

Profile of Aromatic Intermediates of Titanium Dioxide Mediated Degradation of Phenol

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Photocatalysis is green technology for the degradation of recalcitrant organic compounds in water, and have found success in the removal of several water pollutants. Degradation of pollutants is often accompanied by their conversion into other compounds some of which are sometimes feared to be more environmentally harmful than the parent compound. This study profiles aromatic intermediates formed during photocatalytic degradation of phenol in a batch system. Catechol, hydroquinone and resorcinol were identified as the major aromatic degradation intermediates. Maximum concentrations of intermediates obtained is in the order catechol>resorcinol>hydroquinone with all three produced within the first two minutes of phenol degradation. Resorcinol attained steady state concentration of 3.73 mg/L after 2 minutes of phenol photocatalysis with no appreciable change in its concentrations until all phenol is degraded suggesting that production of resorcinol proceeds at approximately the same rate as its removal from solution. Catechol formed rapidly attaining maximum concentration of 7.00 – 7.11 mg/L; after 6 minutes at a rate of 0.764 – 0.868 mg/L/min; decreasing thereafter at rates of 0.241 – 0.348 mg/L/min. Maximum concentration of 0.96 – 1.66 mg/L; of hydroquinone was obtained then decreases steadily until all phenol is degraded. Complete mineralisation of phenol and intermediates was achieved under optimum reaction conditions.

1. Introduction

Technologies for the effective treatment of organic pollutants in water are a major focus for the potable water industry. The advanced oxidation processes especially semiconductor photocatalysis have been the focus of intense study. Photocatalysis is a green technology with the potential to mineralise organic pollutants in water and air.

Phenol and derivatives of phenol are amongst the most common organic water pollutants, because of their wide range of applications and high production volumes. Phenol is an aromatic alcohol with an acidic proton, it is soluble in water, highly mobile in surface and ground waters and widely disposed from agricultural and industrial sources (Barakat et al, 2005). Due to a wide variety of uses of phenolic compounds, their incidence in source waters is very common especially in areas near human settlements. Occurrence of phenolic and aliphatic compounds in natural water is also caused by partial degradation of natural organic materials (NOMs) such as humic acid and fulvic acid. These organic pollutants in water readily form halogenated products such as chlorophenols (CPs), haloacetic acids (HAAs) and trihalomethanes (THMs) during chlorination of the water (Johnstone, 2009).

Phenol is toxic even at low concentrations, and its presence in natural waters can lead to the formation of substituted compounds during disinfection and oxidation processes (Busca et al., 2008). Even at low concentrations, these organic pollutants are a major health risk due to their very high endocrine disrupting potency and genotoxicity (Ahmed et al, 2010). Globally, annual production rate of phenol is estimated at 6 million ton.

Effective utilization of reactive species generated in-situ by photonic excitation of solid catalyst particles for the degradation of primary organic pollutants in water has been demonstrated as an effective technology for the treatment of a variety of organic pollutants in water. Degradation of organic compounds in water is often accompanied by the formation of several intermediate compounds, some of which are feared to be

more toxic than the original pollutant been treated. Effective treatment is expected to mineralise the primary pollutant and intermediate products formed during the treatment process, or reduce the pollutant/intermediates to environmentally insignificant concentrations. Profiling the intermediates produced in the course of the degradation of pollutants in water would provide valuable information on the degradative pathways and the degradability of the intermediates formed.

Although data on photocatalytic degradation of phenol are commonly available in literature (Laoufi et al, 2008) very few of studies have reported results on the degradation pathway analysis and occurrence of potentially harmful intermediates formed during the photocatalytic degradation process. In this study we present results on formation/degradation profile of intermediates that indicate the mode of fragmentation of the cyclic compounds in water. This will contribute to a better understanding of the degradation process of the studied compound. The results will form a framework for understanding degradation pathways in similar and more complex organic pollutants.

2. Materials and Methods

2.1 Chemical and reagents

Phenol as an analytical standard (Fluka 99.7 %) was purchased from Sigma-Aldrich (Sigma-Aldrich Pty Ltd, Johannesburg, South Africa). HPLC grade acetonitrile super gradient HiPerSolv CHROMANORM (99.9 % purity), phenol reagent, and tertiary butanol reagent were purchased from Merck (Johannesburg, South Africa). Anatase titanium dioxide (TiO₂) was purchased from Sigma-Aldrich (Sigma-Aldrich Pty Ltd). All solutions were prepared using ultrapure water produced in a Milli-Q, Millipore Direct Q3 Unit (supplied by Microsep, Johannesburg, South Africa).

