

Surface modifications of activated carbon by gamma irradiation



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ABSTRACT

Four commercial activated carbons with different chemical and textural characteristics were modified by gamma irradiation under five different conditions: irradiated in absence of water, in presence of ultrapure water, in ultrapure water at pH = 1.0 and $1000 \text{ mg L}^{-1} \text{ Cl}^{-}$, in ultrapure water at pH = 7.5 and 1000 mg L^{-1} Br⁻, and in ultrapure water at pH = 12.5 and 1000 mg L^{-1} NO₃⁻. Changes in surface chemistry were studied by X-ray photoelectron spectroscopy; pH of point of zero charge, total acidic groups and total basic groups, which were determined by assessment with HCl and NaOH; and textural changes were determined by obtaining the corresponding adsorption isotherms of N₂ and CO₂. Outcomes show that the activated carbon surface chemistry can be modified by gamma irradiation and that the changes depend on the irradiation conditions. Modifications in the sp² hybridization of the surface carbons suggest that the irradiated carbons undergo graphitization. Measurements of structural parameters indicate that the irradiation treatment does not modify the textural properties of the carbons. Finally, studies of pristine and irradiated activated carbons using diffuse reflectance spectroscopy with the Kubelka-Munk function revealed a reduction in band gap energy in the irradiated carbons associated with an increase in sp² hybridization of the carbon atoms.

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1. Introduction

Activated carbons (ACs) are employed as adsorbents, catalysts, and catalyst supports, among others, and are used to obtain new materials and for energy storage devices [1–6]. All of these varied applications take advantage of their extraordinary textural, and chemical properties (surface area, porous texture, and, surface chemistry), which largely depend on the hetero-atoms on their surface. Various researchers have investigated techniques for modifying the surface chemistry of ACs in order to improve their performance and/or expand their applications [7–10].

Among the hetero-atoms on the surface of ACs, we focus here on oxygen, because the presence of oxygenated groups determines their pH of point of zero charge (pH_{PZC}), their character as electron acceptor/donor, and their hydrophobicity, among other properties. They are also able to anchor functional molecules that can act as ligands or can incorporate other materials, such as oxides and nanoparticles. Various methods have been proposed to modify the oxygen content of ACs and the nature and concentration of their surface groups (Fig. 1) [10,11].

Gaseous or aqueous oxidation [10–14] is widely used to modify activated carbon (AC) surface chemistry, but it also

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Abbreviations: AC, activated carbon; ACs, activated carbons; C, Ceca activated carbon; D, absorbed dose; DRS, Diffuse Reflectance Spectra; Eg, band gap energy; M, Merck activated carbon; S, Sorbo activated carbon; SBW, spectral bandwidth; STP, standard temperature and pressure; W, Witco activated carbon; XPS, X-ray photoelectron spectroscopy 0008-6223/\$ - see front matter © 2013 Elsevier Ltd. All rights reserved.

alters their porosity. Alternative methods have been proposed to avoid this drawback, including electrochemical procedures and the utilization of oxygen plasma [15–19].

In broad terms, the concentration of AC surface oxygenated groups can be increased by gaseous or aqueous oxidation. Aqueous oxidation mainly increases the concentration of carboxylic acids and gaseous oxidation the concentration of carbonyl, and hydroxyl surface groups [12]. Another approach is to selectively remove specific surface groups by heating ACs in an inert atmosphere [20]. Microwave treatment has also been used to modify their surface chemistry, increasing the C/O ratio by removing oxygencontaining acid functional groups and producing ACs with basic surface chemical properties; this treatment also affects the porosity, reducing the size, and volume of micropores [21]. Ozone treatment increased the surface concentration of acid groups, especially carboxyl groups, thereby decreasing the pH_{pzc}, and it reduced the AC surface area and micropore volume [22]. AC oxidation by electrochemical methods were found to increase the surface oxygen content and reduce the AC surface area and micropore volume [15].

