

# Carbon materials as catalysts for the ozonation of organic pollutants in water

## Materiales de carbón como catalizadores para la ozonización de contaminantes orgánicos en agua

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### Abstract

A brief overview about the use of carbon materials as metal free ozonation catalysts is presented. Carbon materials (activated carbons, carbon xerogels, carbon nanofibers and carbon nanotubes) have been shown to be active catalysts in the ozonation of a wide range of organic pollutants. Carbon materials with surface basic properties (i.e. high electron density) and with large pores are the most promising for this process.

### Resumen

En el presente trabajo se resume brevemente el uso de materiales de carbón como catalizadores libres de metales en el proceso de ozonización. Los materiales de carbón (carbones activados, xerogeles de carbón, nanofibras y nanotubos de carbono) han mostrado ser catalizadores activos para una gran variedad de contaminantes orgánicos en dicho proceso, siendo los más adecuados aquellos con propiedades superficiales básicas (alta densidad electrónica) y con mayor tamaño de poros.

### 1. Ozone reactivity in water

The high reactivity of ozone can be attributed to the electronic configuration of the molecule. The two extreme forms of resonance structures of ozone molecule are illustrated in Figure 1. The absence of electrons in one of the terminal oxygen atoms in some of the resonance structures confirms the electrophilic nature of ozone. Conversely, the excess negative charge present in some other oxygen atom imparts a nucleophilic character to the molecule [1, 2].

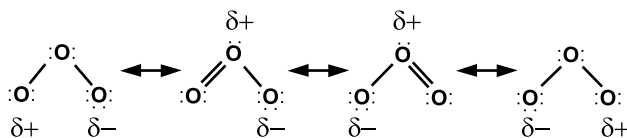


Figure 1. Resonance structures of the ozone molecule. Adapted from [1].

Figura 1. Estructuras de resonancia de la molécula de ozono [1]. Adaptado de [1].

Ozone has one of the highest standard redox potential (2.07 V), only lower than those of fluorine (3.06 V), hydroxyl radical (2.80 V) and atomic oxygen (2.42 V). Because of its high standard redox potential, the ozone molecule has a high capacity to react with numerous compounds by means of redox reactions. Some of these reactions occur by explicit electron transfer, while most of them occur by oxygen transfer from the ozone molecule to the other reactant [1, 2].

The stability of ozone in water largely depends on the water matrix, especially its pH, temperature, chemical composition (such as, the presence of natural organic matter (NOM) and bicarbonate/carbonate ions) [3].

Ozone reactions in water can be classified as direct

and indirect reactions, as presented in Figure 2. Direct reactions occur between ozone molecules and other chemical species (M), while indirect reactions are those between the HO<sup>•</sup> radicals (formed from the decomposition of ozone or from other direct ozone reactions) and compounds present in water. In contrast to other conventional oxidant species, hydroxyl radicals are capable to completely oxidise (i.e. mineralise) even the less reactive pollutants. They react non-selectively with organic compounds, mainly by means of electrophilic addition to unsaturated bonds, addition to aromatic rings, abstraction of hydrogen or by electron transfer. The rate constants of most reactions between HO<sup>•</sup> and organic species are usually in the order of 10<sup>6</sup>–10<sup>9</sup> M<sup>-1</sup> s<sup>-1</sup> [4]. Mineralisation of end products generally results in inorganic carbon, water and inorganic ions.

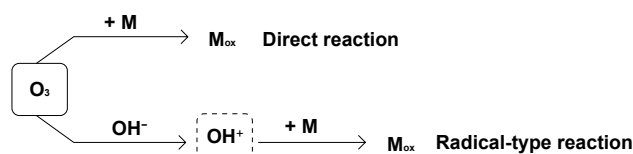
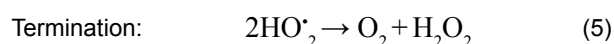
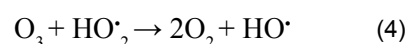
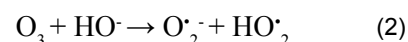
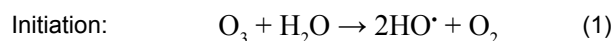


Figure 2. Oxidation reactions of compounds during ozonation in water.

Figura 2. Reacciones de oxidación de compuestos durante la ozonización en agua.

The spontaneous decomposition of ozone in aqueous solution occurs through a series of steps. Since the first model proposed by Weiss in 1935 [5], numerous studies have been developed to clarify the mechanism of decomposition of ozone in water. Presently, the mechanism proposed by Staehelin and Hoigné [6] is generally accepted for the decomposition of dissolved ozone, but alternative reaction steps have been proposed by other authors. A review of the proposed mechanisms is presented in [2]. Briefly, the mechanism for the decomposition of dissolved ozone is described below [7]:



The initiation steps of the ozone decomposition chain mechanism consist in reaction of ozone with water (reaction 1) and hydroxide ions (reaction 2) originating hydroxyl radicals. Nevertheless, the initiation of ozone decomposition in aqueous solution can be artificially accelerated by increasing the pH or by the addition of UV radiation, hydrogen peroxide, reduced metal ions or heterogeneous catalysts, leading to an Advanced

Oxidation Process (AOP) [8]. The contribution of these two steps for ozone decomposition depends strongly on the pH of the solution and on the nature of the substances present in water. Normally, under acidic conditions ( $\text{pH} < 4$ ) the direct pathway rules, whereas for  $\text{pH} > 10$  mainly the radical pathway is present. Under neutral conditions, both pathways can be important [9].

