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Green Mesocarp Coconut For Treatment of Water Contaminated With Paracetamol And Tetracycline

Health Science

KEYWORDS : adsorption, green coconut mesocarp, tetracycline, paracetamol, water

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ABSTRACT

A method involving green coconut mesocarp was developed to remove some pollutants from water. The results show that this natural adsorbent has satisfactory maximum adsorption capacity for paracetamol (0.11mg g-1) and tetracycline (1.61mg g-1). Furthermore, this material was able to remove 95% and 64% of tetracycline and paracetamol, respectively, from enriched water samples. The less efficient activated carbon removed 44% and 39% of tetracycline and paracetamol, respectively. The tested concentrations of these pollutants were higher than the levels commonly found in the aquatic environment. The results showed that coconut is more effective than activated carbon in removing these contaminants. Therefore, this material is suggested as a possible alternative in the treatment of water contaminated with tetracycline, and paracetamol.

INTRODUCTION

The anthropogenic activities associated with industrialization and urbanization has led to a deterioration of water quality due to contamination by toxic substances (Mudiam et al., 2012). Every year, tons of chemical pollutants are discarded in the aquatic environment. Among the main pollutants are heavy metals (Chiba et al., 2011), polycyclic aromatic hydrocarbons (Osman et al., 2012), pesticides (Flores et al., 2004), dyes (Carneiro et al., 2010) and pharmaceuticals (Ziylan and Ince, 2011).

Waste pharmaceuticals are consistently detected in ng L-1 and µg L-1 concentrations in different environmental samples (Hilton and Thomas 2003). These samples include effluents from sewage treatment plants, water supplies, surface water and groundwater. These drugs may persist in the environment and return to humans through the food chain and drinking water (Fatta-Kassinos et al., 2011). Anti-inflammatories and analgesic drugs are commonly used in Brazil with or without a medical prescription (Ribeiro et al., 2011). This fact makes this class of pharmaceuticals one of the main responsible for the pollution caused by drugs in water (Ziylan and Ince, 2011). Paracetamol (PA) is an analgesic and antipyretic drug widely used for the treatment of fever and pain, especially in Dengue epidemics (Guzman et al., 2010). One of the major causes of liver failure in many countries is due to the toxicity of this drug (Craig et al., 2010; Heard et al., 2011). Moreover, studies in mice revealed that this drug can also cause lung damage (Dimova et al., 2000).

Another drug commonly found in the aquatic environment is tetracycline (TC) and its derivatives such as oxytetracycline and chlortetracycline (Yang and Carlson, 2004; Ok et al., 2011). These drugs have been widely used to combat various types of microbial infections. Most of these antibiotics reach the aquatic environment by means of urine and faeces (Yang and Carlson, 2004). The presence of these residues in the environment may cause the onset of pathological microorganisms resistant and induce undesirable biological responses in various types of organisms (Zhao et al., 2011). Just as anti-inflammatories and analgesic drugs, antibiotics are introduced into the water bodies through domestic sewage (Nebot et al., 2007; Reif et al., 2008) and hospitals (Focazio et al., 2008; Feldmann et al., 2008; Verlicchi et al., 2010).

Most treatments for wastewater containing drugs are not suitable. Therefore, the development of efficient and economical techniques to remove these contaminants in the aqueous medium is important (Ribeiro et al., 2011). Among the methods of decontamination, adsorption stands out as an efficient procedure for removing various pollutants, besides being one of the most economical alternatives, especially when using natural adsorbents (Vieira et al., 2011).

Several natural materials have been studied for the removal of chemical pollutants present in water. Among these materials are sugar cane bagasse (Raymundo et al., 2010; Ribeiro et al., 2014), vermicompost (Pereira et al., 2014), babassu coconut mesocarp, walnut shells, Ulva lactuca and Sargassum (Tahir et al., 2008), green coconut mesocarp (Rocha et al., 2012) and others (Ribeiro et al., 2011). The sugar cane bagasse (Ribeiro et al., 2011) and goethite (Zhao et al., 2011) also showed good results in studies for the removal of paracetamol and tetracycline respectively.

