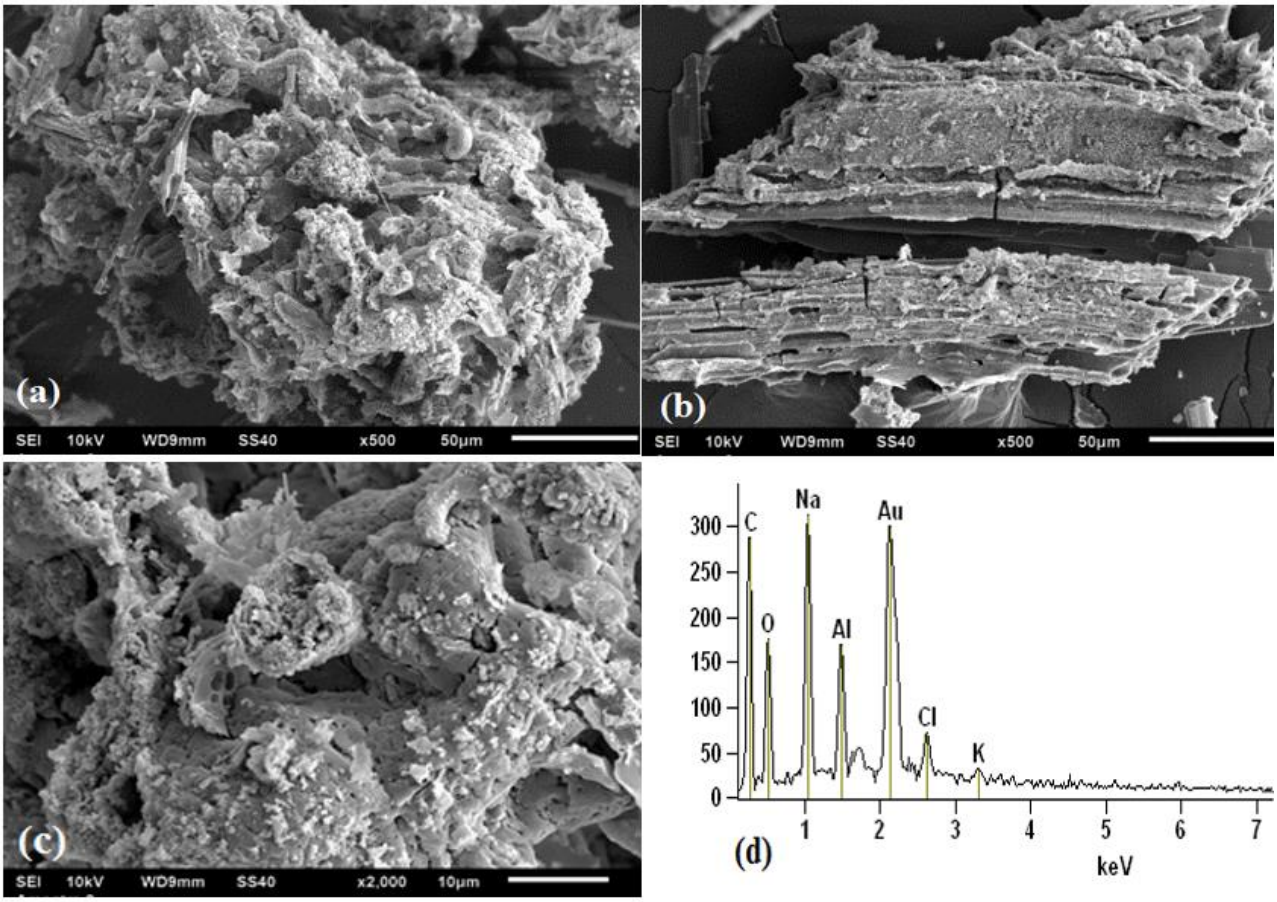

Figure 4. Micrographs with 500x (a and b) and 2000x (c) of magnification and (d) spectrum of cane bagasse activated carbon agglomerated with alumina.

