

# Kinetic modeling of the operational variants in a batch Ozonation-Adsorption process

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**Abstract.** In this work, a mathematical model has been proposed as a basis for the study of the combined adsorption-ozonation process (Ad/Ox) with the complexity involved in a three-phase system. The description of this operation involves the consideration of several parameters regarding kinetic and adsorption phenomena of the system. This paper presents the analysis of Ad/Ox process compared with the simple ozonation, checking the favorable effect of the presence of activated carbon (AC) in ozonation, both primary degradation and mineralization of phenol solutions. The study focuses on Ad/Ox with granular activated carbon (GAC), and analyzes the phenol degradation kinetics depending on the amount of AC. In this way it was possible to establish an order of priority in the relevance of the parameters of the proposed mathematical model. It was found that the adsorption constant may vary meaningfully in the same process.

**Keywords:** Adsorption, activated carbon, ozonation, kinetic modeling, phenol.

## 1. Introduction

It is well-known the difficulty that present the degradation of certain organic compounds as the phenol, chosen as model in this work to study the ozonation process, a possible alternative for already several decades. Nevertheless the unstable character of the ozone makes complicated its application in an effective way, as was demonstrated in quite a few recent studies (Chiang *et al.*, 2006; Rivera-Utrilla *et al.*, 2008). This disadvantage leads us to consider the convenience of combining ozonation with catalytic and adsorbent materials as the AC. In early attempts to add active carbon in the ozonation, the benefits was connected to the high adsorption capacity of activated carbon (AC) observed. Subsequent studies (Rivera-Utrilla, J. and Sánchez-Polo, 2002) have shown that AC catalyzes the decomposition of ozone in aqueous phase by accelerating the transformation of this free hydroxyl radicals. Later another authors like Beltran *et al.* (2006) concluded that with these processes the complete mineralization of many pollutants it's possible. These

authors went into detail about the study of systems ozone/AC and showed that the surface chemistry of activated carbon, along with its textural characteristics, plays a very important role in their behavior as promoter of the process of ozone decomposition to hydroxyl radicals.

There are studies of ozonation combined with AC (Lange *et al.*, 2006; Qu *et al.*, 2007) that operate in batch process but generally they do in a sequential way presenting disadvantages in the application. In this work the simultaneous application of adsorption and ozonation is proposed, analyzing the elimination of phenol as model of pollutant (Pratar *et al.*, 2011). ACs application combined with the ozonation occupies a relevant place in recent works for its undoubted advantages on the catalytic heterogeneous ozonation. The increasing development of new activated carbons and the advantages associated with its double function, adsorptive and catalytic, are the principal reasons of the growing employment of this technology (Lei *et al.*, 2007; Álvarez *et al.*, 2011).

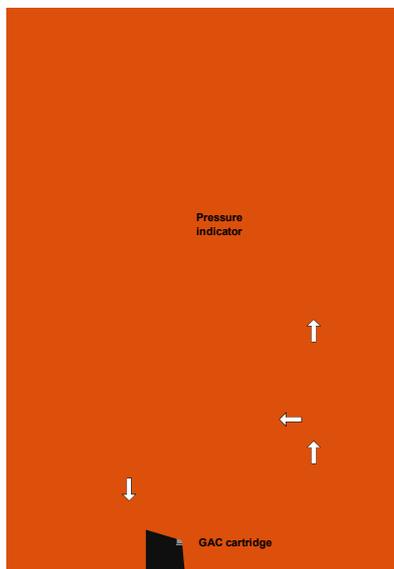
In spite of the findings in this field, it is necessary to go into detail about the combined action of the ozone and activated carbon, to be able to predict and estimate the effects of the process variants and operational on the performances of elimination. This work tries to contribute across a suitable modeling and estimation of the characteristic parameters of the combined system and its influence on the efficiency of the process.

