OIL PRODUCED WATER TREATMENT USING SUGARCANE SOLID RESIDUE AS BIOSORBENT

TRATAMIENTO DE AGUA PRODUCIDA DEL PETRÓLEO USANDO RESIDUO SÓLIDO DE CAÑA DE AZÚCAR COMO BIOSORBENTE

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Abstract

Produced water is a waste generated in the units of petroleum production having as main characteristics the high salinity with presence of emulsified oil, suspended solids, chemical additives, heavy metals and other contaminants. Considering that the inadequate disposal of this water causes environmental contamination, this work aimed to investigate the adsorption of emulsified oil present in the produced water, using sugarcane bagasse (an abundant by-product from sugar/ethanol production) as adsorbent, reducing the pollutant of the effluent according to the parameters accepted by the Brazilian environmental legislation. The adsorption reached equilibrium within 5 minutes of contact and more than 90% of the emulsified oil present in the mixture was removed when 0.1% adsorbent (w/v) was used at 30 °C and 110 rpm. Pseudo first-order and pseudo second-order models were applied to adjust the kinetic data. The best correlation was provided by the pseudo first-order kinetic model demonstrating that chemical sorption was the rate-limiting step, although intraparticle diffusion can not be neglected. From these results, it can be stated that the use of sugarcane residues as an adsorbent agent is an alternative for the efficient removal of the oil present in the produced water. Thus, two partial problems can be solved: wastewater treatment and versatility of agroindustrial waste application.

Keywords: adsorption, petroleum, waste water, agroindustrial residue.

Resumen

El agua producida es un residuo generado en las unidades de producción de petróleo que tiene como características principales la alta salinidad con presencia de petróleo emulsionado, sólidos suspendidos, aditivos químicos, metales pesados y otros contaminantes. Teniendo en cuenta la eliminación inadecuada de esta agua que provoca contaminación ambiental, este trabajo tuvo como objetivo investigar la adsorción de petróleo emulsionado presente en el agua producida, utilizando bagazo de caña de azúcar (un abundante subproducto de la producción de azúcar/etanol) como adsorbente, reduciendo el contaminante del efluente según los parámetros aceptados por la legislación ambiental brasileña. La adsorción alcanzó el equilibrio dentro de los 5 primeros minutos de contacto y más del 90% del petróleo emulsionado presente en la mezcla se eliminó cuando se utilizó un 0.1% de adsorbente (w/v) a 30 °C y 110 rpm. Se aplicaron modelos de pseudo-primer orden y pseudo-segundo orden para ajustar los datos cinéticos. La mejor correlación fue proporcionada por el modelo cinético de pseudo-primer orden que demuestra que la absorción química es el paso limitante de la velocidad, aunque no se puede descuidar la difusión intrapartícula. A partir de estos resultados, se puede afirmar que el uso de residuos de caña de azúcar como agente adsorbente es una alternativa para la eliminación eficiente de petróleo presente en el agua producida resolviendo dos problemas parciales: el tratamiento de aguas residuales y la diversidad en el uso de este residuo agroindustrial.

Palabras clave: adsorción, petróleo, aguas residuales, residuos agroindustriales.

1 Introduction

A significant amount of water is used during the exploration and production of oil onshore and offshore. This water is called produced water and is the largest waste stream during the oil production (Farmen *et al.*, 2010). The produced water incorporates numerous organic (mainly, oils) and inorganic components, and their disposal can contaminate the superficial and underground water and soil. As mentioned by U.S Department of Energy, Office of Fossil Energy (2018) for every barrel of oil produced globally, there are three barrels of produced water. In the United States, the number is closer to 7-10 barrels of water for every barrel of oil, but in the worst scenarios, it can achieve 50 barrels. According to ANP (National Agency of Petroleum, Natural Gas and Biofuels) (2017), Brazil has 29 sedimentary basins with interest for hydrocarbons research (approximately 7.175 million km^2). Between January/15 to March/16 Brazil produced 43.5 million barrels of produced water, i.e., about 273 billion liters of produced water.

The treatment of this effluent is an important issue due to the high cost and expenses involved in the treatment of large flows generated in the process. This justifies the search for technologies and materials in the development of new treatment techniques that are efficient and economically viable (Motta *et al.*, 2014). The biosorption offers the benefits of low operating costs, reduced volumes of chemical and/or biological sludge to be disposed, high detoxification capacity of highly diluted effluent and no nutrient requirement. These benefits served as the main motivations for expanding the biosorption process at large-scale (Wang and Chen, 2006).

