



Behavior of two different constituents of natural organic matter in the removal of sodium dodecylbenzenesulfonate by O_3 and O_3 -based advanced oxidation processes

J. Rivera-Utrilla*, M. Sánchez-Polo, J.D. Méndez-Díaz, M.A. Ferro-García, M.I. Bautista-Toledo

Departamento de Química Inorgánica, Facultad de Ciencias, Universidad de Granada, 18071 Granada, Spain

ARTICLE INFO

Article history:

Received 25 March 2008

Accepted 31 May 2008

Available online 5 June 2008

Keywords:

Ozone

SDBS

Activated carbon

Advanced oxidation processes

NOM

ABSTRACT

The objective of this study was to analyze the role played by two components of natural organic matter (NOM), gallic acid (GAL) and humic acid (HUM), in the removal of the surfactant sodium dodecylbenzenesulfonate (SDBS) from waters by O_3 -based oxidation processes, i.e., O_3/H_2O_2 , O_3 /granular activated carbon (GAC), and O_3 /powdered activated carbon (PAC). It was found that the presence of low concentrations of these compounds (1 mg/L) during SDBS ozonation increases both the ozone decomposition rate and the rate of SDBS removal from the medium. Because of the low reactivity of SDBS with ozone, these effects are mainly due to an increase in the transformation rate of ozone into HO^\bullet radicals. Results obtained demonstrate that the presence of GAL and HUM during SDBS ozonation increases the concentration of $O_2^{\bullet-}$ radicals in the medium, confirming that GAL and HUM act as initiating agents of ozone transformation into HO^\bullet . It was also found that this effect was smaller with a larger molecular size of the acid. Presence of GAL and HUM during SDBS removal by O_3/H_2O_2 , O_3 /GAC, and O_3 /PAC systems also increases the SDBS degradation rate, confirming the role of these compounds as initiators of ozone transformation into HO^\bullet radicals.

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1. Introduction

Surfactants are among the most widely used compounds, since their dual hydrophobic/hydrophilic nature makes them invaluable for flocculation, detergency and stabilization processes in industrial and domestic applications. There has been an exponential increase in the production and use of these substances over the past century. Despite the high biodegradability required by law for these products, the enormous amount of waste they produce has a severe impact on waters and soils [1]. Sodium dodecylbenzenesulfonate (SDBS), a widely applied surfactant belonging to the family of linear alkylbenzene sulfonates (LAS), was selected as model contaminant for these experiments.

The presence of contaminants refractory to conventional physicochemical or biological water treatments has stimulated interest in the use of ozone to degrade organic pollutants in aqueous media. Its use is growing worldwide because of its high oxidizing capacity and potential as a disinfectant agent. The need for more efficient ozonation methods has led to the development of advanced oxidation processes (AOPs) in recent decades [2–4]. The quality and

composition of the water has a major influence on the chemical reactions produced in ozone treatments and therefore on the efficacy of systems. Among compounds found in natural waters, natural organic matter (NOM) can have a major impact on ozonation processes, since it can reduce the effectiveness of disinfectant oxidant species and produce degradation by-products hazardous to human health [5–7]. NOM is present in natural waters at concentrations of 0.3–3 mg/L and, it is considered to be a mixture of humic and fulvic acids that give rise to macromolecules of high molecular weight [8].

Because of its complex nature, it is accepted that NOM can act as inhibitor, promoter or initiator of ozone decomposition reactions to yield highly oxidant radicals, e.g., hydroxyl radicals (HO^\bullet) [9,10]. Therefore, because the degradation of organic contaminants is largely due to their reactivity with HO^\bullet radicals [11,12], the composition of NOM is a determining factor in the ozonation of these contaminants. Hence, it is essential to identify the fractions of NOM that have a positive or negative impact on the process. Due to the lack of knowledge on this topic, the main objective of this study was to analyze the effect of the presence of two constituents of NOM, gallic acid (GAL) and humic acid (HUM), on the removal of SDBS (as model compound) by ozone and by O_3 -based advanced oxidation processes (O_3/H_2O_2 , O_3 /granular activated carbon (GAC), and O_3 /powdered activated carbon (PAC)).