This study analyzes the results obtained when using granular activated carbon (GAC) during the ozonation. In the combination of adsorption and ozonation, two operational modalities have been used: sequential, where the processes acting independently, and the simultaneous (AdOx). The latter proved to be more interesting and will be subject to this study by their better advantages derived by the double function sorption-reactive that occurs on AC surface. It is therefore the objective of this study to assess the extent of the adsorption and reaction in the efficiency of phenol removal, used here as a pollutant model.

## 2. Material and methods

## 2.1. Reaction system

A G-L contactor (cylindrical column of 18 L) was used in the Ad/Ox process (Rodriguez *et al.*, 2016). Ozone gas is introduced into the reactor through a venturi installed in the recirculation stream, thus ensuring a perfect homogenization of the system. The ozone reactor operates in batch with loads of about 10 L of phenol solutions at different concentrations. The different parts of the ozonator are shown in Figure 1.



**Figure 1.** Scheme of the ozonator with essential elements: recirculating system with GAC, O<sub>3</sub> injection and measuring devices.

The operational conditions employed in the experiments were: gas flow  $Q_G=4.0$  L/min (oxygen stream),  $C_A=19.0$  mg/L (ozone concentration in gas),  $C_0=1000$  mg/L (initial phenol concentration), pH=6.5 and  $m_{GAC}=250$  and 500 g (GAC mass for 10 L of phenol solution).

## 2.2. Analytical methods

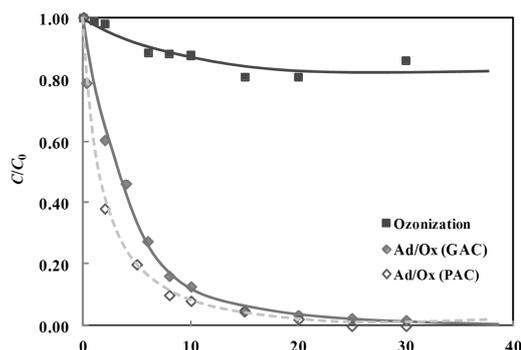
Phenol concentration was analyzed by a high pressure liquid chromatography detector (Waters-2695) coupled with a spectrophotometer UV/Vis (Waters-2487) at 272 nm. Chromatographic separation was performed using a reverse-phase column (Teknokroma-Mediterranea SEA 18) of 1.8  $\mu\text{m}$ , 150 x 4.6 mm and a pre-column. A methanol-buffered water solution at pH=3.0 (40:60) was employed as mobile phase, operating at isocratic flow (1.0 mL/min). Total organic carbon (mgC/L) was analyzed by a TOC analyzer (TOC-V Shimadzu).

## 3. Results and discussion

### 3.1. Comparison of Ad/Ox process versus ozonation

The results obtained through a simple ozonation process were compared, and those obtained through a Ad/Ox process were analyzed and shown in Figure 2. The improvement with the Ad/Ox process in the phenol removal is evident since 100% of removal was achieved. The combination of ozonation and adsorption processes

simultaneously, both with CAP as with GAC, causes a significant increase both in primary degradation kinetics and mineralization degree respect to a simple ozonation.



**Figure 2.** Comparison of phenol removal ( $C_0=1000$  mg/L) by simple ozonation and Ad/Ox process.

Figure 2 shows phenol removal is very important getting a 100% removal in just 30 minutes for a 1000 mg/L phenol concentration and also a good degree of mineralization exceeding 80%. Therefore, the results obtained indicate that the use of GAC in Ad/Ox processes allow best results in the phenol removal and mineralization despite using a lower dose of ozone while the activated carbon kind whether GAC or PAC does not seem important on the oxidation efficiency. The generation of radicals on the AC surface explains the higher speed of reaction in the liquid. After the analysis of the first results about simple ozonation and the different types of Ad-Ox sequential processes, the appropriateness of the simultaneous Ad/Ox process with both GAC and PAC was deduced. Nevertheless, the Ad/Ox with GAC was selected for the rest of the experiments because the handling advantages of the granulated material.

