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Use of Sugarcane Bagasse for Adsorption of Tetracycline in Aqueous Medium

KEYWORDS: adsorption, sugar cane bagasse, tetracycline, water

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ABSTRACT *A system involving sugarcane bagasse (SCB) was developed to remove tetracycline (TC) from water. This system, composed of glass columns and peristaltic pump, was optimized and, for pH and flow rate, the best values were 7.0 and 25 mL min*$^{-1}$ *respectively. After optimization, adsorption isotherm was built and it was possible to calculate maximum adsorption capacity of SCB for TC (*$MAC_{SCB\text{-}TC} = 0.31$ *mg g*$^{-1}$*). Additionally, real samples of pretreated water, from Espírito Santo Sanitation Company, were enriched with TC at 0.1 mg mL*$^{-1}$ *and passed through glass columns paked with SCB or activated carbon (AC) to compare the performance of SCB. The adsorption capacity of TC demonstrated by SCB (98%) was higher than AC (72%). The results encourage more advanced studies of technical and economic applicability of SCB in water treatment.*

INTRODUCTION

The pollutants drugs are constantly detected in the aquatic environmental in concentrations ranging from ng L^{-1} and µg L^{-1} (Hilton and Thomas, 2003; Teijón et al., 2011). The presence of pharmaceuticals in natural waters can be extremely dangerous to wildlife (Shai et al., 2011). Furthermore, these chemicals can reach water supply and return to humans through drinking water causing serious health problems (Fatta-Kassinos et al., 2011). Although antibiotics have been used for decades, the regulatory agencies of various countries have done little to regulate the disposal environment. A significant percentage of antibiotics are excreted in the aquatic environment by means of urine and feces from domestic sewage (Nebot et al., 2007; Reif et al., 2008) and hospitals (Focazio et al., 2008; Verlicchi et al., 2010). Tetracycline (TC) and its derivatives, for example, are commonly found in the aquatic environment (Yang and Carlson, 2004). This antibiotic has been widely used to treatment of infections caused by various types of pathogens (Ok et al., 2011). The occurrence of these substances in the aquatic environment may cause the onset of pathological microorganisms resistant (Gao et al., 2012) and induce undesirable biological responses in various types of organisms (Halling-Sørensen et al., 2002; Shai et al., 2011, Zhao et al., 2011). Therefore, it is important the research for developing economic and efficient methods for the removal of contaminants in drinking water. The adsorption process using activated carbon (AC) (Cabrita et al., 2010) and natural adsorbents (Ribeiro et al., 2011) is one of the most widely used due to its efficiency and economic viability.

The AC is the most used adsorbent for various pollutants removal (Cabrita et al., 2010). However, due to its high cost and considering the huge quantities of effluents to be treated, studies have been made to use the natural adsorbents of considerable availability and lower cost (Crini, 2006). Among these adsorbents include: vermicompost (Pereira et al., 2009), household used black tea (Tahir et al., 2009), *Ulva lactuca* and *Sargassum* (Tahir et al., 2008), green coconut mesocarp (Souza et al., 2010), vegetable sponge (Ribeiro et al., 2011), rice husk (HAN et al., 2008), *Firmiana simplex* wood fiber (Pan and Zhang, 2009), groundnut hull (Qaiser et al., 2009), sugar cane bagasse (Raymundo et al., 2010; Ribeiro et al., 2011; Soliman et al., 2011) and others (Bousher et al., 1997). Recently, Ribeiro et al (2011) show that sugar cane bagasse (SCB) and vegetable sponge were able to remove the analgesic paracetamol present in the aqueous medium. Antunes and colleagues (2012) demonstrated that Isabel grape bagasse was able to remove diclofenac sodium present in aqueous solution whereas Xu and Li (2009) demonstrated the adsorption of TC by marine sediments.

In this study we evaluated the ability of SGB to remove TC present in the aqueous medium. Millions of tons of SGB are produced each year in Brazil (Austin 2009, UNICA and MAPA 2009). Its use as an adsorbent can provide more low-cost alternative to decontaminate drinking water. It also contributes to minimize the environmental impact caused by inadequate disposal of this material in the environment (Raymundo et al., 2010). Our study included the physical and chemical characterization of SCB, the determination of its maximum adsorptive capacity and its efficiency in treating the water sample from the treatment plant. These parameters are critical to establish the efficiency of the adsorbent material.