In the last years, the reduction of adsorption process costs are associated to the development of several categories of activated carbon that are processed from low-cost materials, mainly vegetal residues (Cruz *et al.*, 2018; Andrade *et al.*, 2018). In addition, several of these sources are also available for biosorption processes as untreated raw material, thus, eliminating activation costs, for example, those that are naturally abundant, such as seaweed and clays/sediments, and those obtained from agroindustrial wastes, as fermentation/food wastes (Kleinübing *et al.*, 2011).

Many studies report the use of low cost adsorbents in literature: sugarcane bagasse (Pehlivan *et al.*, 2013;

Guimarães *et al.*, 2012; Brandão *et al.*, 2010); clays (Chen *et al.*, 2012); silica (Gor *et al.*, 2013); chitosan (Sanford *et al.*, 2012); zeolite (Nanoti *et al.*, 2012); corn cob (Nethaji *et al.*, 2013); barley bark (Azizi *et al.*, 2013); wheat straw (Krishnani, 2016); sawdust (Cheng *et al.*, 2012); orange peel (Liang *et al.*, 2010); banana peel (Mohammed and Chong, 2014); rice husk (Xu *et al.*, 2013); passion fruit peel (Dutta *et al.*, 2011); pineapple leaves (Ponou *et al.*, 2011); avocado seed (Bhaumik *et al.*, 2014); peat (Vecino *et al.*, 2013); activated sludge (Rivera-Utrilla *et al.*, 2013); bone from cattle and sheep (Ghanizadeh and Asgari, 2011) and apple (Bello *et al.*, 2013). Sugarcane bagasse is a waste/by-product of the sugar/ethanol industry. It consists predominantly of a polymeric material rich in cellulose (40-50%), hemicellulose (25-30%) and lignin (20-25%) (Guimarães *et al.*, 2012). According to CONAB (National Supply Company) (2017), Brazil produced around 165 million tons of sugarcane bagasse, showing to be an abundant residual biomass.

Dyes adsorption studies with sugarcane bagasse (Deo *et al.*, 2007), heavy metals such as cadmium, chromium and mercury (Yu *et al.*, 2012; Ullah *et al.*, 2013; Khoramzadeh *et al.*, 2013) are described, but the study with this effluent type (oils) is limited. In a special mention, Brandão *et al.* (2010) studied the adsorption of petroleum hydrocarbons (gasoline and n-heptane) applying sugarcane bagasse. However, the parameters used were completely different of that proposed in this article. Contaminants concentration were high, with gasoline concentration changing between 41-370 g/L obtaining a qmax between 8.36-10.99 mL/gbagasse and for n-heptane, 38-157 g/L, and qmax of 2.77-3.06 mL/gbagasse. This research aimed to explore the potential use of sugarcane bagasse to remove oil from a diluted system (low oil concentration - real effluent characteristics, but still out of the legislation parameters) as is the case of produced water (main wastewater from petroleum extraction plants).

2 Materials and methods

2.1 Obtaining and characterization of the adsorbent agent

Sugarcane bagasse was supplied dry and ground by Grupo Toledo LTDA (Marechal Deodoro, Alagoas, Brazil). The fibers provided had a uniform particle

size distribution of 0.5 to 1.5 cm. Initially the bagasse was selected according to the desired fiber diameter through sieving, after which it was washed with running water to remove impurities. After washing, the bagasse was oven dried at 60 °C for 5 hours. Then, upon reaching room temperature, the powder material was stored in hermetic plastic containers until the experiments.

The material was characterized in order to know better the structure of the bioadsorbent and to facilitate the discussion of the adsorption process: moisture, maximum fiber diameter, ashes, scanning electron microscopy (SEM), thermogravimetric analysis, presence of inorganic compounds by X-ray fluorescence spectrometry, X-ray diffraction and Fourier transform infrared spectroscopy (FTIR) were performed. Moisture was determined by heating at 105 °C in a FANEM-model 515 greenhouse, being weighed after 8 hours until constant mass.

The maximum diameter of the sugarcane bagasse was determined by sieving. A set of Tamis, ASTM 20 - Tyler 20 mesh, opening of 0.850 mm was used. Ash content determination was carried out by incineration, heating the dried sample in an electric oven at 500 ºC for 4 h or until obtaining constant ash weight, indicating the absence of organic matter. Bagasse fibers morphology was obtained by scanning electron microscopy (SEM), using a scanning electron microscope (Vega3/Tescan), operating at 20 KV.