The ozone decomposition chain can be terminated when hydroxyl radicals react with inhibitors, which are compounds capable of consuming  $\text{HO}^\cdot$  radicals without regenerating the superoxide radical. The more common inhibitors include tertiary alcohols (e.g. *tert*-butanol), and carbonate and bicarbonate ions. These are also called hydroxyl radical scavengers, because their presence limits or inhibits the action of these radicals on the target compounds. *Tert*-butanol is a well-known radical scavenger, as it reacts with  $\text{HO}^\cdot$  at a rate constant of  $5 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$  [10], which is in the range of the rate constants of reactions between  $\text{HO}^\cdot$  and organic compounds.

## 2. Catalytic ozonation for the degradation of organic compounds

Catalytic ozonation is an AOP for contaminants removal from drinking water and wastewater. Presently, the application of catalytic ozonation is mainly limited to laboratory use. However, due to successful results, further investigation is to be carried out. The target pollutants are organic compounds refractory to biological treatments, such as pesticides, endocrine disrupting compounds (EDCs), pharmaceuticals, and personal care products (PPCPs) and textile dyes. The main weakness of non-catalytic ozonation is related to by-products formation and their future damage in the environment. In contrast, in catalytic ozonation, the problem of toxic by-products formation can be solved by the development of active catalysts capable to promote their mineralisation.

In water treatment, the high reactivity of ozone and the active surfaces of some materials can be used to increase the ozonation efficiency. In this way, several research groups have been focussed on the combined application of ozone and solid catalysts, and consequently numerous papers have been published since the mid 1990s. The most common catalysts proposed for the process of heterogeneous catalytic ozonation are metal oxides such as  $\text{MnO}_2$ ,  $\text{TiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{ZnO}$  and supported metal oxides ( $\text{TiO}_2/\text{Al}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3$ ,  $\text{Co}_3\text{O}_4/\text{Al}_2\text{O}_3$ ,  $\text{MnO}_2/\text{TiO}_2$ ) [11]. Transition and noble metals supported on several oxides ( $\text{Cu-Al}_2\text{O}_3$ ,  $\text{Cu-TiO}_2$ ,  $\text{Ru-CeO}_2$ ,  $\text{Co-Al}_2\text{O}_3$ ) have also been investigated [11, 12]. Activated carbon by itself [13-15], carbon xerogels [16], carbon nanotubes [17], metal oxides supported on activated carbon [18], metal-doped carbon aerogels [19] and platinum supported on carbon nanotubes [20] have also been tested in the ozonation of organic compounds.

The activity of such materials is frequently associated with their ability to catalytically decompose ozone leading to the formation of  $\text{HO}^\cdot$  radicals. The efficiency of the catalytic ozonation process depends, to a great extent, on the catalyst and its surface properties, as well as on the pH of the solution, which influences the properties of surface active sites and ozone decomposition reactions in the aqueous phase. The huge diversity of solid catalyst types, the variety of

the surface properties, and the interactions between catalyst, ozone and organic molecules, make difficult the generalisation of the mechanisms involved. In the following sections a more detailed discussion on the ozonation catalysed by carbon materials is presented.

## 3. Carbon as catalyst for ozonation

### 3.1 Catalytic decomposition of ozone in water

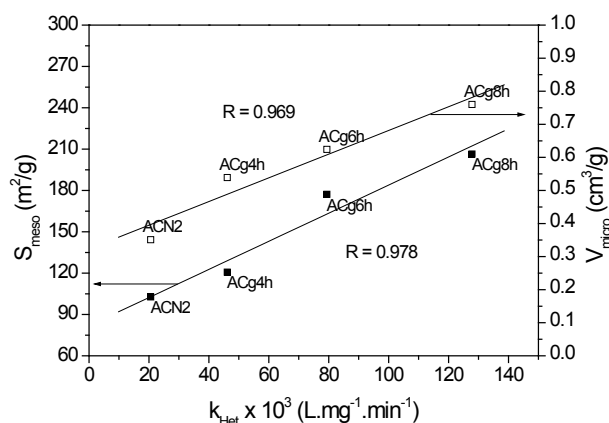
Concerning wastewater treatment, the instability of ozone molecule is an advantage, as the formation of  $\text{HO}^\cdot$  radicals transforms ozonation into an advanced oxidation process [2], enhancing its efficiency for the degradation of organic pollutants.

Carbon materials by themselves were found to be catalysts for the decomposition of  $\text{O}_3$  in water. The pioneer work on this subject was carried out by Jans and Hoigné [21]. Suspensions of activated carbon or carbon black were found to accelerate the depletion of ozone, acting as initiators for the radical type chain reaction that proceed in bulk solution, leading to the transformation of ozone into secondary oxidants, such as  $\text{HO}^\cdot$ . It was suggested that the catalytic decomposition of ozone was preceded by an adsorption step on the activated carbon surface.

More recently, this subject was revisited by different authors [22-24] and the influence of both chemical and textural features of the activated carbon was evaluated.

#### 3.1.1. Influence of the textural properties

Concerning the influence of the textural properties in the catalytic decomposition of ozone, it has been shown that activated carbons with large surface areas clearly favour this reaction [22, 23, 25]. Faria et al. [22] studied the influence of a series of modified activated carbons prepared from the same starting material and differing only in their textural properties. Strong correlations between the heterogeneous apparent rate constant ( $k_{\text{Het}}$ ) and the mesopore surface area and the micropore volume were observed (see Figure 3). Nevertheless, Alvarez et al. [24] did not find any correlation between the textural properties of AC and the rate of ozone decomposition, which may be explained by the fact that the ACs tested were from different origins, possibly masking the textural effects.