Adsorption kinetics

The monitoring of the adsorption kinetics was performed based on the amount of total organic carbon (TOC) present in the pretreated vinasse, as it is a representative parameter that includes the compounds that can be adsorbed. The amount of TOC adsorbed per kg of adsorbent over time, as shown in Figure 5, is actually an equivalent value of adsorbed compounds, counted by measuring the TOC consumed in the liquid phase. From the results presented, it is possible to state that the removal of TOC from the vinasse presented a profile that tends to saturation, reached after six hours of adsorption. The highest adsorbed amount was reached at the minimum temperature of 30°C, with a value of 0.000260 kg kg^{-1} of adsorbent. This result corroborates the literature stating that in general in adsorption processes the amount adsorbed decreases with increasing temperature. Among the kinetic models tested, the pseudo-first-order kinetic model was the one that best fitted the experimental data considering the correlation coefficient (R^2) as presented in Table 3. The activation energy was calculated from the Arrhenius equation and a value of 18.24 KJ mol^{-1} was obtained, which according to the literature characterizes a physical adsorption process (from 5 to 40 KJ mol^{-1}), controlled by intraparticle diffusion and mass transport and less dependent on temperature (Nollet, Roels, Lutgen, Der Meeren, & Verstraete, 2003). The positive sign of activation energy means that, with increasing temperature, the kinetic constant increases (Wang, Mu, Zhao, & Yu, 2006).

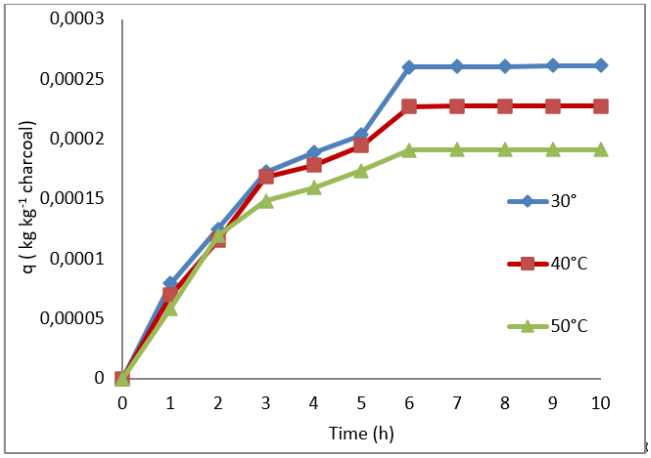

Figure 5. O_2 adsorption for kg of carbon versus time in hours.

Table 3. Parameters for the kinetic adjustment of pseudo-first order reaction and value for E_{at}.

Adsorbent	T (°C)	q_e (exp.) (kgO_2 kg^{-1})	k (s^{-1})	q_e (calc.) (kgO_2 kg^{-1})	R^2	E_{at} (KJ mol^{-1})
Sugarcane bagasse carbon with alumina	30	0.000260	0.0000859	0.000248	0.9876	18.24
	40	0.000227	0.0001094	0.000227	0.9861	
	50	0.000190	0.0001344	0.000195	0.9929	

Adsorption isotherms

The Langmuir and Freundlich models were adjusted to the experimental data, obtained for the three temperatures (30, 40 and 50°C), the isotherms were elaborated and are present in Figures 6a, 6b and 6c. Evaluating the fit by the R^2 and χ^2 values, available in Table 4, it is possible to evaluate that the Langmuir model fitted best to the experimental data, which means, monolayer isotherms, in which adsorption is limited. The R_L parameter of the Langmuir isotherm results in a value between 1 and 0.01 for all temperatures tested, indicating that the isotherms are favorable in the evaluated concentration range (Vargas, Cazetta, Kunita, Silva, & Almeida, 2011). The maximum amount adsorbed was higher at 30°C, but the q_m value was not severely influenced by temperature, as can be seen in Table 3. The values of b were much higher than 1, which is typical of the extremely favorable isotherm (McCabe, Smith, & Harriott, 1993).

