Transformation Pathways and Intermediate Products for the Photocatalytic Oxidation Treatment of 2.4-Dichlorophenol in Aqueous Systems

Zack Khuzwayo[1] and Evans M.N. Chirwa[2]
[1]Researcher, University of Pretoria, Water Utilisation Engineering, Pretoria, South Africa
[2]Project Leader, University of Pretoria, Water Utilisation Engineering, Pretoria, South Africa
Corresponding author's E-mail: zack.khuzwayo@up.ac.za

Abstract

Chlorophenols are highly toxic chemicals that are widely detected in reticulated water and in the environment, the main source being herbicides and precursors applied in industrial manufacturing processes. These micropollutants are unamenable to degradation by conventional treatment methods. Photocatalytic technology is one that can treat and remove these pollutants in the water systems. The exact photocatalytic mechanisms for functional group transformations are not adequately understood, as reactions associated with this protocol are diverse and complicated. This study attempted the determination of molecular entities associated with different semiconductor facilitated reaction schemes. Identification of products and intermediates was performed using advanced GCMS data processing. The analytical objective was to construct an ion trace profile of each intermediate detected and verify the absence of chemical products of reaction groups not detected from the mechanisms evaluated. The more efficient methods to perform this task is through quantification of base peak intensity (BPI), base peak intensity represents the intensity of the most intense peak at every point in the analysis, and these are presented as numerical ratios. It was found that the photocatalytic oxidation process is not one that follows a strict mechanistic reaction scheme. The evaluation of the oxidation pathways through screening of intermediates showed that reductive and oxidation pathways are both involved in the photocatalytic treatment of organics. It was determined and concluded that the degradation mechanisms and reactions pathway schemes are dependent on many factors of the photocatalysis principle, as well as the properties of the chemical groups being investigated along with its manipulations.

Keywords: Photocatalysis, Pathways, Chlorophenol, Intermediate Products.

1. INTRODUCTION

Polychlorinated phenol derivative compounds are amongst those listed as priority pollutants due to their high solubility in aquatic environments and toxicity to microorganisms (Angelini et al., 2014). Chloride substituted phenols have widely found applications as intermediates in manufacture of herbicides and precursors in industrial processes (Di et al., 2017; Du et al., 2016). As a result of intensity of toxicity of chlorophenols, significant attention has been given to determining their presence and removal from the environment (Fukushima and Tsatsumi, 2001). This project investigation was conducted on the degradation of multi-substituted chlorinated phenols under photocatalytic conditions of various manipulations. 2.4-chlorophenol (2,4-DCP) was the compounds evaluated for degradation and intermediate product pathways. 2,4-DCP is used primarily as an intermediate in the preparation of the herbicide 2.4-dichlorophenoxyacetic acid (2,4-D). The oxidation of chlorophenols, especially DCP has been reported to transform the compound into more toxic dimers, such as dibenzo-p-dioxins (PCDDs) and dibenzofurans when general oxidation techniques are applied (Angelini et al., 2014; Pandiyan et al., 2002). Zhao et al., (2012) reported that chlorophenols can easily oxidise into chlorobenzoquinones, which have been confirmed as emerging pollutants. Therefore, studies on the transformation behaviour of chlorophenols via photo-induced reactions are important to understanding efforts of remediation technologies. Photocatalysis is one of the advanced oxidation photochemical processes that is the most efficient nonselective chemical pollutant removal technology. Its principles are founded on semiconductor material properties that facilitate the reaction pathways. Semiconductor surface positive holes are generated through electron ejection, this results in formations of free hydroxyl radicals from water splitting and by mean of hydrogen peroxide reactions. The hydrogen peroxide formed is a product of the conduction band level electron acceptance steps by oxygen molecules. The resultant high oxidation potential at the valence organic chemicals groups, this leads to oxidation of higher level substituted chemical complexes resulting in subsequent formation of a range of intermediate compounds. The advanced oxidation of chlorophenols is reported to be consistent with those of other aromatics when techniques such as photocatalysis, ozonation and Fenton's reactions are applied (Zimbron and Reardon, 2009).

Though photocatalysis as a technology has proven a useful technology in the mineralisation of organic pollutants, the next stage in its theoretical implementation would be the understanding of the technology-induced transformation behaviour of different classes of compounds. Currently, the photocatalytic mechanism and the oxidation reactions associated with it are adequately understood, but the processes of chemical transformation mechanisms are unclear. The proposed study puts emphasis on the chemical kinetic variability of the transformation potential of related species within the photocatalytic process. This study will attempt to determine the kinetic trail and reaction routes undertaken in the oxidation process towards mineralisation using a unique mass spectrum processing method, where ionic populations of compound mass fractions will be statistically analysed for transformed and formed chemical compounds from the depletion of process starting analytes.