* Corresponding author. Fax: +34 958248526.

E-mail address: jrivera@ugr.es (J. Rivera-Utrilla).

Table 1
Chemical and textural characteristics of the activated carbon

Sample	$S_{N_2}^a$ (m ² /g)	S_{ext}^b (m ² /g)	V_2^c (cm ³ /g)	V_3^d (cm ³ /g)	Ash (%)	pH _{pzc} ^e	Acid sites ^f (μeq/g)	Basic sites ^g (μeq/g)
Sorbo	1225	46.9	0.044	0.481	6.07	12.1	271	1285

^a Apparent surface area determined by applying BET equation to N₂ adsorption isotherm at 77 K.

^b External surface area determined by applying α -method to N₂ adsorption isotherm at 77 K.

^c Volume of pores with diameter 50–6.6 nm, determined by mercury porosimetry.

^d Volume of pores with diameter >50 nm, determined by mercury porosimetry.

^e pH of point of zero charge.

^f Determined by NaOH (0.1 N) titration.

^g Determined by HCl (0.02 N) titration.

2. Experimental

2.1. Materials

All reagents used (SDBS, tetranitromethane (TNM), 4-chlorobenzoic acid (*p*CBA), GAL, HUM, indigo, phosphoric acid, hydrochloric acid, sodium hydroxide and hydrogen peroxide) were reagent grade or analytical grade when available and used without further purification. HUM (from Aldrich) and GAL (from Merck) were obtained as tech or analytic grade powder. Stock solutions were prepared in double-distilled water. Concentrated O₃ stock solutions were produced by continuously bubbling O₃-containing oxygen through double-distilled water cooled in an ice bath. The concentration of the resulting stock solution was approximately 0.4 mM (20 mg/L).

Activated carbon from Sorbo was used for SDBS ozonation in the presence of activated carbon. Activated carbon was used in granular (GAC) and powder form (PAC) to check the influence of particle size in SDBS ozonation process. The particle size used was 0.5–0.8 mm and 0.05–0.08 mm for GAC and PAC, respectively. The chemical and textural characteristics of this commercial activated carbon (GAC) are listed in Table 1. The values of PAC characteristics are similar to those of GAC. This activated carbon was selected for its high surface area, basicity and ash content. Previous studies showed [13,14] that these properties make Sorbo activated carbon a good initiator/promoter of ozone transformation into HO• radicals. Because of its high adsorption properties, this activated carbon is widely used for the purification of drinking waters.

2.2. Experimental methods

In each experiment, the reactor was filled with 1 L of the desired pH regulator solution of SDBS 2.87×10^{-5} M. pH was obtained by adding appropriate amounts of phosphoric acid (50 mM) and sodium hydroxide (0.01 M) to the aqueous solution. To this solution was added 1 mg/L of GAL or HUM and, in the corresponding experiments, GAC (25 mg/L), PAC (25 mg/L) or H₂O₂ (3.12×10^{-5} M). Aliquots of the ozone stock solutions were then added to the stirred batch reactor with a sampling dispenser. Ozone stock solutions were prepared in a batch reactor. Ozone was generated from oxygen by means of an OZOKAV ozone generator with a maximum capacity of 76 mg/min. The reactor with SDBS solution was immersed in a thermostatic bath to maintain a constant temperature of 298 K during ozonation experiments. Samples were drawn from the reactor at regular time intervals to measure both SDBS and dissolved ozone concentrations.

