



Activated carbon as photocatalyst of reactions in aqueous phase



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ABSTRACT

The main objective of this study was to identify the origin of the photocatalytic behavior of activated carbons in the presence of ultraviolet (UV) light. For this purpose, we selected four commercial activated carbons and sixteen gamma radiation-modified carbons derived from these. Sodium diatrizoate was considered as model compound for the degradation study. The results demonstrate that the direct diatrizoate photodegradation rate is influenced by the solution pH. The presence of activated carbon during diatrizoate degradation markedly accelerates its rate of removal, regardless of the activated carbon used. Witco commercial carbon exerts the highest synergic effect in diatrizoate removal by the UV/activated carbon system, with a synergic contribution >53% after the first minute of treatment. The synergic activity of all of the activated carbon samples is enhanced by gamma radiation treatment. The textural properties of the activated carbons show no clear relationship with their synergic contribution. However, the synergic activity of the activated carbon is more greatly enhanced in the samples with higher percentages of surface oxygen, and among these, the samples with higher percentages of ester/anhydride groups and of carbon atoms with sp^2 hybridization. Band gap (E_g) determination of activated carbons revealed that they behave as semiconductor materials and, therefore, as photoactive materials in the presence of UV radiation, given that all E_g values are <4 eV. We also observed that the gamma radiation treatment reduces the band gap values of the activated carbons and that, in a single series of commercial carbons, lower E_g values correspond to higher sodium diatrizoate removal rate values. We highlight that the gamma radiation-modified materials show a higher percentage of carbon atoms with sp^2 hybridization, explaining their superior behavior in the process. Finally, we observed that: (i) the activity of the reutilized activated carbons is similar to that of the original carbons, (ii) the presence of dissolved oxygen enhances the rate of diatrizoate removal by UV/activated carbon, and (iii) the UV radiation treatment produces slight chemical modifications in the activated carbons. Based on these results, an action mechanism for the photocatalytic removal of diatrizoate in the presence of activated carbon is proposed, in which the activated carbon acts as a photocatalyst, promoting electrons of the valence band to the conduction band and increasing the generation of HO^\bullet radicals in the medium.

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1. Introduction

Numerous pharmaceutical compounds are being studied as part of a group of emerging unregulated pollutants that pose a potential risk for ecosystems and human health [1,2]. These compounds and their degradation byproducts have been found in both surface

and ground waters [3–5], because many of them resist removal by conventional urban wastewater treatments. Given the increase in the use and types of these products, there is a clear need for research on measures to avoid their presence in the environment. Iodate contrast media are considered to be model compounds of these pollutants due to their persistence and detection in urban wastewaters, surface waters, and ground waters [5–9].

The iodate contrast media used in hospitals include sodium diatrizoate (DTZ), a highly persistent compound that has been detected in treatment plant effluents, surface waters, and ground waters in ranges from $ng\ L^{-1}$ to $mg\ L^{-1}$ [3,5,7,10]. This persistence and its high water solubility mean that DTZ poses a major environmental challenge. DTZ is not mineralized in the environment [11,12] but can be degraded, resulting in stable and potentially more hazardous biodegradation byproducts [12–14]. The resulting concentrations of this contrast medium and its possible metabolites in the environment allow them to accumulate in the food chain,

Abbreviations: AC, activated carbon; AOPs, advanced oxidation processes; E_g , band gap energy; C, activated carbon Ceca; DRS, diffuse reflectance spectra; DTZ, sodium diatrizoate; D_p , mean pore width; HPLC, high performance liquid chromatography; M, activated carbon Merck; pH_{PZC} , pH of point of zero charge; S, activated carbon Sorbo; S_{BET} , surface area determinate by BET; SBW, spectral bandwidth; UV, ultraviolet light; UV/AC, UV/activated carbon system; V_T , total pore volume; W, activated carbon Witco; XFR, X-ray fluorescence; XPS, X-ray photoelectron spectroscopy.

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with the consequent possible noxious effects on living beings. In this context, Advanced Oxidation Processes (AOPs) appear to be a promising technology for removing organic compounds that are resistant to conventional biological treatments, including DTZ. However, the DTZ degradation rate was only 14% with ozone treatment [15,16] and a maximum of 36% with other AOPs (O_3/UV -low pressure mercury lamp, O_3/H_2O_2) [17]; therefore, DTZ continues to be detected at the end of these treatments. Likewise, another study based on competitive kinetics models for treatment with ozone, Fenton, O_3/H_2O_2 , and UV/H_2O_2 obtained similar results in ultrapure water, finding that the highest degradation rates were achieved with UV radiation at 254 nm (96.6%) and photo-Fenton (64.7%) [18].

AOPs include photocatalytic processes, which require the use of luminous radiation capable of producing electronic activation of the catalyst. The energy of this radiation must be in the visible or UV region, and the photocatalyst must be a semiconductive material with an electronic band structure that can generate electron–hole pairs after irradiation at a given wavelength. The electron–hole pairs favor the formation of highly reactive radical species that participate in pollutant degradation. These radicals will derive from reduction or oxidation reactions on whether they are promoted by the electron or hole generated, respectively.

