Ozonation of o-cresol in aqueous solutions

F. J. Beltrán*, J. M. Encinar and J. F. García-Araya
Departamento de Ingeniería Química y Energetica, Universidad de Extremadura, 06071 Badajoz, Spain
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Abstract—The o-cresol aqueous solution ozonation of concentrations similar to those encountered in some wastewaters has been studied. The degradation rate of o-cresol is increased with temperature, pH, gas flow rate, agitation speed and ozone partial pressure. For a 10^{-3} M initial concentration of o-cresol a mass rate of 11.7 mg of ozone per minute leads to o-cresol conversions of about 70% in less than 20 min of ozonation, the k_L a of the reactor being between 2.8 and 13.0 h^{-1}. From the variation observed in the o-cresol ozonation yield with time a competitive effect of secondary reactions has been shown. The ozone absorption rate was always higher than 3 times the maximum ozone absorption in organic-free water (value defined as reaction factor). This fact indicates that the reactions involved develop in the proximity of the gas-liquid interface and the kinetic regime is fast.

Key words—ozone, ozonation, ozone absorption, o-cresol, water ozonation

NOMENCLATURE

\[ a \] = specific interfacial area (m^{-1})
\[ [B] \] = o-cresol or phenol concentration (mol·l^{-1})
\[ [B]_0 \] = initial o-cresol or phenol concentration (mol·l^{-1})
\[ D_a \] = o-cresol diffusivity (m^{2}·s^{-1})
\[ D_{O_2} \] = oxygen diffusivity (m^{2}·s^{-1})
\[ D_{O_3} \] = ozone diffusivity (m^{2}·s^{-1})
\[ E \] = experimental reaction factor defined by equation (5)
\[ E_i \] = instantaneous reaction factor defined by equation (6)
\[ k \] = empirical first order pseudokinetic constant (l·mol^{-1}·s^{-1})
\[ k_l \] = liquid side mass transfer coefficient for the o-cresol-ozone system (m·s^{-1})
\[ k_{lO} \] = liquid side mass transfer coefficient for the cuprous cloride-oxygen system (m·s^{-1})
\[ m_c \] = molar flux rate of ozone at the reactor inlet (mol·s^{-1})
\[ m_l \] = molar flux rate of ozone at the reactor outlet (mol·s^{-1})
\[ N \] = agitation speed (rpm)
\[ N_t \] = ozone absorption rate defined by equation (3) (mol·l^{-1}·s^{-1})
\[ N_a \] = actual ozone absorption rate defined by equation (2) (mol·l^{-1}·s^{-1})
\[ [O_3] \] = equilibrium ozone concentration at the gas-aqueous interface (mol·l^{-1})
\[ P_{O_3} \] = ozone partial pressure (Pa)
\[ Q \] = gas flow rate (l·h^{-1})
\[ T \] = temperature (°C)
\[ t \] = absorption time (s)
\[ V \] = reaction volume (liters)
\[ z \] = stoichiometric yield ratio (mol O_3 consumed·mol o-cresol consumed^{-1})
\[ Z \] = total stoichiometric yield ratio (mol O_3 consumed·mol o-cresol consumed^{-1}).

Greek letters

\[ \alpha \] = coefficient defined in equation (7)
\[ \beta \] = coefficient defined in equation (7)
\[ \gamma \] = coefficient defined in equation (7)
\[ \delta \] = coefficient defined in equation (7)
\[ \varphi \] = coefficient defined in equation (8)
\[ \eta \] = o-cresol ozonation yield defined by equation (4)
\[ \omega \] = coefficient defined in equation (8).

INTRODUCTION

o-Cresol, as other phenols, is a common pollutant of wastewaters (Turner, 1989). The presence of the hydroxyl and methyl groups in its molecule activates their ortho and para positions so that an electrophile agent can attack them very quickly. This property allows some oxidant agents such as chlorine or ozone to be used for its degradation.

