

## GUIDE FOR AUTHORS

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The reviews of doctoral theses will be published in English.

The extension for each review is 4 pages maximum (Times New Roman 11, spacing 1.5).

The profiles consist of the following sections:

1. Title of Doctoral Thesis.
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3. Supervisors of the doctoral thesis and their affiliations.
4. Wording and presentation. It will ensure that the wording is clear and concise as possible, including: Objectives and Novelty, Results, Conclusions and Related Publications.

Special emphasis should be given to the objectives and novelty of the research presented and the final conclusions reached.

Figures and Tables should be inserted at an appropriate place in the text.

Regarding to the Related Publications section, the references should be limited to that directly related to the Doctoral Thesis. References should be presented in a numbered list at the end of the manuscript in accordance with the format shown in the instructions for articles of this Bulletin.

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## DEGRADATION AND REMOVAL OF NAPHTHALENESULPHONIC ACIDS IN AQUEOUS SOLUTION BY MEANS OF OZONATION PROMOTED BY ACTIVATED CARBON

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### **OBJECTIVES AND NOVELTY**

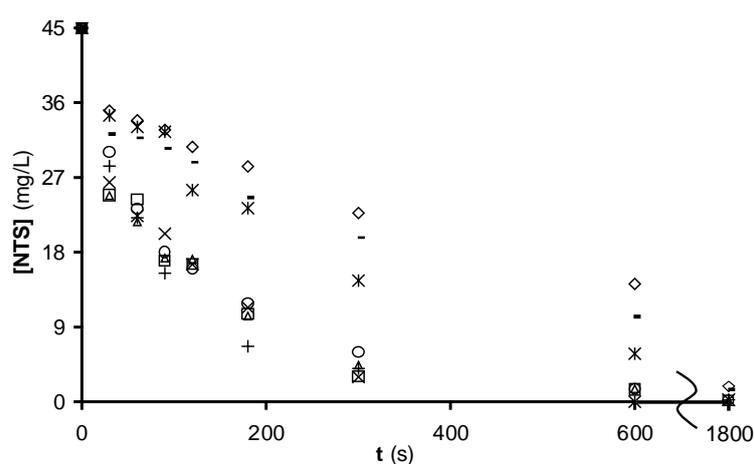
Effluents from the textile industry present elevated concentrations of sulphonated polyphenols (dyestuffs), ranging between 10 and 80 mg/L and with a mean concentration of 31 mg/L. Biological water treatments are not effective in eliminating this type of compound, so that alternative treatments are necessary. At present, activated carbon and ozone are widely used to treat organic compounds that are resistant to biological treatments, taking advantage of their respective adsorbent and oxidizing properties. Activated carbon has been signaled as a promising catalyst of ozonation because of its chemical and textural properties and low cost. However, there are no data on the physical and chemical processes that take place to enable the correct design of a reactor for this method. Thus, it is not known which properties of activated carbon are involved in increasing the extension of the ozonation process or what reactions are implicated. Moreover, the influence of operational variables on the adsorption/ozonation process is still unknown.

The present work aimed to outline results obtained during the development of a wider project to design a new reactor based on the combined use of ozone and activated carbon for the depuration of waters that contain a large concentration of non-biodegradable organic matter. Knowledge of the ozonation process of naphthalenesulphonic acids in the absence of activated carbon (reaction mechanism and kinetics, influence of operational variables, oxidation subproducts) and of the interactions involved in the adsorption of these contaminants on activated carbon will also help us explain more precisely the behavior of activated carbon both as catalyst and adsorbent in the treatment system based on the combined use of ozone and activated carbon.

## RESULTS

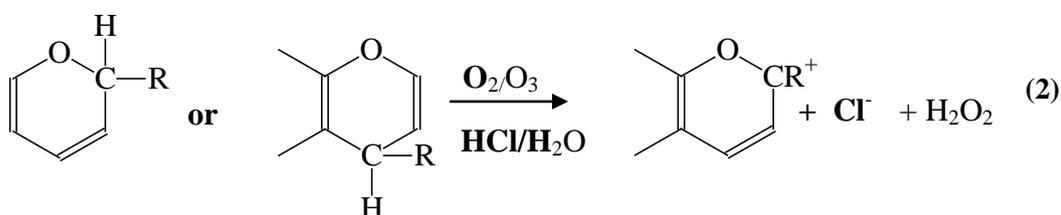
Naphthalenesulphonic compounds were observed to present genotoxic activity at elevated concentrations. The study revealed that the genotoxic activity of naphthalenesulphonic acids reduces as the number of sulphonic groups on the aromatic ring increases. Ames test findings indicate that the mechanism that produces the DNA damage is by substitution of nitrogenated bases. The aromatic acids studied showed a low reactivity to ozone. The greater the number of sulphonic groups in the molecule, the lower was the reactivity. The prolonged exposure of activated carbon to ozone modifies the chemical composition of the surface of activated carbon. The basic sites are transformed into acid ones due to their oxidation. The action of ozone also impacts on the textural characteristics of the carbon; the surface area diminishes. On the other hand, the adsorption of naphthalenesulphonic acids on activated carbons is regulated both by  $\pi$ - $\pi$  dispersion interactions and by electrostatic interactions. We reported that the reactivity of naphthalenetrisulphonic acid (NTS) to ozone was very low ( $k_D = 6.72 \text{ M}^{-1} \text{ s}^{-1}$ ). However, NTS showed an elevated affinity for free radicals ( $k_{OH} = 3.68 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ ), so that we can consider NTS an ideal compound to detect the presence of highly oxidizing radicals in the medium.