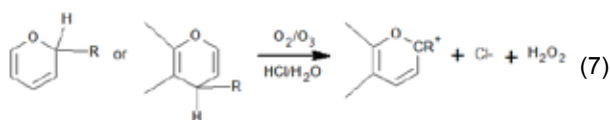
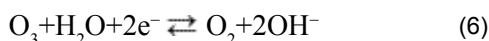


**Figure 3.** Variation of  $k_{\text{Het}}$  with selected textural properties of activated carbons. ACN2 is the original AC and ACgxh, where x is the duration (hours) of gasification at 900 °C under  $\text{CO}_2$ , are the treated samples. Reprinted with permission from [22]. Copyright (2006) American Chemical Society.

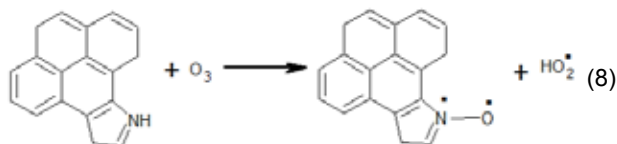
**Figura 3.** Variación de  $k_{\text{het}}$  con las propiedades texturales indicadas de los carbones activados. ACN2 es el AC original y ACg<sub>x</sub>h, dónde x indica la duración (horas) de gasificación a 900 °C con CO<sub>2</sub>, son las muestras tratadas. Reproducido con permiso de [22]. Copyright (2006) American Chemical Society.

### 3.1.2. Influence of the surface chemistry

It is already established that ozone decomposition is controlled by the surface chemical properties of the carbon materials, the most efficient ones being those with high basicity. Rivera-Utrilla and collaborators [15, 23] and Alvarez et al. [24] concluded that O<sub>3</sub> reduction on the AC surface generated OH<sup>-</sup> ions and H<sub>2</sub>O<sub>2</sub>, which initiate the O<sub>3</sub> decomposition into highly oxidative species [26]. The delocalised π electron system (reaction 6) and the oxygenated basic surface groups, such as chromene and pyrone (reaction 7), were identified as the catalytic centres, according to the following reactions [15]:



The same authors [23, 27] tested nitrogen-containing AC and concluded that pyrrolic groups were the nitrogenated active centres for O<sub>3</sub> decomposition. The attack of pyrrolic groups by ozone yields N-oxide-type groups and the superoxide radical (reaction 8), which enhances the rate of ozone transformations into hydroxyl radicals [6].

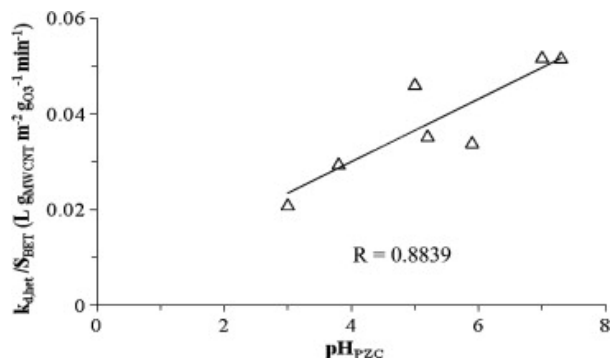


Faria et al. [22] studied the effect of pH on the catalytic decomposition of ozone and proposed that the electrostatic interactions between activated carbon surface and the solutes involved in the mechanism (including OH<sup>-</sup> ions) may also play a role. When the pH<sub>PZC</sub> of the activated carbon is higher than the pH of the solution, the surface of the material becomes positively charged, enhancing the attraction of hydroxide ions and the heterogeneous decomposition of ozone.

Successive ozone decomposition runs carried out with the same AC sample showed that the surface chemistry is mainly important in the first cycles of reaction, its effect decreasing thereafter due to a slightly progressive oxidation of the surface, which causes the increase of acidic surface groups, mainly carboxylic acids and therefore the loss of basicity [22-24]. Based on these results, Sánchez-Polo et al. and Alvarez et al. [23, 24] proposed that AC could not be a catalyst for ozone decomposition, but rather an initiator of the O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> system. Nevertheless, Faria et al. [22] concluded that basic activated carbons tended to behave as acid ACs, which were shown to still be active catalysts.

The effect of the surface chemistry of MWCNTs was recently discussed in detail in the ozone decomposition [28], and a correlation was observed between the normalized rate constant for heterogeneous ozone

decomposition ( $k_{\text{d,het}}/S_{\text{BET}}$ ) and pH<sub>PZC</sub> (see Figure 4), showing that the trend of the catalytic activity for the decomposition of ozone follows the decrease of acidity, according to what was observed for activated carbons.



**Figure 4.** Correlation of the normalized rate constants for heterogeneous ozone decomposition ( $k_{\text{d,het}}/S_{\text{BET}}$ ) with pH<sub>PZC</sub>. Reproduced with permission from [28].

**Figura 4.** Correlación de las constantes de velocidad normalizadas para la descomposición heterogénea de ozono ( $k_{\text{d,het}}/S_{\text{BET}}$ ) con el pH<sub>PZC</sub>. Reproducido con permiso de [28].

