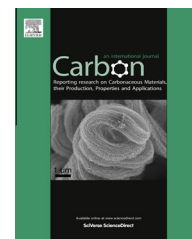


Available at [www.sciencedirect.com](http://www.sciencedirect.com)

ScienceDirect

journal homepage: [www.elsevier.com/locate/carbon](http://www.elsevier.com/locate/carbon)

# Role of activated carbon on micropollutants degradation by ionizing radiation



Inmaculada Velo-Gala, Jesús J. López-Peñalver, Manuel Sánchez-Polo\*, José Rivera-Utrilla

Department of Inorganic Chemistry, Faculty of Science, University of Granada, 18071 Granada, Spain

## ARTICLE INFO

### Article history:

Received 3 July 2013

Accepted 30 September 2013

Available online 10 October 2013

## ABSTRACT

The objective of this study was to analyze the influence of the presence of activated carbon on the degradation of the triiodinated contrast medium diatrizoate (DTZ) by the simultaneous use of gamma radiation and activated carbon. Four commercial activated carbons (Ceca, Witco, Sorbo, and Merck) with different textural and chemical characteristics were used for this purpose. The percentage DTZ removal obtained was considerably higher with the gamma radiation/activated carbon (GM/AC) system than with radiolysis in the absence of activated carbon, and it depended on the specific activated carbon employed. First, we optimized the amount of activated carbon required to maximize the amount of DTZ removed by the GM/AC system (0.06 g). The degradation constants were higher with the GM/AC system than with radiolysis alone, evidencing a synergic effect that favors pollutant removal. This synergic effect is independent of the textural but not the chemical characteristics of the activated carbon, observing a higher synergic activity for carbons with a higher surface content of oxygen, specifically quinone groups. We also highlight that the synergic effect of the activated carbon requires adsorbent–adsorbate electrostatic interaction and is absent when this interaction is hindered.

© 2013 Elsevier Ltd. All rights reserved.

## 1. Introduction

Numerous chemical compounds pose an environmental challenge because of their resistance to removal by conventional wastewater treatments. This is the case of sodium diatrizoate (DTZ), a contrast medium derived from triiodinated benzene that is widely used (3500 tons/year) in medical diagnostic imaging [1,2]. Various studies have demonstrated that conventional biological wastewater treatments are not effective to remove DTZ [3], which is found in concentrations ranging from  $\mu\text{g L}^{-1}$  to  $\text{mg L}^{-1}$  in all stages of the water cycle [4–7],

including groundwaters and surface waters intended for human consumption [7–9]. This compound has also been detected in  $\mu\text{g L}^{-1}$  concentrations in irrigation systems and in water treatment plant sludge reutilized as agricultural fertilizer [10,11].

DTZ has been shown to resist physicochemical treatments, including advanced oxidation processes (AOPs), which have achieved percentage removal values ranging widely from 14% with ozone treatments [12,13] to 64.7% with the photo-Fenton technique [14]. Other systems have been tested for DTZ degradation, including those using catalysts [15–17],

\* Corresponding author: Fax: +34 958243856.

E-mail address: [mansanch@ugr.es](mailto:mansanch@ugr.es) (M. Sánchez-Polo).

Abbreviations: ACs, activated carbons; AOPs, advanced oxidation processes; AORPs, advanced oxidation/reduction processes; BE, XPS binding energy; D, absorbed dose; DTZ, sodium diatrizoate;  $D_B$ , mean pore width; C, ceca AC-40 activated carbon; GM/CA, gamma radiation/activated carbon system; HPLC, high performance liquid chromatography; M, Merck activated carbon;  $\text{pH}_{\text{PZC}}$ , pH of point of zero charge; S, Sorbo-Norit activated carbon;  $S_{\text{BET}}$ , surface area determinate by BET;  $S_{\text{EXT}}$ , external surface determined by the t method;  $V_T$ , total pore volume; W, Witco activated carbon; XPS, X-ray photoelectron spectroscopy  
0008-6223/\$ - see front matter © 2013 Elsevier Ltd. All rights reserved.

<http://dx.doi.org/10.1016/j.carbon.2013.09.091>

membrane filtration [18], and non-thermal plasma oxidation [19], in which high percentage degradation values were obtained but at very low initial concentrations of the compound. Although researchers have reported widely varying results, they all conclude that DTZ is not mineralized [3,20] and that the byproducts are more toxic than the original compound [3,21–23]. Iodinated contrast media are the main contributors to the total environmental burden of absorbable halogenated organic compounds [1,2,24].