According to reports in the literature, practically all of the above procedures augment the surface oxygen content, generally by increasing the concentration of surface acidic groups, but they also modify the textural properties of the ACs. However, few data are available on the use of ionizing radiation to modify AC surface chemistry, we propose the utilization of ionizing radiation as an alternative approach to the modification of AC surface chemistry.

When ionizing radiation falls on a material, ionization, and excitation are produced, with the former predominating over the latter. This interaction can produce numerous chemical transformations, including oxidations, reductions, and polymerizations. The interaction of ionizing radiation with water deserves special mention, because its energy is transferred by non-elastic collisions with the water molecules, generating highly reactive species, as shown in (Reaction (1)):

$$\begin{split} H_2 O &\longrightarrow [2.8] HO^{\cdot} + [2.7] e^-_{aq} + [0.6] H^{\cdot} + [0.72] H_2 O_2 + [2.7] H_3 O^+ \\ &+ [0.45] H_2 \end{split} \tag{1}$$



Fig. 1 – Surface oxygenated groups present in ACs.

where the values in square brackets are the number of molecules formed on absorption of an energy of 100 eV, i.e., the mean radiochemical yield of the process, G-value, for a pH range of 6.0–8.5 and in an air-free medium [23]. The degree to which each species is formed depends on the solution pH, temperature, energy imparted by the incident radiation per unit distance traveled in the aqueous medium, absorbed dose, dose rate, and presence of dissolved gasses, among other factors. It is therefore possible to obtain media with a predominance of oxidizing species (HO', H₂O₂, or O₂) or reducing species (H' or e_{ao}^{-}).

With this background, the objective of this study was to evaluate the utilization of ionizing radiation to modify the electrical, chemical and textural properties of four commercial ACs, irradiating them directly in the air or in aqueous medium. In the latter case, selection of the appropriate radical scavengers yields reaction media with a predominance of the oxidizing species HO^o or one of the two main reducing species formed in radiolysis, H^o or e_{aq}^- . The influence of each of these species on the characteristics of the treated activated carbons will also studied.

2. Experimental

2.1. Materials

All chemical reagents used (hydrochloric acid, potassium bromide, sodium nitrate, sodium hydroxide) were of high purity analytic grade and supplied by Sigma–Aldrich. All solutions were prepared with ultrapure water obtained with Milli-Q[®] equipment (Millipore). Four commercial ACs were used as starting material: Sorbo (S), Ceca (C), Merck (M), and Witco (W). They were sieved to a particle size <0.25 mm, washed with ultrapure water to remove dust, then dried in oven at 383 K for 24 h and stored in desiccators. The commercial ACs were previously characterized [24,25], and some of these characteristics are given in Tables S1 and S2 (Supplementary data).

2.2. Irradiation sources

Irradiation studies were performed using a model 30 J MARK-I gamma irradiator (Shepherd & Associates) in the Experimental Radiology Unit of the Scientific Instrumentation Center (CIC) of the University of Granada (Spain). The equipment includes four ¹³⁷Cs sources with a total combined activity of 3.70×10^{13} Bq (1000 Ci) and has three irradiation positions for different dose rates: position 1 (3.83 Gy min⁻¹); position 2 (1.66 Gy min⁻¹); and position 3 (1.06 Gy min⁻¹).

2.3. Activated carbon irradiation experiments

All irradiations were conducted at a dose rate of 3.83 Gy min⁻¹ in irradiation position 1, administering a total dose of 25 kGy. The four ACs, C, M, S, and W, were irradiated in the air (i.e., in absence of water) by placing 5.0 g of previously dried AC into 15 mL plastic tubes. Irradiation in aqueous solution was conducted by introducing 5.0 g AC into 50 mL plastic tubes and filling them with ultrapure water previously bubbled with N₂ for 1 h. Before the irradiation, samples were bubbled with N₂ to avoid the presence of dissolved O₂, and the tubes were

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