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Tetracycline removal with activated carbons produced by hydrothermal carbonisation of Agave americana fibres and mimosa tannin

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ABSTRACT

Two series of carbons were prepared from *Agave americana* fibres (A) mixed with *mimosa* Tannin (T) at different T to A weight ratios $W = 0/4$; 1/3; 2/2; 3/1 and 4/0. The first series, CTAW, was produced by direct pyrolysis of the precursors (T, A, or blends) and the second one, CHTAW, was produced in two steps, hydrothermal carbonisation (HTC) and then pyrolysis. Materials from the CHTAW series presented higher surface areas, H/C atomic ratios and carbon yields than those of the CTAW series. CHTA2/2 was next activated with CO_2 during 1, 2 or 3 h. The appropriate selection of the synthesis conditions allowed obtaining high-surface area activated carbons (ACs) with similar carbon yields and average pore diameters as non-activated, low-surface area, carbon materials. CHTA2/2 activated for 2 h was tested for tetracycline (TC) adsorption, and the equilibrium was reached much faster than for a reference commercial AC due to the presence of macropores and mesopores provided by carbonised A. TC adsorption was spontaneous, and adsorption kinetics was adequately fitted by a pseudo-second-order model. TC adsorption essentially depends on surface area, and the results reported herein are in the range of those reported in the open literature.

1. Introduction

Activated carbons (ACs) are porous materials characterised by highly developed pore texture, specific area and surface functionalities. ACs are produced from many different precursors, biomass among them, the selection of which being mainly conditioned by availability and cost. Among biomass, coconut shells (Rodríguez-Estupiñan et al., 2013), algae (Altenor et al., 2012), rice straw (Fierro et al., 2010a; Schaefer et al., 2017), lignin (Fierro et al., 2007) or ramboutan (*Nephelium lappaceum*) skin (Njoku et al., 2014) can be mentioned but are just examples. Pore texture, surface area and amount of functional groups in ACs can be enhanced by physical activation in which the precursor is pyrolysed under inert gas, usually nitrogen at high temperature, at least 800 °C, and further exposed to an oxidising gas. The latter is usually steam or CO_2, at temperatures within the range from 800 to 1000 °C (Ghouma et al., 2015). Physical activation with CO_2 allows obtaining ACs with high surface areas and amount of surface functionalities (Molina-Sabio and Rodríguez-Reinoso, 2004). Activation time and flow of oxidising gas are the main parameters influencing the final AC characteristics (Acosta et al., 2016), and these parameters are sometimes optimised by experimental design (Zhao et al., 2011). Unlike for chemical activation, the resultant ACs doesn't need washing, which is a time-consuming step.

In the last decade, the interest for hydrothermal carbonisation (HTC) treatment significantly increased (Braghiroli et al., 2014; Braghiroli et al., 2015; Schaefer et al., 2016), although this process is known since 1913 (Bergius, 1915). HTC indeed allows transforming biomass precursors into hydrochars with a hydrophilic shell and a hydrophobic core (Braghiroli et al., 2015) in a very simple way. In brief, biomass and water are introduced in an autoclave which is then placed in an oven at moderate temperature (150–250 °C), and in which the pressure is auto-generated. In these conditions, hydrolysis of the soluble biopolymers takes place, followed by fragmentation (Braghiroli et al., 2015). Next, the resultant monomers condensate and the as-obtained nuclei grow through a diffusion process, usually leading to carbonaceous microspheres. Different biomasses have been submitted to HTC to produce carbon materials, such as corn stalk and *Tamarix ramosissima* (Ling-Ping et al. (2012)), cellulose (Luca et al., 2014) or tannin (Braghiroli et al., 2015). HTC is also an interesting method for producing carbons doped with heteroatoms such as nitrogen. Thus, nitrogen-

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rich carbonaceous materials were synthesised from tannin submitted to HTC in concentrated ammonia (Braghiroli et al., 2012). However, hydrochars must be pyrolysed for obtaining true carbon materials, and have to be further activated to enhance their porosity and functionalities and hence to produce activated carbons (ACs).

