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Research article

Pyrolysis wastewater treatment by adsorption on biochars produced by poplar biomass

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ABSTRACT

Pyrolysis is a widely studied thermochemical process, however the disposal of the produced byproducts is an unexplored field. In particular, the acqueous phase, characterized by a high organic load (TOC), must be necessarily treated. Aims of this work is to study the potentiality of biochar as adsorbent material for the treatment of this wastewater. For this aim, pyrolysis wastewater and biochar produced in the same plant were used. Two biochars produced at different temperatures (550 and 750 °C) and an activated biochar produced by chemical activation with NaOH of the raw biomass were tested. The study shows that higher temperature in the biochar production leads to higher sorption capacity of the organic compounds due to an increase of the surface area. The activation process further increases the surface area of the biochar that becomes similar to that of a commercial activated carbon while the sorption capacity exceeds that of commercial activated carbon of 2.5 times.

1. Introduction

The interest on the exploitation of biomass to produce biofuels and chemicals has continuously increased in the last decade. Biofuels are considered one of the most attractive alternative to fossil fuels but their production is not yet competitive due to several limitation in the bio-fuels production processes (de Caprariis et al., 2015a). Among biofuels, biooil has received a lot of attention from scientific community and industrial sector due to the lack of candidates for the substitution of diesel and gasoline in the transportation sector, which is so far supplied almost only by fossil fuels. Biooil is for the most part produced by biomass pyrolysis. During pyrolysis the biomass is decomposed to form a solid residue, biochar, a gas product, composed principally by CO_2, CO, CH_4, H_2 and light incondensable hydrocarbons, and a liquid product composed by an organic phase, the biooil and an aqueous phase in which soluble organic species are dissolved (de Caprariis et al., 2015b). This process presents several criticality such as the high energy required for the process to occur, the low quality of the biooil obtained and the expensive treatments needed for the by-products (water phase) discharge.

In the last years, many improvements have been made to improve the biooil quality but the water disposal still remains an unexplored issue. In literature, very few works are present on the pyrolysis wastewater treatments. Mehrjouei et al. used heterogeneous advanced oxidation processes to abate the organic content of water (Mehrjouei et al., 2015). Other works are focused on the recovery of acetic acid from this water (Lee et al., 2010; Rasrendra et al., 2011). The valorisation of this by-product by means of acetic acid recovery could be feasible only for big scale plant. However, for small scale applications, that are the most common applications for pyrolysis plants, other solutions must be considered.

Adsorption is one of the most used technique for wastewater purification to remove organic molecules at industrial scale (Makrigianni et al., 2015). Among several adsorbents used for wastewater treatment, the activated carbons have the most suitable characteristics, due to their porosity, well-developed internal surface area and high adsorption capacity (Djilani et al., 2015). However, the expensive activated carbons production costs lead to a serious drawback for their use as commercial adsorbents (Karakoyun et al., 2011). Recently, there is a growing interest in the production of activated carbon from biochars produced by biomass pyrolysis (Tan et al., 2015). A wide variety of agricultural and industrial wastes are frequently used as precursors of activated

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carbon (Mohan et al., 2007; Torrellas et al., 2015; Xu et al., 2011; Yuan et al., 2011; Zhang et al., 2015).

In this work, sorption capacities of poplar wood biochars were tested on the removal of organic compounds from pyrolysis wastewater. The influence of the temperature on the sorption capacity was investigated. An activated biochar was produced by chemical activation with NaOH of the poplar wood biomass. Few works are present in literature on the chemical activation of the biomass (Benadjemia et al., 2011) while many articles are present on the activation of biochars (Park et al., 2013; Pezoti et al., 2016). The sorption capacities of biochars produced at different temperatures and of activated biochar were compared with those of a commercial activated carbon. Adsorbate and sorbent were obtained as by-products of the same biooil production plants, minimizing in this way the sorption production costs.

2. Materials and methods

2.1. Adsorbate

The absorbate is composed by the organic species contained in the water obtained as by-product in a pyrolysis process for the production of biooil. Water is generated mainly by the decomposition reactions of cellulose and hemicellulose composing the biomass and by the evaporation of the initial amount of moisture (Mathew and Zakaria, 2015). The water content produced in this kind of process is typically 15–30% by weight with respect to the former biomass. The water fraction contains the soluble organic species produced during the process. In this study the water was produced by a fixed bed pyrolysis process performed at temperature of 450 °C and fed with poplar biomass.

