Reaction Mechanism of the Photocatalytic Degradation of Phenol and 4-Chlorophenol with Ozone

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Introduction
Phenol (ph) and chlorophenols (4clph) represent an important class of environmental water pollutants. These organic compounds have been considered on the EPA’s priority pollutants list since 1976 [1]. Therefore, they must be completely mineralized by an advanced oxidation processes (AOPs). It has widely reported that phenol and chlorophenols can be degraded by photocatalytic processes using TiO$_2$ as catalysts and oxygen as electron acceptor [2]. The photocatalytic degradation of 4-chlorophenol can be described by three parallel reaction pathways resulting in stable intermediates including hydroquinone, benzoquinone and 4-chlorocatechol that are decomposed to water and CO$_2$ [3]. Phenol also undergoes complete mineralization by a reaction mechanism that also includes hydroquinone, catechol, 1,2,4-benzenetriol and benzoquinone as intermediate reaction products. Since the photocatalytic process can be improved with the use of ozone, the photocatalytic degradation of phenol and 4-chlorophenol with TiO$_2$, oxygen and ozone has been studied in our laboratories.

Materials and Methods
Phenol, 4-chlorophenol, catechol, 1,2,4-benzenetriol, hydroquinone and benzoquinone were purchased from Aldrich. Several organic and inorganic acids and salts used in the product studies were purchased from J. T. Baker. Spectroscopic and chromatographic grade solvents were purchased from Mallinckrodt. Titanium dioxide, used in the product studies were purchased from J. T. Baker. Spec.

Results and Discussion
The experimental results confirm that the photocatalytic degradation of phenol and 4-chlorophenol (250 mL of a 100 ppm solution and 2gL$^{-1}$ of catalyst) indicated that the reaction mechanism of the parent organic compound depends on the gas bubbled through the system. In the presence of oxygen, benzoquinone and hydroquinone are the main intermediate organic products. In the presence of ozone, catechol and 1,2,4-benzenetriol are easily formed due to the presence of an extra amount of HO$^*$ radicals. Kinetic rate constants of the pseudo first order kinetic model [4] for the photocatalytic degradation of phenol indicate that the initial reaction rates are increased 10 times fold when oxygen is substituted by ozone. Whereas the mineralization reaction, which is described by a zero order kinetic model, increased three times fold when ozone is injected to the reaction system. In the case of 4-chlorophenol, the reaction rate constants increase 5 and three times fold when ozone is bubbled to the system instead of oxygen.

<table>
<thead>
<tr>
<th>gas</th>
<th>Phenol degradation rate constant</th>
<th>Phenol mineralization rate constant</th>
<th>4-chlorophenol degradation rate constant</th>
<th>4-chlorophenol mineralization rate constant</th>
</tr>
</thead>
<tbody>
<tr>
<td>oxygen</td>
<td>$k_d$ (min$^{-1}$)</td>
<td>$k_m$ (ppm min$^{-1}$)</td>
<td>$k_a$ (min$^{-1}$)</td>
<td>$k_m$ (ppm min$^{-1}$)</td>
</tr>
<tr>
<td>ozone</td>
<td>0.0087</td>
<td>0.1813</td>
<td>0.0112</td>
<td>0.2261</td>
</tr>
</tbody>
</table>

The numerical analysis of all the experimental data are being carried out in order to obtain all the kinetic parameters of the LH-HW kinetic model for the photocatalytic degradation of phenol, 4-chlorophenol and their intermediate organic reaction products.

Acknowledgments
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References
4. Moctezuma, E., Gonzalez, R., Zamarripa, H., Palestino, G., Oros, accepted for publication, J. Environ. Managment, manuscript SF94002