MATERIALS AND METHODS

Reactants and instruments

Sugar cane bagasse (SGB) was obtained from DISA, an alcohol distillery located in Conceição da Barra, north of the Espírito Santo State, Brazil. The reactants of analytical degree and deionized water ($18.2\ M\Omega\ cm^{-1}$) were used to prepare all the solutions. Tetracycline (TC) was obtained from Sigma-Aldrich Company (St Louis, MO, USA), hydrochloric acid were purchased from Vetec (Duque de Caxias-RJ, Brazil) and sodium hydroxide from Dinâmica (Diadema-SP, Brazil). Samples of potable water were collected at a water treatment station from Espírito Santo Sanitation Company. The following equipment was used: an analytical scale (Shimadzu AY 220 model), UV/Vis spectrophotometer (Biospectro SP-220 model), infrared (Perkin-Elmer Spectrum-100 model), pH meter (PHTEK), magnetic stirrer (Nova Ética and Biomixer), laboratory oven (Quimis Q-317 B model), industrial blender (FAET), ultrasonic device (Ultracleaner 1400), scanning electron microscope (SHIMADZU, SSX 550 model), sputter coater (SHIMADZU, IC-50 Ion Coarter model), automated physisorption instrument (Autosorb-1, Quantachrome Instruments), peristaltic pump (Instrutherm, BP 1000) and specific particle size sieves (Granutest).

SCB preparation

To remove the maximum amount of contaminants from the SCB, this was washed with hydrochloric acid 0.2 M, water (pH 7.0) and then dried in a laboratory oven (60°C) for 15 hrs. In the next step, the material went to an industrial blender with posterior sieving to obtain particles sizes between 1.19 mm and 4.76 mm (Figure 1). Polyethylene containers were used to stock the adsorbent material.

Fig. 1. Particles of SGB after preparation

Physical and chemical characterization of SCB

The procedures of scanning electron microscopy and spectroscopy infrared analysis described below were adopted or modified from the literature (Ribeiro et al., 2011; Pereira et al., 2009).

Scanning electron microscopy

The SCB samples were covered with a thin layer of gold, using the sputter coater, and they were analyzed with the scanning electron microscope. An electron beam of 10 kV was used, which allowed for obtaining micrographs of the physical structure of the natural adsorbent surfaces

Spectroscopy infrared analysis

The organic functional groups were characterized by Fourier transform infrared spectroscopy using KBr discs to prepare the SCB samples. The spectral range varied from 4,000 to 500 cm^{-1}.

The maximum adsorptive capacity

In this experimental set, the onset of saturation conditions at the adsorbent front was estimated for TC. For this purpose, the following tetracycline concentrations (0.01 – 0.08 $mg.mL^{-1}$) were tested. The pH of maximum adsorption (pH 7.0) was obtained in our laboratory. This value was used because of its use in waste treatment stations. For this purpose, 2,5 g of adsorbent were utilized in glass columns (75 x 30 cm) at flow rate of 25 mL min^{-1}. The mass and flow rate parameters also been optimized in our laboratory. The TC concentrations were indirectly quantified by absorbance measurements (l = 357 nm) of the eluates. The maximum adsorptive capacity of SCB for TC (MAC_{SCB-TC}) was determined according to the mathematical model of Langmuir to calculate MAC also in .static-batch mode (Robinson et al., 2002; Kannan and Murugavel, 2007; Farinella et al., 2008; Ribeiro et al., 2011).

TC removal from enriched water samples

In this stage, was to evaluate the efficiency of adsorptive process for treating water samples provided by Espírito Santo Sanitation Company and enriched with 0.1 mg mL^{-1} TC. The pH of these samples was around 7.0 and they had the following values for colour (4 mg PT-Co/L; Hazem Unity), total dissolved solids (160 mg L^{-1}) and turbidity (2.17 NTU; Nephelometric Turbidity Unity) in accordance with the requirements of the Brazilian government (CONAMA, 2004). Glass columns (75 x 30 cm) were filled with 2.5 g of SCB and five aliquots (100 mL) of the enriched water samples were percolated at 25 mL min^{-1}. The quantification of TC was carried out by the previously described procedure. It must be noted that, at this stage, the columns were also filled with sand and gravels besides SCB, exactly as is done at the water treatment station (Figure. 2). An identical column containing activated carbon (AC), commonly used in water filtration, was also assembled in order to compare the performance of the SCB. The procedure was performed as described by Ribeiro et al., 2011.