The thermogravimetric analysis (TG/DTG) was performed in a Shimadzu DTG 60H thermobalance with a heating rate of 10 ºC/min from room temperature to 800 ºC under a dynamic atmosphere of synthetic air with a flow rate of 50 mL/min. Samples were packed in 70 μL platinum crucibles and approximately 4 mg in mass. The presence of inorganic compounds was determined by energy-dispersive X-ray (EDX) in EDX-7000/8000. X-ray diffraction (XRD) analyze of the materials was performed using a Shimadzu XRD 7000 diffractometer employing Ni filters using CuKα of radiation of 1.54060Å. The data were collected in an angular range (2θ) 10-90°.

The bands of the chemical bonds were obtained by Fourier Transform Infrared Spectroscopy (FTIR) technique recorded in a Thermo Scientific Nicolet iS10 spectrophotometer with precision: 4000 to 400 cm^{-1} using the KBr pellet technique.

2.2 Synthetic produced water obtention and adsorption tests

The effluent used in this paper was produced synthetically, however, simulating the characteristics of the real produced water according to Motta *et al.* (2014) who prepared an Oil/Water emulsion using petroleum (API density of 28.3ºC and relative density of 0.8824 kg/L) in water to achieve an effluent with 200-400 mg/L of oil. The synthetic effluent was obtained from the emulsion of 40 mL of petroleum with 50 L of water, as mentioned, simulating the real oil concentration, which contains about 80-200 mg/L of oil. In the preparation of the emulsion, a pilot unit consisting of 100 L feed tank, a 1/2 hp centrifugal pump for emulsion recirculation with flow of 90 L/h (P1), a peristaltic pump to supplying oil (P2) and a stirrer with rotation of 1000 rpm as outlined in Figure 1.

Two hours after the beginning of the emulsification process, an ideal and homogeneous mixing was obtained, and then the effluent was used in the batch adsorption experiments. The tests were conducted with 0.2 g of the adsorbent (sugarcane bagasse) in 200 mL of water produced (0.1% w/v) and then placed in a Shaker Incubator SL 222 (SOLAB) at 30°C under constant stirring at 110 rpm.
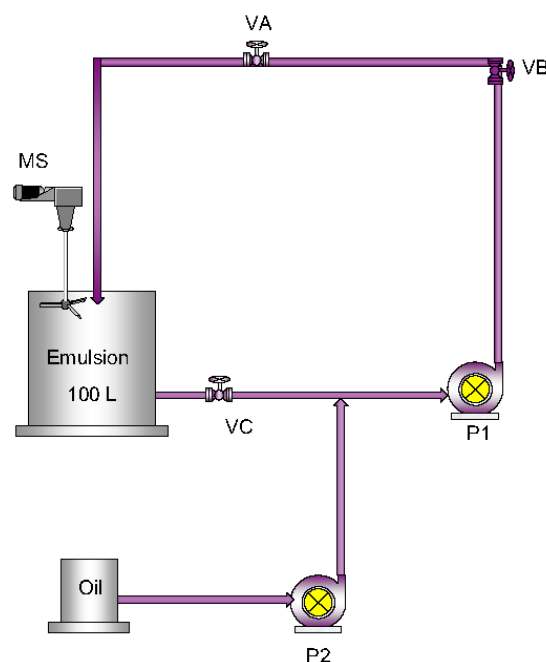

Fig. 1. Emulsion preparation system.

The pH of the emulsion was maintained acid (∼ 4.0) as suggested by Brandão *et al.* (2010), since for hydrocarbons adsorption, this parameter does not change significantly. After the adsorption process, the suspension was filtered and the oil and greases content (TOG) was extracted from the filtrate with solvent S-316.

The determination of oils and greases (C_t) was conducted in an HORIBA analyzer, model OCMA-350, with the samples collected at different reaction times: 5, 10, 15, 20, 25 and 30 min. The adsorption capacity of the bagasse in mg/g (q_t) was calculated according to Equation 1 which relates the concentration of oil in the liquid phase at a given moment in mg/L (C_t), the initial concentration of oil in the mixture in mg/L (C_0), the volume of the mixture in L (V) and the mass of adsorbent in g (W).

$$q_t = \frac{(C_0 - C_t)V}{W} \tag{1}$$

The kinetic models of pseudo first-order (Equation 2) (Lagergren, 1898) and pseudo second-order (Equation 3) (Ho and McKay, 1998) were used to adjust the experimental data:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \tag{2}$$

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t \tag{3}$$

where: q_e is amount of oil adsorbed in equilibrium by biomass (mg/g), q_t is amount of oil adsorbed at any time t (mg/g), k_1 is constant adsorption rate (min^{-1}) and k_2 is adsorption of pseudo second-order (g/(mg.min)).