### 3.2. Mathematical model of Ad/Ox process

For the description of the Ad/Ox discontinuous process it was proposed a mathematical model to determine the kinetic constants of adsorption and phenol oxidation. In addition the model allows the calculation of the variation of phenol concentration along the reaction considering the oxidation that takes place not only in the liquid but also on the surface of the activated carbon. The variation of the concentration of phenol keeping all these phenomena in mind follows Eq. 1:

$$\left(\frac{dC}{dt}\right) = \left(\frac{dC}{dt}\right)_{oxL} + \left(\frac{dC}{dt}\right)_{oxS} + \left(\frac{dC}{dt}\right)_{ads} \quad (1)$$

On the other hand the terms due to the reaction in the liquid and solid medium suppose a consumption of ozone that must be corresponded with the flow from the gas phase. From the total flow of ozone transferred to the liquid,  $N_{O_3}$ , a part,  $N_{O_3}^I$ , is consumed through the reaction in the liquid phase and other,  $N_{O_3}^{II}$ , through the reaction on the surface of the GAC. The term of the flow of ozone consumed in the liquid can be expressed as Eq. 2, where  $P_A^*$  is the partial pressure of ozone in equilibrium with the liquid and He, the Henry's constant.

$$N_{O_3}^I = k_C C C_{AL} = k_C C (C_{AL} - 0) = k_C C \left( \frac{P_A^*}{He} \right) \quad (2)$$

being,

$k_C$ : kinetic constant of the reaction between the phenol and the ozone in the liquid (mg/L min)

$C, C_{AL}$ : concentrations of phenol and ozone, respectively (mg/L)

The part of the flow of ozone consumed on the surface of the activated carbon is expressed by:

$$N_{O_3}^{II} = k_{CS} C_{AS} C_S = k_{CS} z_{AS} z_S w^2 \quad (3)$$

$$z_S = q_e = K_F (C^*)^{1/n_F} \quad (4)$$

In Eq. 3,  $k_{CS}$  is the kinetic constant of reaction between the ozone and the phenol on the surface of the activated carbon, (mg/Lmin); and  $z_{AS}$  and  $z_S$  are the ozone concentration on the surface of the activated carbon, and on the surface of the activated carbon respectively in mg/gAC. By means of the parameter  $w$ , GAC mass per volume (g AC/L), is possible to obtain the concentrations  $C_{AS}$  and  $C_S$ .

The minimal diffusion resistance is supposed for phenol with regard to the surface of the activated carbon (Álvarez *et al.*, 2001), considering, therefore, that phenol concentration is the same in the liquid and in the solid phase in equilibrium, following Freundlich's equation:

$$C^* = \left( \frac{z_S}{K_F} \right)^{n_F} \approx C \quad (5)$$

The concentration  $C^*$  is usually very similar to  $C$ , due to high mass transfer coefficients of the liquid film surrounds the particle of activated carbon. This argument is used in a similar way for the ozone through the equilibrium between the liquid and solid, expressed by the  $m$  coefficient:

$$C_A^* = m z_{AS} \cong C_{AL} \quad (6)$$

In Eq. 6,  $C_A^*$  it is the concentration of ozone in the liquid in equilibrium with the concentration of ozone adsorbed on AC surface. In Eqs. 2-3, the kinetic constants are re-defined from the equations that together with the kinetic one of adsorption (Alhamed, 2009) are showed in the following expressions:

$$\left( -\frac{dC}{dt} \right)_{oxL} = z k_C C_{AL} C = k_{oxL} C \quad (7)$$

$$\left( -\frac{dC}{dt} \right)_{oxS} = z k_{CS} z_{AS} z_S w^2 = k_{oxS} q_t \quad (8)$$

$$-\frac{dq_t}{dt} = k_{ads} (q_e - q_t)^2 \quad (9)$$

In the previous equations  $z$  is the effective stoichiometric coefficient of the phenol removed per mole of ozone at the primary degradation reaction. Eq. 7-8 represent kinetics for the liquid and solid respectively, where  $k_{ads}$  is the stoichiometric coefficient of phenol removal per ozone consumed in primary oxidation. Eq. 9 is the adsorption

kinetic in presence of ozone, where  $k_{ads}$  values are different from those obtained without ozone.