2. EXPERIMENTAL

2.1. Materials

2.4-Dichlorophenol, anatase 99.7% titanium dioxide (TiO2) were purchased from Sigma-Aldrich Logistik GmbH (Schnelldorf, Germany). Phenol and GC grade methanol were purchased from Merck (South Africa). Ultra-pure (UP) water was dispensed by the Millipore Direct Q3 with pump instrument. Reference standard were purchased from PerkinElmer (South Africa division).

2.2. Instrumental analysis

Organic compound tracking was performed using a gas chromatography (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 (30 m, 250 µm) from PerkinElmer. Helium (He) carrier gas of 99.999% purity and applied at a flow rate of 1 mL min-1. MS interface comprised of an Electron Ioniser (EI) and a high performance mass analyser.

2.3. Reactor configuration

The photocatalytic process setup is presented in Figure 1. The reactor vessel had a 1 L capacity up to the solution level and it rested on a magnetic stirrer with an rpm setting of 200. 15 cm on either side of the vessel were quarts sleeved long-arc UV lamps (Phillips HOK 4/120 SE), Table 1. A fizzling oxygen tube was attached to a flow regular, a sensor probe (HQd MTC 101) was fitted on the top side, and a glass sampling tube was attached to precision pump tubing (Masterflex), and all were immersed in the solution. The setup was installed in a temperature regulated walk-in reactor room that is wall-connected to a cold-room of 4 ◦C set temperature, the wall connection has small port-openings that allow transfer of cooled air. The reactor room has a driven air-vacuum that constantly drives the cooling system.

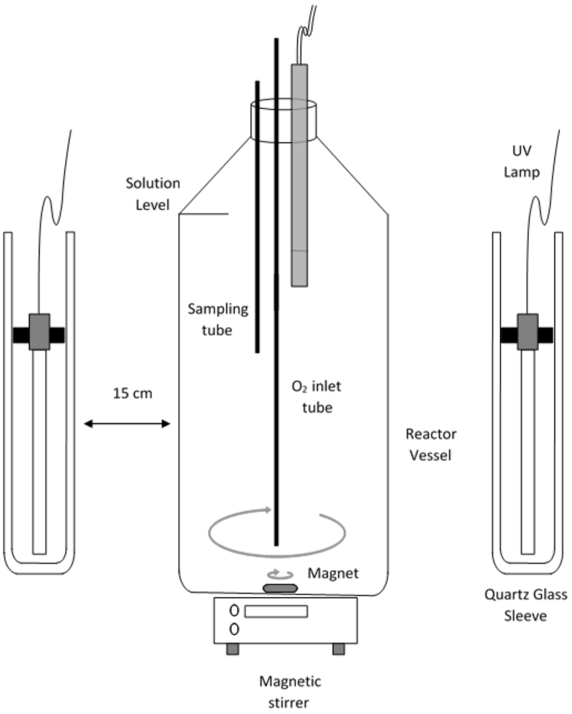

Figure 1. Schematic of the laboratory photocatalytic reactor setup

2.4. Experimental process

The reactor setup process included solution temperature determinations over the irradiation period, this was conducted by control pseudo-experimental runs using water solution. It was determined that at shorter distances the irradiation intensity was enough to offset the reactor room cooling system. There was a relationship between the fractional increases in solution temperature and the distance of the radiation sources. Progressive increases in UV lamp distances were conducted to determine the distance at which the solution temperature would remain relatively unchanged. The distance of 15 cm from the outer surface of the vessel and the outer surface of the quarts sleeve was determined to be the minimum distance required not to interfere with cooling, this is depiction in Figure 1. Analyte spiked solution were prepared accordingly, catalyst dispensation took place after chemical application, this was followed by sonication (8891 Cole-Parmer) for 10-15 minutes. Oxygen flow (20 mL min^{-1}) was initiated prior to solution transfer, only when the system was set did the UV irradiation take place. 1.5 mL sample volumes were removed at predetermined intervals, centrifuged (eppendorf minispin) for 20 minutes at 5000 rpm before instrumental analysis.

2.5. Data processing

Sigmaplot 11 (Systat Software, San Jose, CA) scientific data analysis graphics computation software was used for data processing and statistical analysis. The program was designed for the identification and simulation of aquatic systems in the laboratory, in technical plants, and in nature. The program is used to simulated experimental data profiles using derived and known expressions through mathematical modelling. Kinetic parameter estimations are conducted with input values and constraints determinations. Calculated error estimations are used to perform model sensitivity analysis.