Chlorine, widely applied in water treatment due to its low cost and disinfectant power, forms organohalogen compounds with phenols (trihalomethanes, chlorophenols, etc.) (Dore et al., 1979) which give the water a bad taste and disagreeable odours. On the other hand, ozone, with a higher oxidant power, does not have these drawbacks when applied to waters containing those organics and hence it appears a more convenient oxidant for these cases (Dore and Legube, 1983).

Literature presents an exhaustive list of works dealing mainly with the ozonation of phenol (Eisenhauer, 1968, 1971; Gould and Weber, 1976; Roth et al., 1982; Singer and Gurol, 1983; Gurol and Singer, 1983; Whitlow and Roth, 1988). These works include reaction pathways, identification of oxidation species, overall water properties such as COD, TOC, kinetic models, total stoichiometric values and so on. In other work, Dore et al. (1978) studied the ozonation of different phenol derivatives containing chlorine, nitro and methyl substituting groups in their molecules. They report values of absorbances of...
phenolic aqueous solutions at different wavelengths and reaction times with the aim of observing the aromaticity evolution with time.

In this paper the ozonation of o-cresol in water has been carried out. The main aims of the work have been, on the one hand, to study the operating variable influence and stoichiometry and on the other hand, given the fact that the process involves gas-liquid reactions, to determine the yields of ozonation, the reaction factor and its evolution with pH and temperature, parameters affecting the kinetic regime of the absorption. Finally, a modified model of Kingsley (Kingsley and Bliss, 1952; Roth et al., 1982), use for a catalytic reactor, has been applied for fitting the experimental results.

EXPERIMENTAL

The experiments were carried out in a 750 cm² cylindrical semicontinuous agitated glass vessel, the gas stream being fed through a 1 mm i.d. tube. The vessel had an inside diameter of 10 cm and contained four submerged baffles and a two flat bladed stirrer (4 cm in dia) for the agitation. Other details can be found elsewhere (Sotelo et al., 1989a). For the ozonations the vessel was always charged with 500 cm³ of a 10⁻³ M buffered o-cresol aqueous solution. For determining the liquid side mass transfer coefficient, k_L, and the specific interfacial area, a, a chemical method based on the oxygen absorption in cuprous chloride aqueous solutions was used (Camacho and Paez, 1983, 1984). The stoichiometric yield factor of the reaction z, was obtained by mixing aqueous o-cresol and ozone solutions of known concentrations. In order to avoid, as much as possible, the interferences of other reactions (i.e. between ozone and subproducts), in all cases, the o-cresol concentration was much higher than that of ozone as a guarantee that the ozone was consumed exclusively by its reaction with o-cresol. This procedure has been applied in a previous work (Sotelo et al., 1989b).

Before starting the experiment, the ozone concentration (produced in a Constrema ozonator fed with oxygen) was measured in the gas stream, iodometrically. Likewise, during the absorption, ozone at the reactor outlet was also determined by the same procedure. In this way, the ozone absorption rate could be evaluated from the difference between the ozone molar flux rates at the reactor inlet and outlet. On the other hand, liquid samples were withdrawn from the reactor at time intervals to analyze the possible interferences of other reactions (i.e. between ozone and subproducts), in all cases, the o-cresol concentration was much higher than that of ozone as a guarantee that the ozone was consumed exclusively by its reaction with o-cresol. This procedure has been applied in a previous work (Sotelo et al., 1989b).

Table 1. Values of k_L and a determined

<table>
<thead>
<tr>
<th>T(°C)</th>
<th>Q0(h⁻¹)</th>
<th>N(rpm)</th>
<th>k_L·10⁶(m⁻¹s⁻¹)</th>
<th>a(m⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
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<td>4.75</td>
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<tr>
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<td>6.50</td>
<td>37.11</td>
</tr>
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<td>300</td>
<td>7.15</td>
<td>38.08</td>
</tr>
<tr>
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<td>4.40</td>
<td>17.91</td>
</tr>
<tr>
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<td>39.30</td>
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<td>20</td>
<td>50</td>
<td>500</td>
<td>8.13</td>
<td>44.50</td>
</tr>
</tbody>
</table>

