



Adsorption of odorous sulfur compounds onto activated carbons modified by gamma irradiation



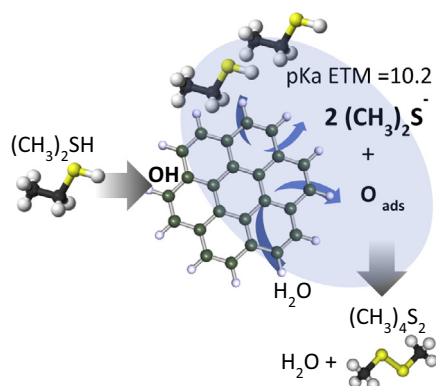
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GRAPHICAL ABSTRACT



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ABSTRACT

A commercial activated carbon (AC) was modified by gamma irradiation and was tested as adsorbent for the removal of ethyl mercaptan, dimethyl disulfide and dimethyl sulfide in wet conditions. Modifications were carried out under five different conditions: irradiation in absence of water, in presence of ultrapure water, in ultrapure water at $\text{pH} = 1.0$ and $1000 \text{ mg L}^{-1} \text{ Cl}^-$, in ultrapure water at $\text{pH} = 7.5$ and $1000 \text{ mg L}^{-1} \text{ Br}^-$, and in ultrapure water at $\text{pH} = 12.5$ and $1000 \text{ mg L}^{-1} \text{ NO}_3^-$. The chemical properties of each AC were characterized by elemental analysis, temperature programmed desorption and X-ray photoelectron spectroscopy. Outcomes show that a large number of oxygen functional groups were incorporated in the AC surface by gamma irradiation, especially in the AC irradiated in the presence of ultrapure water. The dynamic adsorption test results reveal that the incorporation of oxygen functional groups did not enhance the adsorption capacities for dimethyl sulfide and dimethyl disulfide. A significant improvement in the ethyl mercaptan adsorption capacity was correlated with the incorporation of phenolic groups in the AC surface. Moreover, diethyl disulfide was detected as by-product of ethyl mercaptan oxidation process under wet conditions and its formation depended on the chemical properties of ACs.

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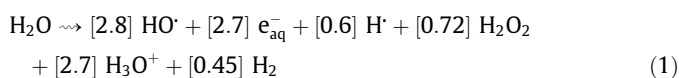
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1. Introduction

Volatile sulfur compound (VSC) emissions from waste water treatment plants (WWTPs), among other facilities, have become a public concern. The low odor threshold (OT) of these compounds [1] implies the requirement of highly effective technologies for reducing the impact on the quality of life of the population.

Adsorption by activated carbons (ACs) is a widely applied technique to remove VSCs in an extended variety of fields [2–5]. Several researchers have proposed different methodologies to modify the chemical surface of ACs in order to improve their performance. It has been shown that the incorporation of oxygen groups in the surface can improve the adsorption capacity. These modifications can be achieved by means of oxidation, chemical impregnation or thermal treatments [6–9]. However, these treatments involve the modification of the textural properties, causing the loss of porosity of the adsorbent.

In order to avoid this loss of porosity, the use of ionizing radiation as a treatment for modifying ACs has been recently investigated by Velo-Gala et al. [10]. The authors demonstrated that the use of ionizing radiation can incorporate different surface groups on the carbon surface without altering the porosity of the material. 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):



where the values in square brackets are the radiochemical yield of the process (G-value) for a pH range 6.0–8.5 and in an air free medium, i.e., the number of molecules formed on absorption of an energy of 100 eV [11]. The degree to which each species is formed depends on the solution pH, temperature, energy imparted by the incident radiation per unit distance travelled in the aqueous medium, absorbed dose, dose rate, and presence of dissolved gasses, among other factors. Thereby, it is possible to obtain a medium with a predominance of oxidizing species (HO^\cdot , H_2O_2 , or O_2) or reducing species (H^\cdot or e_{aq}^-). The effect of the incorporation of different oxygen surface groups in an ACs on the adsorption of VSCs, such as ethyl mercaptan (ETM), dimethyl sulfide (DMS) and dimethyl disulfide (DMDS), has been previously investigated in inert conditions (N_2 stream) [9]. From the results of this work, it was concluded that on one hand, DMDS adsorption was unaffected by the incorporation of oxygen functional groups in AC surface. On the other hand, only a massive incorporation of oxygen functional groups, especially hydroxyl groups, compensated the loss of porosity and thereby improved the adsorption capacities for ETM and DMS. The observed experimental results were confirmed by simulations with the quantum-chemical COSMO-RS model which established the role of each oxygen surface functional groups of the AC in the VSCs adsorption process.