The pyrolysis wastewater was analysed by a GC-MS analyser (Agilent) using a thin film (30 m × 0.32 mm, 0.5 μm film thickness) HP-MS5 capillary column supplied from HP, to individuate the dissolved organic species, and characterized by its Total Organic Carbon (TOC) measured using a Shimadzu analyser. The adsorption performances were quantified measuring the total organic carbon of the pyrolysis wastewater before and after the adsorption tests.

2.2. Adsorbent preparation and characterization

The adsorption tests were performed using four different adsorbents, two biochars, one activated biochar and a commercial activated carbon, this last as reference material.

Biochars were produced by the pyrolysis of fresh poplar biomass grounded to pass in 500 μm sieve The pyrolysis was performed at two different temperatures, 550 °C and 750 °C, in a fixed bed reactor with a heating rate of about 20 °C/min under a nitrogen flow of 0.4 L min^{-1}; the maximum reaction temperature was kept constant for 1 h in order to assure the completion of the reactions. In the following, the biochar produced at 550 °C will be referred to as BC-550, while the char produced at 750 °C will be referred to as BC-750.

To improve the sorption properties of biochar, an activated biochar was produced by NaOH treatment, as previously reported in literature (Park et al., 2013), of the fresh poplar biomass followed by a pyrolysis step at 750 °C. In the following, this activated biochar will be referred as ABC-750.

The performances of the produced adsorbent materials were compared with those of a commercial activated carbon (Acquacarb 207EA), which is a materials largely used in the adsorption processes of water pollutants.

The elemental analysis (C, H, N, O) of the obtained samples was performed using an Elemental analyser (Eurovector, EA3000). The ash content was determined gravimetrically, heating the sample in a muffle with air till 600 °C for 4 h. The porosity of the adsorbents was evaluated by the Iodine number (nI) which gives an indirect indication of the surface area (Mianowski et al., 2007; Ying et al., 2006). The Iodine number was performed following the ASTM D 4607-86.

Microstructure and morphology of materials were investigated by scanning electron microscope (SEM) analysis using a FESEM Zeiss Auriga 405 (Carl Zeiss Microscopy, Oberkochen, Germany).

The chemical characteristics of biochar surfaces were evaluated by Boehm titration, which is based on the assumption that NaOH neutralizes all acidic groups, Na_2CO_3 neutralizes carboxyl groups and lactonic groups, $NaHCO_3$ neutralizes carboxyl groups only, while HCl neutralizes all basic groups (Boehm, 2002).

X-ray diffraction (XRD) was performed on all the samples. XRD patterns were obtained using an X-ray microdiffractometer, Rigaku D-max-RAPID, using Cu-Kα radiation.

2.3. Batch adsorption studies

All the experimental tests were performed in a set of Erlenmeyer flasks (100 ml) where an amount of pyrolysis wastewater was put in contact with the adsorbents in an orbital shaker at a constant temperature of 25 °C. To confirm the reproducibility of the results all the tests were carried out in triplicate, under identical conditions. The average of these measurements were used to express each assessment.

Equilibrium studies were performed to investigate the sorption capacities of the different adsorbents and to carry out the isothermal adsorption curves. The tests were conducted with 40 ml solutions; the performances of the adsorbents mixed with pyrolysis wastewater containing different content of organic carbon ranging between 5700 and 82 700 mg/l and using different adsorbent quantities (ratio between solution volume and adsorbent amount ranging between 5 and 50 ml/g) were investigated. The samples of pyrolysis wastewater having variable carbon content were obtained by diluting the original one, featuring a TOC of 82 700 mg/l.

The equilibrium tests lasted 24 h and afterwards the suspensions were filtered and the TOC of the recovered water measured. The sorption capacity at the equilibrium, q_e (mg/g), was calculated as:

$$q_e = \frac{(C_0 - C_e)V}{W} \quad (1)$$

where C_0 and C_e (mg/l) are the initial and equilibrium TOC of the pyrolysis wastewater, respectively, V (l) is the volume of the solution and W (g) is the dry mass of the adsorbent.

Batch kinetic experiments were conducted in the same set-up used for the equilibrium tests by using 80 ml of solution; the ratio between the volume of water and the adsorbent amount was fixed to 50. The tests were conducted on pyrolysis wastewater samples with different initial TOC (35 000, 58 000, 82 700 mg/l). Aliquots of water (1 ml) were withdrawn from the suspension at fixed time intervals, filtered through a 0.45 μm filter and then analysed. The adsorption capacity at time t, q_t (mg/g) was calculated as:

$$q_t = \frac{(C_0 - C_t)V}{W} \quad (2)$$

where C_t (mg l^{-1}) is the TOC at time t.

2.4. Isotherm adsorption models

Adsorption isotherms are of fundamental importance to design