CHEMICAL ENGINEERING TRANSACTIONS

VOL. 76, 2019

A publication of
AIDIC
The Italian Association
of Chemical Engineering
Online at www.aidic.it/cet

Guest Editors: Petar S. Varbanov, Timothy G. Walmsley, Jiří J. Klemeš, Panos Seferlis

ISBN 978-88-95608-73-0; **ISSN** 2283-9216

DOI: 10.3303/CET1976230

The Effect of Dissolved Oxygen on the UV/TiO_2 Photocatalytic Degradation Mechanism of Phenol

Lindelwa Jay, Evans E.M.N. Chirwa*, Sheperd M. Tichapondwa

Department of Chemical Engineering, University of Pretoria, Pretoria 0002, South Africa
evans.chirwa@up.ac.za

Photocatalysis is a green technology for the degradation of persistent organic compounds in water and has been successful in the removal of several water pollutants. Degradation of organic compounds in water is often accompanied by the formation of degradation by-products, which are not well researched. In this study, aromatic intermediates formed during the photocatalytic degradation of phenol were profiled in a batch system. The carbon-13 isotopic labelling technique was used to track the degradation pathway. Photocatalytic degradation of phenol was conducted in 1L solutions of phenol (20 mg/L) in ultrapure water in a batch system. Catalyst concentration was constant at 8 mg/L Titanium dioxide (TiO_2). Concentration of phenol and detection of the aromatic intermediates of phenol degradation were monitored on a Waters High Performance Liquid Chromatograph (HPLC) and Gas Chromatogram- Mass Spectrometer (GC-MS), respectively. Aromatic intermediates identified during the course of photocatalysis of the phenol include Benzoquinone, Hydroquinone and Maleic acid. Photocatalysis has shown potential 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. The distribution of the degradation intermediates confirms that the dominant degradation pathway is via hydroxyl radical mechanism.

1. Introduction

The widespread occurrence of phenols and its derivatives in the environment has raised serious concerns and has become a threat to our water supply network. Phenols occur in surface waters, groundwater, wastewater and sludge products (Gami et al., 2014). Due to the toxicity effects and endocrine disrupting properties of phenolic compounds, their removal from water and wastewater has gained widespread global attention.

It has been frequently observed that pollutants not amenable to biological treatment may also be characterised by high chemical stability or by strong difficulty to be completely mineralized (Bamuza-Pemu and Chirwa, 2013). In these cases, it is necessary to adopt reactive systems much more effective than those adopted in conventional purification processes.

Semiconductor-mediated photocatalysis is a well-established technique for pollutant degradation leading to complete mineralization. Photocatalysis can be defined as a “catalytic reaction involving the use of a catalyst by absorption of light” (Fujishima et al., 2008). The appropriate positioning of valence (VB) and conduction (CB) bands in semiconductors (Figure 1) makes them suitable materials for the absorption of light and photocatalytic action (Marzo et al., 2018). The model compound used is phenol in this study. The kinetics of its disappearance have already been reported (Trinh et al., 2016) but the detailed description of the main steps of the whole degradation process was not studied. The present study attempted to study the degradation pathway of phenol using a carbon-13 isotope labelling technique. This is a technique used to track the passage of an isotope through a reaction. The position of the isotope in the products is measured to determine the sequence the isotopic atom followed in the reaction. In this study, a phenol-1-^{13}C reagent (Figure 2) was used to track the degradation of phenol in the photocatalytic system.

