



Development and characterization of activated hydrochars from orange peels as potential adsorbents for emerging organic contaminants



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HIGHLIGHTS

- Orange peel-derived hydrochars are obtained by hydrothermal carbonization.
- New adsorbents are developed by thermal and chemical activation of the hydrochars.
- Adsorption of emerging contaminants depends on the adsorbents' characteristics.
- Kinetic studies are performed and adsorption isotherms are determined and modeled.

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ABSTRACT

Activated hydrochars obtained from the hydrothermal carbonization of orange peels (*Citrus sinensis*) followed by various thermochemical processing were assessed as adsorbents for emerging contaminants in water. Thermal activation under flows of CO₂ or air as well as chemical activation with phosphoric acid were applied to the hydrochars. Their characteristics were analyzed and related to their ability to uptake three pharmaceuticals (diclofenac sodium, salicylic acid and flurbiprofen) considered as emerging contaminants. The hydrothermal carbonization and subsequent activations promoted substantial chemical transformations which affected the surface properties of the activated hydrochars; they exhibited specific surface areas ranging from 300 to ~620 m²/g. Morphological characterization showed the development of coral-like microspheres dominating the surface of most hydrochars. Their ability to adsorb the three pharmaceuticals selected was found largely dependent on whether the molecules were ionized or in their neutral form and on the porosity developed by the new adsorbents.

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1. Introduction

Hydrothermal carbonization (HTC) of biomass residues has been recently revived and employed as a way to obtain a solid product with higher carbon content than the original material. The HTC of a biomass is achieved using water as the reaction medium and applying mild temperatures (180–250 °C) under saturated pressure (autogenous or provided by a gas) for several hours. The thermochemical process applied to biomass includes simultaneous reactions of hydrolysis, dehydration, decarboxylation, condensation, polymerization and aromatization of the original precursor,

although detailed reaction mechanisms are yet unknown due to the complexity of this type of natural materials (Funke and Ziegler, 2010). The resulting carbon-rich product, known as hydrochar, usually exhibits increased heating values when compared to the natural biomass (Román et al., 2012), showing potentiality as an energy source; moreover, functional groups on its surface have been identified, which may improve their chemical reactivity and potentialities towards certain applications such as adsorption (Román et al., 2013).

In this regard, available agro-industrial residues have been investigated as precursor of hydrochars. They include materials as diverse as sunflower stems, walnut shells and olive stones (Román et al., 2012), poultry manure and corn silage (Oliveira et al., 2013), and palm empty fruit bunches (Parshetti et al.,

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2013), among others. In particular, orange peels discarded from juice processing industry are a valuable waste material ubiquitously available. Global orange production for 2013/14 is currently estimated at 51.8 million metric tons, with a substantial fraction destined to industrialization (FAS-USDA, 2014). These peels represent a significant disposal problem, especially in those regions where orange cultivation is a major industry (Fernandez et al., 2014). As far as the authors know, their conversion into hydrochars has only been reported by Titirici et al. (2007) who compared mechanical soft and hard biomass as precursors.

Most of the hydrochars developed have been investigated as a mean to upgrade biomass feedstock quality for energy generation (Parshetti et al., 2013; Román et al., 2012), for CO₂ storage (Hao et al., 2013) or for soil amendment (Oliveira et al., 2013). However, recently, hydrochars have also been regarded as potential carbonaceous adsorbents. In general, carbonaceous adsorbents can be defined as materials mainly composed of carbon, which have porosity and/or surface chemistry characteristics suitable to enhance the adhesion of molecules to their surface. Several carbon adsorbents have been developed so far. In particular, activated carbons (ACs) still stand out mainly due to their ease of preparation, which does not require very sophisticated experimental set-up in comparison with other methods and the possibility of using heterogeneous sources such as biomass as starting materials. This also allows giving an added value to agro-industrial wastes. ACs are usually produced by physical or chemical activation. Both processes require a pyrolysis stage either prior or after the reaction with the gasifying or oxidizing agent (Rodríguez Reinoso, 2002). Usually the pyrolytic stage involves the use of high temperatures (above 600 °C) as well as the use of high purity inert gases. In this frame, the possibility of performing the carbonization step via HTC instead of pyrolysis can result in important energy and economical cost reduction, apart from other handling advantages derived from the greater simplicity of the process (such as tar formation, which is an important issue specially with materials with high content of volatile matter, such as biomass). Because of these advantages, the possibility of activating hydrochars has recently become a hot topic for research (Román et al., 2013; Hao et al., 2013).