In this work we evaluated the green coconut mesocarp (GCM) for the removal of TC and PA. These studies were realized in fixed beds employing glass columns containing GCM. This material was selected due to its high adsorptive capacity for some pollutants and due to its abundance and low cost in Brazil (Sousa et al., 2007; Leal et al., 2010; Rocha et al., 2012). Furthermore, this study aimed to provide a new alternative for the reuse of GCM, which is abundant on Brazilian beaches and represents an enormous problem of environmental impact due to solid waste generation.

MATERIALS AND METHODS

Chemicals and instruments

GCM was obtained from beaches of Guarapari city, Espírito Santo State, Brazil. The reactants of analytical degree and deionised water (18.2MΩ cm^{-1}) were used to prepare all of the solutions. Paracetamol (PA) was obtained from Farma Derm (Vitória-ES, Brazil); tetracycline (TC) was obtained from Sigma-Aldrich Company (St Louis, MO, USA), hydrochloric acid was 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 (CESAN). 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).

Adsorbent preparation

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

Scanning electron microscopy (SEM)

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

Surface area and porosity determination (SAAP)

The GCM samples were analyzed through N2 adsorption/desorption isotherms at 77K at different times, using an automated physisorption instrument. This equipment was used with a programme to calculate the material's surface area and its average pore size, according to Brunauer-Emmett-Teller, BET (Brunauer et al., 1938).

Spectroscopy infrared analysis (IR)

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

Adsorption isotherm building

In this experimental set, the onset of saturation conditions at the adsorbent front was estimated for PA and TC. For this purpose, the following paracetamol (1–100 μM) and tetracycline (0.01–0.08 mg mL^{-1}) concentrations were tested. The pH of maximum adsorption (pH 7.0) was obtained in our laboratory. Although the tetracycline demonstrates three pKa values, the pH 7.0 value was used in our studies because of its common use in waste treatment stations. For this purpose, 3g of adsorbent were utilized in glass columns (75 x 30 cm) at flow rate of 30 mL min-1. The mass and flow rate parameters were also optimized in our laboratory. The eluent concentrations were indirectly quantified by absorbance measurements utilizing 250 nm for PA and 357 nm for TC.

PA and TC removal from enriched water samples

In this stage, the efficiency of the adsorptive process for treating water samples provided by CESAN and enriched with 20 μM PA or 0.1 mg mL^{-1} TC. The pH of these samples was around 7 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 (Cabrita et al et al., 2010). Glass columns (75 x 30 cm) were filled with 3g of GCM, and then aliquots (100 mL) of the enriched water samples were percolated at 30 mL min-1 (optimized in our laboratory). The quantification of PA e 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 gravel besides GCM, which is exactly what is done at the water treatment station (Fig. 1). An identical column containing activated carbon (AC), commonly used in water filtration, was also assembled in order to compare the performance of the GCM.

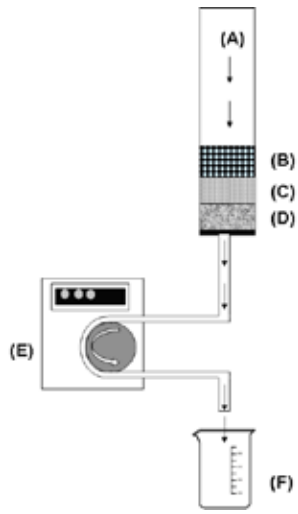

Figure 1. Columns simulating real filter in water treatment plants. Direction of flow of the sample contaminated with pollutants (A) through the column containing gravel (B), sand (C) and AC or GCM (D). Presence of peristaltic pump (E) and system for collecting the filtered sample (F).