3. RESULTS

Figure 2 shows the typified graphical representations of the photocatalytic oxidation behaviour of DCP in aqueous matrices. The oxidation degradation of the chlorophenols is viewed purposely towards mineralisation, meaning that each intermediate product formed may itself behave as a parent compound to lesser chemical species and associated derivatives. Depending on which reaction schemes are favoured, all plausible and preferred photocatalytic steps may be involved.

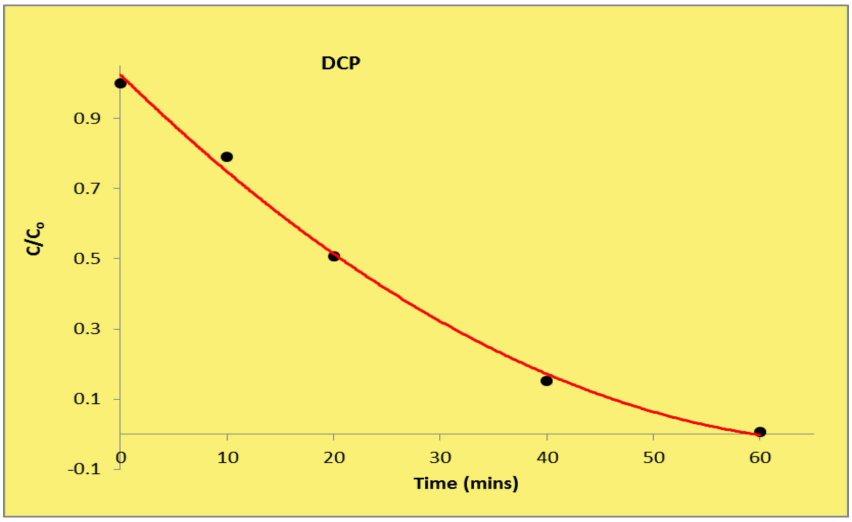

Figure 2. Typified DCP photocatalytic oxidation profile

The data processing was performed as a function of the photocatalytic time course at each sampled interval of the determined oxidation profile. The results though not interval specified represent a complete scan of the mass spectroscopy chromatograms range. The registered intermediate and derivative compounds alongside complementary transitional groups are a collective of detectable ions spectrums above the instrument limit of detection. The principal is reliant on the ability to generate and amplify enough populations of individual ions that can match a spectrum list which can be attributed with statistical confidence to a known intermediate or known compound.

3.1. DCP oxidation intermediate products and oxidation pathways

Chromatogram details and mass spectrum data were extensively screened for particular ions related to potential intermediate products from various oxidation reaction pathways reported. The absence of ions of interest from quantitative mass spectrum analysis would deem that particular pathway statistically unfavourable or absent, while the presence of ions that were not initially detected and their correspondence to intermediate products associated with a particular mechanism will be verification of that particular pathway. Plausible reaction scheme are proposed for the detected ions. Tab.1 shows the ions detected from the oxidation of 2,4-DCP at different irradiation time intervals. The analytical objective was to construct an ion trace profile of each intermediate detected and verify the absence of chemical products of reaction groups not detected from the mechanisms evaluated. One of the more efficient methods to perform this task was through quantification of base peak intensity (BPI), base peak intensity represents the intensity of the most intense peak at every point in the analysis. BPI is different to total ion chromatogram (TIC), total ion chromatogram represents the summed intensity across the entire range of masses being detected at every point in the analysis thus taking all ions into account.

Table 1 shows the intermediate compounds of identified ions that recorded measurable intensities, there were two noticeable peaks on the chromatograms after 10 minutes of irradiation had lapsed, at retention times of 12.12 and 11.89. The %BPI recorded steady influx of the ions after an illumination period of 10 minutes that decreased upon the disappearance of DCP from the system. This is similar to the findings reported by Zhang et al., (2015) on the degradation of DCP using modified carbon Fenton's oxidation process, the study also reported that in the presence of chloride ions the atom located in the para-position on the aromatic ring was substituted by radical OH◦ to form 2-chlorohydroquinone. The intermediate compounds associated with the oxidation of DCP are expected to further oxidise to organic acid products until complete mineralisation is achieved. Chlorohydroquinone was not detected from the system, this may suggest that the hydroxyl radical attack pathway reaction scheme is dynamically favoured and not the substitution reaction steps. This is partial agreement with findings by Kilic and Cinar (2008) where results show that the major intermediates of the photocatalytic degradation of 4-Chlorophenol are 4-chlorocatechol and hydroquinone (HQ). The semi-direct dehalogenation of the chloride ions reaction from the para-positions, though not registered as a viable mechanism, is suggested to take place. This explains the presence of monochlorophenol in solution, Table 1 shows that 2-chlorophenol and/or 3-chlorophenol ions were present in the system in low mass concentrations.

