Chemical Engineering Journal 279 (2015) 788–798

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

Chemical-activated carbons from peach stones for the adsorption of emerging contaminants in aqueous solutions

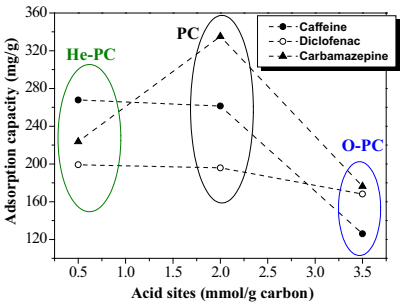
Silvia Álvarez Torrellas [a,b], Rafael García Lovera [b], Néstor Escalona [b], Catherine Sepúlveda [b], José Luis Sotelo [a], Juan García [a,*]

[a] Grupo de Catálisis y Procesos de Separación (CyPS), Departamento de Ingeniería Química, Facultad de Ciencias Químicas, Universidad Complutense de Madrid, Avda. Complutense s/n, 28040 Madrid, Spain
[b] Grupo de Materiales Microporosos en Catálisis y Adsorción, Departamento de Físico-Química, Facultad de Ciencias Químicas, Universidad de Concepción, Edmundo Larenas 129, Concepción, Región del Biobío, Chile

HIGHLIGHTS

- Chemical activation and characterization of raw peach stones based-activated carbons.
- Chemical and thermal treatments in order to modify the chemical surface carbons.
- Batch and dynamic adsorption tests of several emerging contaminants were performed.
- Competitive effect occurring between adsorbate and water for the active sites.
- TPD studies played an important role in the interpretation of chemical surface groups.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 8 April 2015
Received in revised form 26 May 2015
Accepted 27 May 2015
Available online 1 June 2015

Keywords:
Adsorption
Chemical activation
Fixed-bed column
Mesoporous carbons
Emerging contaminants

ABSTRACT

Activated carbons from peach stones by chemical activation with $H_3PO_{4(s)}$ have been prepared, leading to high surface area and well-developed mesoporous materials. Further oxidation and gas phase treatments were applied in order to analyze the influence of the chemical surface groups on the adsorption behavior. The adsorption of three emerging compounds: a stimulant (caffeine), an anti-inflammatory drug (diclofenac) and a psychiatric drug (carbamazepine) from ultrapure water through batch and dynamic tests was investigated. The characterization of the adsorbents was conducted by N_2 adsorption–desorption isotherms, scanning electron microscopy (SEM), infrared spectrometry (FTIR), thermal programmed decomposition (TPD), zero charge and isoelectric points (pH_{ZPC}, pH_{IEP}) determination and the evaluation of the total acidity by potentiometric titration with n-butylamine. TPD profiles and FTIR spectra revealed the presence of carboxylic, phenolic, carbonyl and quinonic functionalities in the carbonaceous surfaces. S-type adsorption isotherms, as Giles classification, were obtained, indicating a competitive effect between aqueous solution and the target adsorbates. Carbamazepine adsorption capacity was higher than caffeine and diclofenac, reaching 335 mg/g, attributed to its hydrophobic character and water solubility properties. The oxidation of the activated carbon greatly enhanced the hydrophilic character of the material, decreasing the adsorption capacity and highly affecting on the breakthrough times and adsorption capacity values in the fixed-bed adsorption process.

* Corresponding author. Tel.: +56 220 4324, +34 91 394 5207.
E-mail addresses: rgarcia@udec.cl, jgarciar@ucm.es (J. García).

http://dx.doi.org/10.1016/j.cej.2015.05.104
1385-8947/

1. Introduction

Activated carbon is a carbon-based material which is not truly amorphous but has a microcrystalline structure. These materials have been used as excellent and versatile adsorbents in several gas and liquid phase applications due to their highly developed porosity and extended apparent surface area. The volume of the pores in activated carbons is generally defined as being higher than 0.2 cm^3/g, and the internal surface area is larger than 400 m^2/g as measured by Brunauer–Emmett–Teller (BET) equation. The physicochemical properties of the material and subsequent adsorbent behavior highly depend on the nature of the raw material used, the activating agent and the conditions of the carbonization and activation processes [1].

Most organic materials rich in carbon, mainly coals, wood [2], coconut shell, peat [3], agricultural by-products such as fruit stones [4], seeds hulls [5], straw and stalks [6], lignite, coal, petroleum, coke, etc. can be used as precursor materials for activated carbon preparation. The selection of the material is based mainly on (i) low in inorganic matter; (ii) availability and cost; (iii) low degradation upon storage and (iv) ease of activation. The most common processes of activation are physical and chemical. The physical activation involves two steps: (i) carbonization and (ii) the control gasification of a carbonaceous precursor using a gas stream (O_2, CO_2, steam water, etc.) at high temperatures. In the chemical activation process, the raw material is impregnated using a chemical agent (H_3PO_4, $ZnCl_2$, H_2SO_4, H_3BO_3, KOH, NaOH, etc. solutions) and the resulting solid is activated at lower temperatures than those used in the physical methodology [7,8]. Some previous works report several conditions using different precursors and chemical activating agents [9,10].