Paper Received: 10/07/2019; Revised: 05/08/2019; Accepted: 09/08/2019
Please cite this article as: Jay L., Chirwa E.M.N., Tichapondwa S.M., 2019, The Effect of Dissolved Oxygen on the UV/TiO_2 Photocatalytic Degradation Mechanism of Phenol, Chemical Engineering Transactions, 76, 1375-1380 DOI:10.3303/CET1976230

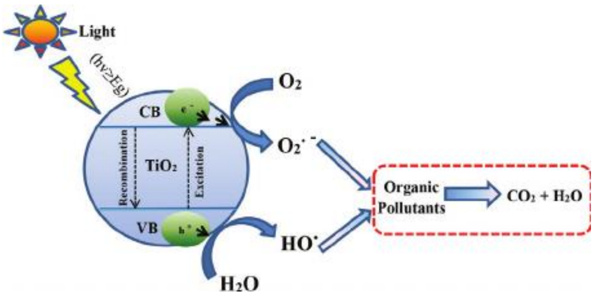


Figure 1: Photocatalytic mechanisms taking place during on a semiconductor surface

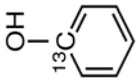


Figure 2: The chemical structure of phenol-1-^{13}C

Methods and materials

2.1 Experimental setup

Degradation studies were conducted in a fed-batch reactor with photons for catalyst activation supplied by a medium pressure 400 W UV lamp immersed just above the pollutant solution housed in a double jacket quartz sleeve, which served as the cooling system for the lamp (Tshuto et al, 2017). 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 at a flow rate of 10 mL/min. Thorough mixing of the contents of the reactor was achieved by continuous agitation with a magnetic stirrer. The experimental reaction time was set at 100 min. Aliquots of 2 mL were withdrawn from the reactor at 10 min intervals using a micro-syringe for further analysis. The reactor system was a closed system as UV light is very harmful (Figure 3).

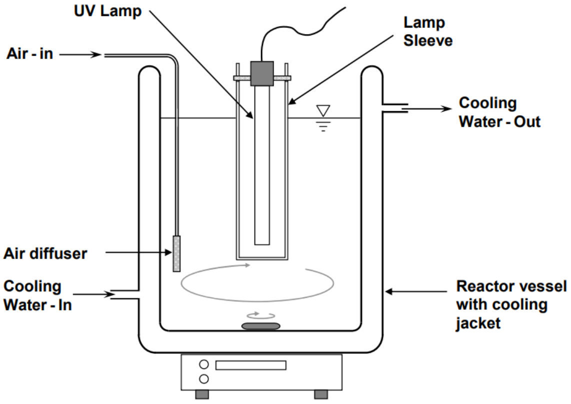


Figure 3: Photocatalytic reactor set-up (Adopted from Bamuza-Pemu and Chirwa).

2.2 Batch studies

Experiments were run in triplicates and average values are reported. ^{12}C phenol degradation experiments and ^{13}C labelled phenol degradation experiments were running separately for each batch and results were compared. Samples were then transferred into 0.5 mL micro-centrifuge tubes where they were then centrifuged for 10 min to separate suspended catalyst from the solution before GC-MS analysis.

2.3 Analytic methods

2.3.1 Phenol degradation analysis

Concentrations of the phenol 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 60 % acetonitrile (A) and 40 % water (B) was used for elution of compounds at a flow rate of 1.2 mL/min at 25 °C, injection volume was 10 μL with B operated in the isocratic mode.

2.3.2 Pathway analysis by carbon-13 tracking

The phenol solution samples were analysed using a GC system comprising of a Clarus 600 GC, Clarus 600T mass spectrometer (MS), attached to a Turbomatrix 40 trap headspace sampler (PerkinElmer, South Africa division). The chemical separation component was the Elite 5MS GC system capillary column from PerkinElmer. Helium (He) carrier gas of 99.99 % purity and applied at a flow rate of 1 mL/min. MS interface comprised of an electron ioniser (EI) and a high-performance mass analyser. This was used to measure the concentration of phenol during the course of photocatalysis. The selective ion recording (SIR) function on the GC-MS was used for carbon-13 isotope tracking. SIR is a mass spectrometry scanning mode in which only a limited mass-to-charge ratio range is transmitted or detected by the instrument, as opposed to the full spectrum range. This mode of operation typically results in significantly increased sensitivity.