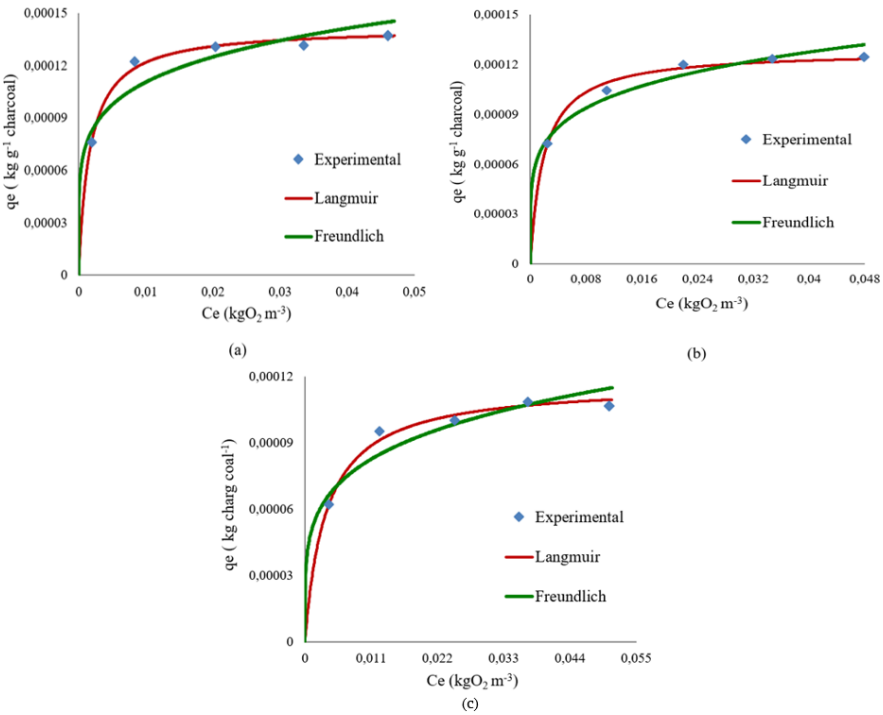

Figure 6. Adsorption isotherms at temperatures of (a) 30°C, (b) 40°C and (c) 50°C.

Table 4. Parameters calculated by isotherm models of Langmuir and Freundlich.

Adsorbent	T	Langmuir			Freundlich		
	(°C)	q_m ($kgO_2\ kg^{-1}$)	b ($m^3\ kg^{-1}O_2$)	R^2	K	n	R^2
Sugarcane bagasse carbon with alumina	30	0.00014	608.92	0.9952	0.00025	5.6274	0.8685
	40	0.00012	518.84	0.9903	0.00023	5.2493	0.9543
	50	0.00011	283.48	0.9897	0.00021	4.6446	0.8868

According to the classification of McCabe et al. (1993) the isotherms presented the characteristic shape of extremely favorable isotherms, which indicates that the adsorption capacity tends to be high for a low equilibrium concentration. Regarding the classification proposed by Giles, MacEwan, Nakhwa, and Smith (1960), the isotherms can be classified as L2, which are typical Langmuir isotherms, characterized by a decrease in the slope of the curve as the available sites for adsorption decrease, due to the surface coverage of the adsorbent, and indicates that at low concentrations the surface has high affinity for the components that generate TOC in vinasse, and this affinity decreases at higher concentrations.

Estimation of thermodynamic parameters

The thermodynamic parameters (ΔG°, ΔS° and ΔH°) values of the adsorption process are presented in Table 5. The adsorption process was shown to be exothermic and favored at lower temperature justified by the negative value of ΔH° for lower temperature, like most adsorption processes. The value of ΔH° was less than 25,000 J mol^{-1}, which is a indicative of physisorption (Varshney, Gupta, & Singhal, 1995). The ΔG° values were negative, indicating the occurrence of a spontaneous adsorption process. These values are in accordance with the concepts of adsorption, which is a spontaneous process in nature. The negative value of positive ΔS° indicates an increase in entropy, according to Wang et al. (2006) this phenomenon is associated with a perturbation of the adsorbent structure by the replacement of adsorbed water molecules by adsorbate molecules. Furthermore, the vinasse has several substances with potential for adsorption, which causes competition resulting in global variations of enthalpy and entropy different than when a single substance is adsorbed.

Table 5. Thermodynamic parameters.

Adsorbent	T (°C)	ΔG° (J mol^{-1})	ΔH (J mol^{-1})	ΔS° (J $mol^{-1}K^{-1}$)
Sugarcane bagasse carbon with alumina	30	-16350.45	-3093.40	-48.09
	40	-15869.46		
	50	-15388.48		

Efficiency of the coagulation-flocculation/adsorption process

Evaluating the coagulation-flocculation process along with adsorption with activated carbon from bagasse, it was noticed that the combined process was efficient in reducing the toxic parameters of the evaluated vinasse. Table 6 shows the values of the parameters of color, turbidity, TOC, COD and toxicity of untreated vinasse and vinasse treated by coagulation-flocculation/adsorption at the lowest temperature (30°C), and the percentage of reduction of each parameter.

Table 6. Color, turbidity, COT, COD and toxicity of untreated vinasse, and vinasse treated by coagulation-flocculation/adsorption at the lowest temperature (30°C).

Parameter	Color (mg PtCo L^{-1})	Turbidity (FAU)	COD (mg $O_2\ L^{-1}$)	TOC (mg L^{-1})	LC50 [a]	Dilution [b]	Mortality [c] (%)
Vinasse in natura	40 600	10 756	74 650	20 250	1.54	0.35:1	100
Vinasse treated with coagulation/ adsorption	10 756	423	20 416	9 842	2.57	1.24:1	22
Reduction (%)	73.50	96.06	72.65	51.47	-	-	78

[a] Lethal concentration of vinasse that causes death of 50% Artemia nauplii after 24h of exposition; [b] Dilution (mL of vinasse for 1 mL of synthetic seawater (35 g L^{-1})); [c] Mortality: percentage of accumulated dead organisms (to a dilution of 1:1).