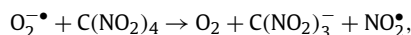
The adsorption kinetics of GAL and HUM on GAC and PAC were obtained by adding 0.25 g of activated carbon to 1 L of solution with 10 mg/L of acid (GAL or HUM) at a constant temperature of 298 K. The adsorption kinetics of SDBS on activated carbon in the presence of GAL or HUM were obtained by adding 0.25 g of GAC or PAC to a 1-L solution of SDBS 2.87×10^{-4} M and 10 mg/L of the

corresponding acid. In all experiments, the concentration of SDBS in the system was measured at regular time intervals.

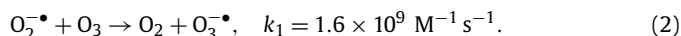
2.3. Analytical methods

Ozone in solution was measured by means of the indigo method [15]. The pH of the solution was determined by using a Crimson pH meter, calibrated with reference buffer solutions with pH of 4 and 7. SDBS was measured by high-resolution liquid chromatography (HPLC) in gradient [16] with detection by fluorescence ($\lambda_{ex} = 225$ nm, $\lambda_{em} = 295$ nm). The acids were determined by spectrophotometry (GAL, 268.5 nm; HUM, 260 nm) using a Genesys 5 spectrophotometer.

The O₂• radicals generated were detected by their reaction with TNM (reaction (1)), determining the anion formed ((C(NO₂)₃)[−], ϵ (350 nm) = 15,000 M^{−1} cm^{−1}) [17].



$$k_2 = 2 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}, \quad (1)$$



In order to minimize the extent in which the reaction of O₂• radicals with ozone is produced (reaction (2)), a concentration of 5×10^{-3} M of TNM was used. Thus, the fraction of the radicals reacting with ozone was ≤ 0.01 (Eq. (3)):

$$f_{O_2^{\bullet}} = \frac{k_1[O_3]}{k_1[O_3] + k_2[C(NO_2)_4]} = 0.01. \quad (3)$$

The HO• radicals generated during ozonation were measured by evaluating the concentration of *p*CBA as a function of treatment time. *p*CBA has a low reactivity with ozone ($k_{O_3} = 0.15 \text{ M}^{-1} \text{ s}^{-1}$) and a high reactivity with HO• radicals ($k_{OH} = 5.2 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$), making it an ideal compound for detecting HO• radicals in the medium. The *p*CBA concentration was determined by HPLC-UV. The mobile phase was 45% of 10^{-2} M H₃PO₄ and 55% methanol at 1 mL/min, using a wavelength of 234 nm to detect *p*CBA.

The techniques and methods used for the chemical and textural characterization of the activated carbon are described in detail elsewhere [13,14,18].

3. Results and discussion

3.1. Influence of GAL and HUM on the SDBS degradation rate using ozone

Fig. 1 and Table 2 (experiments 1, 6, and 11) show the results of ozonation of SDBS at pH 7 in the absence or presence of GAL and HUM as a function of the exposure of the system to ozone. This exposure was determined from Fig. 1b as $\int_0^t [O_3] dt$, which represents the time integrated concentration of O₃ during ozonation process. The addition of 1 mg L^{−1} of either acid to the system increased the SDBS oxidation rate and the value of the ozone decomposition constant (k_D), determined by a first-order kinetic model (Table 2, experiments 1, 6, and 11). Because of the low reactivity of SDBS with ozone ($k_{O_3} = 3.68 \text{ M}^{-1} \text{ s}^{-1}$) [19], these results (Fig. 1) may indicate that the presence of these acids during SDBS ozonation increases the transformation rate of ozone into HO• radicals, which would be responsible for the increased SDBS degradation rate. Ozone can also be decomposed in pure water, on carbon and in the presence of sunlight [2,3] however the magnitude of this effect is negligible under the experimental conditions used.

A characteristic parameter of this treatment system is $\Delta[SDBS]/\Delta[O_3]$, which represents the efficacy of the system to remove SDBS as a function of the ozone consumed. Determination of this parameter in the presence and absence of GAL and HUM (Table 2,

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