To determine the properties of activated carbons involved in the decomposition of ozone in highly oxidizing species, NTS was ozonized in the presence of different commercial activated carbons. Figure 1 shows experimental results of NTS ozonation in the presence of the different activated carbons.



**Figure 1.** NTS ozonation in the presence of commercial activated carbons. pH 2.3, T 298 K. ( $\diamond$ ), without carbon; (O), Filtrisorb 400; ( $\Delta$ ), Merck; ( $\square$ ), Ceca GAC; ( $\ominus$ ), Ceca AC40; (x), Norit; (+), Sorbo; (-) Witco.

The greater rate of NTS ozonation in the presence of these carbons could, therefore, be explained by an increase in free radical hydroxyl concentration. The carbons that most enhanced the NTS ozonation rate were those with greatest  $\text{pH}_{\text{PZC}}$  values and highest concentrations of surface basic groups. However, no clear relationship was observed between the NTS ozonation rate and the  $S_{\text{N}_2}$  of the activated carbon. On the other hand, the carbons that most favored the removal of NTS from the medium (Sorbo and Norit) were those with greatest macropore volumes. The results obtained suggest that the catalytic activity of these activated carbons in NTS ozonation is mainly a function of the carbon basicity. The basicity of an activated carbon is due to the presence of basic oxygen-containing functional groups (e.g. pyrones or chromenes) and/or graphene layers acting as Lewis bases and forming electron donor-acceptor (EDA) complexes with  $\text{H}_2\text{O}$  molecules. According to the above results, we proposed that the delocalised  $\pi$  electron system of basic carbons and oxygenated basic groups (chromene and pyrone) would, therefore, act as catalytic centres of reaction, reducing the ozone molecules to hydroxyl ion and hydrogen peroxide following the reactions (1, 2), which act as ozone decomposition initiators.



## CONCLUSIONS

**The aromatic acids studied showed a low reactivity to ozone. The greater the number of sulphonic groups in the molecule, the lower was the reactivity.**

The prolonged exposure of activated carbon to ozone modifies the chemical composition of the surface of activated carbon. The basic sites are transformed into acid ones due to their oxidation. The action of ozone also impacts on the textural characteristics of the carbon; the surface area diminishes because of the ozone attack and because the increase in oxygenated groups prevents the diffusion of nitrogen by obstructing the entrances of the micropores.

The adsorption of naphthalenesulphonic acids on activated carbons is regulated both by  $\pi$ - $\pi$  dispersion interactions and by electrostatic interactions. However, the  $\pi$ - $\pi$  interactions have a more determining influence on this process.

The presence of basic activated carbon during the ozonation of NTS increases the rate of degradation and produces the removal of part of the organic matter by its mineralization.

### **RELATED PUBLICATIONS**

- [1] Sánchez-Polo M, Rivera-Utrilla J, Zaror CA, Advanced oxidation with ozone of 1,3,6-naphthalenetrisulphonic acid in aqueous solution, J Chem Tech Biotech, 2002; 77, 148-154.
- [2] Valdés H, Sánchez-Polo M, Rivera-Utrilla J, Zaror CA, Effect of ozone treatment on surface properties of activated carbon, Langmuir, 2002; 18, 2111-2116.
- [3] Rivera-Utrilla J, Sánchez-Polo M, Zaror CA Degradation of naphthalenesulphonic acids by oxidation with ozone in aqueous phase, Phys Chem Chem Phys 2002; 4, 1129-1134.
- [4] Rivera-Utrilla J, Sánchez-Polo M, Mondaca MA, Zaror CA, Effect of ozone and ozone/activated carbon treatments on genotoxic activity of naphthalenesulphonic acids, J Chem Tech and Biotech 2002; 77, 883-890.
- [5] Sánchez-Polo M, Rivera-Utrilla J, Adsorbent-adsorbate interactions in the adsorption of Cd(II) and Hg(II) on ozonised activated carbons, Env. Sci. Tech., 2002; 36, 3850-3854.
- [6] Rivera-Utrilla J, Sánchez-Polo M, Ozonation of 1,3,6-naphthalenetrisulphonic acid catalysed by activated carbon in aqueous phase, App. Catal. B: Environ. 2002; 39, 319-329.
- [7] Rivera-Utrilla J, Sánchez-Polo M, The role of dispersive and electrostatic interactions in the aqueous phase adsorption of naphthalenesulphonic acids on ozone-treated activated carbons, Carbon 2002; 40, 2685-2691.
- [8] Sánchez-Polo M, Rivera-Utrilla J, Effect of O<sub>3</sub>/carbon reaction on the catalytic activity of activated carbon during degradation of 1,3,6-naphthalenetrisulphonic acid with ozone, Carbon, 2003; 41, 303-307.
- [9] Valdés H, Sánchez-Polo M, Zaror CA Effect of ozonation on the activated carbon surface chemical properties and on 2-mercaptobenzothiazole adsorption, Latin America Applied Research, 2003; 33, 219-223.
- [10] Rivera-Utrilla J, Sánchez-Polo M, Adsorption of Cr(III) on ozonized activated carbon. Importance of C $\pi$ -cation., Wat. Res., 2003; 37, 3335-3340.
- [11] Rivera-Utrilla J, Sánchez-Polo M, Degradation and removal of naphthalenesulphonic acids by means of adsorption and ozonation catalyzed by activated carbon in aqueous phase, Water Resources Research 2003; 39, 1232-124.

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