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Research article

Preparation of biomass-based activated carbons and their evaluation for biogas upgrading purposes

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ABSTRACT

The use of waste biomass to produce adsorbent materials for the process of biogas upgrading might be a sustainable way to improve the energy matrix and help developing waste disposal technologies. The objective of this study was to prepare and evaluate activated carbons from coconut shell and babassu coconut, a waste biomass highly available at low cost. Both carbon samples were prepared by physical activation with CO_2 and characterized by N_2 adsorption isotherms at 77 K. The biosorbents produced from babassu and coconut shells presented BET surface areas of 1452 m^2/g and 809 m^2/g, respectively. Their applicability to upgrade biogas was assessed by experimental evaluation of pure (CO_2 and CH_4) and mixture (CO_2/CH_4) adsorption equilibrium data at 293 K and pressures up to 10 bar. The results were used to compare the performance of the samples prepared in this work with a commercial sample. Adsorption capacity for carbon dioxide was similar for both synthesized samples, but the activated carbon from coconut shell presented better properties for CO_2/CH_4 separation, as its selectivity (4.2 at 1 bar) and working capacity (1.0 mmol/g at 3 bar) are comparable to those of the commercial adsorbent over the low pressure range studied. This indicates that biomass waste is an interesting precursor for the production of activated carbons for biogas upgrading.

1. Introduction

Waste generation and management have been increasingly turning into a major global concern. It's estimated that approximately 2 billion tons of municipal solid waste (MSW) are currently generated and about 38% is disposed in dumpsites (ISWA, 2015; D-Waste, 2013). Not differently, in Brazil, 41.3% of total MSW collected in recent years were disposed of inappropriately, corresponding to almost 30 million tons of solid waste (ABRELPE, 2016). Besides, more than 40% of global MSW is composed by organic matter (D-Waste, 2013; Hoornweg and Bhada-Tata, 2012), as it occurs similarly in Brazil, with a percentage of 51.4% from the total collected (ABRELPE, 2013).

These facts warn about the need to improve the organic waste management. A solution that has become the main alternative for sustainable organic waste treatment is the anaerobic digestion (Zupančič and Grilc, 2012). This process has the advantage of producing biogas, a mixture predominantly composed of methane and carbon dioxide, which can be employed as a fuel for heat and electricity generation (Papurello et al., 2015, 2014; Van Foreest, 2012). To increase its usage possibilities, biogas has to be upgraded to biomethane by treatment technologies and injected into the natural gas grids. In that way, this renewable energy can be applied in different manners, depending on the society needs (Nielsen and Oleskowicz-Popiel, 2008).

Adsorption based processes have been widely used and studied in gas purification, including biogas upgrade, CO_2 capture and storage, due to their relative low energy requirements, easy control and low operating costs (Bae et al., 2008; Kim et al., 2015; Xiao et al., 2016). For CO_2/CH_4 separation using adsorption, many studies have focused on the use and development of carbon-based adsorbents (Goetz et al., 2006; Mestre et al., 2014; Yuan et al., 2013). The most evident advantages of activated carbons (ACs) are (i) hydrophobicity, which prevents an early deactivation by water saturation and dismisses a prior moisture removal for separation process; (ii) relatively low heat of adsorption, thereby requiring low energy for its regeneration and (iii) low cost, which are aspects that make them a potential adsorbent for CO_2/CH_4 mixtures (Álvarez-Gutiérrez et al., 2014; Tagliabue et al., 2009). Therefore, their application for biogas upgrading has been studied worldwide (Esteves et al., 2008; Mestre et al., 2014; Ribeiro et al., 2008).

The use of waste biomass (e.g. sugarcane bagasse, olive stones,

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Nomenclature

A	Adsorption potential (J/mol)
BC	Babassu coconut
CS	Coconut shell
b_i	Parameter related to the affinity gas-adsorbent of species i (bar^{-1})
n_i	Number of moles of component i (mol)
P_i	Equilibrium pressure in a system containing the component i (bar)
q_i	Adsorbed amount of component i (g/g or mmol/g)
$q_{max,i}$	Maximum adsorbed amount of component i (g/g or mmol/g)
R	Universal gas constant (= 8.314 J/mol/K)
S_{CO_2/CH_4}	Adsorption selectivity of CO_2 over CH_4
T	Temperature (K)
t_i	Parameter related to the heterogeneity
V_{micro}	Volume of micropores (cm^3/g)
V_{tot}	Total pore volume (cm^3/g)
x_{CO2}	Mole fraction of carbon dioxide in adsorbed phase
x_{CH4}	Mole fraction of methane in adsorbed phase
WC	Working capacity (mmol/g)
y_{CO2}	Mole fraction of carbon dioxide in gas phase
y_{CH4}	Mole fraction of methane in gas phase
$\Pi*_i$	Reduced spreading pressure of component i (mol/m^3)
π_i	Spreading pressure of component i (J/m^3)

almond shells, rice hulls and corn stalks) as precursor for AC production has also been subject of recent researches (Álvarez-Gutiérrez et al., 2014; Gonçalves et al., 2016; Islam and Rouf, 2013; Li et al., 2016; Serafin et al., 2017; Zubrik et al., 2017). This precursor is highly available at a low cost. Furthermore, its use to produce adsorbents with low ash content and good adsorption properties is not only an attractive solution, but it also might contribute to the development of waste disposal technologies (Savova et al., 2001).