### 3.2 Catalytic ozonation of organic pollutants in water

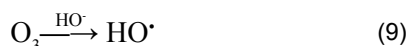
Catalytic ozonation may be included in the so-called advanced oxidation processes. These processes are based on the formation of HO<sup>•</sup> radicals, which are highly reactive towards most organic pollutants. Among these processes, the combination of ozone and carbon materials in a single step was found to be an attractive alternative to the treatment of water and wastewater containing organic contaminants. The large variety of compounds tested in this process includes small carboxylic acids, such as oxalic [29, 30], oxamic [30], pyruvic [31], and succinic acids [32], and aromatic compounds such as aniline [33], naphthalenesulfonic acid [15, 27, 34, 35], sulfonated aromatic compounds [36], phenolic compounds [37-39] and benzothiazole solutions [40]. The simultaneous use of ozone and activated carbon has been shown to be a promising method for the mineralisation of dye solutions [41-47] and for the treatment of textile wastewater [14, 41, 46-50], especially when used as a final oxidation treatment for biotreated effluents. Recently, the application of simultaneous use of ozone and activated carbon to remove emerging organic pollutants, such as EDCs and PPCPs, has been successfully investigated. The mineralization of diclofenac [51], sulphonamide antibiotics (including sulfamethoxazole [52, 53]), nitroimidazole antibiotics [54, 55], hormones [56] and atrazine [57]) has been reported in the literature.

The scheme presented in Figure 5 summarizes the main possible reaction pathways occurring in the ozonation of organic compounds catalysed by carbon materials.

The removal of organic pollutants, as well as the respective oxidation by-products, via ozonation in the presence of carbon materials is a result of a complex combination of homogeneous and heterogeneous reactions. Both direct and indirect ozone reactions occur in the liquid phase. Additionally, reactions between adsorbed species and oxygen radicals formed on the surface of the activated carbon are assumed to occur.



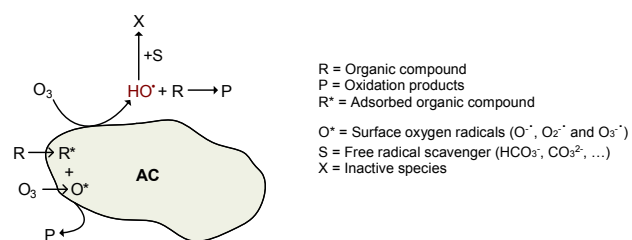
Regarding the non-catalytic decomposition of ozone in aqueous solution, it is established that it is initiated by the presence of  $\text{HO}^\cdot$  ions; so pH plays a major role in this process.



As shown in the previous section, carbon materials accelerates the decomposition of ozone and is consensual that both textural and surface chemical properties influence that decomposition, but doubts on the mechanism still remains. Two possible pathways can explain the decomposition of  $\text{O}_3$  in the presence of carbon materials. The first one assumes that activated carbon acts as an initiator of the decomposition of ozone, eventually through the formation of  $\text{H}_2\text{O}_2$  [10], yielding free radical species, such as  $\text{HO}^\cdot$ , in solution [15]. Another possibility is the adsorption and reaction of ozone molecules on the surface of the activated carbon, yielding surface free radicals ( $\text{O}^*$ ) [12], which can react with adsorbed organic species ( $\text{R}^*$ ) [27]. This results in the formation of several intermediates that are further transformed into saturated compounds (P), which cannot be mineralized by direct ozone attack. Additionally,  $\text{HO}^\cdot$  radicals in solution can also contribute to the oxidation of the organic compounds. The mineralization of the oxidation intermediates into inorganic carbon and inorganic ions (e.g.  $\text{NO}_3^-$ ,  $\text{NH}_4^+$ ,  $\text{SO}_4^{2-}$ ), occurs both in the liquid phase through  $\text{HO}^\cdot$  radical attack, or on the surface of the activated carbon.

Even though there is no experimental evidence, it is necessary to consider that adsorbed reactants might also react with dissolved ozone, or hydroxyl radicals from the aqueous phase [28].

It has been shown that the presence of a radical scavenger (S) induced different results depending on the organic compound studied. The effect of the radical scavenger is expected mainly when the reactions proceed in the bulk solution.



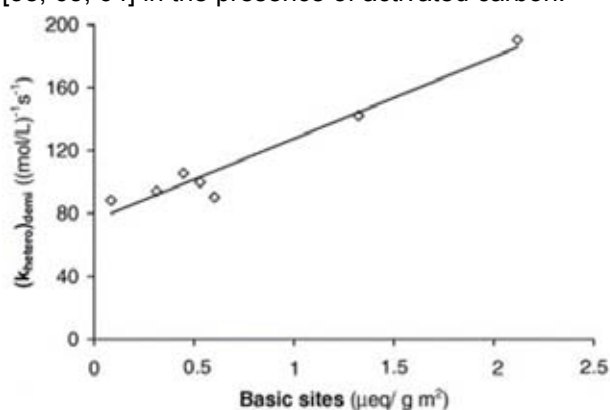
**Figure 5.** Schematic representation of the main reaction pathways occurring during ozonation catalysed by activated carbon (AC). Reproduced with permission from [58].

**Figura 5.** Esquema de las principales rutas de reacción producidas durante la ozonización catalizada con carbón activado (AC). Reprodcido con permiso de [58].

