



Research article

Evaluation of waste biomasses and their biochars for removal of polycyclic aromatic hydrocarbons



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ABSTRACT

This work evaluates the use of biomasses and their biochars as adsorbents to remove polycyclic aromatic hydrocarbons from water. Coconut waste (CW) and orange waste (OW) were pyrolyzed at 350 °C to produce the corresponding biochars (BCW and BOW). Adsorption tests using a mixed solution of benzo(a)anthracene, benzo(b)fluoranthene, benzo(k)fluoranthene, benzo(a)pyrene, and dibenzo(a,h)anthracene showed removal percentages of 30.33–83.43% (CW), 47.09–83.02% (BCW), 24.20–74.25% (OW), and 23.84–84.02% (BOW). The adsorption mechanisms appeared to involve π - π interactions of similar groups of the adsorbate and adsorbent, together with hydrophobic effects. There was no indication of competition between the PAHs for the adsorption sites, and there was evidence of cooperative adsorption. The PAHs could be desorbed from the adsorbents with efficiencies in the range 34.88–72.32%, and the reuse of the adsorbents in two further cycles demonstrated their potential for use in the removal of PAHs from water.

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1. Introduction

The aim of United Nations Sustainable Development Goal 12 is to reduce resource use, environmental degradation, and pollutant emissions. One approach that can help to achieve this is the rational use of the large quantities of waste biomass generated during production and processing in the agriculture and forestry sectors, as well as during other economic activities. This can decrease the quantities of wastes discharged into the environment, adding value to them while at the same time minimizing the extraction of feedstocks from the environment.

In Brazil, enormous amounts of waste are generated from agricultural activities. The country is currently the world's largest producer of oranges (around 18 million tons in 2013) and the fourth largest coconut producer (around 2.8 million tons in 2013) (FAO, 2013). The processing and extraction of orange juice leaves almost 50% of the fruit as a byproduct (Chon and Chon, 1997). In the processing of green coconuts, between 80% and 85% of the gross weight remains as waste (shells) (Rosa et al., 2002).

These wastes typically have no added value and can constitute

an environmental problem, since millions of tons are generated annually worldwide. It is therefore necessary to identify potential uses of these wastes, and one possibility is as adsorbents for the removal of pollutants from aqueous media. Various wastes have been studied as adsorbents for the removal of both organic and inorganic contaminants (Santos et al., 2007; Araújo et al., 2013; Mimura et al., 2010; Costa et al., 2012).

The expansion of industrial activities, especially those related to oil extraction, can lead to problems of water pollution due to leakage from underground storage tanks, distribution points, industries, and residences (Namkoong et al., 2003). Pollutants derived from petroleum include polycyclic aromatic hydrocarbons (PAHs), which are compounds characterized by the presence of two or more condensed aromatic rings (Hu et al., 2014). PAHs also can be formed by pyrolysis of organic matter at temperatures in the range 500–900 °C, especially above 700 °C (Bartle, 1991). Due to their semi-volatile nature, PAHs can be transported long distances in the air and in water. These compounds can reach marine environments as a result of urban runoff, wastewater effluent discharges, industrial emissions, and spillages and leakages during the production and transport of fossil fuels (Latimer and Zheng, 2003).

Some of these compounds are important from an environmental perspective because they are, or may become (after chemical modification), carcinogenic and/or mutagenic (Lamichhane et al.,

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2016), so it is important to understand their dispersion in the environment and the potential risks to human health.

The United States Environmental Protection Agency has identified sixteen priority PAHs for environmental monitoring purposes (US EPA, 1993). In Brazil, National Environment Council Resolution No. 357, of March 17, 2005 (CONAMA, 2000), sets maximum permissible limits for benzo(a)anthracene, benzo(a)pyrene, benzo(b)fluoranthene, benzo(k)fluoranthene, chrysene, dibenzo(a,h)anthracene, and indeno(1,2,3-c,d)pyrene of $0.05 \mu\text{g L}^{-1}$ for Class 1 freshwater and $0.018 \mu\text{g L}^{-1}$ for Class 1 saltwater.

There is little information in the literature concerning the mechanisms of adsorption of PAHs by biomasses. Crisafulli et al. (2008) studied the potentials of biomasses including green coconut shells for the adsorption of several PAHs (naphthalene, acenaphthene, anthracene, and pyrene) and concluded that the adsorption processes were governed by π - π interactions between the PAHs and the adsorbents. Chen et al. (2011) studied the adsorption of lower molecular weight PAHs (naphthalene, acenaphthylene, fluorene, phenanthrene, and pyrene) using plant residues including orange peel, and reported a negative correlation between adsorption and higher polarity of the adsorbent, while a positive correlation was obtained with increasing aromaticity of the material. However, information is scarce concerning the adsorption of higher molecular weight PAHs. Hence, there is a need for further research targeting the adsorption of higher molecular weight PAHs, since these compounds present greater carcinogenicity and/or mutagenicity risks towards humans.