Lignocellulosic materials constitute the more commonly used precursors (around 45 wt% of the total raw materials used for the manufacture of activated carbons). Low contents of inorganic materials are important in the preparation of activated carbons with low ash content, but relatively high volatile content is also needed for the control of the carbon porosity. Both characteristics are common to most of lignocellulosic materials used for the production of activated carbons. These cellulose-type materials such as wood, sawdust, nutshells and fruit stones are mainly used in the chemical activation methodology [7].

In the chemical activation the porosity is generated through dehydration reactions in the carbonaceous structure [7]. Earlier studies have shown that chemical activation using phosphoric acid solutions at moderate temperatures generates, in some lignocellulosic materials, a high surface area and a balanced degree of micro and mesoporosity percentages, useful for a wide range of applications as adsorbents. The development of surface area appears to be greatly dependent on the subsequent heat treatment temperature [11]. The authors have selected peach stones as precursor material due to their availability and desirable physical characteristics as activated carbon precursor.

Carbon-oxygen surface groups are the most important surface groups that influence the surface characteristics such as the wettability, polarity, and acidity, and the physico-chemical properties such as catalytic, electrical, and chemical reactivity of the activated carbons. In chemical activation the carbon material develops oxygenated functional groups (more reactive), which has an important role on the adsorption capacity of water and other polar compounds [12]. Therefore, these surface groups could be modified by chemical and/or thermal treatments in order to improve the adsorption properties.

Emerging contaminants of concern are new substances detected in waste waters at low concentration levels, ranging from μg/L to ng/L. The results of advanced water analysis have revealed the presence of pharmaceuticals, personal care products (PPCPs), endocrine disrupting compounds, polybrominated flame retardants (PBDEs), perfluorinated compounds (PFCs), etc. even in drinking waters. Some representative compounds of these categories are the well-known stimulant substance, caffeine, an alkaloid occurring in more than 60 plant species and whose consumption is very regular over the world, about being the global data 70 mg per person per day. Caffeine is a compound detected in wastewater, surface water, and groundwater worldwide [13].

Therefore, there is evidence that pharmaceutical compounds can reach detectable concentrations in wastewaters due to they are not completely degraded after consumption. Diclofenac, a popular analgesic belonging to the group of the non-steroidal anti-inflammatory drugs, has been frequently identified in effluents from domestic wastewater treatment plants and in rivers [14]. Carbamazepine, an antiepileptic drug, is one of the most frequently detected pharmaceutical residues in water bodies. This drug, together with caffeine, has been proposed as an anthropogenic marker in water streams in numerous studies [15].

Activated carbon adsorption has revealed worldwide as effective in the removal of organic compounds at the concentration range in they are present in waste waters, no generating secondary by-products which can be more harmful than the original compounds. In addition, it has no high energy costs associated and it is easy of operate [16,17]. Numerous studies have evaluated the efficiency of adsorption technique in the removal of emerging contaminants, such as pharmaceuticals and endocrine disruptors, onto activated carbons in ultrapure water and in the presence of natural organic matter [18].

One of our goals has been to develop a granular activated carbon using peach stones as a starting material by acid phosphoric solution-activation, obtaining a high surface area and mesoporosity activated carbon for the removal of several polar emerging compounds, such as caffeine, diclofenac and carbamazepine. Another goal has also been to study the overall changes on the carbon surface after an oxidation treatment with HNO_3 and a thermal treatment under inert atmosphere, studying the influence of these surface modifications on the aqueous phase adsorption properties. Therefore, from our knowledge, this is the first work testing the role of the external media, i.e. atmosphere on the regeneration of oxygen-surface functionalities in the modified activated carbons.

2. Materials and methods

2.1. Materials

The target compounds, caffeine, diclofenac and carbamazepine, were purchased from Sigma to Aldrich (Steinheim, Germany), with a purity higher than 98% and used as received in the experiments.

Ortho-phosphoric acid (85 wt%) was purchased from Panreac and nitric acid (69.5 wt%) was obtained from Carlo Erba.

The working solutions were obtained by diluting a stock solution previously prepared using ultrapure water. The physicochemical properties of the compounds are shown in Table 1. The molecular structures of the substances are depicted in Fig. S1 (Supplementary Material).

In the dynamic experiments, before column packing, the activated carbons were sieved at 0.5–0.589 mm and washed with boiling water to remove the impurities into the pores and finally they were dried in oven at 110 °C for 24 h.

2.2. Preparation of the activated carbon

The activated carbon was prepared by chemical activation using phosphoric acid as activating agent. The precursor material, peach