



Role of activated carbon surface chemistry in its photocatalytic activity and the generation of oxidant radicals under UV or solar radiation



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ABSTRACT

We have studied the role that activated carbon surface chemistry plays in its photocatalytic activity under UV radiation and simulated solar radiation. In this study, we have used the commercial activated carbon Witco and five carbon samples obtained after its gamma radiation treatment, as this procedure allows the modification of the superficial chemistry of the carbon but not its physical properties. Sodium diatrizoate was used as a model compound for the degradation study. Its degraded percentage depends on the type of radiation and activated carbons used. To explain the carbon photocatalytic activity, we have demonstrated the formation of the electron hole as well as the formation of hydroxyl radicals and the superoxide anion in the UV/activated carbon and the Solar/activated carbon systems, and that the concentration of these oxidant species depends on the superficial chemistry of these materials. Moreover, the activated carbons, which have a smaller band gap allow higher concentrations of hydroxyl radicals, whilst those carbons with a larger band gap favour the formation of the superoxide anions. The degradation of the contaminant by UV/activated carbon and Solar/activated carbon systems has also been compared with the results obtained when the photocatalyst used is the traditional TiO_2 . The activated carbon efficiency as a photocatalyst is higher than TiO_2 under UV radiation, which is due to the different concentrations of oxidant species produced in both systems.

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1. Introduction

Treatment systems based on heterogeneous photocatalysis are one of the technologies to be considered in the treatment of contaminated water with organic compounds, which resist conventional processes [1,2]. In these systems, the radiation in the visible-ultraviolet range originates electronic activation in the

Abbreviations: AC, activated carbon; AOPs, advanced oxidation processes; Eg, band gap energy; DRS, diffuse reflectance spectra; DMSO, dimethyl sulfoxide; DNPH, 2,4 dinitrophenylhydrazine; DNPHo, formaldehyde-2,4-dinitrophenylhydrazone; DTZ, sodium diatrizoate; EDTA, ethylenediaminetetraacetic acid; ESR, electron spin resonance; HPLC, high performance liquid chromatography; NF^- , nitroform anion; Solar/AC, simulated solar radiation and activated carbon system; TNM, tetranitromethane; UV, ultraviolet light; UV/AC, ultraviolet light and activated carbon system; W, Pristine activated carbon Witco; W-H^+ , Witco carbon irradiated in the presence of H^+ ; W-e^-_{aq} , Witco carbon irradiated in the presence of e^-_{aq} ; $\text{W}\cdot\text{OH}$, Witco carbon irradiated in the presence of $\cdot\text{OH}$; W-O , Witco carbon irradiated in the presence of all radicals; W-a , Witco carbon irradiated in the air (without water); XPS, X-ray photoelectron spectroscopy.

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semiconductor material or catalyst. After its irradiation with a suitable wavelength, this material generates pairs of electron/holes, which are responsible for the formation of highly reactive species (hydroxyl radical, hydroperoxyl radical, superoxide anion, hydrogen peroxide, etc.) that will be involved in pollutant degradation [3–7]. In the processes of heterogeneous photocatalysis, the material used as a photocatalyst is essential because it determines the required wavelength of radiation to be applied to carry out the process. Therefore, the development of new materials that allow the use of sunlight is of great interest since most photocatalyst materials absorb UV light, which constitutes only a small fraction (3–5%) of the solar spectrum [8,9]. In addition, the use of traditional photocatalyst materials has other disadvantages, such as their complicated removal of the treated effluent and their high level of recombination of electron/hole pairs generated. Most of studies performed to solve these problems are based on the application of doping techniques of metal oxides, such as TiO_2 , either by replacing a small fraction of the corresponding metal by another metal, such as iron, gold, copper, platinum and palladium, among others [10–14], or by replacing part of the oxygen of the photocatalyst by non-metallic elements, such as nitrogen, carbon and sulphur [10,11,14–16]. But

in all these cases the necessity to remove the photocatalyst from the effluent persists. To resolve this question photocatalysis immobilization on supports is proposed, with the use of porous materials being particularly interesting. Due to their high surface area and morphology, this type of support provides the advantage of the accommodation of the semiconductor material, without affecting its properties and the approximation of pollutants to the photocatalyst is facilitated [17–25]. Carbon materials have significantly improved the efficiency of the degradation process, which is largely attributed to their textural properties [22,26,27]. However, it has recently been shown that the improvement of the photocatalytic performance observed with some carbon materials exceeds their simple textural contribution. The complete degradation of contaminants in aqueous solution has been achieved by oxidation systems with UV radiation in the presence of activated carbon without the typical semiconductor materials [28–32]. In addition to this behaviour, it should be added that the consideration of some activated carbons as photocatalyst materials is correct as they maintain the role of preserving their physicochemical characteristics after the photocatalytic process and their reuse has demonstrated that these materials conserve their initial photoactivity after several cycles [30,33]. These results confirm that activated carbons have an important photocatalytic activity just under the action of UV radiation, so more studies are necessary to allow us to elucidate the action mechanisms and the properties of activated carbons that can explain this behaviour. F. Velasco et al. showed that the photoactivity of carbons was related by the combination of high porosity and the presence of photoreactive sites that favour the splitting of the exciton inside the pores. They pointed out that the incorporation of O-containing groups in carbon matrix decreased the photoconversion inside the pores [34]. Within this context, we think it is necessary to study in depth how influences the superficial chemistry of activated carbon in their photoactivity. Therefore, in our study, we have used a commercial activated carbon (Witco) and five new carbon samples obtained after its ionizing radiation treatment, because this procedure allows the modification of the superficial chemistry of the carbon but not its physical properties [35]. The present study represents a great breakthrough in the clarification of the origin of the photocatalytic activity of activated carbons. We directly analyse the phases that form the photocatalytic processes and the influence of the type of irradiation source used. Furthermore, it is expected that the chemistry of the activated carbon surface will have an important role in the processes of photo-oxidation. To analyse the photocatalytic activity, these activated carbon samples have been exposed to radiation with different energy sources, such as UV light and simulated solar radiation, the analysis of activated carbon photo-activity in this latter system being novel.