RESULTS AND DISCUSSION

SEM, SAAP and IR analysis

The image obtained by scanning electron microscopy revealed that the surface of GCM is irregular and characterised by the presence of concavities of different sizes (Fig. 2). Furthermore, the data obtained through the SAAP analysis revealed that the GCM have a larger surface area (11.2 m2 g-1), pore diameter between 4 and 50 nm, and pore volume of 1.4 x 10-8 m3.g-1. These data indicate that the material is characterized by the presence of mesopores, as observed by Lima et al.(2012). These characteristics may represent a relative disadvantage with regard to the physical interaction with contaminants (Guo et al., 2008). However, other studies have shown that some natural adsorbents, with similar characteristics to the GCM, were also able to interact with water pollutants. The occurrence of chemical interactions between pollutants and functional groups were suggested to be present in the adsorbents and not only due to the deposition of the pollutants on adsorbents pores (Yurtsever and Şengil, 2009). Our results obtained through infrared analysis (Fig. 3) revealed the presence of important chemical groups. It was possible to determine the presence of O-H groups (band at 3415 cm-1) from the alcohol function. This band possibly refers to the vibration of cellulose and lignin structures present in the coconut fiber (Brígida et al., 2010). The presence of C-H sp3 carbon was also determined, which was characterized by the infrared band at 2920 cm-1. The band at 1742 cm-1 indicated the occurrence of C=O groups from esters of lignin and hemicellulose (Farinella et al., 2008). The bands at 1618 cm-1 and 1520 cm-1 refer to the presence of aromatic rings. The bands between 1450 cm-1 and 1000 cm-1 are unspecific and may indicate the presence of C-O groups from esters (band at 1250 cm-1) and alcohols (band at 1100 cm-1). It is possible that these groups form C-O esters due to the presence of wax in the epidermal tissue Herrera-Franco and Valadarez-Gonzálea, (2005). Observation of PA and TC structures (Fig. 4) suggests that their functional groups are able to establish weak interactions with the chemical groups in the GCM structures. Recently, Fourier transform infrared analysis of sugarcane bagasse containing adsorbed CR indicated interactions between the carboxyl and hydroxyl groups of bagasse and CR functional groups (Fatta-Kassinos et al., 2011).

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Studies realized by Cabrita et al. (2010) demonstrated the importance of chemical interactions in the adsorption of PA in chemically modified activated carbon.

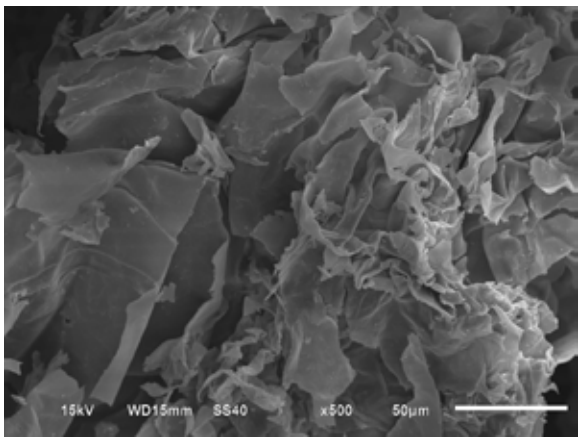


Figure 2. Scanning electron microscopy of GCM with magnifications of 500 x.

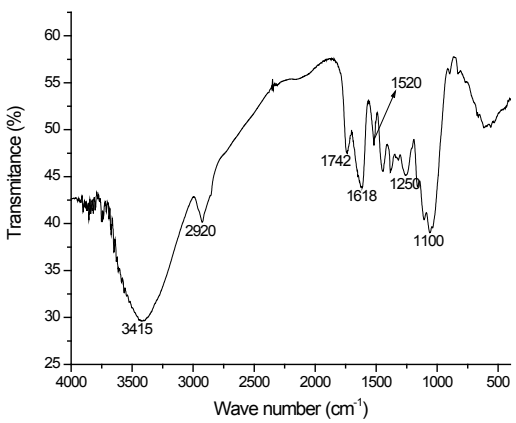


Figure 3. Infrared spectrum of GCM.