2. Results and discussion

Although a balanced chemical equation for a reaction describes the quantitative relationships between the amounts of reactants present and products formed, it gives no information about how fast a given reaction occurs. This information is obtained by studying the chemical kinetics of a reaction, which depend on various factors: reactant concentrations, temperature, physical states and surface areas of reactants, and solvent and catalyst properties if either is present. This study investigates the effect of dissolved oxygen on the photoactivity insight into how to control reaction conditions to achieve the desired outcome.

3.1 Effect of electron scavenger on phenol degradation

Reactions were carried out with a phenol concentration of 20 mg/L and 8 mg/L TiO_2. Experiments were run in triplicates and average results were reported. A phenol removal of 88.9 % was achieved when the reactor was continuously bubbled with oxygen (Figure 4a). The phenol removal amount reduced to 50 % when the solution was not bubbled with oxygen. These results clearly show that continuous addition of oxygen to the reaction mixture is required to sustain the photocatalytic reaction and to effect complete degradation. Oxygen acts as the electron scavenger for the conduction band electrons, thereby preventing recombination of the electron-hole pair and thus promoting photocatalysis. Without subsequent addition of oxygen, the reaction rate is slow as the rate of dissolved oxygen (DO) addition by surface aeration is less than what is required by the reaction.

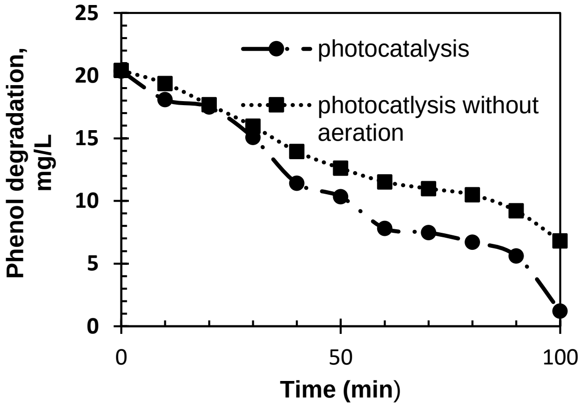


Figure 4(a): A comparison of phenol photocatalytic degradation with and without aeration.

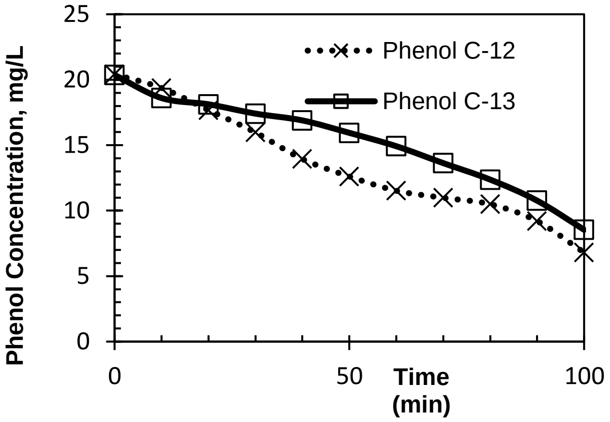


Figure 4(b) The photodegradation profile of phenol ^{13}C and ^{12}C over TiO_2.

Kinetic Isotope Effect:

$$KIE = \frac{k_{c-12}}{k_{c-13}} = \frac{0.0149}{0.0129} = 1.16 \qquad (1)$$

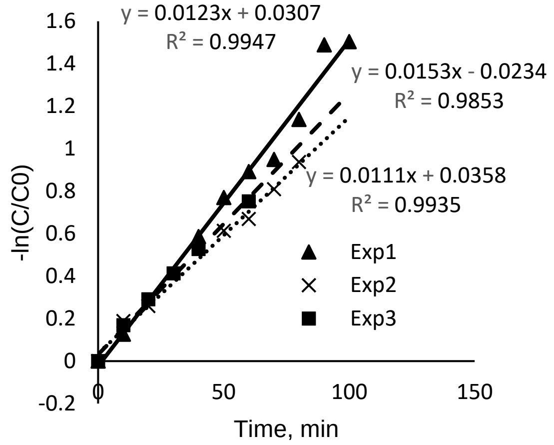


Figure 5(a): A linear plot of the Langmuir-Hinshelwood equation to determine rate constant, k, for phenol-^{13}C experiments