When describing the chemical reaction on GAC surface in Eq. 8,  $z_S$ , local in nature, was expressed in terms of  $q_t$  that is the global charge of phenol g phenol/g GAC. In this case, both,  $z_S$  and  $q_t$  have the same meaning same due to the system homogeneity. On the other hand,  $q_t$  is the term used usually in the kinetic for adsorption, while the  $q_t$  and  $q_e$  are obtained experimentally taking into account the global removal of phenol in the liquid. In consequence, Eq. 10 expresses the fall of phenol concentration in a discontinuous Ad/Ox process as the sum of the three previous terms:

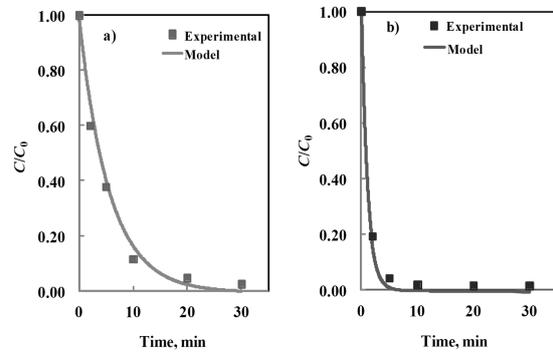
$$-\frac{dC}{dt} = k_{oxL} C + k_{oxS} q_t w + k_{ads} (q_e - q_t)^2 w \quad (10)$$

where  $k_{ads}$  is the kinetic constant by adsorption in units of gGAC/(mg phenol min),  $k_{oxL}$  in the oxidation constant in the liquid, and  $k_{oxS}$  is the oxidation constant on the solid surface, both in units of liquid  $\text{min}^{-1}$ .

### 3.3. Kinetic analysis of Ad/Ox process

Results from the degradation of phenol, both primary degradation and mineralization, were obtained through the measurement of total organic carbon (TOC) in the treated solution. The degradation kinetics was adjusted to the proposed model by solving Eqs. 10 and 5. The solving process of such equations was carried out with the aid of the FlexPDE calculation tool, which is a simulation program that was used here to determine, through the corresponding fitting process, the kinetic constants of adsorption and ozonation and modeled kinetics of phenol concentration and TOC during degradation.

The GAC was assumed perfectly mixed in the reacting volume. In other words, the GAC load, confined inside a cartridge, behaves as it was perfectly distributed in the reactor due to the vigorous agitation of the reaction medium through the recirculation system. Consequently, the kinetic parameters of oxidation and adsorption will be affected by the stirring and mixing conditions in the ozonator through G-L and L-S flows and corresponding mass transfer parameters.



**Figure 3.** Experimental and modeled (fitted with FlexPDE) kinetic profiles of phenol degradation in an Ad/Ox process of 1000 mg/L of phenol: a)  $m_{GAC}=250$  g and b)  $m_{GAC}=500$  g.

Initial conditions or value of the dependent variables involved in differential equations at time zero, time at which begins the Ad/Ox phenol removal process were defined before the calculus process. The concentration at any position within the reactor is  $C=C_0=1000$  mg/L and therefore the load placed on the bed of activated carbon is zero,  $q_t=0$  mg/L, the GAC amount, depending on the experiment was of 250 or 500 g, the volume of 10 L dissolution and the flow and the concentration of ozone was  $Q_G=4.0$  L/min and  $C_A=19$  mg/L, respectively. The program simulates the kinetics of degradation on the basis of the value of the initial variables, varying parameters to calculate:  $k_{ads}$ ,  $k_{oxL}$  and  $k_{oxS}$ , to achieve the best fit to the experimental degradation kinetics.