ACs are widely used as adsorbents and are applied in many fields such as, among others, air purification (Choi et al., 2016), drinking water and wastewater treatment (Zietzschmann et al., 2016), gas storage (Sethia and Sayari, 2016), or purification of pharmaceutical products (Li et al., 2015). The gradual increase of antibiotics presence in natural water and antibiotics bioaccumulation, tetracycline (TC) among them, is a serious threat to the environment. Therefore, antibiotics removal is a scientific and technological challenge, and a matter of public concern. Antibiotics removal can be achieved by membrane filtration (Kovalova et al., 2012), electrochemical treatments (Dirany et al., 2012) or adsorption onto porous materials (Acosta et al., 2016; Ncibi and Mika, 2015).

The main objective of the present study was to remove TC using ACs produced from a low-cost, easily available and highly abundant local biomass in Tunisia: *Agave americana* fibres (A). *Mimosa* tannin (T) was used to increase the carbon yield, and ACs were synthesised by varying several experimental conditions: T/A weight ratio, addition of an HTC step or not, and activation time. We showed that the ACs prepared here had higher performances than a commercial AC in terms of TC adsorption. Traditional studies including basic thermodynamic calculations, pH effect, equilibrium and kinetics aspects were also carried out. A review of the TC adsorption capacities reported in the open literature was finally provided in order to compare with the performances of the ACs prepared herein.

2. Material and methods

2.1. Raw materials

Agave americana fibres (A) were collected at Ben Salem, in the central Tunisian region of Kairouan. The relevant fibre extraction method was described in the literature (Ben Hamissa et al., 2007). Briefly, *Agave americana* plants were treated in a NaCl-salt solution at 80 °C for 8 h. Afterwards, they were beaten with a mallet and vigorously thrashed with a scraper in order to separate the fibres (Ben Hamissa et al., 2013). Fibres were washed several times with distilled water to remove non-cellulosic particles, and were dried in an oven at 70 °C until constant weight. Then, the fibres were finely cut and sieved using an electric sifter. The particle size used in the experiments was comprised between 1 and 5 mm.

Tannin (T) was extracted from *Mimosa* tree barks (*Acacia mearnsii*, De Wild), and was kindly supplied by the company SilvaChimica (San Michele Mondovi, Italy). This material is commercially available under the name "Fintan OP", and its extraction protocol has been described in detail elsewhere (Braghiroli et al., 2014). Briefly, fresh barks were subjected to leaching in a diluted sodium bisulphite aqueous solution at 70 °C. The resultant solutions were concentrated and then spray-dried to yield a light-brown powder containing 1 wt.% of amino and imino acids, 4–6 wt.% of water, 80–82 wt.% of phenolic flavonoid materials. The remainder consists in monomeric and oligomeric carbohydrates, mainly broken pieces of hemicelluloses (Braghiroli et al., 2014).

A commercial AC, F300 provided by the company Calgon, was used as reference material for Tetracycline (TC) adsorption. TC, 98% pure, was provided by Sigma Aldrich.

2.2. Activated carbon synthesis

Two series of carbons were prepared from 4 g of different precursors obtained by mixing *Agave americana* fibre (A) and tannin (T) at several T to A weight ratios (W) and maintaining the final mass to 4 g (i.e., $W = 0/4$; 1/3; 2/2; 3/1 and 4/0). The carbon precursors were labelled TA0/4; TA1/3; TA2/2; TA3/1 and TA4/0, respectively, and this series was called TAW.

The first carbon series was prepared by direct pyrolysis of the aforementioned TAW precursors in a horizontal tubular furnace (Carbolite CTF). 1 g of carbon precursor was placed in a quartz boat and transferred into a quartz tube continuously flushed with nitrogen at a flow rate of 100 mL/min. The tube was heated in the furnace at 1 °C/min up to 900 °C, and such final temperature was held for 1 h. Then, the furnace was allowed to cool down to room temperature under nitrogen flow. The resultant samples after pyrolysis and drying at 105 °C were labelled CTAW, where "C" means carbon.