2.2 Degradation studies

Degradation studies were conducted in a batch reactor with photons for catalyst activation supplied by a medium pressure 400 W UV lamp immersed in the pollutant solution housed in a double jacket quartz sleeve, which served as the cooling system for the lamp. Temperature control in the reactor was achieved by circulating cold water through the outer cavity of the quartz sleeve. The reactor contents in all batches were aerated through a perforated quartz disc at a flow rate of 10 mL/min. Thorough mixing of the contents of the reactor was achieved by continuously agitation with a magnetic stirrer. The initial experimental reaction time was set at 60 min.

Photocatalytic and photolytic degradation of phenol were conducted in batch systems with 1 L solutions of phenol (30 mg/L) in ultrapure water with varying TiO₂ concentration. Catalyst concentration was varied from 30-100 mg/L (TiO₂) (Sigma-Aldrich Pty Ltd) were irradiated with a medium pressure 400W UV lamp (Philips, Netherlands, supplied by Technilamps, South Africa). UV radiation intensity in reactors was measured with Goldilux UV Smartmeters, Model GRP-1 (USA, supplied by MIT, South Africa) and calibrated by the National Metrology Institute of South Africa (NMISA).

2.3 Analysis

Concentration of the phenols and the aromatic intermediates of phenol degradation were monitored on a Waters HPLC (Waters 2695 separation module with a photo diode array – Waters 2998 PDA detector. Phenol and the intermediate compounds were separated on Synergi Fusion-RP C18 (150 x 4.6 mm, 4 µm) column (Phenomenex) and Empower software for data analysis. A binary mobile phase consisting of 1% acetic acid in water (A) and 1 % acetic acid in acetonitrile (B) was used for elution of compounds at a flow rate of 1.2 mL/min at 25 °C, injection volume was 20µL with B operated in the gradient mode (gradient: B 70 % at 0 min, to 100 % at 20 min). Concentration of phenol, hydroquinone, catechol, resorcinol and benzoquinone was determined from calibration curves of standards of each compound.

3. Results and discussion

3.1 Aromatic intermediates of phenol degradation

Phenol has an electron rich aromatic ring which is susceptible to both electrophilic aromatic substitution and to oxidation reactions. Phenol oxidation is believed to produce several aromatic intermediates such as quinones (benzoquinone) (McMurry, 2012), hydroxylated phenols, notably catechol (benzene-1,2-diol), hydroxyquinone (1,4-Dihydroxybenzene) (Sobczyński et al, 2004) and resorcinol (benzene-1,3-diol); and some acyclic compounds including oxalic acid, formic acid, maleic acid, glyoxalic acid and fumaric acid. Alapi and Dombi (2006) reported obtaining 1,2-Dihydroxybenzene and 1,4-Dihydroxybenzene during UV and UV/VUV photolysis of phenol. Sobczyński et al. (2004) identified resorcinol in solution during photocatalysis of phenol in non-quantifiable amounts.

Aromatic intermediates identified in solution during the course of photocatalysis of the phenol include catechol, hydroxyquinone and resorcinol whose structures are presented in Figure 1.

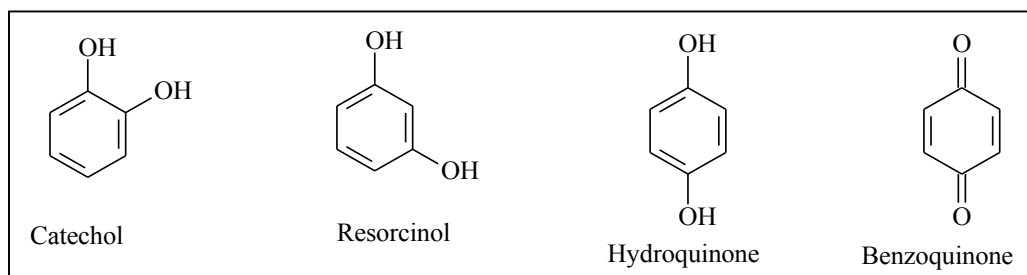


Figure 1: Structures of catechol, resorcinol, hydroquinone and benzoquinone

Trace amounts of benzoquinone was transiently observed in a few of the systems studied. Quantitative HPLC analysis of concentrations of aromatic intermediates revealed that all three aromatic intermediates are produced within the first two minutes of treatment. Maximum concentrations of intermediates obtained is in the order catechol>resorcinol>hydroquinone (Figure 2). Formation rates were calculated as the rates at which the maximum concentrations were obtained and the degradation rates of intermediates were calculated as the rate of disappearance of the intermediate from the maximum concentrations obtained. All aromatic intermediates formed during the course of phenol degradation were in turn completely degraded in solution as indicated by their degradation profiles in Figure 2.