Adsorption on activated carbons (ACs) has been proposed as a method to remove this type of recalcitrant pollutant from effluents. The utilization of AC to eliminate organic and inorganic compounds from water is currently considered one of the best options available for the tertiary treatment of urban wastewater treatment plant effluents. AC can remove a large amount of pollutants of different types [25–33] due to the physicochemical properties of its surface [34]. These properties can be modified by using different activation methods, allowing the preparation of carbons to be tailored for specific objectives [35–38]. This versatility in their application is widened by their combination with other physical and chemical processes, such as AOPs, or by their application in catalysis, yielding innumerable possibilities for the treatment of all kinds of pollutants [39–43]. The utilization of ACs to enhance conventional treatment systems is therefore of great interest. Thus, after conducting studies on DTZ removal by adsorption on AC and by radiolytic degradation [44], in the present work, the simultaneous use of both systems was proposed as a means to remove both the original toxic compounds and the degradation products from the medium.

The oxidizing pathway used to treat certain pollutants can be very slow, and the use of reducing radicals is more effective, including solvated electrons ( $e_{aq}^-$ ) or hydrogen radicals ( $H\cdot$ ). Hence, the application of technologies that simultaneously generate oxidizing and reducing species, as in the case of ionizing radiations, may be of value in the treatment of pollutants resistant to conventional techniques. Thus, currently the ionizing radiation is applied to treat water contaminated with pollutants resistant to advanced oxidation processes [45–48]. However, there has been little research on the effects of the presence of catalysts, specifically AC, during the irradiation of contaminated waters. The utilization of AC in radiolysis may induce a synergic effect that enhances the compound degradation, producing higher percentage degradation values than could be expected by adding together the effects of oxidizing and reducing radicals from the radiolysis and of oxidizing groups from the AC with its adsorptive effect.

The use of AC in the presence of energy sources represents a novel procedure that could be applied in current radiolysis-based effluent treatment systems and improve their effectiveness [45–48] because in the same treatment contaminants can be (i) adsorbed on AC, and/or (ii) oxidized due to the generation of  $HO\cdot$  species, and/or (iii) reduced due to the formation of solvated electrons, increasing the benefit of the process.

With this background, the objective of this study was to analyze the effect of adding different ACs on the radiolytic degradation of pollutants, using DTZ as reference compound and investigating: (i) the kinetics of the radiolysis in the presence of different types of AC; (ii) the mechanisms involved in DTZ removal with the combined use of AC and radiolysis, and

(iii) the influence of the physical and chemical characteristics of the ACs on the outcomes of this combined treatment.

## 2. Experimental

### 2.1. Materials

All chemical products used (sodium diatrizoate, phosphoric acid, sodium chloride, potassium bromide, sodium nitrate, sodium carbonate, sodium bicarbonate) were high-purity analytical grade and supplied by Sigma–Aldrich. All solutions were prepared with ultrapure water obtained using Milli-Q® equipment (Millipore). Four commercial activated carbons were used: Ceca AC-40 (C), Merck (M), Sorbo-Norit (S), and Witco (W). Activated carbon particle had a size less than 0.25 mm.

### 2.2. Irradiation source

Irradiation experiments were conducted using a JL Shepherd Mark 1 gamma irradiator (model 30J) in the Experimental Radiology Unit of the Scientific Instrumentation Center of the University of Granada (Spain). The equipment includes four  $^{137}\text{Cs}$  radioactive sources with a total combined activity of  $3.70 \times 10^{13}$  Bq (1000 Ci). The irradiation chamber has a useful volume of 8.25 L and is equipped with a rotation system that guarantees uniform dose application throughout the irradiation volume. The apparatus has three irradiation positions for different dose rates: position 1,  $3.83 \text{ Gy min}^{-1}$ ; position 2,  $1.66 \text{ Gy min}^{-1}$ ; and position 3:  $1.06 \text{ Gy min}^{-1}$ .

DTZ samples were irradiated at room temperature ( $298 \pm 2 \text{ K}$ ) in 2 mL vials sealed with screw tops to avoid the entry of air. Before the irradiation, nitrogen was bubbled through the samples to avoid the presence of dissolved oxygen in the medium.

### 2.3. DTZ determination 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–visible detector and an autosampler with capacity for 120 vials. The chromatographic column was a Nova-Pak® C18 ( $4 \mu\text{m}$  particle size;  $3.9 \times 150 \text{ mm}$ ). The mobile phase was 80% of 1% phosphoric acid solution and 20% ultrapure water, in isocratic mode, with  $2.0 \text{ mL min}^{-1}$  flow; the detector wavelength was set at 254 nm and injection volume was 100  $\mu\text{L}$ .

### 2.4. Physical and chemical characterization of the activated carbons

All AC samples were texturally ( $\text{N}_2$  adsorption at 77 K,  $\text{CO}_2$  adsorption at 273 K) and chemically (elemental analysis, percentage mineral matter, X-ray photoelectron spectroscopy (XPS)) characterized. The techniques used in the chemical and textural characterization of the samples can be found in previous publications by our group [40,49,50].

Table 1 shows the textural and chemical characteristics obtained for the four ACs studied.

Download English Version:

<https://daneshyari.com/en/article/7854993>

Download Persian Version:

<https://daneshyari.com/article/7854993>

[Daneshyari.com](https://daneshyari.com)