Various materials have been used as photocatalysts, and TiO_2 is one of the most widely applied in water treatments. The considerable research carried out since the publication of the first studies in the 1970s [19] has yielded wide knowledge of the technological possibilities offered by the use of titanium oxides with UV radiation in their elemental polymorphic forms (anatase, rutile, and brookite) and in combination with other materials that act as doping and/or support agents [20–23]. Documented drawbacks of utilizing these materials include: the difficulty of their removal from the treated effluent treated, the need for their recovery and reutilization, the reduced percentage absorption of the solar spectrum, and the high level of recombination of electron–hole pairs. Recent investigations have centered on photocatalysis processes that reduce these disadvantages. The immobilization of these photocatalysts in porous carbon materials is a research line of special interest, as reflected by the exponential increase in the number of publications over the past few years [24–30].

The photocatalytic process can be improved by the physical and chemical properties of activated carbons, especially their large specific surface area, which is usually attributed to the increase in contact surface area between catalyst and pollutant, favored by the action of the carbon as porous support [28,31–33]. However, some carbons play more than a mere support role, as concluded by recent studies [34–36] that obtained 80% mineralization of phenol by photooxidation using UV radiation in the presence of activated carbons and in the absence of semiconductors. These findings are consistent with the capacity of activated carbon to favor photocatalysis in well-known oxidation processes, including ozonation or the use of hydrogen peroxide, in which the carbon itself acts as catalyst [15,16,37] and in which the physical and chemical properties of the carbon influence the ozone decomposition [15,38–40].

With this background, the main aim of this study was to identify the origin of the photocatalytic behavior of activated carbons to remove DTZ in the presence of UV light. For this purpose, we selected four commercial carbons and sixteen gamma-radiated carbons derived from these. The specific objectives were to study: (i) the adsorption kinetics of DTZ on the commercial activated carbons and the gamma-radiated carbons under different experimental conditions; (ii) the DTZ degradation kinetics by direct photolysis with low-pressure UV radiation; (iii) the DTZ photodegradation in the presence of activated carbons; and (iv) the mechanism underlying DTZ degradation with UV light in the presence of activated

carbon, determining the role of the physical and chemical properties of the activated carbon in this process.

2. Experimental

2.1. Materials

All chemical products used (sodium diatrizoate, phosphoric acid, and sodium chloride) were high-purity analytical grade and supplied by Sigma–Aldrich. All solutions were prepared with ultrapure water obtained using Milli-Q® equipment (Millipore). The molecular structure of DTZ and its species distribution as a function of solution pH are depicted in Fig. S1 in the Supplementary Materials.

2.2. Determination of DTZ in aqueous solution

DTZ concentrations in solution were determined by high performance liquid chromatography (HPLC) in inverse phase using a chromatograph (Thermo-Fisher) equipped with UV–vis detector and an autosampler with capacity for 120 vials. The chromatographic column was a Nova-Pak® C18 (4 μ m particle size; 3.9 \times 150 mm). The mobile phase was 80% of water solution (1% phosphoric acid) and 20% ultrapure water, in isocratic mode, with 2.0 mL min^{-1} flow; the detector wavelength was set at 254 nm and injection volume was 100 μ L.

2.3. Analysis of DTZ UV–vis absorption spectrum

The DTZ absorption spectrum was determined by using a spectrophotometer (Genesys 5), running a wavelength scan for a DTZ concentration of 25 mg L^{-1} at pH values of 2, 6, 9, and 12.

2.4. Gamma radiation treatment of activated carbons

We used commercial activated carbons Sorbo (S), Merck (M), Ceca (C), and Witco (W) in their original form and after gamma radiation treatment.

Activated carbons were treated using a model 30J MARK-I gamma irradiator (Shepherd & Associates) at the Experimental Radiology Unit of the Granada University Scientific Instrumentation Center (Spain). The equipment includes four sources of ^{137}Cs with a total combined activity of 3.70×10^{13} Bq (1000 Ci). It 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}). In the present study, carbons were irradiated in position 1, receiving a total dose of 25 kGy.

The four activated carbons were irradiated by introducing 5.0 g of each in 50 mL plastic tubes and adding ultrapure water to fill the tubes. Before their irradiation, samples were bubbled with nitrogen to avoid the presence of dissolved oxygen, and the tubes were sealed to avoid air entry. These irradiated samples were designated C-0, M-0, S-0, and W-0, respectively. The predominant radiolytic species in the medium were modified by irradiating the samples in the presence of: (i) 1000 mg L^{-1} Cl^- and pH = 1.0, because the chloride ion acts as scavenger of OH^\bullet and e_{aq}^- radicals [41] (Reactions 1–8) and Reaction 9 takes place at this pH [42], producing a majority concentration of H^\bullet in the medium (samples C– H^\bullet , M– H^\bullet , S– H^\bullet , and W– H^\bullet , were obtained under these conditions); (ii) 1000 mg L^{-1} Br^- and pH = 7.5, because the bromide ion acts as scavenger of the HO^\bullet radical, giving rise to Reactions 10–13 [43–45], and this medium pH favors Reaction 14 [42], so that the majority species in the medium is e_{aq}^- (samples C– e_{aq}^- , M– e_{aq}^- , S– e_{aq}^- , and W– e_{aq}^-); and (iii) 1000 mg L^{-1} NO_3^- and pH = 12.5, because Reactions 14–16 take place under these conditions [37,42,45] and anion nitrate acts as H^\bullet and e_{aq}^- scavenger, so that the majority

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