Kinetics modeling of the experimental degradation was carried out for two different amounts of GAC: 250 and 500 g. In Figure 3, fittings of the experimental data are shown to the kinetic model proposed for the two different GAC quantities loaded in the reaction media. The fitting results was good, presenting a determination coefficient  $R^2=0.99$ . Likewise, Table 2 also shows the values of the kinetic constants of adsorption and oxidation obtained to get the fit of the experimental kinetics for a simultaneous Ad/Ox process.

In Table 2, the analysis of constants obtained in the fitting process reveals that the increase of GAC amount does not affect the constant of oxidation in the solid which is similar in both cases, but contributes to the increase of the oxidation constant in liquid. This apparent constant includes the ozone concentration in the liquid and coefficient  $z$  that depends strongly on the efficiency and concentration of  $OH^\bullet$  (Eq. 7), clearly influenced by the catalytic activity of GAC surface that competes with the adsorptive capacity. An equilibrium balance is essential in the dual role of the GAC to develop a good efficiency of the Ad/OX process (Nunoura *et al.*, 2002).

**Table 2.** Kinetic constants of adsorption and oxidation related to the removal of phenol and mineralization for AdOx. 1000 mg/L of phenol and  $m_{GAC}=250$  and 500 g.

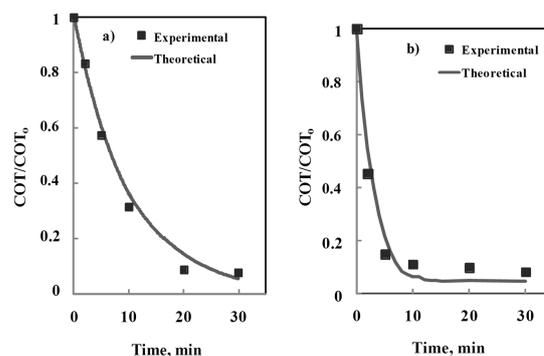
$m_{GAC}$	$m_{GAC}=250$ g	$m_{GAC}=500$ g
$k_{ads} 10^5$	4.0	9.0
$k_{oxL} 10^1$	2.5/1.0	7.0/1.0
$k_{oxS} 10^1$	0.1	0.1
$k_{adsm} 10^5$	4.0	9.0
$k_{oxLm} 10^1$	1.4/0.9	3.0/0.1
$k_{oxSm} 10^1$	0.1	0.1

Units of variables:  $m_{CAG}=g$ ;  $k_{ads}=g$  GAC/(mg fenol min);  $k_{oxL}=\text{min}^{-1}$ ;  $k_{oxS}=(\text{mg/L})/[(\text{mg/g GAC}) \text{min}]$

### 3.4. Kinetic modeling of the mineralization process

The previously mentioned kinetic model was also employed in the analysis of mineralization. TOC values were used in this case as experimental results. Similarly to done with the primary degradation TOC results were fitted to the proposed model with the results shown in Figure 4. Fittings shown in Figures 4 a) and b), correspond to primary degradation and mineralization, which give rise to

values of the correlation coefficient ( $R^2$ ) of 0.95 and 0.99, respectively. Both in the case of in the mineralization as in the primary degradation, the oxidation constant in solid,  $k_{oxS}$ , does not seem affected, it is always the same. On the contrary, the value of the oxidation constant in liquid,  $k_{oxL}$ , becomes half in mineralization of primary degradation value, no doubt because of the more refractory nature of degradation intermediates. Other effect observed in the  $k_{oxL}$  is the continuous declining as the process goes on as a result the progressive occupation of the GAC surface by the phenol and its derivatives.



**Figure 4.** Modeled kinetics after fitting (FlexPDE) to the experimental results of mineralization, for an Ad/Ox process of 1000 mg/L phenol solution with a)  $m_{GAC}=250$  g of and b)  $m_{GAC}=500$  g.