Determination of k_L and a

These parameters were obtained by the procedure of Camacho and Paez (1983, 1984) which is based on the absorption of oxygen in cuprous chloride aqueous solutions whose kinetics are known. This gas-liquid reaction is of first-order with respect to the oxygen and develops in the fast pseudo-first order kinetic regime. So, the application of Danckwerts surface renewal theory (Danckwerts, 1970) allows the determination of k_L and a. Table 1 shows the values obtained for both parameters at different operating conditions. In all of the cases, k_L was corrected by applying the equation:

\[ k_L = k_0^L \cdot \frac{[D_{O_3}]/[D_0]}{1.5}. \]  (1)

Determination of the stoichiometric yield factor, z

This was conducted by the procedure described previously. Several series of experiments at different pHs (2, 7 and 8.5) were carried out. The average value obtained for z was 2.03 ± 0.10 mol of ozone consumed per mol of o-cresol consumed. This value agrees with the two strongest nucleophilic positions in the o-cresol molecule. The nucleophilic character of these positions (see Fig. 1) is mainly
due to the nature of the hydroxyl group which activates the ortho and para positions promoting the electrophilic aromatic substitution (Morrison and Boyd, 1983) and then a 1,3 dipolar addition of a second ozone molecule which breaks the aromatic ring. This sequence of reactions has been proposed for the case of phenol (Decoret et al., 1984).

Other authors report values of stoichiometry, although these referred to the ozonation of phenol. Thus, Eisenhauer (1978), Gould and Weber (1976) and Roth et al. (1982) found that for the total destruction of phenol, between 4–6 mol of ozone are required to remove 1 mol of phenol. On the other hand, Dore et al. (1978) report that the stoichiometric ratio increases with ozonation time reaching a plateau value of about 6. Finally, Hoigne (1982) indicates that for the ozonation of phenol-like compounds, 3 mol of ozone are needed to consume 1 mol of phenol. These values are higher than those found in this work, however, they do not distinguish between the amount of ozone that self-decomposes, if any, and the amount that reacts with phenol and with the intermediates formed. So, they could be called the total stoichiometric yield factors, $z_t$. In this work, values of $z_t$ can also be obtained from the o-cresol concentration profiles versus time and the molar flux rates of ozone at the reactor outlet (see equation (2) below). Thus, Fig. 2 depicts the total stoichiometric yield factor for the case of o-cresol ozonation as a function of time obtained at different experimental conditions. It can be seen that $z_t$ increases with time up to a stationary value between 4–6, as it occurs with phenol ozonation. By analyzing more carefully the data obtained it was observed that at a given time the higher the conversion reached the higher the corresponding value of $z_t$.

### Table 2. Ranges of application for variables studied

<table>
<thead>
<tr>
<th>Variable</th>
<th>Values applied</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature (°C)</td>
<td>10, 20 and 30</td>
</tr>
<tr>
<td>Agitation speed (rpm)</td>
<td>100, 300 and 500</td>
</tr>
<tr>
<td>Gas flow rate (1·h⁻¹)</td>
<td>10, 30, 50 and 70</td>
</tr>
<tr>
<td>Ozone partial pressure (Pa)</td>
<td>10.3–1064.5*</td>
</tr>
<tr>
<td>pH</td>
<td>2, 7 and 8.5</td>
</tr>
</tbody>
</table>

*Minimum and maximum values applied.

### Influence of variables

The ozone partial pressure applied was always within the range indicated in Table 2. This table also presents all the values taken for the rest of variables studied.

Experimental results allowed us to observe that the variables studied have a positive effect on the o-cresol degradation. As an example, Figs 3 and 4 show the disappearance curves of o-cresol versus time corresponding to experiments developed at different ozone partial pressures and pH, the rest of the variables being kept constant. On the other hand, Table 3 indicates the o-cresol conversion reached for different operating variables. These results seem to indicate that ozone absorption is controlled jointly by mass transfer and chemical reaction because of the positive effect of fluidodynamic (agitation speed, gas flow rate) and chemical reaction variables (temperature, pH) on o-cresol degradation rate and hence on the ozone absorption rate, as indicated later.