On the other hand, the effect of adding chemicals during the HTC of biomass and pure carbohydrates has been examined before, regarding the control of pH during the process by addition of citric acid (Titirici et al., 2007). Also, the effect of acetic acid and lithium chloride on the energy and mass yields and on the constituents of the original biomass (Lynam et al., 2011) or the use of KOH for the activation of glucose-derived carbon spheres with potential as functional materials (Li et al., 2011) have been investigated. However, adding chemicals to tailor the surface chemistry of a biomass-derived hydrochar and to provide a specific functionalization or to improve its textural characteristics has been scarcely studied (Falco et al., 2013; Hao et al., 2013). Despite the number of pieces of research on the improvement of chemical or structural properties of hydrochars has increased during last years, there is still a gap on the use of novel precursors which had been traditionally discarded for classical activation methods, such as biomass with high humidity content. To the best of the authors' knowledge, no studies dealing with the activation of hydrochar obtained from orange peels and their potential use as adsorbents have been reported.

As it is well-known, the versatility of carbonaceous adsorbents like ACs makes them suitable to be used in a large variety of systems such as drinking water and wastewater treatments, and applications in the food, beverage and chemical industries. The literature offers a wide spectrum of studies on their use to remove a large variety of organic molecules with different toxicity, abundance, polarity or size characteristics, including phenolic compounds (in the form of phenol or its derivatives, such as

nitrophenol, aminophenol or chlorophenol), volatile organic compounds (benzene, toluene or n-hexane) and synthetic dyes (methylene blue, methyl orange or acid green), to name a few (Bansal and Goyal, 2001; Fernandez et al., 2014). Lately, the organic compounds categorized as emerging have driven some attention. They include pharmaceuticals, steroid hormones, pesticides, personal care products and other industrial chemicals in very low concentrations (ng/L to µg/L). Discharge guidelines and standards do not exist for most of them and their removal within wastewater treatment facilities is commonly variable and incomplete (Luo et al., 2014). Although their environmental significance and fate remain poorly understood, their presence has been associated to toxic and ecological effects on biota (Delgado et al., 2012). With respect to adsorption of emerging contaminants onto ACs, many publications have given evidence about the suitability of these adsorbents for removal of herbicides and pesticides, drugs, and personal care products (Delgado et al., 2012). However, few attempts have been made to test activated hydrochars for contaminants removal from water such as atrazine and tetracycline.

With these premises, the present study is devoted to investigate the feasibility of obtaining adsorbents through the conversion of orange peels into hydrochars by means of HTC and their further processing by thermal and chemical activation. The resulting activated hydrochars are characterized and comparatively analyzed, and their behavior in the adsorption of three emerging pharmaceutical contaminants is examined. Particularly, two non-steroidal anti-inflammatory drugs: diclofenac sodium (DFS), frequently detected in wastewaters, and flurbiprofen (FP), of more recent occurrence (Verlicchi et al., 2012) were selected; also, salicylic acid (SA), an aspirin metabolite frequently found in municipal and industrial discharges, was investigated (Luo et al., 2014). To the authors' knowledge, the removal of these compounds has not been studied before onto hydrochar-based ACs.

2. Methods

2.1. Materials

Oranges (*Citrus sinensis*) from southeastern Spain, were purchased from a local market, washed and peeled. The orange peels were chopped and oven-dried at 100 °C. The dried samples were then crushed, milled and screen-sieved (0.5–1 mm). The precursor material obtained is hereafter abbreviated as OPP.

Pharmacopoeia grade SA (M.W. 194.2 g/mol, Standard[®]), FP (M.W. 244.3 g/mol, Gador[®]), DFS (M.W. 318.1 g/mol, Henan Dongtai Pharm Co. Ltd.) and analytical grade H₃PO₄ acid (Biopack[®]) were employed.

2.2. Hydrochar production

A mass of 10 g of OPP was soaked with 100 mL of distilled water and allowed to hydrate for 2 h within a Teflon vessel. The HTC of the precursor was carried out in a stainless steel autoclave (Berghof, Germany), heated at 200 °C for 20 h under self-generated pressure conditions. These experimental conditions were chosen based on previous works with agricultural residues (Román et al., 2012; Titirici et al., 2007). Then, the sample was rapidly cooled to room temperature immersing the reactor in an ice bath, and the solid was collected by filtration and sequentially washed with warm distilled water and finally dried at 100 °C. The hydrochar obtained is hereafter abbreviated as HC.

2.3. Hydrochar activations

Thermal activation of the HC (4 g) was performed inside a cylindrical stainless steel atmospheric pressure reactor described

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