

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

Edgar Moctezuma*, Brenda Zermeño, Raúl González, Manuel Salaiques
Universidad Autónoma de San Luis Potosí,
Av. Manuel Nava # 6, San Luis Potosí, S.L.P.,
52-444-8262440 ext. 535, MEXICO 78290
*edgar@uaslp.mx

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 TiO₂ 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 CO₂ [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 TiO₂, 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, Degussa P25, a known mixture of 80% anatase and 20% rutile with a 30 nm average particle size, a non-porous material with a 50.10 m²/g reactive area was used as received.

Photocatalytic degradation experiments were carried out in a reactor system already described in previous publications [4, 5]. This unit is configured with a Pyrex glass tube reactor irradiated with four UV light lamps (Cole-Parmer E-09815-55, $\lambda_{\max} = 365$ nm). For each set of experiments, 250 mL of a **ph** or **4clph** standard solution were placed inside the glass reactor and slurried with 0.2 g of TiO₂. A pure oxygen or ozone was bubbled through the system at a constant rate of 100 mL/min. For the determination of **ph**, **4clph** and intermediate organic compounds, the samples were analyzed by high performance liquid chromatography (HPLC) in a 600E Waters instrument equipped with a UV Waters 486 detector. A Nova Pack Phenyl column was used for separation. The mobile phase was a mixture of EDTA water solution and methanol (60/40) that was delivered at a rate of 1.5 mL/min. The wavelength of detection was set at 276 nm.

Results and Discussion

The experimental results confirm that the photocatalytic degradation of **ph** and **4clph** can be described by a series-parallel reaction scheme. The experimental results also

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 1. Reaction rate constants for the photocatalytic degradation and mineralization of phenol and 4-chlorophenol (250 mL of a 100 ppm solution and 2g/L⁻¹ of catalyst)

gas	Phenol degradation rate constant	Phenol mineralization rate constant	4-chlorophenol degradation rate constant	4-chlorophenol mineralization rate constant
	k_d (min ⁻¹)	k_m (ppm min ⁻¹)	k_d (min ⁻¹)	k_m (ppm min ⁻¹)
oxygen	0.0087	0.1813	0.0112	0.2261
ozone	0.0674	0.5775	0.0583	0.5612

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

The financial support of Fundación PRODUCE and the Universidad Autónoma de San Luis Potosí through the research C04-FAI-10-17.60 is kindly appreciated. The catalyst (Degussa P25) was donated by the Degussa Corporation.

References

- Leyva, E., Moctezuma, E., Ruiz, M.G., Torres-Martinez, L.M., *Catal. Today* 40, 4, 1998, 367-376
- De Lasa, H., Serrano, B., Salaiques, M., *Photocatalytic reaction engineering*, Springer, 2005
- Li, X., Cubbage, J., Troy, A., Jenks, W., *J. Org. Chem.*, 64, 1999, 8509-8524
- Moctezuma, E., Gonzalez, R., Zamarripa, H., Palestino, G., Oros, accepted for publication, *J. Environ. Management*, manuscript SF94002
- Moctezuma, E., Leyva, E., Zamarripa, H., *Rev. Intern. Contam. Amb.*, 19, 3, 115-123, 2003