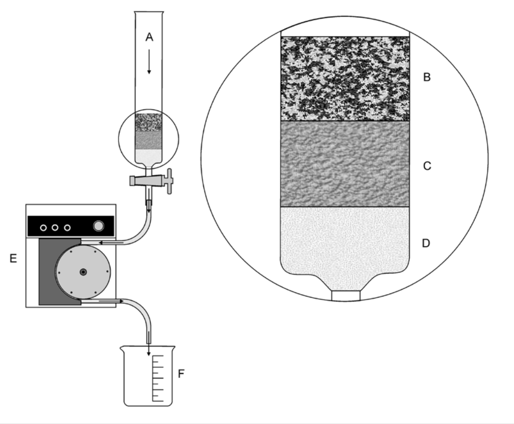


Fig. 2. Columns simulating real filter in water treatment plants. Direction of flow of the sample contaminated with TC (A) through the column containing gravel (B), sand (C) and SCB or AC (D). Presence of peristaltic pump (E) and system for collecting the filtered sample (F).

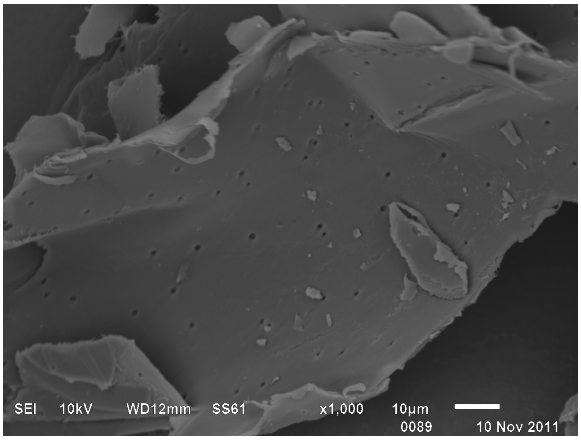
RESULTS AND DISCUSSION

Physical and chemical characterization of SCB

The Scanning electron microscopy images obtained in this study are in agreement with those presented by Ribeiro et al., 2011. The SCB surface is irregular and presents macropores of about 1 µm in diameter (Figure 3). The presence of macropores in SCB was demonstrated by Ribeiro et al., 2001 and indicates a small surface area, which suggests low efficiency in adsorption. Adsorbents which have micropores (< 2 nm) and high surface area are more efficient in adsorption process (Guo et al., 2008, Tseng et al., 2003). The morphological characteristics of SCB suggest relative disadvantage in this physical interaction between this natural adsorbent and TC. However, it was observed that some adsorbents which have low surface area and macropores, are also capable of interacting with pollutants in an aqueous medium (Yurtsever and Sengil 2009; Ribeiro et al., 2011). These interactions occur due to the presence of chemical groups of the adsorbents and not only to the deposition of the pollutants molecules on pores. These functional groups bind with the pollutants through hydrogen bond, electrostatic, hydrophobic and Van der Walls interactions. Recently Cabrita et al., 2010 demonstrated the importance of chemical interactions in the adsorption of paracetamol by activated carbon.

Our results obtained through infrared analysis (Figure 4) revealed the presence of important chemical groups. It was possible to determine the presence of O-H groups in 3,333 cm^{-1} from the alcohol function. This band indicates axial deformation in intramolecular hydrogen bond and possibly refers to the occurrence of vibrations in the macromolecules of SCB structure. According to Meza et al. (2006), SCB is composed of about cellulose, hemicellulose and lignin, in varying proportions, depending on soil properties and the plant's development stage. The presence of infrared band at 2,920 cm^{-1} indicates the occurrence of CH$_3$, while the small band in 1,720 cm^{-1} revealed the existence of C=O from esters probably of lignin and hemicellulose (Brigida et al., 2010). The bands at 1,618cm^{-1} and 1,520cm^{-1} refer probably to the presence of aromatic rings while the bands between 1,450cm^{-1} and 1,000cm^{-1} are unspecific and may indicate the presence of C-O groups from esters and alcohols (Herrera-Franco and Valadarez-Gonzálea, 2005; Brigida et al., 2010). These chemical functional groups determined by spectroscopy infrared analysis probably bind with TC through hydrogen bond, hydrophobic and Van der Walls interactions. The TC structure (Figure 5) has hydroxyl groups, CH$_3$, C=O, aromatic rings among others capable of performing interactions with SCB.