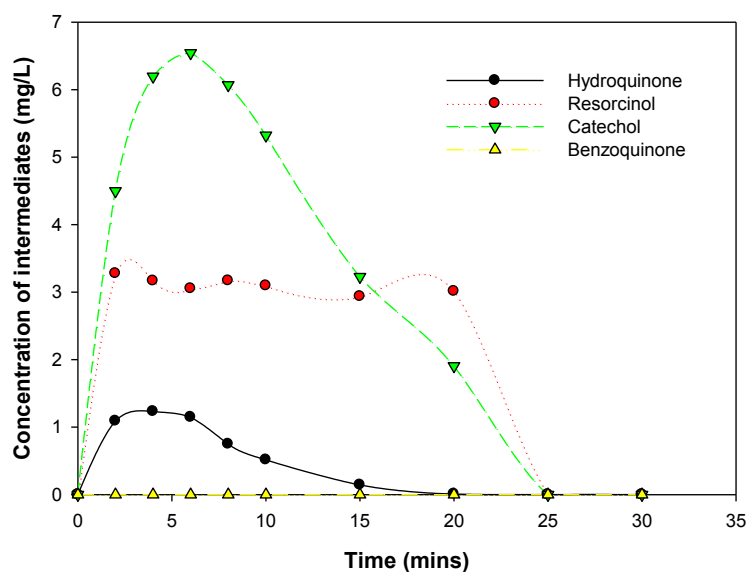


Figure 2: Concentration profile of aromatic intermediates formed from phenol degradation

3.2 Catechol

The formation and degradation profiles of catechol with different catalyst concentrations are presented in Figure 3. The degradation of phenol produced higher concentration of catechol than any other aromatic intermediate.

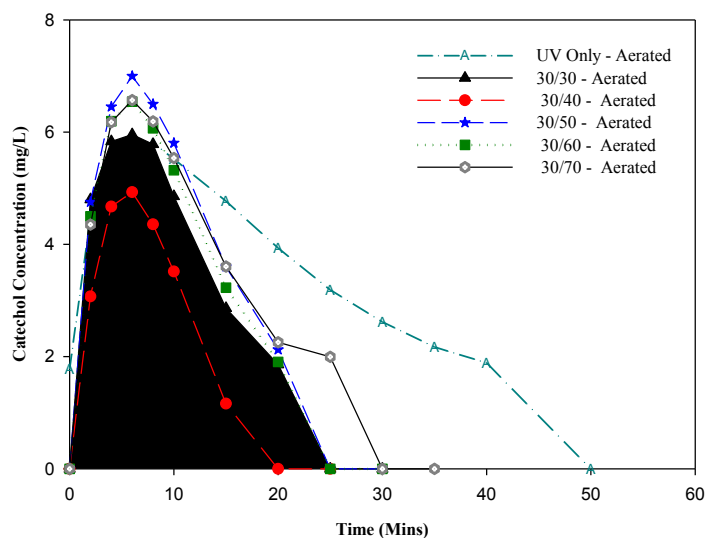


Figure 3: Formation/degradation profile of catechol

This could be attributed to the ortho directing properties of the hydroxyl group of phenol. Catechol was formed rapidly within the first 2 min of phenol degradation and its concentrations in solution increased to a maximum of 7.00 – 7.11 mg/L; after 6 min at a rate of 0.764 – 0.868 mg/L/min (Figure 3). Concentration of catechol decreased gradually thereafter at rates of 0.241 – 0.348 mg/L/min. A study of the degradation profiles of phenol and catechol show that there is a steady increase in catechol concentration as long as the concentration of phenol is higher than that of catechol and a decrease in concentration starts to occur once the concentration of phenol is approximately the same as that of catechol is the same as that of phenol in solution. Catechol is completely removed from solution after the precursor compound is completely degraded.

3.3 Resorcinol

Resorcinol is formed from the electrophilic substitution of a meta aromatic hydrogen atom. Steady state concentrations of 3.4975 ± 0.15 mg/L of resorcinol were obtained after 2 min of phenol photocatalysis with no appreciable change in its concentrations to the point of disappearance of phenol from solution. The relatively unchanged concentration of resorcinol in solution suggests that production of resorcinol in solution proceeds at approximately the same rate as its removal from solution until all phenol is removed from solution (Figure 4).