The parameter with the highest percentage of removal was turbidity (96.06%), and this is due to the good performance of the pre-treatment used in the coagulation-flocculation vinasse that removed most of the

suspended and colloidal particles, which are mainly responsible for the turbidity of the effluent associated with inorganic compounds. This removal of suspended material also contributed, to a smaller scale, to the reduction of other parameters: color, COD, TOC and toxicity.

For the color parameter, the removal achieved was 73.50%. The decolorization of vinasse is mainly associated with the removal of polyphenolic and colored compounds present in the vinasse, mainly melanoidins, tannic acid and humic acid, and that are difficult to remove by oxidation with classical biological treatments. The adsorption process with activated carbon, with significant distribution of micropores and mesopores, has been shown to be very efficient in the adsorption of melanoidins and dark composites in vinasse. The result achieved in this work confirms the affinity of the produced activated carbon for the compounds responsible for the color of the vinasse (Caqueret, Cagnon, Bostyn, & Fauduet, 2012; Ahmedna, Marshall, & Rao, 2000; Satyawali & Balakrishna, 2007).

The reduction of COD reached 72.65%, quite considerable value given the large amount of organic matter present in the effluent. The value is similar to that achieved by Chingono, Sanganyado, Bere, and Yalala (2018) (72% reduction) that used the adsorption process with sugarcane bagasse ashes, higher than the value achieved by Guerreiro et al. (2016) (43.6% reduction) that used a combined coagulation-flocculation and Fenton oxidation process and also higher than the reduction achieved by Seixas et al. (2006) (69% reduction) that used sugarcane bagasse activated carbon in multiple adsorption steps.

Regarding the reduction of the TOC parameter, the removal value obtained was 76.08%, higher than that obtained by Guerreiro et al. (2016) (reduction of 51.6%) and Santana et al., 2008 who used the process of heterogeneous photocatalysis with light and reached a removal percentage of 55%. The reduction of organic matter achieved in this work is of extreme importance, because the application of vinasse to the soil, as is done in many regions of Brazil, causes the leaching of this organic matter that can contaminate groundwater, causing microbiological growth and oxygen consumption.

To confirm the reduction of the vinasse pollution potential, bioassays were performed with *artemia salina*, and the result is presented in Table 6. As can be seen, there was a reduction in the toxicity of the vinasse after the combined coagulation-flocculation/adsorption process. The toxicity of the treated vinasse showed less toxicity than the control (potassium dichromate) with LC_{50} of 1.69, which corresponded to a dilution of 0.46:1 (0.46 mL of control to 1 mL of saline solution (35 g L^{-1})). The reduction in toxicity is also evident when analyzing the mortality of nauplii for a 1:1 dilution of vinasse (1 mL of vinasse to 1 mL of saline solution (35 g L^{-1})). As shown in Table 6 mortality dropped from 100% for untreated vinasse to 22% after the applied treatment.

In general, the combined coagulation-flocculation/adsorption process was efficient in reducing the polluting potential of the vinasse, due to the reduction of the parameters already presented and discussed. It is important to highlight the efficiency of the activated carbon from sugarcane bagasse agglomerated with alumina. The use of bagasse made the adsorbent a low cost and efficient alternative in reducing the toxic parameters of the vinasse. The agglomeration with alumina showed to be an alternative with great potential because it provided the adsorbent greater granulometry and possibility of application in fixed bed systems, in addition to a great efficiency in the treatment of vinasse, which can be associated with the presence of alumina (Al_2O_3), although the agglomeration reduced the specific area of the adsorbent, alumina is recognized as an efficient inorganic adsorbent due to its excellent physicochemical properties, low toxicity, large surface area and high porosity (Asencios & Sun-Kou, 2012).

Conclusion

The results showed that the activated carbon of sugarcane bagasse agglomerated with alumina is a promising adsorbent and when applied in conjunction with the coagulation-flocculation process it was possible to obtain removals of color, turbidity, COD, TOC and toxicity of vinasse with removal percentages of 73.50%, 96.06%, 72.65%, 76.08%, 78% respectively. The isothermal Langmuir model fitted the experimental data best and the pseudo-first-order model best represented the adsorption kinetics. The process was spontaneous, exothermic and with increased entropy.

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