In addition, the intraparticle diffusion was verified through the (Weber and Morris 1963) equation, which determines that the removal of adsorbate varies with time square root. Thus, the intraparticle diffusion coefficient (k_{int}) can be obtained from Equation 4.

$$q_t = k_{int} t^{0.5} + C \tag{4}$$

where: k_{int} is the intraparticle diffusion rate constant (mg g^{-1} min$^{-0.5}$) while C is a constant related to the thickness of the diffusion layer; that is, higher values of this constant reflect in greater effects of this layer (Ho *et al.*, 2000).

3 Results and discussion

3.1 Physical and chemical characterization of sugarcane bagasse

The biomass chemical composition is related to several factors, such as sugarcane type, soil, climatic conditions and even the handling and storage (Santos *et al.*, 2012). For this reason, a characterization was carried out aiming to compare the biomass used in this research with other publications. The physical characterization of the sugarcane bagasse was based on the analysis of moisture and ash content. The moisture of the dried biomass was 10.6%, Brandão *et al.* (2010) found 8.1%. The ash content was 18.8%, Paula *et al.* (2009) determined a content of 10% of ashes for sugarcane bagasse. In general, the main inorganic elements in biomass are Si, Fe, Ca and K, as discussed by Umamaheswaran and Batra (2008) and Paula *et al.* (2009). Elemental analysis of crude fiber determined with energy-dispersive X-ray (EDX) is presented in Table 1 and it is observed that Si is the predominant element in sugarcane bagasse, in accordance with the results presented by Paula *et al.* (2009).

Figure 2 shows the scanning electron microscopy of sugarcane bagasse. In the image (A) was possible to observe a compact structure with the presence of bound fibers, probably due to the presence of hemicellulose and lignin. This result agrees with that obtained by Yu *et al.* (2012) that justifies this image as the presence of homogeneous elongated cells in the sugarcane bagasse. In addition, these fibers may participate in adsorptive processes (Boniolo *et al.*, 2010). Images (B) and (C) show irregularities in the material surface which may be related to the pores of the material and help in the internal diffusion and adsorption of organic molecules (Weber *et al.*, 2013).

Table 1. Chemical analysis: elemental composition of sugarcane bagasse, determined by EDX analysis.

Element	Percentage (%)
Si	54.43
Fe	16.14
Ca	11.40
K	10.84
S	2.99
Ti	2.13

(A) 236 x
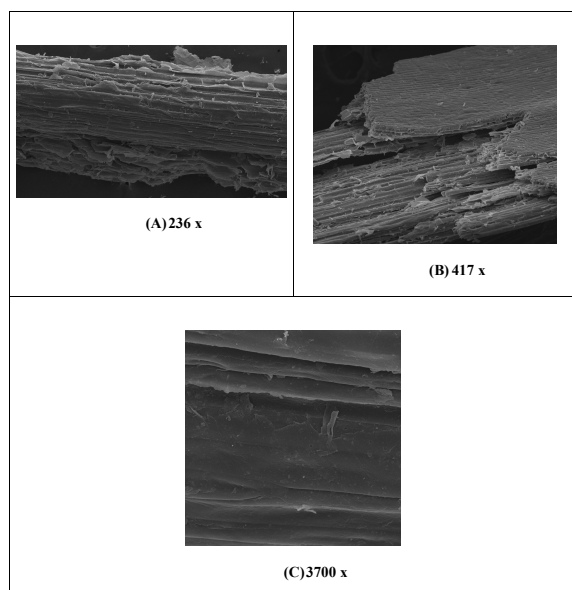
(B) 417 x

(C) 3700 x

Fig. 2. SEM examination of sugarcane bagasse: A) 236X, B) 417X and C) 3.7 kx.