The babassu coconut has been considered for producing AC given to its local abundance. The seeds of babassu are largely exploited for oil extraction, generating a waste biomass with considerable potential for other uses. Literature reports some applications for the fruit and seed components (Lima et al., 2006; Teixeira, 2008; Vieira et al., 2011), but practically nothing related to the production of activated carbons for gas adsorption purposes.

The production of activated carbons from lignocellulosic materials involves carbonization at low temperatures (700–800 K), in the absence of oxygen, to eliminate volatile materials, and subsequent activation at higher temperatures (1100–1300 K) to increase the porosity and the surface area of the solid (Yang, 1997). The process of activation can be carried out through different ways: (i) with chemical agents (e.g. KOH, H_3PO_4, $ZnCl_2$), known as chemical activation; (ii) with CO_2, air or water vapor for physical or thermal activation or; (iii) these two methods combined (Marsh and Rodríguez-Reinoso, 2006). One advantage and relevant aspect of physical activation is that it causes relatively lower environmental impact in comparison with the other methods (Plaza et al., 2015; Hjaila et al., 2013).

Among the processes of thermal activation, the use of CO_2 is reported to increase the development of narrow micropores in the solid structure (Rodríguez-Reinoso et al., 1995), which is a very important feature of an adsorbent used to remove CO_2 from gas mixtures (Wickramaratne and Jaroniec, 2013).

The physical activation with carbon dioxide is usually performed in one or two steps: carbonization and activation at the same time or separately, respectively. In the first case there (one step) is energy saving, lower processing time and it also produces adsorbents with satisfactory textural properties as well as or even better than in a two-step activation process (Yang et al., 2010).

In this work, two AC samples were prepared from babassu and coconut shell, which are abundant regional resources, by one-step CO_2 activation. Their suitability to separate CO_2 from CO_2/CH_4 mixtures in a Pressure Swing Adsorption (PSA) process (Ruthven et al., 1993; Yang et al., 1997) were investigated based on their textural properties, adsorption capacity for carbon dioxide, selectivity over methane at 293 K and working capacity, compared to a commercial AC sample.

2. Materials and methods

2.1. Preparation and characterization of chars

2.1.1. Preparation

Coconut shells (*Cocos nucifera*) and babassu coconut (*Orbignya speciosa*) were used as carbon precursors for the preparation of activated carbons. These materials were washed with distilled water and dried at 373 K for 24 h. Then, the samples were crushed and sieved to a particle size between 3 and 5 mm.

A one-step CO_2 physical activation was applied in the production process (Ello et al., 2013; Plaza et al., 2015; Yang et al., 2010). About 6 g of precursor were introduced and spread in a quartz tube of 609 mm length and 16 mm diameter, which was placed inside of a horizontal tube furnace. The samples were heated at 1173 K for 140 min, at a heating rate of 10 K/min, as reported by Yang et al. (2010), under a CO_2 flow rate of 200 cm^3/min. At the end, carbon dioxide flow was interrupted and the system was kept under N_2 atmosphere until room temperature was reached.

2.1.2. Characterization

The samples were weighed before and after the AC synthesis process to determine the yield, which was calculated according to Eq. (1) (Rashidi et al., 2012):

$$Yield = \left(\frac{mass\ \ after\ \ activation\,(g)}{inicial\ \ mass\,(g)}\right) \times 100\% \tag{1}$$

The produced activated carbons were characterized by means of N_2 adsorption isotherms at 77 K using an Autosorb-1 MP (Quantachrome, USA) gas sorption analyzer. The specific surface area, micropore volume and total pore volume were then determined. Surface area and micropore volume were calculated by Brunauer–Emmett–Teller (BET) method and Dubinin–Radushkevich (DR) equation, respectively (Rouquerol et al., 2014). Total pore volume was determined according to the volume of N_2 adsorbed at reduced pressure $P/P_0 \approx 1$ and the pore size distribution was obtained by the Density Functional Theory (DFT) with Monte Carlo simulation method using Quantachrome's software (Lastoskie et al., 1996; Rios et al., 2009).

2.2. Single and binary adsorption isotherms

Adsorption isotherms of carbon dioxide, methane and their mixture (30% CO_2, 70% CH_4) were evaluated at 293 K and up to 10 bar using a magnetic suspension balance (), which provides data with a reproducibility of more or less 0.02 mg under an uncertainty of < 0.002%. The isotherms were used to assess the performance of adsorbents prepared for biogas upgrading purposes. Data handling was carried out according to the literature (Dreisbach et al., 2002; Rios et al., 2009).

The Tóth equation (Tóth, 1971, 2002) (Eq. (2)) and the Ideal