Rivera-Utrilla and collaborators [15, 27, 34, 59, 60] proposed the basal plane electrons, the oxygenated basic groups (chromene and pyrone) and the pyrrole groups (in the case of N-containing samples) as the active sites responsible for ozone decomposition in aqueous phase, according to equations 6 to 8, by initiating the decomposition of  $\text{O}_3$  into highly oxidative species, and increasing the naphthalene-1,3,6-trisulfonic acid (NTS) (an organic molecule representative of several dyes) ozonation rate [15]. They showed that the heterogeneous rate constant for NTS ozonation ( $(k_{\text{hetero}})_{\text{demi}}$ ) was well correlated

with the basicity of ACs, as can be seen in Figure 6 [59]. Similar correlation was found by Beltran et al. for the ozonation of succinic acid [32]. The advantage of the basic surface groups has also been highlighted for the catalytic ozonation of aniline [33] and different classes of dyes and textile effluents [43]. Recently, the same trend has been observed when carbon xerogels were used for the ozonation of several dyes [16] and when carbon nanotubes with different surface chemistries were used in the ozonation of oxalic and oxamic acids [28], sulfamethoxazole (SMX) [61] and bezafibrate [62].

Another additional advantage of using ozone and carbon materials simultaneously is the possibility of in-situ regeneration of the carbon material, avoiding the costly ex-situ treatment of the exhausted carbon material. This fact was observed experimentally in the catalytic ozonation of textile effluents [14] and phenol [38, 63, 64] in the presence of activated carbon.



**Figure 6.** Relationship between the heterogeneous rate constant ( $(k_{\text{hetero}})_{\text{demi}}$ ) for the ozonation of NTS and the concentration of basic groups in demineralised ACs. Reproduced with permission from [59].

**Figura 6.** Relación entre la constante de velocidad heterogénea ( $(k_{\text{hetero}})_{\text{demi}}$ ) para la ozonización de NTS y la concentración de grupos básicos de ACs desmineralizados. Reprodcido con permiso de [59].

### 3.3. Catalytic ozonation using nanocarbon materials on macrostructured catalysts.

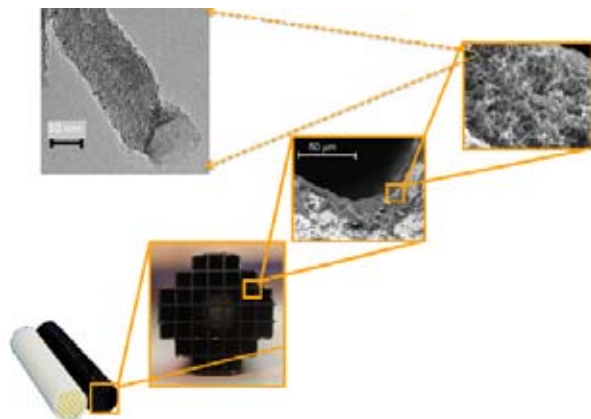
Carbon nanotubes (CNT) and nanofibers (CNF) constitute a new family of supports offering a good compromise between the advantages of activated carbon and high surface area graphite [65]. The main drawback of activated carbons in liquid media is that they are predominantly microporous and the diffusion of solutes in this type of pores may be very slow. Diffusion limitations in the micropores of activated carbons are even more dramatic in aqueous media than in organic media due to the hydrophobic nature of carbon surface. Hence, solutes in aqueous media have hindered access to micropores, unless the surface is made hydrophilic by functionalization with e.g. oxygenated groups. In contrast, the mesoporous nature of nanocarbon materials (NCM) favours the diffusion through the pore network. Moreover, solutes have good access to mesopores of NCM, even if the pore walls are hydrophobic, i.e. without functionalization [66]. Indeed, CNTs represent an interesting alternative to conventional supports. Carbon nanotubes were barely applied as ozonation catalysts of organic pollutants. Nevertheless, the few studies found on their use in ozonation processes have reported multi-walled carbon nanotubes (MWCNT) as a very promising material. Actually, a

commercial sample of MWCNT was successfully used in the catalytic ozonation of oxalic acid [17, 67], SMX [61], bezafibrate [62] and atrazine [68]. Similarly to activated carbon, the mechanism involves a combination of bulk and surface reactions.

Most of the mentioned studies use nanocarbon catalysts in the powder form, which is a problem for their practical application in water treatment. A solution to overcome this drawback is to grow these nanomaterials onto a macrostructure. In this way, it is possible to enhance oxidation in catalytic ozonation by facilitating mass transfer across the different phases, and the ease of operation associated to a macrostructure is seen as a very important advantage of this technology. The process eliminates the need for filtration of catalyst particles, while reducing pressure drop when compared to packed bed reactors.

An example of this type of macrostructure catalyst is shown in Figure 7 [69]. It consists of a commercial honeycomb cordierite structure, upon which CNFs were grown after coating the monolith with an alumina wash coat impregnated with nickel, which acts as a catalyst for carbon growth. In this particular case, CNFs were formed under a gas flow of ethane and hydrogen (50:50) at 600 °C.

The utilization of this type of structured catalysts in continuous ozonation experiments has been already applied in the removal of oxalic acid as well as several emerging organic micropollutants (atrazine, bezafibrate, erythromycin, metolachlor and nonylphenol) with very promising results [69-71].



**Figure 7.** Honeycomb monolith covered with CNFs used in the catalytic ozonation of emerging organic pollutants. Reproduced with permission from [69].

**Figura 7.** Monolitos de panel de abeja recubiertos con CNFs usados en la ozonización catalítica de contaminantes orgánicos emergentes. Reproducido con permiso de [69].