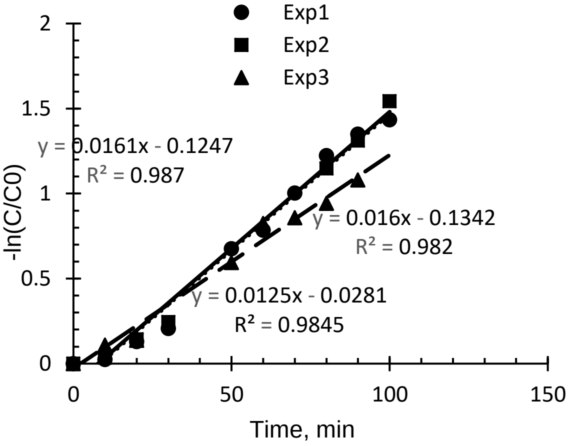


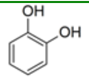
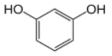
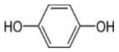
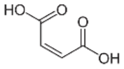
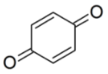
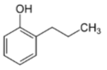
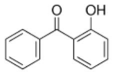
Figure 5(b): A linear plot of the Langmuir-Hinshelwood equation to determine rate constant, k, for phenol-^{12}C experiments

A kinetic study was carried (Figure 4b – Figure 5b) out, and KIE values were calculated Eq (1). From the above-calculated KIE, it can be concluded that the isotopically labelled phenol atom is part of the rate-determining step. This is referred to as a primary isotope effect. It is also noted that the above-calculated KIE is slightly above the 'normal' KIE values (1.0-1.10) for heavy isotope atoms (Simmons et al., 2012). This can be attributed to inaccuracies during experiments.

3.2 Pathway analysis by carbon-13 tracking

The movement of the c-13 isotope was followed by GC-MS analysis in order to understand the route taken by the isotope and therefore postulate a reaction mechanism. The intermediates reported in Table 3 were detected during the tracking of c-13 under UV/TiO_2 photocatalytic degradation of phenol. These intermediates contained the c-13 isotope in the highest relative abundance. The degradation mechanism depicted in Figure 6 was postulated based on these results.

Table 1: The phenol photodegradation intermediates detected by GC-MS analysis for phenol ^{12}C under anaerobic conditions (absence of electron scavenger)

	Structure	Molecular weight	Mass/charge (m/z) ratio
Catechol		110.1	110;111;92;82;81;64;63;53;39;27
Resorcinol		110.1	111;110;82;81;69;55;53;39;27
Hydroquinone		110.1	111;110;82;81;55;54;53;39;27;26
Maleic acid		116.1	99;98;72;55;54;53;46;45;27;26
Benzoquinone		108.1	109;108;82;80;54;53;52;50;26;25
2-propylphenol		136.2	136; 108; 107; 91; 79; 78; 77; 51; 39; 27
2-hydroxybenzophenone		198.2	199; 198; 121; 97; 93; 105; 77; 65; 51; 39

Phenol can undergo either a direct ring-opening process via pathway 1 or an indirect ring cleavage process via pathways 2 or 3, where the hydroxylated phenolic intermediates and its oxidized form, mainly hydroquinone, and p-benzoquinone, are generated by the nonselective attack of •OH radicals. All these intermediates can eventually be oxidized to CO_2 via various sub-intermediates following the ring-opening processes. The optimum efficiency is only reached if all the photogenerated electrons participate in the oxidation of phenol and its intermediates. If, however, electrons are consumed by the benzoquinone reduction reaction (Equation 2), the overall efficiency decreases (Su et al., 2012).