Figure 3 shows the thermogravimetric curve of TG and DTG of the sugarcane bagasse. It is possible to observed a mass loss of approximately 6.2% between 25 and 170 ºC (Region I). According to the literature, this event is attributed to the desorption of water physically adsorbed on the surface (Kruk and Jaroniec, 2000). Another region of mass loss was observed between 171 and 390 ºC (Region II) which is associated with the removal of organic compounds, such as fats, waxes, alkaloids, terpenes, etc. In addition to these two losses, a third region of mass loss was detected between 391 and 800°C due to the decomposition of lignin, hemicellulose and cellulose (Mothé and Miranda, 2009).
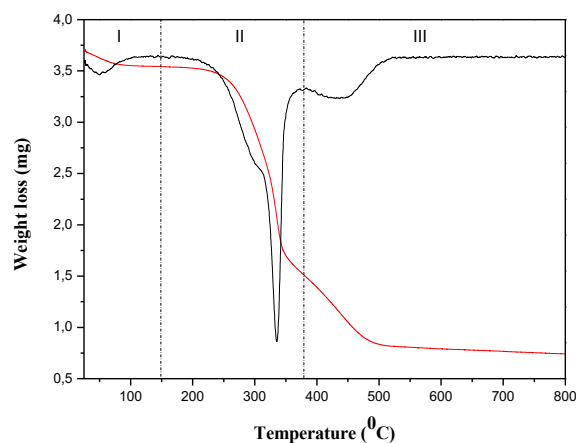

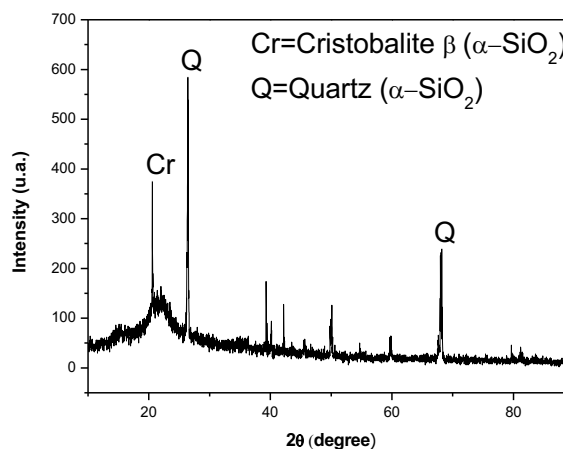Fig. 3. Thermogravimetric curve of sugarcane bagasse.

Fig. 4. XRD pattern of sugarcane bagasse.

The X-ray diffraction spectrum obtained for sugarcane bagasse is shown in Figure 4. It is possible to observed the presence of three main peaks, two more intense in the region $2\theta = 21.9º$ and $2\theta = 25.9º$ and another less accentuated in region $2\theta = 67.7º$. These peaks are referred to as the presence of cristobalite β (SiO_2) and quartz (α-SiO_2), being the main crystalline phase of the material. A wide range of dispersion is observed between $2\theta = 12º$ and $2\theta = 33º$, which implies the presence of amorphous compounds in the sugar cane bagasse (Ríos-Parada *et al.*, 2017).

Based on these results Ríos-Parada *et al.* (2017) concluded that the material is semi-crystalline. The result is in agreement with energy-dispersive X-ray analysis, where the chemical element Si is predominant.

With the infrared spectrum (Figure 5), it was possible to observe the presence of characteristic bands of lignocellulosic material (Yun *et al.*, 2010). According to Pehlivan *et al.* (2013) and Yu *et al.* (2012) the broadband around 3490 cm^{-1} is attributed to the elongation vibration of the hydroxyl groups OH.

This result is in accordance with thermogravimetric analysis, which presents a significant loss of mass relative to humidity. Bands around 2300 and 1600 cm^{-1} refer to the C−H stretch of alkanes present in cellulose and hemicellulose and the aromatic skeletal vibrations of the C = O bond present in lignin (Zhang *et al.*, 2013). The presence of the band in the 1300 cm^{-1} range is attributed to the C−H and C−O stretching vibrations in the acetyl group in hemicellulose (Zhang *et al.*, 2013).
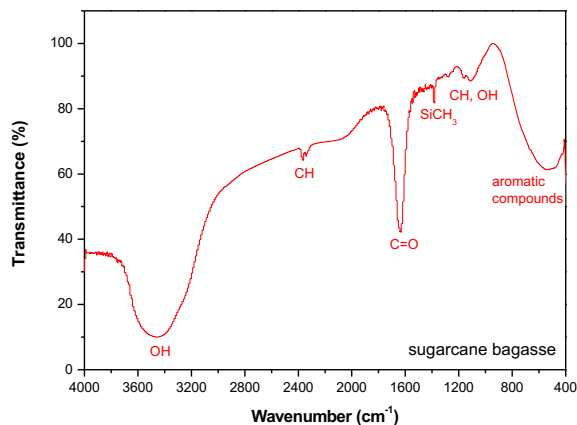
Fig. 5. Infrared spectroscopy of sugarcane bagasse.