#### 4. Conclusions

Intensive research has been carried out on the ozonation of several organic pollutants in the presence of carbon materials. Two catalytic pathways may occur simultaneously: 1) decomposition of  $O_3$  into  $HO\cdot$  or other highly active oxygen-containing radicals on the surface of the carbon materials, with sequent oxidation in the homogeneous phase; and 2) adsorption of the organic compounds on carbon, which then react on the surface with  $O_3$  or oxygenated radicals. Therefore, the surface chemistry of carbon samples plays a key role in the catalytic ozonation of organic pollutants. In general, catalytic ozonation

is favoured by carbons with basic or neutral properties. Recently, the use of carbon nanofibers and nanotubes supported on macrostructures (like monoliths or foams) has been appointed as a very promising system, since it overcomes the problem of mass transfer resistances usually observed in the case of microporous materials.

#### 5. Acknowledgements

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#### 6. References

- [1] Oyama ST. Chemical and catalytic properties of ozone. *Cat Rev* 2000; 42(3):279-322.
- [2] Beltrán FJ. Ozone reaction kinetics for water and wastewater systems. Boca Raton, Florida: Lewis Publishers. 2004.
- [3] Hoigné J. Chemistry of ozone and transformation of pollutants by ozonation and advanced oxidation processes. In: Hubrec J, editor. The handbook of environmental chemistry Vol 5, Part C, Quality and treatment of drinking water II. Weinheim: Wiley-VCH; 1998.
- [4] Buxton GV, Greenstock CL, Helman WP, Ross AB. Critical review of rate constants for the reaction of hydrated electrons, hydrogen atoms and hydroxyl radicals ( $OH/O\cdot^-$ ) in Aqueous Solution. *J Phys Chem Ref Data* 1988; 17(0):513-886.
- [5] Weiss J. Investigations on the radical  $HO_2$  in solution. *Trans Faraday Society* 1935; 31(0):668-81.
- [6] Staehelin J, Hoigné J. Decomposition of ozone in water: Rate of initiation by hydroxide ions and hydrogen peroxide. *Environ Sci Technol* 1982; 16(10):676-81.
- [7] Sotelo JL, Beltran FJ, Benitez FJ, Beltran-Heredia J. Ozone decomposition in water: kinetic study. *Ind Eng Chem Res* 1987; 26(1):39-43.
- [8] von Gunten U. Ozonation of drinking water: Part I. Oxidation kinetics and product formation. *Water Res* 2003; 37(7):1443-67.
- [9] Hoigné J, Bader H. Rate constants of reactions of ozone with organic and inorganic compounds in water - I: Non-dissociating organic compounds. *Water Res* 1983; 17(2):173-83.
- [10] Hoigné J. Inter-calibration of OH radical sources and water quality parameters. *Water Sci Technol* 1997; 35(4):1-8.
- [11] Kasprzyk-Hordern B, Ziólek M, Nawrocki J. Catalytic ozonation and methods of enhancing molecular ozone reactions in water treatment. *Appl Catal B: Environ* 2003; 46(4):639-69.
- [12] Legube B, Karpel Vel Leitner N. Catalytic ozonation: a promising advanced oxidation technology for water treatment. *Catal Today* 1999; 53(1):61-72.
- [13] Beltrán FJ, Rivas FJ, Montero-de-Espinosa R. Catalytic ozonation of oxalic acid in an aqueous  $TiO_2$  slurry reactor. *Appl Catal B: Environ* 2002; 39(3):221-31.
- [14] Lin SH, Lai CL. Kinetic characteristics of textile wastewater ozonation in fluidized and fixed activated carbon beds. *Water Res* 2000; 34(3):763-72.
- [15] Rivera-Utrilla J, Sánchez-Polo M. Ozonation of 1,3,6-naphthalenetrisulphonic acid catalysed by activated carbon in aqueous phase. *Appl Catal B: Environ* 2002; 39(4):319-29.
- [16] Orge CA, Sousa JPS, Gonçalves F, Freire C, Órfão JJM,