Table 2: The phenol photodegradation intermediates detected by GC-MS analysis for phenol ^{13}C under anaerobic conditions (absence of electron scavenger)

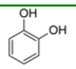
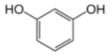
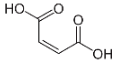
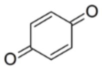
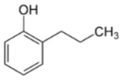
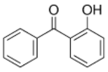
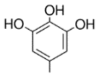
	Structure	**Molecular weight**	**Mass/charge (m/z) ratio**
Catechol		110.1	110;111;92;82;81;64;63;53;39;27
Resorcinol		110.1	111;110;82;81;69;55;53;39;27
Hydroquinone		110.1	111;110;82;81;55;54;53;39;27;26
Maleic acid		116.1	99;98;72;55;54;53;46;45;27;26
Benzoquinone		108.1	109;108;82;80;54;53;52;50;26;25
2-propylphenol		136.2	136; 108; 107; 91; 79; 78; 77; 51; 39; 27
2-hydroxybenzophenone		198.2	199; 198; 121; 97; 93; 105; 77; 65; 51; 39
Benzene-1,2,3-triol		126.1	284; 228; 79; 78; 77; 65; 52; 51; 50; 39

Table 3: The table reports the intermediates detected from ^{13}C tracking results in the absence of electron scavenger

	Phenol ^{13}C
Intermediates	Hydroquinone
	Maleic acid
	Benzoquinone

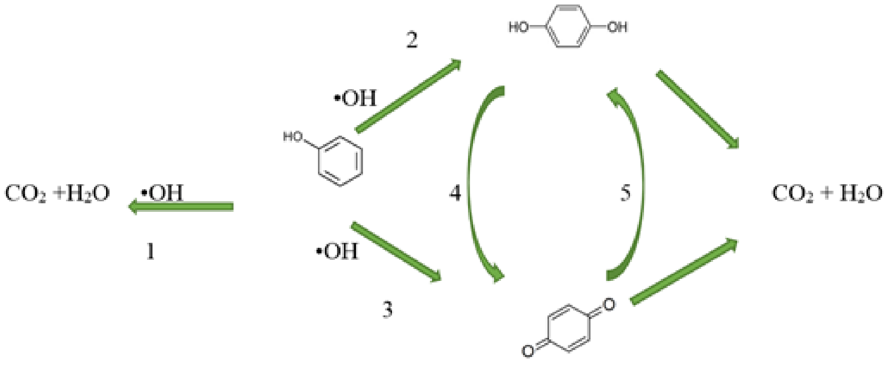


Figure 6: The proposed degradation pathway of Phenol, Hydroquinone and Benzoquinone

Photo-oxidized benzoquinone produced from phenol or hydroquinone is rapidly reduced to hydroquinone using the photogenerated electrons (Su et al., 2012). This redox reaction rapidly consumes both free electrons and oxygen in an ineffective manner and consequently inhibits the overall photodecomposition efficiency. Researchers believe that the ·OH radicals are the main active oxygen species in the ring-opening step due to their high oxidative ability (Pang et al., 2014). However, electrochemical studies suggest that the aromatic rings cannot be efficiently cleaved by the OH radicals in the absence of O_2, indicating the ·OH radicals are not a good active species for the cleavage of aryl rings (Pang et al., 2014).

$$\text{Benzoquinone} + 2e^- + H^+ \xrightarrow{k_{BH}} \text{Hydroquinone} + H_2O \qquad (2)$$

$$\text{Hydroquinone} + 0.5O_2 \xrightarrow{k_{HB}} \text{Benzoquinone} + H_2O \qquad (3)$$

Where k_{BH} and k_{HB} are the rate constants for the conversion of benzoquinone-to-hydroquinone Eq (2) and hydroquinone-to-benzoquinone Eq(3).

Conversely, the accumulation of benzoquinone can be associated with the strongly depressed k-value, which suggests that far less free electrons and oxygen molecules have been consumed in the redox reactions (Su et al., 2012), thus resulting in an improvement of the overall photooxidation efficiency of phenol.