The results obtained with the characterizations agree with the literature when it comes to lignocellulosic materials, which are materials consisting predominantly of cellulose, hemicellulose and lignin (Meili *et al.*, 2016; Vlaev *et al.*, 2011; Kenes *et al.*, 2012).

3.2 Batch adsorption experiments

Figure 6 shows the results of oil adsorption tests in water with 0.1% (w/v) adsorbent, pH 4.0 at 30 °C and 110 rpm, changing the reaction time (0-30 minutes) and initial concentration of oil (77.7, 99.8, 164.5, 179.0 and 212.0 mg/L). All curves appear to stabilize after an initial adsorption peak (the treated effluent was firstly collected in 5 min where the peak of adsorption was observed), suggesting a fast process (i.e., reaching the equilibrium in the first 5 min of reaction time) and the transient period of the curve was not verified. The considerable variation of the points in this equilibrium phase is a frequent behavior for these compounds which may be associated to the analytical variation of the oils adsorption or desorption after the saturation process. This effect was obtained by Brandão *et al.* (2010) treating hydrocarbons (gasoline and n-heptane) with sugarcane bagasse (at 400 rpm for 60 minutes) reaching the equilibrium phase after 5 minutes. In addition, water contaminated with crude oil was treated with corn cob and reached the equilibrium phase in 2 minutes of reaction (Nwadiogbu *et al.*, 2016).

In Table 2 it is possible to see the kinetic parameters for the pseudo first-order model which provided good adjustments with standard error between 2.6-15%.
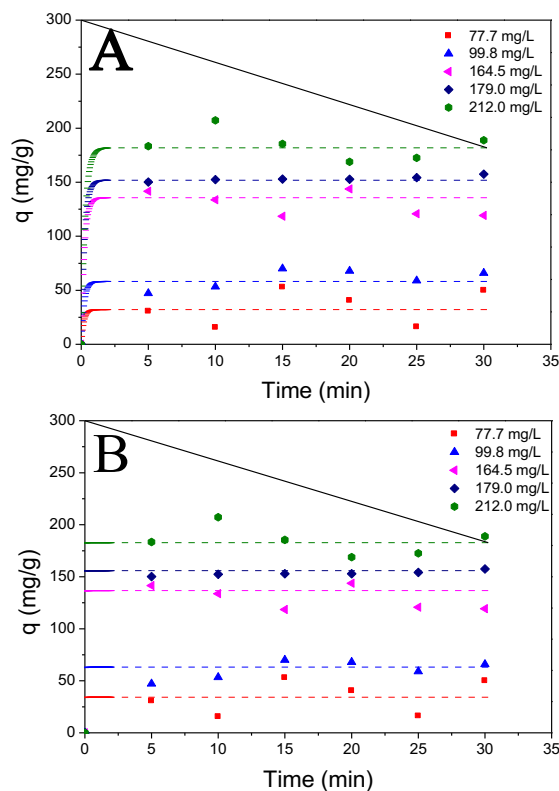

Fig. 6. Kinetic models. A) Pseudo first order and B) Pseudo second order model adjustment of kinetic data.

In the second-order pseudo-model an adjustment with the smallest standard error shows adsorption rates (k_2) that predict an almost instantaneous process but without evaluating a transient period, it is a little bit difficult to confirm. Kinetic models are used to determine the rate of the adsorption process and how this rate controls the equilibrium time. The adsorption mechanism depends on the physical and/or chemical characteristics of the adsorbent as well as the mass transport process (Xue *et al.*, 2014).

It is important to note that the concentrations of oil used in this paper changed between 20-212 mg/L, simulating the real produced water obtained in the region of this study, as previously mentioned, which has between 80-200 mg/L of oil concentration and is very low in comparison with other published papers that commonly have used concentrations up to 2000 mg/L (Okiel *et al.*, 2011; Fathy *et al.*, 2017) or in special cases of 13.000 mg/L (García-Alcántara *et al.*, 2016; Melgarejo-Torres *et al.*, 2017). However, this value (80-200 mg/L) is still higher than the minimum requirement of the Brazilian legislation, thus requiring disposal and treatment before discharger or reuse and will be discussed below.