A technique that can be used to improve the performance of these biomasses in the adsorption of contaminants is their pyrolysis to produce biochars. Due to its high surface area and the presence of a non-carbonized fraction, biochar has been found to be an effective adsorbent for the removal of contaminants from soil and water (Ahmad et al., 2014; Tang et al., 2013; Nautiyal et al., 2016). Chen and Chen (2009) used biochars derived from orange peel pyrolyzed at different temperatures for the removal of naphthalene and 1-naphthol from water. The biochar produced at 700°C showed the highest capacity for adsorption of the compounds present at low concentrations.

The present work evaluates the use of biochars and their precursor biomasses for application in the removal of polycyclic aromatic hydrocarbons present in water, as well as their reuse in several desorption cycles. The adsorption behaviors are related to the chemical and morphological characteristics of the materials, and results are presented for the application of the adsorbents using real samples.

2. Materials and methods

2.1. Sample collection and preparation

The waste coconut (CW) and orange (OW) biomasses were collected from snack bars (as processing byproducts) and were then dried in an oven at 105°C for 24 h, before grinding in a knife mill fitted with a 10 mesh sieve. The biochars of coconut (BCW) and orange (BOW) waste were prepared by pyrolysis of the dried biomasses in a furnace (EDG model FTHV-20 10P), with heating to 350°C at a rate of 5°C min^{-1} (without a residence time), followed by milling as described above.

2.2. Characterization of the biomasses and biochars

2.2.1. Infrared spectroscopy

Infrared spectra of the samples were obtained at 4000 – 400 cm^{-1} using a Varian 640-IR spectrometer operated in transmittance mode with resolution of 2 cm^{-1} . The samples were

prepared in the form of pellets with a KBr:sample ratio of 95:5.

2.2.2. Thermogravimetric analyses

Thermogravimetric curves were obtained using a Shimadzu TGA-50 analyzer. The samples were placed in platinum crucibles and heated from 26 to 900°C , at $10^\circ\text{C min}^{-1}$, under a 40 mL min^{-1} flow of nitrogen.

2.2.3. Elemental analysis

Elemental (CHN) analyses were performed with a LECO CHN628 instrument and the results were treated using CHN628 v. 1.30 software. The gases used were helium (99.995%) and oxygen (99.99%), and the furnace temperature was 950°C . Calibration was performed using EDTA as a standard, and the carbon, nitrogen, and hydrogen contents of the samples were obtained using approximately 100 mg portions deposited on thin sheets of tin.

2.2.4. Surface area measurements

The surface areas of the materials were determined by the adsorption of nitrogen at 77 K, using a Quantachrome NOVA 1200 instrument, according to the Brunauer-Emmett-Teller (BET) method. The samples were degassed for 2 h at 100°C , prior to the nitrogen adsorption/desorption procedure.

2.3. Chromatographic analyses

The analyses were performed using a Shimadzu Prominence high performance liquid chromatograph (HPLC) consisting of the following modules: degasser (model DGU-20A3), binary pumping system (model LC-20AT), automatic injector (model SIL-20A), column oven (model CTO-20A), fluorescence detector (model RF-20A), and communication module (CBM-20A). A Shimadzu Shim-Pack VP-ODS column ($250 \times 4.6 \text{ mm}$) was employed, and the system was controlled with LCSolution software. The injection volume was $20 \mu\text{L}$ and the column temperature was 30°C .

For analysis of the individual PAHs, the mobile phase consisted of a binary mixture of water and acetonitrile (10:90), at a flow rate of 1 mL min^{-1} . The run time was 15 min and the excitation/emission wavelengths for detection of BaA, BbF, BkF, BaP, and DahA were 266/384, 290/430, 290/430, 290/430, and 290/430 nm, respectively.

For analysis of the mixed PAHs solution, the mobile phase consisted of a binary mixture of water and acetonitrile, with the following elution program: 75% acetonitrile for 5 min, a linear ramp to 95% acetonitrile in 25 min, return to 75% acetonitrile in 30 min, and constant 75% acetonitrile for another 5 min. The flow rate was 1 mL min^{-1} and the detector was maintained at excitation/emission wavelengths of 266/384 nm up to 20 min, followed by a switch to 290/430 nm for the remainder of the period.

2.4. Batch adsorption tests

In the evaluation of contact time, experiments were performed using individual PAHs solutions and a mixed solution. The contact time experiments were conducted using 10 mL aliquots of individual PAHs solutions containing $100 \mu\text{g L}^{-1}$ of each compound, as well as using a mixed solution containing $100 \mu\text{g L}^{-1}$ of each PAH. After addition of 50 mg of biochar or biomass, the mixtures were agitated at 150 rpm (Marconi MA 832/1 agitator) and 25°C . At predetermined intervals, the samples were filtered through glass wool and analyzed by HPLC.

In order to determine the influence of the initial concentration, 50 mg portions of biochar or biomass were placed in flasks together with 10 mL of mixed PAHs solutions at concentrations of 20, 50, 75, and $100 \mu\text{g L}^{-1}$. After equilibrating for 180 min, the samples were

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