A



B

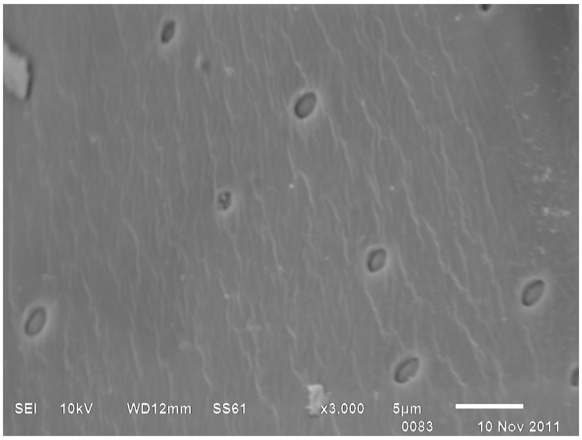


Fig 3. Scanning electron microscopy of SCB

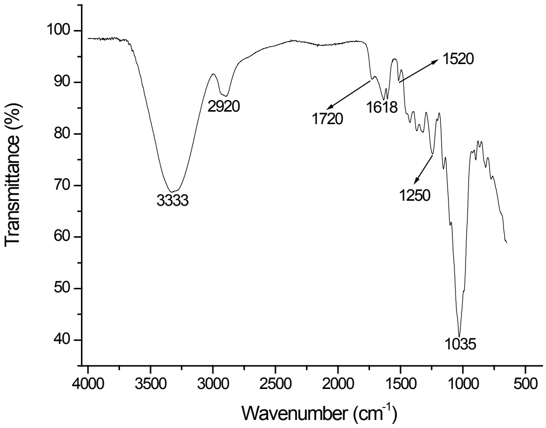


Fig 4. Infrared spectrum of SCB.

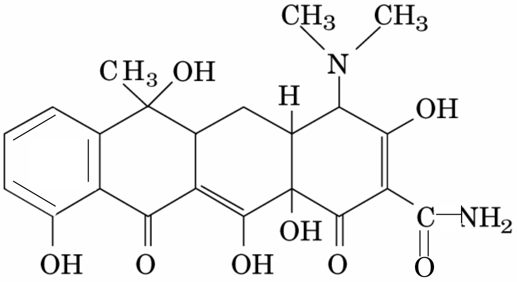


Fig 6. Tetracycline structure

The maximum adsorptive capacity

Through Langmuir mathematical model was constructed a isotherm (Figure 7) that after linearized (Figure 8) provided the value of MAC$_{SCB-TC}$ (0.31 mg g^{-1}). It is suggested that this MAC$_{SCB-TC}$ value is appropriate, since the drugs are found in the aquatic environment at ng/L or µg/L levels (Hilton and Thomas, 2003; Rabiet et al. 2006; Conley et al. 2008). Choi and colleagues (2009), for example, found TC and its derivatives, in order of 0.37 µg/L in a Korean river. Zhang et al. (2012) found TC and others antibiotics with the median concentrations ranged from 0.89 to 117.97 ng/L in Jiulongjiang River, South China. Recently, Locatelli et al (2011), using a liquid chromatography–electrospray tandem mass spectrometry (LC–MS/MS) method, detected the presence of some antibiotics in surface water samples from the Atibaia watershed (São Paulo State, Brazil) at concentrations of ng/L. These concentrations levels ensure quantitative retention of TC by SCB, before column saturation is reached.