Table 2. Kinetic parameters for the adsorption of oil in sugarcane bagasse. Experimental conditions: pH = 4.0, T = 30 °C; Adsorbent mass = 0.1% (m/v).

C_0	PFO		PSO		PFO	PSO
(mg/L)	k_1	q_e	k_2	q_e	Standard Error (%)	
77,7	5,21	32,11	52,12	34,25	15,02	14,8
99,8	4,72	58,12	49,75	63,12	8,56	7,96
164,5	4,31	135,70	48,15	136,70	12,17	12,48
179	4,07	151,90	44,98	155,85	2,63	1,7
212	3,52	181,90	44,34	182,79	12,67	14,75

PFO - pseudo-first and PSO - pseudo-second order models. Nonlinear adjustments were performed to determine the values of k_1 (min^{-1}), k_2 (g/(mg.min)) and q_e (mg/g).

Figure 7 shows a behavior of the oil removal rate at very diluted concentrations, which is not discussed in the mentioned articles. In this research, the percentage of oil removal increases when the initial oil concentration is higher achieving an optimum point from which the removal rate starts to decrease. In studies with higher concentrations of hydrophobic compounds (water produced and crude oil - up to 2000 mg/L, and exceptionally 50% (v/v) by Brandão *et al.* (2010)), this behavior was not observed, which probably showed the results after the optimum point where the removal rate decrease when the oil concentration increases, i.e., an inverse behavior (Okiel *et al.*, 2011).

One explanation of this phenomenon is that by increasing the concentration of the contaminant (at very diluted mixtures), the driving force for mass transfer also increases. It is also possible to affirm that at low concentrations there will be available active sites in the surface of the adsorbent (i.e., saturation does not occur).
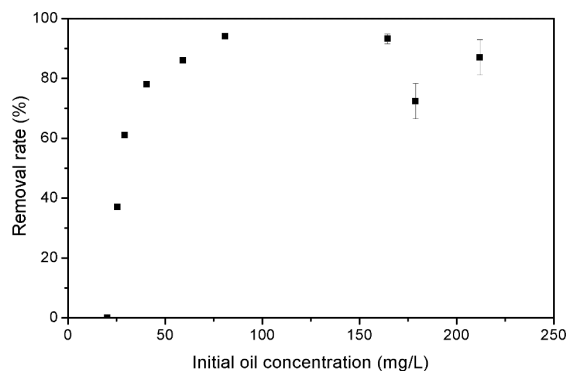

Fig. 7. % Removal rate as a function of initial oil concentration.

From this explanation, the gradual increase of the contaminant will reflect in better removal rates, reaching an optimum point (saturation/equilibrium) (Pathania *et al.*, 2017). In this research, all experiments with initial oil concentration up to 100 mg/L, final concentrations lower than 10 mg/L in liquid phase were obtained, which made it difficult to adjust the equilibrium isotherms.

According to Brazilian legislation (CONAMA Resolution No. 393/2007), the disposal of produced water in water bodies requires a monthly average concentration of oils and greases up to 29 mg/L, with a daily maximum value of 42 mg/L. The results of this work demonstrated that produced water with oil concentrations up to 100 mg/L can be efficiently treated with 0.1% (w/v) of adsorbent (sugarcane bagasse). For higher concentrations of contaminant, the increase of adsorbent concentration or multi-stage processes would solve the problem.

As seen in Table 3, the removal of hydrophobic compounds by bioadsorbents had some similarities with this study. Some studies (generally those with lower contaminant concentrations) reported fast adsorption with equilibrium times within the first 10 minutes of reaction. On the other hand, the maximum adsorption capacities reached were much higher than those observed in this article, emphasizing the hypothesis of adsorbent unsaturation and justifying the results found in Figure 7.

To conclude, the results of intraparticle diffusion in the adsorption process of oil (produced water) in sugarcane bagasse are presented in Figure 8. An increase of the diffusivity constant is observed when the oil concentration is higher (initial oil concentration between (77.5-212 mg/L).

Table 3. Literature references for the adsorption of hydrophobic compounds in bioadsorbents.