The use of ionizing radiation has been studied with the objective of incorporating oxygen surface groups in an AC without modifying the porosity of the adsorbent. The irradiated ACs were used for the adsorption of ETM, DMS and DMDS under wet conditions and in the presence of oxygen, in order to understand the adsorption behavior in operational conditions more similar to those applied at real-life applications.

2. Materials and methods

2.1. Materials

All chemical reagents used (hydrochloric acid, potassium bromide, sodium nitrate, sodium hydroxide) were of high purity and supplied by Sigma–Aldrich. All the solutions were prepared with ultrapure water obtained with Mili-Q® equipment (Millipore). Steam activated extruded RB3 carbon supplied by Norit was used as the as-received material (AC-R). The AC-R was grounded and sieved in order to achieve a particle size lower than 212 μm . All AC samples were dried overnight at 105 $^\circ\text{C}$ before being used and stored in desiccators. All liquid sulfur compounds were supplied by Acros Organics (Belgium) and Merck (Germany) as well as nitric acid supplied by Scharlau (Spain) had purities higher than 99%.

2.2. Irradiation source

Irradiation studies were performed using a MARK-I gamma irradiator model 30J (Shepherd & Associates) in the Experimental Radiology Unit of the Scientific Instrumentation Center (CIC) of the University of Granada (Spain). The equipment includes four ^{137}Cs 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 modifications

All irradiations were conducted at a dose rate of 3.83 Gy min^{-1} , administering a total dose of 25 kGy. The as-received material (AC-R) was irradiated in air (in absence of water) by placing 5.0 g of the previously dried AC into 15 mL plastic tubes (AC denoted as AC-A). 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 N_2 for 1 h (AC-0). Before the irradiation, the samples were bubbled with N_2 to avoid the presence of dissolved O_2 , and the tubes were sealed to prevent entry of air. As noted above, the interaction of gamma irradiation with water molecules gives rise to multiple highly reactive radical species (Reaction (1)). The predominance of specific radiolytic species in the media was obtained by irradiating 5.0 g samples of the ACs in 50 mL plastic tubes under different experimental conditions: (i) $1000 \text{ mg L}^{-1} \text{ Cl}^-$ and $\text{pH} = 1.0$, because the chloride ion acts as HO^\cdot and e_{aq}^- radical scavenger [12] (Reactions (2)–(9)) and Reaction (10) is favored at this pH [13], producing the predominance of H^\cdot species in the medium (AC-H); ii) $1000 \text{ mg L}^{-1} \text{ Br}^-$ and $\text{pH} = 7.5$, because the bromide ion acts as HO^\cdot radical scavenger, giving rise to Reactions (11)–(14) [14–16], and Reaction (15) is favored at this pH [13], producing the predominance of e_{aq}^- species (AC-e); iii) $1000 \text{ mg L}^{-1} \text{ NO}_3^-$ and $\text{pH} = 12.5$, because Reactions (15)–(17) take place under these conditions [13,16,17], and the nitrate anion acts as H^\cdot and e_{aq}^- scavenger, producing the

Table 1
Designations of the AC samples obtained.

AC designation	Irradiation
AC-R	As-received activated carbon
AC-H	Activated carbon irradiated in the presence of H^\cdot
AC-e	Activated carbon irradiated in the presence of e_{aq}^-
AC-OH	Activated carbon irradiated in the presence of HO^\cdot
AC-0	Activated carbon irradiated in the presence of all radicals
AC-A	Activated carbon irradiated in the air (without water)

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