Work similar to that presented in this paper was carried out by Singer and Gurol (1983) on the ozonation of phenol. By comparing the conversions of phenol and o-cresol reached by both works it is observed that phenol is consumed faster than o-cresol. From kinetic data reported by Hoigne and Bader (1983) it is known that o-cresol reacts with ozone faster than phenol does (thus, at pH 2 and 22°C the kinetic constants for phenol and o-cresol ozone direct reactions are $10^3$ and $12 \times 10^3$ M⁻¹·s⁻¹, respectively.)
respectively). According to this, it should be expected that the o-cresol conversions obtained, herein at least, are a little higher than those of phenol reported by Singer and Gurol (1983). These discrepancies could be explained if it is admitted that mass transfer of ozone into the water notably affects the ozonation of these phenols and hence the ozone absorption rate and the degradation rate of o-cresol, in our case, depends strongly on the fluidodynamic parameters \( k_L \) and \( a \). Thus, values of \( k_La \) for the work of Singer and Gurol ranged from 43 to 75 h\(^{-1}\) while those of this research ranged from 2.8 to 13.0 h\(^{-1}\). These different values of \( k_La \) can account for the conversion results obtained from both works. In addition, it has indicated that the ozone partial pressures applied by Singer and Gurol were between 1600 and 5030 Pa and the ozonation of o-cresol was carried out with ozone partial pressures lower than 1100 Pa.

**Ozonation yield**

Absorption of ozone in aqueous o-cresol solutions was followed for 30 min during which dissolved ozone was never detected. This fact suggests that the absorption can be fast or instantaneous according to the film theory (Danckwerts, 1970). Since temperature and pH notably influence the o-cresol degradation rate, it can be assumed that the kinetic regime is fast so that ozone absorption depends both on mass transfer and chemical reaction. On the other hand, although ozone is mainly consumed in its reaction with o-cresol it also reacts with the secondary products, mainly non-saturated dicarboxylic acids, resulting from the aromatic ring opening (Decoret et al., 1984). This competitive set of reactions is corroborated after determining the ozone absorption rate by means of the equation given below:

\[
N_i = \frac{m_o - m_e}{V}
\]  

where \( m_e \) and \( m_o \) being the molar flux rates of ozone at the reactor inlet and outlet, respectively, and \( V \) the reaction volume at time \( t \). Hence, \( N_i \), represents the total rate consumed by all the reactions developed in the water. In addition, the amount of ozone exclusively consumed by o-cresol can be determined from the following equation:

\[
N_i = -z \frac{d[B]}{dt}
\]  

where \([B]\) represents the o-cresol concentration at time \( t \).

From equations (2) and (3) the o-cresol ozonation yield \( \eta \), defined as the percentage of absorbed ozone which is consumed in the destruction of o-cresol can be determined:

\[
\eta = \frac{N_i}{N_r} \times 100.
\]

This parameter is highly significant and can be of great use for economic reasons because it would allow the knowledge of the ozone dosage necessary for the degradation yield of a given pollutant present in the water. For determining \( \eta \) it was necessary to calculate \( N_r \) and \( N_i \) from equations (2) and (3). In so doing, a polynomial regression analysis of o-cresol concentration–time data was made, which gave us the o-cresol disappearance rates at different times. Figures 5 and 6 show the variation of \( N_r \), \( N_i \) and o-cresol ozonation yield with absorption time for experiments carried out at different ozone partial pressures.