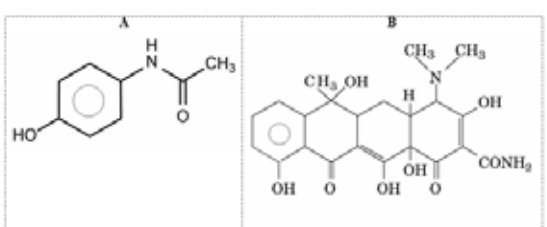


Figure 4. Structures of PA (A) and TC (B).

Adsorption isotherm building

In order to verify the maximum adsorptive capacity (MAC) of the GCM front for PA and TC, adsorption isotherms were constructed (Fig. 5). Following this, the isotherms were linearized (Fig. 6) according to the mathematical model of Langmuir in order to calculate MAC also in static-batch mode (Robinson et al., 2002; Kannan et al., 2007; Farinella et al., 2008; Ribeiro et al., 2011) for paracetamol (MAC_pA) and tetracycline (MACTC). The MACTC (1.61 mg g-1) value obtained was considerably higher than that of MACPA (0.11 mg g-1). These values indicate the amount of pollutant retained per gram of GCM. The difference between PA and TC structures (Fig. 4) can explain the occurrence of distinct MAC values. It may be noted that TC has more chemical groups than PA that are capable of interacting with the functional groups of the GCM adsorbent. It is suggested that the chemical groups of these structures are able to interact with GCM through hydrogen bonding and hydrophobic, van der Waals and electrostatic interactions.

It is possible that MAC values are satisfactory for the two pollutants, because pharmaceuticals are commonly found in drinking water at µg L-1 or ng L-1 levels (Hilton and Thomas 2003). These concentrations ensure quantitative retention of TC and PA before column saturation is reached. Recently, Ribeiro et al. (2014) and Ribeiro et al. (2011) found similar MACTC and MACPA values when they investigated the retention of TC and PA by natural adsorbent sugar cane bagasse. Interesting MAC values, obtained from different mathematical models, were also found by several authors who investigated the adsorption of organic pollutants by different adsorbents in stirring system (IS) or columns (Chatterjee et al., 2007; Dogan et al., 2008; Wang and Chen, 2009; Gupta et al., 2009; Perju and Dragan, 2010).

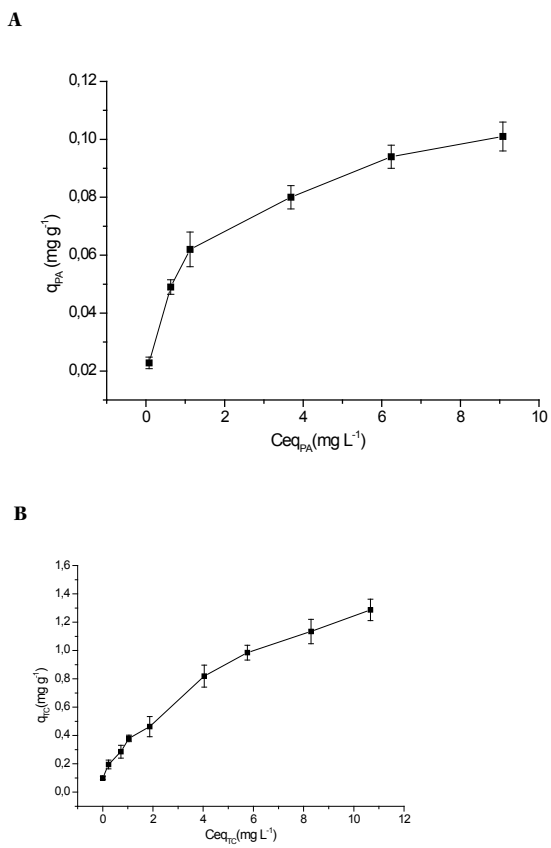
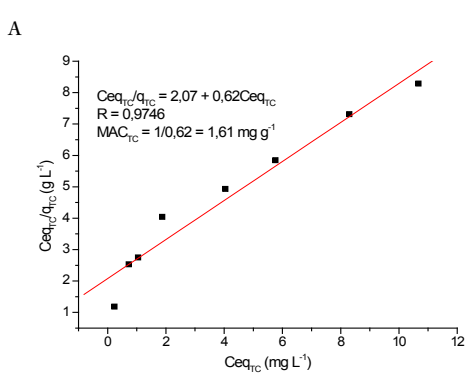
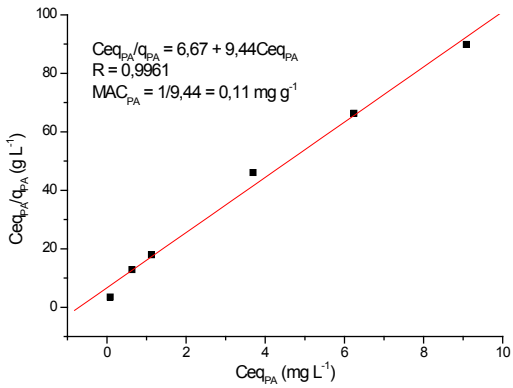