## 4. Conclusions

The combination of adsorption and ozonation or Ad/Ox process, simultaneously with CAP or CAG, produces an improvement of both the kinetics of phenol removal and the mineralization degree with respect to a simple ozonation process, even using low dosages. A favourable effect of the addition of GAC was proven. Improvement in the amount of phenol eliminated is evident with values exceeding the 100% in all analyzed cases. The succession of consecutive cycles, so for mineralization as for primary degradation does not affect the oxidation constant observed in solid,  $k_{oxS}$ , and can be deduced the decisive participation of surface phenomena on mineralization. On the contrary, the value of the oxidation constant in liquid,  $k_{oxL}$ , becomes half during mineralization than for phenol removal, because the more refractory nature of degradation intermediates. Other effect observed is the continuous decreasing of  $k_{oxL}$  as a consequence of the progressive occupation of the GAC surface by the phenol and its derivatives all along the process.

## References

- Chiang Y.P., Liang Y.Y., Chang C.N. and Chao A.C. (2006), Differentiating ozone direct and indirect reactions on decomposition of humic substances. *Chemosphere*, **65(11)**, 2395-2400.
- Rivera-Utrilla J., Sánchez-Polo M., Prados-Joya G., Ferro-García M.A. and Bautista-Toledo I. (2008), Removal of pharmaceutical compounds, nitroimidazoles, from waters by using the ozone/carbon system. *Water Research*, **42(15)**, 4163-4171.
- Rivera-Utrilla J. and Sánchez-Polo M. (2002), Ozonation of 1, 3, 6-naphthalenetrisulphonic acid catalysed by activated carbon

- in aqueous phase. *Applied Catalysis B-Environmental*, **39(4)**, 319-329.
- Beltran F.J., Garcia-Araya J.F., and Giraldez I. (2006), Gallic acid water ozonation using activated carbon. *Applied Catalysis B-Environmental*, **63(3-4)**, 249-259.
- Lange F, Cornelissen S., Kubac D., Sein M., Sonntag J., Hannich C.B., Golloch A., Heipieper H.J., Möder M. and Sonntag C. (2006), Degradation of macrolide antibiotics by ozone: A mechanistic case study with clarithromycin. *Chemosphere*, **65(1)**, 17-23.
- Qu X., Zheng J. and Zhang Y. (2007), Catalytic ozonation of phenolic wastewater with activated carbon fiber in a fluid bed reactor. *Journal of Colloid and Interface Science*, **309(2)**, 429-434.
- Pratar W., Pornsiri T., Swasdisevi T., Tawatchai C. and Wiwut T. (2011), Adsorption and Ozonation kinetic Model for Phenolic Wastewater Treatment. *Chinese Journal of Chemical Engineering*, **19(1)**, 76-82.
- Lei L., Gu L., Zhang X. and Su Y. (2007), Catalytic oxidation of highly concentrated real industrial wastewater by integrated ozone and activated carbon. *Applied Catalysis A-General*, **327**, 287-294.
- Álvarez P.M., Pocostales J.P. and Beltrán F.J. (2011), Granular activated carbón promoted ozonation of a food-processing secondary effluent. *Journal of Hazardous Materials*, **185**, 776-783.
- Alhamed Y.A. (2009), Adsorption kinetics and performance of packed bed adsorber for phenol removal using activated carbon from dates stones. *Journal of Hazardous Materials*, **170(9)**, 763-770.
- Nunoura T., Lee G. H., Matsumura Y. and Yamamoto K. (2002), Modeling of supercritical water oxidation of phenol catalyzed by activated carbon. *Chemical Engineering Science*, **57(15)**, 3061-3071.
- Rodriguez C., Lombraña J.I., De Luis A. and Sanz J. (2016), Oxidizing efficiency analysis of an ozonation process to degrade the dye rhodamine 6G, *Whiley online library*, DOI 10.1002/jctb.5051.