In order to avoid experimental errors as much as possible the unreacted ozone mass at the reactor outlet was determined for 5 min periods and then equation (2) was applied. Assuming that for the very first few seconds of the absorption ozone is only consumed by o-cresol, it can be accepted that at \( t = 0 \) both ozone absorption rates \( N_i \) and \( N_r \) are the same. Next, as long as absorption time increases it has been observed that \( N_i \) goes through a maximum (dotted line of curves in Fig. 5) due to the ozone consumption by o-cresol and first intermediate products and then decreases to become closer to \( N_r \). On the other hand, from Fig. 5 it is also observed that \( N_i \) is continuously decreasing with time. Regarding the effect of ozone partial pressure, it can be said that the higher the value of this variable the higher the time in which the

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**Table 3. o-Cresol conversion values reached**

<table>
<thead>
<tr>
<th>( T (\degree C) )</th>
<th>( Q (\text{l.h}^{-1}) )</th>
<th>( N ) (rpm)</th>
<th>( t = 600 \text{s} )</th>
<th>( t = 1200 \text{s} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>50</td>
<td>300</td>
<td>30</td>
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</tr>
<tr>
<td>20</td>
<td>50</td>
<td>500</td>
<td>32</td>
<td>64</td>
</tr>
</tbody>
</table>

*pH = 7; \( P_{O_2} = 357.3 \text{ Pa}; \) tSD 6.6; tSD 10.8.

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Fig. 4. pH influence on o-cresol ozonation. \( T, 20\degree C; P_{O_2}, 362.8 \text{ Pa}; \) \( Q, 50 \text{l.h}^{-1}; N, 300 \text{ rpm} \).
maximum total ozone absorption rate is reached. This is also in accordance with the presence of reactive intermediates which logically are very quickly consumed when the amount of ozone fed to the reactor is high.

As for the ozonation yield of o-cresol, its evolution with time (see Fig. 6) decreases within the first few minutes of the process to a minimum and then increases. As expected, the influence of ozone partial pressure on the o-cresol ozonation yield seems to be negative because the increase of this variable triggers the formation of intermediate products which consume ozone. Although the application of high ozone partial pressures leads to important ozone absorption rates, the ozonation yield of the priority organic, o-cresol in this case, diminishes as mentioned above. So, from these results it can be deduced that there exists an optimum value of the ozone partial pressure. Above this value the concentration of intermediate products is very high and the o-cresol ozonation yield diminishes (i.e. in Fig. 6, $\eta$ at $P_{O_3} = 577$ Pa). On the other hand, below the optimum ozone partial pressure value the ozone absorption and the specific o-cresol degradation rates decrease (i.e. in Fig. 3, $B$ at $145$ Pa or in Fig. 5, $N_t$ or $N_i$ at $51$ Pa).

**Reaction factor**

Another important feature of the ozonation is the knowledge of the kinetic regime of the absorption. In this case, it is necessary to know the reaction factor defined as the ratio between the actual and maximum physical absorption rates (Charpentier, 1981):

$$E = \frac{N_t}{k_L a [O_3]}$$

Figures 7 and 8 show the variation of $E$ with temperature and pH at different reaction times. With respect to the absorption time, it can be observed that the reaction factor first increases with the increase of time due to several competitive and ozone-consuming reactions taking place during the first few minutes, then the reaction factor decreases. The less reactive products that probably appear at elevated times can explain this situation because at these conditions the kinetic regime will become diffusional (Astarita, 1967) and the process will be controlled exclusively by mass transfer. This also justifies that $N_t$ and $N_i$ are similar at high absorption times because the process will not be dependent on chemical reaction rates.