Figure 5. . Adsorption isotherms for PA (A) and TC (B) using columns packed with GCM



B



B

Figure 6. Linearization of the adsorption isotherms for PA (A) and TC (B).

Paracetamol and tetracycline removal from enriched water samples

In this step the efficiency for removing PA and TC from enriched pre-treated water samples was tested. Finally, GCM efficiency was compared with activated carbon (AC), which is commonly utilized in treatment plants. The results are shown in Figure 7. It can be observed that the GCM is more efficient than the activated carbon in removing the two pollutants. The GCM was able to remove 95% and 64% of TC and PA, respectively. The less efficient AC removed 44% of TC and 39% of PA. The tested concentrations of PA (20 μM) and TC (0.1 mg mL-1) were higher than the levels commonly found in the aquatic environment. AC is currently the most widely used in wastewater treatment. However, a high cost is ascribed to AC when employed in decontamination processes. Furthermore, AC has a low efficiency in removing some contaminants in the water when compared to other adsorbents. It is suggested also that GCM may be more economically viable when compared to AC, since GCM is an agroindustrial residue abundantly produced and often wasted in Brazil. The GCM discarded on the beaches and accumulate in the garbage is an environmental problem for the coastal cities of Brazil.

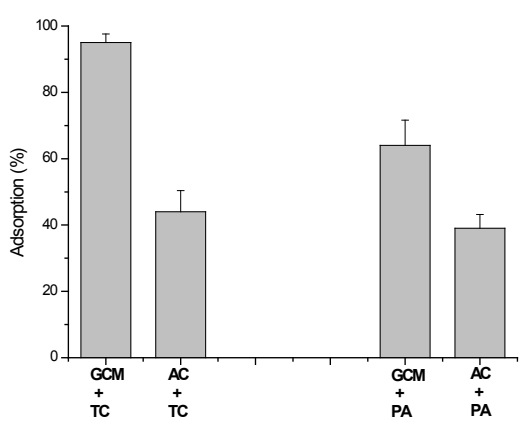


Figure 7. Percentage of TC and PA removal for GCM and AC in columns that simulate the treatment plants.

CONCLUSION

The results suggest that GCM has physical and chemical structures that qualify it as an adsorbent for water treatment. This natural adsorbent has satisfactory maximum adsorption capacity for paracetamol and tetracycline. Furthermore, this material is more efficient than activated carbon for removing the pollutants utilized 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 and paracetamol. Finally, the results encourage more detailed studies, including economic viability.

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