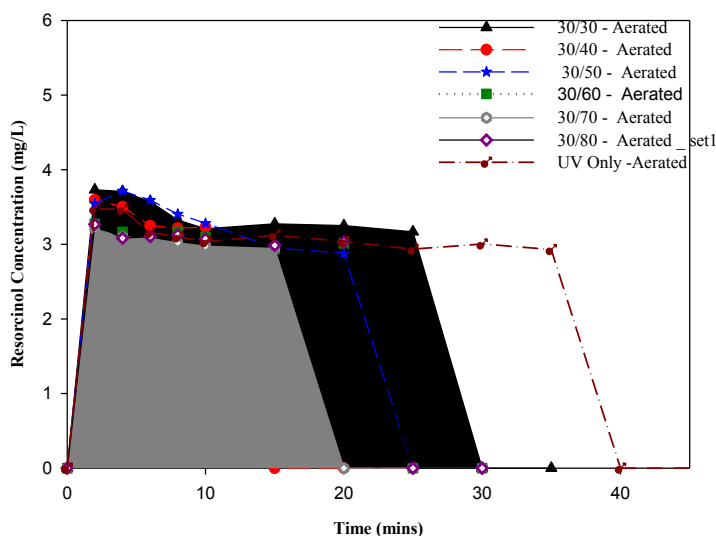


Figure 4: Formation/degradation profile of resorcinol

Maximum concentrations of resorcinol obtained were higher than expected as higher concentrations of the para directed product (hydroquinone) was expected. This could be attributed to the non-selective nature of attack of the hydroxyl radical in solution which is a stronger effect than the ortho, para directing effect of the hydroxyl group of phenol. A second contributing factor is the fact that the ortho- and meta- positions present two possible points of attack. Catechol is formed from substitution of an aromatic hydrogen atom on carbon atoms at positions C₂ and C₆ of the aromatic ring and resorcinol is formed from substitution of an aromatic hydrogen atom on carbon atoms at positions C₃ and C₅, while hydroquinone formation is possible only from substitution at the para carbon atom at position (C₄). The non-selective nature of hydroxyl radical attack is supported by the fact that degradation in non-aerated system produced resorcinol transiently (results not shown).

3.4 Hydroquinone

Hydroquinone formation and degradation profiles at different catalyst concentrations are presented in Figure 5. Hydroquinone formation peaks after 2-4 min of phenol degradation obtaining maximum concentrations of 0.956 – 1.447 mg/L and its concentration decreases steadily and gradually until all phenol is removed from solution. Higher concentrations of hydroquinone than resorcinol was expected but for reasons of positioning and possible points of attack as discussed in Section 3.3, lower concentration of hydroquinone the other two aromatic intermediates were obtained.

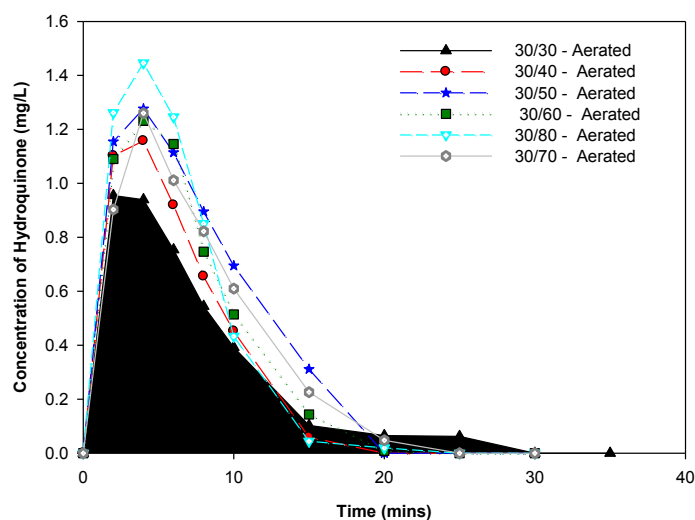


Figure 5: Formation and degradation profile of hydroquinone

All three aromatic intermediates are measured in solution as long as the parent phenol is still in solution and are rapidly removed completely when all phenol is degraded in solution.

4. Conclusions

Photocatalysis is a promising technology for the complete mineralisation of aromatic organic pollutants as it has been demonstrated that both the pollutant and its direct intermediates can be completely removed from solution.

Phenol degradation produces first aromatic dihydroxy substituted compounds that are further degraded forming acyclic compounds on cleavage of the aromatic ring.

Dominant degradation pathway is via hydroxyl radical mechanism as shown by the distribution of aromatic intermediates formed.

Concentration of aromatic intermediates formed is in the order catechol>resorcinol>hydroquinone.

Profiling of intermediates formed serves to give valuable information as to the degradation pathway of not only the parent pollutant but the intermediates formed.

Modelling the intermediate formation can give vital information which can be used to obtain kinetic parameters to describe similar compounds.

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