From Figs 7 and 8 it can be seen that the reaction factor is always higher than 3 which corroborates that the ozone absorption kinetic regime is fast (Charpentier, 1981) and the reactions involved develop in the proximity of the gas–aqueous interface. It is also observed that $E$ increases strongly with the increase of temperature and pH for ranges of 10–20°C and 2–7, respectively, and then slightly with
pH while it remains practically constant with temperature. The increase of $E$ with pH can be due to either the action of hydroxyl radicals coming from the ozone decomposition (Staehelin and Hoigne, 1985) or to the presence of the dissociated form of o-cresol which reacts with electrophilic agents, such as ozone, faster than its non-dissociated form (Hoigne and Bader, 1983). The radical way can be promoted by the presence of organic intermediates which can accelerate the ozone decomposition in radicals (Staehelin and Hoigne, 1985), although the fact that the o-cresol–ozone stoichiometric yield ratio is kept constant with pH seems to indicate that the radical contribution to the o-cresol disappearance rate is negligible. This is also corroborated by the fact that the kinetic constant of the o-cresolate ion–ozone reaction is much higher than that of the o-cresol–ozone reaction, even at pH 7 and 8.5 for which the o-cresol degree of dissociation is still low [the kinetic constant of the reaction of ozone with a phenol-type compound increases by a factor of ten per unit of pH according to Hoigne and Bader (1983)]. In summary, for the range of pH studied whichever way o-cresol is consumed, the reaction seems to proceed in the liquid film. The reaction factors obtained (see Figs 7 and 8 and Table 4) confirm this statement. Regarding the temperature effect, the constancy observed in the reaction factor when the temperature is higher than 20°C can be interpreted, at first sight, as if the total ozone absorption rate would be independent of the chemical reaction and if so, the reaction, proceeding within the liquid film, would be instantaneous (Danckwerts, 1970). However in these conditions there can be two opposite effects: an increase in temperature yields on one side an increase of the chemical reaction rate and on the other side a decrease of the Henry coefficient of ozone defined as $[O_3^*] = H_3PO_4$, and hence of the ozone concentration at the gas–aqueous interface. Therefore, for the same ozone partial pressure, the reaction factor can even diminish with the increase of temperature. This explanation can be applied to the slight increase observed in the reaction factor when pH increases above 7 because the ozone concentration at the gas–liquid interface also decreases with the pH (Sotelo et al., 1989a). Furthermore, according to the film theory (Charpentier, 1981) if the reaction is instantaneous, the reaction factor determined experimentally should equal that obtained theoretically from this theory, given by the following equation:

$$E_i = 1 + \frac{zDB}{D_0[O_3^*]}.$$  

Table 4 shows a list of values of $E$ and $E_i$ deduced from equations (5) and (6) for different experimental conditions and at $t = 0$ [because at the start of the ozonation only the o-cresol–ozone second order irreversible reaction would develop and equation (6) can then be applied]. As can be seen from Table 4 in any case the experimental reaction factor $E$ is between 2 and $E_i$. This means that the reaction takes place in a zone in the film region near the gas–liquid interface and hence the kinetic regime is fast (Charpentier, 1981).

**Empirical kinetic model**

The results obtained in this work indicate that the o-cresol ozonation is a simultaneous mass transfer–reaction kinetic process which involves competitive reactions, and this results in it being very difficult to find a model which incorporates both mass transfer parameters and chemical rate constants. In this sense, empirical models provide a useful method for relating these parameters to the kinetic absorption of ozone. Eisenhauer (1968) and Gould and Weber (1976) found that the total decomposition of phenol in a gaseous ozone reactor can be correlated by a first order kinetic expression whose constant involves the ozone concentration in the gas fed to the reactor, the reaction volume and the gas flow rate. Later, Roth et al. (1982) found that a modified Kingsley's model

![Fig. 8. Reaction factor evolution with pH. T: 20°C; $P_{0_3}$: 357.7 Pa; $Q$: 501·h$^{-1}$; $N$: 300 rpm.](image)
corresponds to a gas absorption accompanied by fast irreversible reactions in the water. The presence of the hydroxyl and methyl groups in the aromatic ring strongly enhances the ozone absorption rate so that the reaction factor can reach values of 20 during the first few minutes of ozonation. On the other hand, for an initial o-cresol concentration of $10^{-3}$ M during the first 20 min of ozonation, 11.7 mg of ozone per min permit us to obtain conversions of 70%, the $k_a$ being $8.7 \text{ h}^{-1}$ in spite of the competitive effect of secondary products which also consume ozone. It was proved that an empirical model, based on the work of Kingsley and Bliss (1952) and first used by Roth et al. (1982) and Whitlow and Roth (1988) for the ozonation of phenol and other organics, adequately fits the kinetic data obtained in this work.