3. Conclusion

Reaction conditions were manipulated, and a different set of results was obtained. This suggests that the photocatalytic degradation of phenol can proceed via different reaction pathways depending on reaction conditions (Jay and Chirwa, 2018). Under anaerobic conditions (absence of O_2), ^{13}C tracking results revealed Benzoquinone, Maleic acid and Hydroquine as the main intermediates containing the ^{13}C isotope. The benzoquinone-to-hydroquinone conversion occurs in the absence of electron scavenger (oxygen), however, it ineffectively consumes the photogenerated radicals, and thus reducing the photo-oxidation efficiency of phenol as was observed with the depressed phenol degradation rate (k).

References

Bamuza-Pemu E.E., Chirwa E.M.N., 2013. Profile of aromatic intermediates of titanium dioxide mediated degradation of phenol. Chemical Engineering Transactions, 35,1333–1338, DOI: 10.3303/CET1335222.

Fujishima A., Zhang X., Tryk D.A., 2008. TiO2 photocatalysis and related surface phenomena. Surface Science Reports, 63(12), 515–582. doi: 10.1016/j.surfrep.2008.10.001.

Gami A.A., Shukor M.Y., Khalil K.A., Dahalan F.A., Khalid A., Ahmad S.A., 2014. Phenol and Phenolic Compounds Toxicity. Journal of Environmental Microbiological and Toxicology, 2, 11-23.

Jay L., Chirwa E.M.N., 2018. Pathway analysis of phenol degradation by UV/TiO_2 photocatalysis utilising the C-13 isotopic labelling technique, Chemical Engineering Transactions, 70, 181-186, DOI: 10.3303/CET1870031.

Marzo L., Pagire S.K., Reiser O., Kçnig B., 2018. Visible-Light Photocatalysis: Does It Make a Difference in Organic Synthesis? Angew. Chem. Int. Ed., 57, 10034–10072, DOI: 10.1002/anie.201709766.

Pang X., Chen C., Ji H., Che Y., Ma W., Zhao J., 2014. Unraveling the Photocatalytic Mechanisms on TiO_2 Surfaces Using the Oxygen-18 Isotopic Label Technique. Molecules, 19, 16291–16311. DOI: 10.3390/molecules191016291.

Simmons E. M., Hartwig J.F., 2012, On the Interpretation of Deuterium Kinetic Isotope Effects in C-H Bond Functionalizations by Transition-Metal Complexes, Angew. Chem. Int. Ed., 51, 3066 – 3072, DOI: 10.1002/anie.201107334.

Su R., Tiruvalam R., He Q., Dimitratos N., Kesavan L., Hammond C., Lopez-Sanchez J.A., Bechstein R., Kiely C.J., Hutchings G.J., Besenbacher F., 2012. Promotion of Phenol Photodecomposition over TiO_2 Using Au, Pd, and Au–Pd Nanoparticles. ACS Nano, 6, 6284–6292, DOI: 10.1021/nn301718v.

Tshuto T., Kitoto E., Ranamane L., Chirwa E.M.N., 2017. Simultaneous degradation of phenol and reduction of chromium (VI) using UV/TiO_2 photocatalysis, Chemical Engineering Transactions, 57, 895-900 DOI: 10.3303/CET1757150.

Trinh D. T. T., Le S. T. T., Channei D., Khanitchaidecha W., Nakaruk A., 2016. Investigation of Intermediate Compounds of Phenol in Photocatalysis Process, International Journal of Chemical Engineering and Applications, 7(4), 273-276, doi: 10.18178/ijcea.2016.7.4.588

Wang L., Wang N., Zhu L., Yu H., Tang H., 2008. Photocatalytic reduction of Cr(VI) over different TiO_2 photocatalysts and the effects of dissolved organic species. Journal of Hazardous Materials, 152, 93–99. DOI: 10.1016/j.jhazmat.2007.06.063.