- Pereira MFR. Development of novel mesoporous carbon materials for the catalytic ozonation of organic pollutants. *Catal Lett* 2009; 132(1):1-9.
- [17] Liu Z-Q, Ma J, Cui Y-H, Zhang B-P. Effect of ozonation pretreatment on the surface properties and catalytic activity of multi-walled carbon nanotube. *Appl Catal B: Environ* 2009; 92(3-4):301-6.
- [18] Ma J, Sui M, Zhang T, Guan C. Effect of pH on MnOx/GAC catalyzed ozonation for degradation of nitrobenzene. *Water Res* 2005; 39(5):779-86.
- [19] Sánchez-Polo M, Rivera-Utrilla J, von Gunten U. Metal-doped carbon aerogels as catalysts during ozonation processes in aqueous solutions. *Water Res* 2006; 40(18):3375-84.
- [20] Liu Z-Q, Ma J, Cui Y-H. Carbon nanotube supported platinum catalysts for the ozonation of oxalic acid in aqueous solutions. *Carbon* 2008; 46(6):890-7.
- [21] Jans U, Hoigné J. Activated carbon and carbon black catalyzed transformation of aqueous ozone into OH radicals. *Ozone Sci Eng* 1998; 20(1):67-90.
- [22] Faria PCC, Órfão JJM, Pereira MFR. Ozone decomposition in water catalysed by activated carbon: influence of chemical and textural properties. *Ind Eng Chem Res* 2006; 45(8):2715-21.
- [23] Sánchez-Polo M, von Gunten U, Rivera-Utrilla J. Efficiency of activated carbon to transform ozone into OH radicals: Influence of operational parameters. *Water Res* 2005; 39(14):3189-98.
- [24] Álvarez PM, García-Araya JF, Beltrán FJ, Giráldez I, Jaramillo J, Gómez-Serrano V. The influence of various factors on aqueous ozone decomposition by granular activated carbons and the development of a mechanistic approach. *Carbon* 2006; 44(14):3102-12.
- [25] Guiza M, Ouerdeni A, Ratel A. Decomposition of dissolved ozone in the presence of activated carbon: An experimental study. *Ozone Sci Eng* 2004; 26(3):299-307.
- [26] Gurol MD, Singer PC. Kinetics of ozone decomposition: A dynamic approach. *Environ Sci Technol* 1982; 16(7):377-83.
- [27] Rivera-Utrilla J, Sánchez-Polo M. Ozonation of naphthalenesulphonic acid in the aqueous phase in the presence of basic activated carbons. *Langmuir* 2004; 20(21):9217-22.
- [28] Gonçalves AG, Figueiredo JL, Órfão JJM, Pereira MFR. Influence of the surface chemistry of multi-walled carbon nanotubes on their activity as ozonation catalysts. *Carbon* 2010; 48(15):4369-81.
- [29] Beltrán FJ, Rivas FJ, Fernandez LA, Alvarez PM, Montero-de-Espinosa R. Kinetics of catalytic ozonation of oxalic acid in water with activated carbon. *Ind Eng Chem Res* 2002; 41(25):6510-7.
- [30] Faria PCC, Órfão JJM, Pereira MFR. Activated carbon catalytic ozonation of oxamic and oxalic acids. *Appl Catal B: Environ* 2008; 79(3):237-43.
- [31] Beltrán FJ, Acedo B, Rivas FJ, Gimeno O. Pyruvic acid removal from water by the simultaneous action of ozone and activated carbon. *Ozone Sci Eng* 2005; 27(2):159-69.
- [32] Beltrán FJ, García-Araya JF, Giráldez I, Masa FJ. Kinetics of activated carbon promoted ozonation of succinic acid in water. *Ind Eng Chem Res* 2006; 45(9):3015-21.
- [33] Faria PCC, Órfão JJM, Pereira MFR. Ozonation of aniline promoted by activated carbon. *Chemosphere* 2007; 67(4):809-15.
- [34] Sánchez-Polo M, Rivera-Utrilla J. Effect of the ozone-carbon reaction on the catalytic activity of activated carbon during the degradation of 1,3,6-naphthalenetrisulphonic acid with ozone. *Carbon* 2003; 41(2):303-7.
- [35] Rivera-Utrilla J, Sánchez-Polo M. Degradation and removal of naphthalenesulphonic acids by means of adsorption and ozonation catalyzed by activated carbon in water. *Water Resour Res* 2003; 39(9):1-13.
- [36] Faria PCC, Órfão JJM, Pereira MFR. Catalytic ozonation of sulfonated aromatic compounds in the presence of activated carbon. *Appl Catal B: Environ* 2008; 83(1-2):150-9.
- [37] Beltrán FJ, García-Araya JF, Giráldez I. Gallic acid water ozonation using activated carbon. *Appl Catal B: Environ* 2006; 63(3-4):249-59.
- [38] Lin SH, Wang CH. Ozonation of phenolic wastewater in a gas-induced reactor with a fixed granular activated carbon bed. *Ind Eng Chem Res* 2003; 42(8):1648-53.
- [39] Giráldez I, García-Araya JF, Beltrán FJ. Activated carbon promoted ozonation of polyphenol mixtures in water: Comparison with single ozonation. *Ind Eng Chem Res* 2007; 46(24):8241-7.
- [40] Valdés H, Zaror CA. Heterogeneous and homogeneous catalytic ozonation of benzothiazole promoted by activated carbon: Kinetic approach. *Chemosphere* 2006; 65(7):1131-6.
- [41] Soares OSGP, Faria PCC, Orfao JJM, Pereira MFR. Ozonation of textile effluents and dye solutions in the presence of activated carbon under continuous operation. *Sep Sci Technol* 2007; 42(7):1477-92.
- [42] Kawasaki N, Ogata F, Yamaguchi I, Fujii A. Removal of orange II, methylene blue and humic acid by ozone-activated carbon combination (OZAC) treatment. *J Oleo Sci* 2008; 57(7):391-6.
- [43] Faria PCC, Órfão JJM, Pereira MFR. Mineralisation of coloured aqueous solutions by ozonation in the presence of activated carbon. *Water Res* 2005; 39(8):1461-70.
- [44] Gul S, Bahar G, Yildirim OO. Comparison of ozonation and catalytic ozonation processes for the decolourization of reactive red 195 azo dye in aqueous solution. *Asian J Chem* 2010; 22(5):3885-94.
- [45] Gul S, Ozcan O, Erbatur O. Ozonation of CI Reactive Red 194 and CI Reactive Yellow 145 in aqueous solution in the presence of granular activated carbon. *Dyes Pigm* 2007; 75(2):426-31.
- [46] Gul S, Eren O, Kir S, Onal Y. A comparison of different activated carbon performances on catalytic ozonation of a model azo reactive dye. *Water Sci Technol* 2012; 66(1):179-84.
- [47] Faria PCC, Órfão JJM, Pereira MFR. Activated carbon and ceria catalysts applied to the catalytic ozonation of dyes and textile effluents. *Appl Catal B: Environ* 2009; 88(3-4):341-50.
- [48] Arsian-Alaton I, Seremet O. Advanced treatment of biotreated textile industry wastewater with ozone, virgin/ozonated granular activated carbon and their combination. *J Environ Sci Health, Pt A: Toxic/Hazard Subst Environ Eng* 2004; 39(7):1681-94.
- [49] Arslan-Alaton I. Granular activated-carbon assisted ozonation of biotreated dyehouse effluent. *AATCC Review* 2004; 4(5):21-4.
- [50] Alvarez PM, Beltran FJ, Masa FJ, Pocostales JP. A comparison between catalytic ozonation and activated carbon adsorption/ozone-regeneration processes for wastewater treatment. *Appl Catal B: Environ* 2009; 92(3-4):393-400.
- [51] Beltrán FJ, Pocostales P, Alvarez P, Oropesa A. Diclofenac removal from water with ozone and activated carbon. *J Hazard Mater* 2009; 163(2-3):768-76.
- [52] Beltrán FJ, Pocostales P, Alvarez PM, Lopez-Pineiro F. Catalysts to improve the abatement of sulfamethoxazole and the resulting organic carbon in water during ozonation. *Appl Catal B: Environ* 2009; 92(3-4):262-70.
- [53] Pocostales JP, Alvarez PM, Beltran FJ. Kinetic modeling of powdered activated carbon ozonation of sulfamethoxazole in water. *Chem Eng J* 2010; 164(1):70-6.
- [54] Sánchez-Polo M, Rivera-Utrilla J, Prados-Joya G, Ferro-García MA, Bautista-Toledo I. Removal of pharmaceutical compounds, nitroimidazoles, from waters by using the ozone/carbon system. *Water Res* 2008; 42(15):4163-71.