In other studies [34,36–42], the authors only detected the generation of hydroxyl radical in carbon materials using spin trapping and electron spin resonance (ESR) spectroscopy to detect radicals, measuring a spin trapping agent (5-diethoxyphosphoryl-5-methyl-1-pyrroline-N-oxide (DEPMPO) or 5,5-dimethylpyrroline-N-oxide (DMPO)). In our study, we propose a different method of mean to detect and quantify hydroxyl radicals and superoxide anion photogenerated. It is noteworthy that this is the first time that the quantification of reactive species concentrations produced by the photocatalytic activity of the activated carbons has been made by this methodology.

On the other hand, the efficiency of the UV radiation/activated carbon system (UV/AC system) and solar radiation/activated carbon system (Solar/AC system) is evaluated in terms of degradation of the sodium diatrizoate (DTZ) contrast media as the pollutant model. In our previous studies we obtained high degradation percentages of this compound by a photooxidation process in the presence of activated carbon under UV light but in the absence of a typical semi-

conductor [30] or using gamma radiation in presence of activated carbon [43]. In both studies, experimental data for DTZ adsorption kinetics on Witco activated carbon were obtained, and the results showed its low adsorption. This behaviour facilitates the study of the role of activated carbon surface chemistry in the photocatalytic activity of activated carbon.

With this background, the present work aims to demonstrate the photocatalytic behaviour of activated carbons in the presence of UV light and simulated solar radiation, by analysing the different reactions which form the photocatalytic processes such as the generation of electron/hole pairs and the formation of highly reactive species. For this purpose, our specific objectives were: (i) Propose a new methodology to detect and quantify hydroxyl radicals and superoxide anion photogenerated by the photocatalytic activity of the activated carbons; (ii) the study of the influence of the activated carbon amount in the photocatalysis processes with UV light and solar radiation; (iii) to evidence the existence of photogenerated positive holes in the materials; (iv) the quantification of the concentrations of superoxide and hydroxyl radicals formed by photocatalysis processes under UV light and simulated solar radiation; (v) to determine the role of dissolved oxygen in the medium in these photocatalytic processes; and (vi) the analysis of the influence of surface chemical properties of activated carbon in the formation of the different radical species quantified.

2. Experimental

2.1. Materials

All the chemical products used (sodium diatrizoate, formic acid, acetonitrile, methanol, hydrochloric acid, sodium chloride, tetranitromethane, dimethyl sulfoxide, ethylene diamine tetraacetic acid, atrazine) were high-purity analytical grade and supplied by Sigma–Aldrich, with the exception of Aeroxide TiO₂ P-25 (CAS-N° 13463-67-7), which was provided by Evonix Industries. All the solutions were prepared with ultra-pure water obtained using Milli-Q® equipment (Millipore). The original activated carbon used has the commercial name Witco. The rest of carbon samples used in this study are changes produced on Witco by applying gamma radiation under different conditions (Section 2.5).

2.2. Photoreactor of simulated solar radiation

The solar simulator used was a model 1500 Solarbox, Neurtek instruments brand, equipped with a Xenon lamp of 1500 W (PHILIPS XOP-15-OF, 1500 W), which supplies radiant energy in a spectral range from 280 to 825 nm (Fig. 1S). The photodegradation experiments were conducted in an irradiance of 450 W m⁻². The experiments were conducted in quartz tubes (wall-width of 3 mm, inner diameter of 22 mm and height of 220 mm) that have a 92% transmittance across the 200–2500 nm range, which were previously sealed to prevent the effect of evaporation. The activated carbon used was kept in suspension by a magnetic agitation system.

The photonic flux entering in the quartz tubes provided by the Xenon lamp, installed inside the solar radiation simulator, was determined by 2-nitrobenzaldehyde (o-NB) actinometry, adapting the method proposed by Willett and Hites [44]. Thus, 0.5 L solution of 2-nitrobenzaldehyde 2.5 × 10⁻³ M was prepared, using as solvent a mixing of ethanol in water 50:50. This solution was irradiated an irradiance of 450 W m⁻² and samples were drawn every 5 min. o-NB concentration was plotted as a function of irradiation time and the curve was fitted to first-order kinetics. The incident photon flow (I₀) was calculated through Eq. (1).

$$I_0 = \frac{d[\text{Act}]}{dt} \times \left(\frac{1}{\phi}\right) \times \left(\frac{1}{1 - 10^{-\epsilon \cdot b \cdot [\text{Act}]_0}}\right) \quad (1)$$

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