In this equation the contribution of the initial concentration of o-cresol has been eliminated because this variable was not changed in this work. The experimental data (thirty experiments) were found to fit first order kinetic equation with correlation coefficients higher than 0.96. A multilinear regression analysis was then performed in order to find the coefficients of equation (8). Table 5 indicates the results obtained along with those found from other works related to the ozonation of phenol which used equation (7).

CONCLUSIONS

From the results obtained in this work it can be finally concluded that the ozone–o-cresol reaction corresponds to a gas absorption accompanied by fast irreversible reactions in the water. The presence of the hydroxyl and methyl groups in the aromatic ring

**Table 5. Comparison of the regression results from experimental data**

<table>
<thead>
<tr>
<th>Work</th>
<th>$\alpha$</th>
<th>$\beta$</th>
<th>$\gamma$</th>
<th>$\delta$</th>
<th>$\omega$</th>
<th>$\psi$</th>
<th>$R^+$</th>
<th>No. points</th>
</tr>
</thead>
<tbody>
<tr>
<td>Eisenhauer (1968)$^*$</td>
<td>0.088</td>
<td>0.829</td>
<td>—</td>
<td>-1.004</td>
<td>—</td>
<td>—</td>
<td>0.966</td>
<td>13</td>
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<tr>
<td>Gould and Weber (1976)$^+$</td>
<td>0.593</td>
<td>0.724</td>
<td>0.068</td>
<td>-0.783</td>
<td>—</td>
<td>—</td>
<td>0.832</td>
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<tr>
<td>Roth et al. (1982)$^+$</td>
<td>0.885</td>
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<td>—</td>
<td>—</td>
<td>0.860</td>
<td>79</td>
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<tr>
<td>This work$^*$</td>
<td>0.180</td>
<td>0.864</td>
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<td>—</td>
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<td>0.152</td>
<td>0.958</td>
<td>30</td>
</tr>
</tbody>
</table>

$^*$Correlation coefficient. $^+$Ozonation of phenol with equation (7). $^\ddagger$Ozonation of o-cresol with equation (8).

(Kingsley and Bliss, 1952) better described the ozonation of phenol and other organics (Whitlow and Roth, 1988). The empirical model is represented too by another first order kinetic equation of the following form:

$$\frac{d[B]}{dt} = k \cdot [B] = \alpha \cdot (m_e/V) \cdot [OH^-] \cdot [B]^\beta. \quad (7)$$

Equation (7), in this work, has been modified some with the aim of accounting for the temperature and agitation speed effects. So the following equation was used for the constant $k$:

$$k = \alpha \cdot (m_e/V) \cdot [OH^-] \cdot \exp(\omega/T) \cdot N^\psi. \quad (8)$$

In this equation the contribution of the initial concentration of o-cresol has been eliminated because this variable was not changed in this work. The empirical model (thirty experiments) were found to fit first order kinetics with correlation coefficients higher than 0.96. A multilinear regression analysis was then performed in order to find the coefficients of equation (8). Table 5 indicates the results obtained along with those found from other works related to the ozonation of phenol which used equation (7).

From Table 5 it can be observed that the influence of gas flow rate and ozone partial pressure (coefficient $\beta$) is similar for the ozonation of both the phenols compared. The coefficient $\gamma$ (effect of pH) is, however, higher in the ozonation of o-cresol. According to Hoigne and Bader (1983), due to the presence of the methyl group o-cresol reacts with ozone at pH 2 approx. 12 times faster than phenol does. Since the ozonation rate of phenols increases with pH it can be expected that the o-cresolate ion reacts with ozone even faster than the phenolate ion, accounting for the values of $\gamma$ obtained. Finally, the values of the coefficients $\omega$ and $\psi$ clearly indicate the important effects of temperature and agitation speed on the degradation rate of o-cresol.

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REFERENCES