- [55] Rivera-Utrilla J, Sánchez-Polo M, Prados-Joya G, Ferro-García MA, Bautista-Toledo I. Removal of tinidazole from waters by using ozone and activated carbon in dynamic regime. *J Hazard Mater* 2010; 174(1-3):880-6.
- [56] Beltran FJ, Pocostales P, Alvarez P, Aguinaco A. Ozone-activated carbon mineralization of 17 $\alpha$ -ethynylestradiol aqueous solutions. *Ozone Sci Eng* 2009; 31(6):422-7.
- [57] Guzman-Perez CA, Soltan J, Robertson J. Kinetics of catalytic ozonation of atrazine in the presence of activated carbon. *Sep Purif Technol* 2011; 79(1):8-14.
- [58] Figueiredo JL, Pereira MFR. The role of surface chemistry in catalysis with carbons. *Catal Today* 2010; 150(1-2):2-7.
- [59] Sanchez-Polo M, Leyva-Ramos R, Rivera-Utrilla J. Kinetics of 1,3,6-naphthalenetrisulphonic acid ozonation in presence of activated carbon. *Carbon* 2005; 43(5):962-9.
- [60] Sánchez-Polo M, Rivera-Utrilla J. Ozonation of naphthalenetrisulphonic acid in the presence of activated carbons prepared from petroleum coke. *Appl Catal B: Environ* 2006; 67(1-2):113-20.
- [61] Gonçalves AG, Órfão JJM, Pereira MFR. Catalytic ozonation of sulfamethoxazole in the presence of carbon materials: catalytic performance and reaction pathways. *J Hazard Mater* 2012; 239-240(0):167-74.
- [62] Gonçalves A, Órfão JJM, Pereira MFR. Ozonation of bezafibrate promoted by carbon materials. *Appl Catal B: Environ* 2013; 140-141(0):82-91.
- [63] Polaert I, Wilhelm AM, Delmas H. Phenol wastewater treatment by a two-step adsorption-oxidation process on activated carbon. *Chem Eng Sci* 2002; 57(9):1585-90.
- [64] Qu X, Zheng J, Zhang Y. Catalytic ozonation of phenolic wastewater with activated carbon fiber in a fluid bed reactor. *J Colloid Interface Sci* 2007; 309(2):429-34.
- [65] Serp P. Carbon nanotubes and nanofibers in catalysis. In: Serp P, Figueiredo JL, editors. *Carbon materials for catalysis*. New Jersey: John Wiley & Sons, Inc.; Hoboken; 2009.
- [66] Job N, Sabatier F, Pirard J-P, Crine M, Léonard A. Towards the production of carbon xerogel monoliths by optimizing convective drying conditions. *Carbon* 2006; 44(12):2534-42.
- [67] Liu Z-Q, Ma J, Cui Y-H, Zhao L, Zhang B-P. Influence of different heat treatments on the surface properties and catalytic performance of carbon nanotube in ozonation. *Appl Catal B: Environ* 2010; 101(1-2):74-80.
- [68] Fan X, Restivo J, Órfão JJM, Pereira MFR, Lapkin AA. The role of multiwalled carbon nanotubes (MWCNTs) in the catalytic ozonation of atrazine. *Chem Eng J* 2014; 241(0):66-76.
- [69] Restivo J, Órfão JJM, Armenise S, Garcia-Bordejé E, Pereira MFR. Catalytic ozonation of metolachlor under continuous operation using nanocarbon materials grown on a ceramic monolith. *J Hazard Mater* 2012; 239-240(0):249-56.
- [70] Restivo J, Orfao JJM, Pereira MFR, Garcia-Bordeje E, Roche P, Bourdin D, Houssais B, Coste M, Derrouiche S. Catalytic ozonation of organic micropollutants using carbon nanofibers supported on monoliths. *Chem Eng J* 2013; 230(0):115-23.
- [71] Restivo J, Órfão JJM, Pereira MFR, Vanhaecke E, Rönning M, Iouranova T, Kiwi-Minsker L, Armenise S, Garcia-Bordejé E. Catalytic ozonation of oxalic acid using carbon nanofibres on macrostructured supports. *Water Sci Technol* 2012; 65(10):1854-62.