The second carbon series was prepared by submitting the TAW precursors to hydrothermal carbonisation (HTC) before pyrolysis at 900 °C. In a typical experiment, 4 g of TAW were introduced in a glass vial containing 40 g of distilled water, and the vial was introduced into a 200 mL Teflon-lined autoclave (Anton Parr). The autoclave was then introduced for 6 h in a ventilated oven pre-heated at 180 °C. The choice of HTC conditions ensured total HTC conversion (Braghiroli et al., 2014).

After HTC and drying at 105 °C, the samples were labelled HTAW, where "H" means HTC, and they were pyrolysed in the same conditions as for the first series. The resultant samples were then labelled CHTAW, where C, H, T, A and W have the same meaning as before.

One of the carbon samples, CHTA2/2, was chosen for physical activation with CO_2 in order to further develop its textural properties. CO_2 activation was carried out in a horizontal tubular furnace. 1 g of CHTA2/2 was placed in a quartz boat and transferred into a quartz tube flushed with high-purity nitrogen at a flow rate 100 mL/min, then heated at 5 °C/min up to 900 °C. Once the final temperature was reached, N_2 was replaced by CO_2 at a flow rate of 60 mL/min during 1, 2 or 3 h. Next, the furnace was allowed to cool under nitrogen flowing at 100 mL/min. ACs were labelled act_CHTA2/2, where "t" stands for the activation time (h), from 1 to 3 h, i.e., ac1_CHTA2/2, ac2_CHTA2/2, ac3_CHTA2/2, respectively.

Carbon yield: Y_C, total carbon yield: $Y_{T,C}$, HTC yield: Y_H, HTC total yield: $Y_{T,H}$, carbon yield after HTC: $Y_{C,H}$, and total carbon yield after HTC: $Y_{T,CH}$, were calculated according to equations SI1, SI2, SI3, SI4, SI5, and SI6, respectively, in the supplementary information (SI).

The activation yield, Y_{ac} (%), on dry basis, was calculated as:

$$\boldsymbol{Y_{ac}}(\%) = \left(\frac{\boldsymbol{actCHTA}2/2(\boldsymbol{g})}{CHTA2/2(\boldsymbol{g})}\right)_{\boldsymbol{db}} \times 100 \tag{1}$$

and the total yield of the process after HTC, pyrolysis and activation, Y_{T,act_CH} (%), as:

$$\boldsymbol{Y_{T,act\,CH}}(\%) = \frac{\boldsymbol{Y_{ac}}(\%) \times \boldsymbol{Y_{T,CH}}(\%)}{100} = \left(\frac{\boldsymbol{actCHTA}2/2(\boldsymbol{g})}{TA\boldsymbol{2}/2(\boldsymbol{g})}\right)_{\boldsymbol{db}} \times 100 \tag{2}$$

The total yield, Y_T, is thus either Y_H, $Y_{T,C}$, $Y_{T,CH}$ or $Y_{T,act\text{-}CH}$ for the series HTAW, CTAW, CHTAW or act_CHTA2/2, respectively, depending on the process considered.

Theoretical yields of processes such as HTC (H), direct pyrolysis (C) or HTC + pyrolysis (CH), for $W = 1/3$, 2/2 or 3/1, were calculated by a linear expression taking into account the experimental yields of pure T or pure A submitted to the process considered, and the value of W. For instance, for a TA mixture at $W = 1/3$ submitted to direct pyrolysis, one gets:

$$\boldsymbol{Y_{C,th}}(1/3) = \frac{\boldsymbol{Y_{C,exp}}(\boldsymbol{T}) + \boldsymbol{Y_{C,exp}}(\boldsymbol{A}) \times 3}{4} \tag{3}$$

where the subscripts "exp" and "th" stand for experimental and theoretical, respectively.

2.3. Materials characterisation

Carbon, hydrogen, oxygen, nitrogen and sulphur contents were