Biosorbent	Adsorbate	Inicial oil concentration	Equilibrium time	Adsorption capacity q_e	References
Amorphous carbon thin film	Produced water	100-2500 mg/L	6 h	50-300 mg/g	Fathy *et al.*, 2017
Activated carbon, bentonite and deposited carbon	Oil-water emulsion	800-1600 mg/L	2 h	127-920 mg/g	Okiel *et al.*, 2011
Corncob	Crude oil	-	2 min	1000-2000 mg/g	Nwadiagbu *et al.*, 2016
Rice husk ash	Crude oil	-	2 min	1000-6000 mg/g	Vlaev *et al.*, 2011
Rice husk	Petroleum	-	5-10 min	12-15 g/g	Kenes *et al.*, 2012
Sugarcane bagasse	Petroleum hydrocarbons (gasoline and n-heptane)	5-50%	5 min	2-12 mL/g	Brandão et al., 2010
Sugarcane bagasse	Synthetic produced water	20-212 mg/L	5-10 min	207 mg/g	This study

The ratio between the constants of the different oil concentrations provide an indication of the increase in diffusivity, and consequently of mass transfer, even if qualitatively (transient period needed to be observed as well to provide a quantitative affirmation). k_{int} values were of 0.56, 0.72, 0.90, 1.82 and 1.88 mg g^{-1} min$^{-0.5}$, respectively according to the increase of oil concentration.
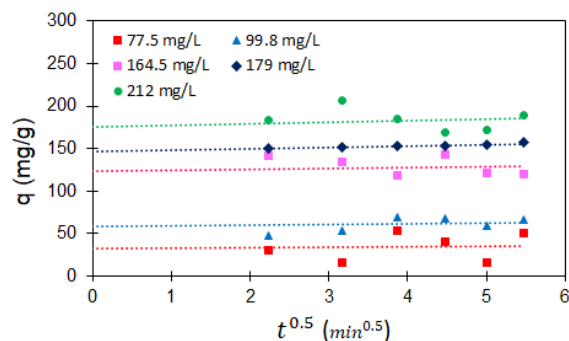
Estimating mass transfer or transfer coefficient can be important to understand if is possible to remove the oil present in the effluent, because this is one of the main phenomenon responsable to adsorb oil in biomass (Tec-Caamal *et al.*, 2018; Lizardi-Jiménez *et al.*, 2011; Lizardi-Jiménez *et al.*, 2012).

A similar behavior was observed by Weber *et al.* (2013), in the adsorption process of a tannery dye (70-400 mg/L) using papaya seed, however, higher values of k_{int} can be visualized, as a consequence of higher q_e found of 129.94-415.96 mg/g (k_{int} 0.58-6.65 mg g^{-1} min$^{-0.5}$ in comparison with this work. As well as by Bayramoglu *et al.* (2013), during the adsorption of the textile dyes RG-19 and RR-2 (20-400 mg/L) using amine-modified plant biomass of *A. caricum* (q_e between 16.5-63.4 mg/g and e k_{int} of 0.61-3.85 mg g^{-1} min$^{-0.5}$). As aforementioned, the adsorption was fast and the transitory phase was not properly viewed, and for this reason it is possible that the adsorption ploted in the Figure 8 have multilinearity, even though only the intraparticle diffusion coefficient was presented in this article.

Fig. 8. % Plot of intraparticle diffusion model for oil adsorption on sugarcane bagasse.

Conclusions

The residue used (sugarcane bagasse) was characterized and showed similarities with other published researches in terms of biomass structure emphasizing its potential for adsorption studies. EDX analyze show the characteristic signal of Si, the SEM showed a porous surface of the biosorbent, TGA analysis indicated the thermal stability, the FTIR spectra presented to better understand of the functional groups present in the material and X-ray diffraction (XRD) analysis showed the presence of amorphous compounds and that cristobalite and quartz being the main crystalline phase of the material.

Sugarcane bagasse, an important agricultural waste, proved to be very efficient for the oil removal in the water produced by adsorption. The equilibrium phase was achieved within 5 minutes of contact and removal rates higher than 90% were obtained using oil concentrations up to 212.0 mg/L. The maximum adsorption capacity was 207.3 mg/g at pH 4 and 110 rpm at 30 °C. Adsorption kinetics was better described by the pseudo first-order model, indicating that some chemical adsorption can occur. It was also observed that the intraparticle diffusion is involved in the adsorption process.

This paper emphasizes a sustainable solution to two industrial issues: the contamination of water generated in the oil industry and the solid residue generated by sugar/ethanol production.

Acknowledgements

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