Some authors have obtained interesting MAC values for the adsorption of TC and others pharmaceuticals by different natural and synthetics adsorbents in stirring system or columns (Bui and Choi, 2009; Ji et al., 2009; Ji et al., 2010; Ribeiro et al., 2011; Antunes et al., 2012). Liu and colleagues (2012) obtained considerable the maximum adsorption capacities of TC on the on organo-montmorillonite (1000–2000 mmol/kg). Recently, Ribeiro et al. (2011) found satisfactory MAC values when they investigated the retention of paracetamol by natural adsorbents sugar cane bagasse (120.5 μg/g) and vegetable sponge (37.5 μg/g). Significant removal of diclofenac sodium by Isabel grape bagasse was observed by Antunes et al., (2012). Cuerda-Correa and colleagues (2010) found excellent adsorption of non-steroidal anti-inflammatory drugs (NSAIDs), naproxen and ketoprofen, on the carbon blacks. The experimental results of these authors proved that, under the optimal operation conditions, up to 517mg/g of naproxen and 400mg/g of ketoprofen may be adsorbed. Although there are significant differences between the MAC values, all these studies, the adsorption capacities determined are greater than the concentrations of drugs in the aquatic environment.

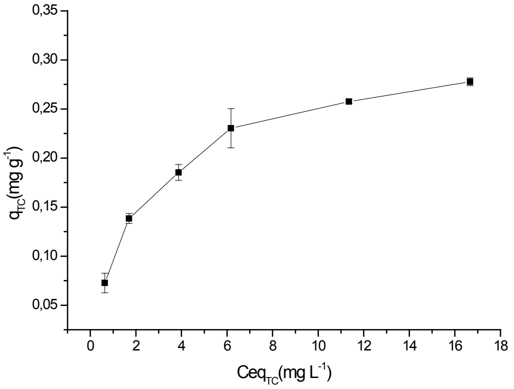


Fig. 7. Adsorption isotherm for TC using columns with SCB

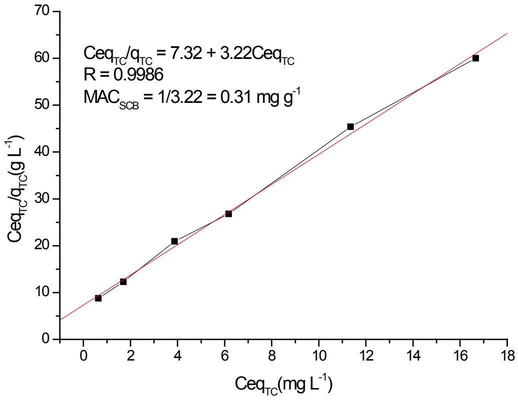


Fig 8. Linearization of the adsorption isotherm according to the mathematical model of Langmuir.

TC removal from enriched water samples

The efficiency of SCB for removing 0.1 mg mL^{-1} TC from enriched water samples was verified and compared with activated carbon (AC), commonly used in treatment plants. The results show that SCB and AC were able to remove 98% and 72% of TC respectively (Figure 9). The concentrations removed by these adsorbents were higher than the levels of drugs commonly found in aquatic environmental. In this way, the adsorption capacity demonstrated by SCB was higher than AC, justifying its use in the removal of tetracycline in contaminated water. The AC is currently the most widely used in the wastewater treatment. However, a high cost is ascribed to AC when employed in decontamination processes (Brandão et al., 2010). Futhermore, SCB is, possibly, more economically feasible when compared to AC, since SCB is an agroindustrial residue abundantly produced in Brazil. The results obtained in this work encourage more advanced studies of technical and economic applicability.

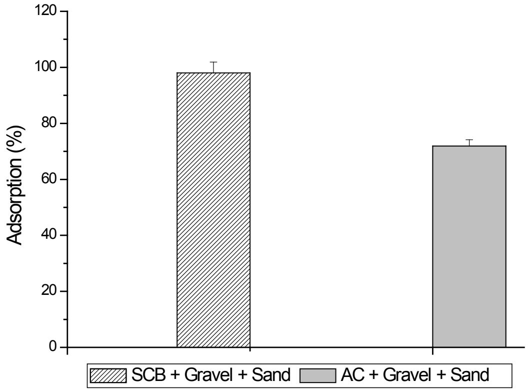


Fig. 9. Percentage of TC removal for SCB in columns that simulate the treatment plants.

CONCLUSION

The results suggest that SCB has physical and chemical structures that qualify it as an adsorbent for water treatment. This natural adsorbent has satisfactory maximum adsorption capacity for tetracycline. Furthermore, this material is more efficient than activated carbon for removing the tetracycline utilised in this study from the water supply. Therefore, this adsorbent it is suggested as a possible alternative in the treatment of water contaminated with tetracycline. Finally, the results encourage more detailed studies, including economic viability.

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