Table 1. Mass spectrum derived intermediate ions of DCP oxidation at different intervals

Compound identified	Retention time (min)	m/z	T0	T10	T20	T40	T60	T80
			%BPI	%BPI	%BPI	%BPI	%BPI	%BPI
Dichlorophenol	9.31	162	100	94.03	93.07	11.8	(unresolved peak)	0
		164	58.83	55.2	53.42	3.89		0
3,5-dichloro-benzene-1,2-diol	12.12	178	0	1.68	5.55	6.76	2.36	0.91
		180	0	1.47	4.96	7.13	2.74	0.72
1,3-benzenediol-4,6-dichloro	11.89	178	0	2.19	3.26	3.18	2.65	1.08
		180	0	1.93	2.85	3.12	2.11	0.56
Chlorohydroquinone	Not detected	144	na	na	na	na	na	na
		52						
Monochlorophenol	9.9	128	0.11	1.02	1.21	0.53	(unresolved peak)	(unresolved peak)
		64	0.09	0.69	0.78	0.41		

The photo-induced semiconductor catalyst oxidation process cannot be evaluated in isolation from the simple parts of its principle application of the form of photolysis and the formation of hydroxyl radical in the absence of the catalyst. The effects of all the degradation processes in isolation, though near impossible to quantify separately are additive in the overall resultant photocatalytic process. The degradation pathways and reaction schemes preferred may encompass the complete range of possible oxidation routes from each oxidation process followed. The photolytic oxidation process is one that may be responsible for a significant degree of organic compound degradation. The photolytic oxidation process is one that may be responsible for a significant degree of organic compound degradation. Data from preliminary studies represented recorded complete oxidation of DCP in 40 minutes of irradiation under photocatalytic conditions, while approximately 38 percent of DCP was reduced photolytically in the same period of illumination. It is statistically justifiable to deduce that a significant reduction in the concentration of organics in solution is due to photolysis, though as indicated previously that this does not take place in isolation under semiconductor photocatalytic applications.

4. CONCLUSION

This study determined transitional and intermediate compounds from the active photocatalytic degradation of dichlorophenol in aqueous systems. The hypothesis was formulated on the basis that different reactions schemes may be responsible for the overall process. The photocatalytic oxidation process is not one that follows a strict mechanistic reaction scheme. The evaluation of the oxidation pathways through screening of intermediates showed that reductive and oxidation pathways are both involved in the photocatalytic treatment of organics. That is one of the few ways to explain some of the derived products and intermediates detected in the system which has largely been attributed to the formation of free radical charges, their source being purely based on the positive surface-hole moiety. The photocatalytic mechanistic reaction schemes are very versatile and complex, to such an extent that an extensive review of the literature provides little uncontested knowledge regarding the processes undergone. The degradation mechanism is dependent on many factors of the photocatalysis principle, as well as the properties of the chemical groups being investigated.

ACKNOWLEDGMENTS

Funding from the Water Research Commission (WRC) South Africa, WRC Project No. K5/1125//3 awarded to Prof Evans M.N. Chirwa of the University of Pretoria.

REFERENCES

Angelini VA, Agostini E, Medina MI, Gonzalez PS (2014) Use of hairy root extracts for 2,4-DCP removal and toxicity evaluation by Lactuca sativa test, Environmental Science and Pollution Research, 21,2531-2539.

Di J, Chen J, Ji M, Zhang Q, Xu L, Xia J, Li H (2017) Reactable ionic liquid induced homogeneous carbon super-doping of $BiPO_4$ for superior photocatalytic removal of 4-chlorophenol. Chemical Engineering Journal, 313, 1477-1485.

Du P, Zhaon H, Li H, Zhang D, Huang C, Deng M, Liu C, Cao H (2016) Transformation, products, and pathways of chlorophenols via electro-enzymatic catalysis: How to control toxic intermediate products, Chemosphere, 144, 1674-1681.

Fukushima M, Tsatsumi K (2001) Degradation Pathways of Pentachlorophenol by Photo-Fenton Systems in the Presence of Iron(III), Humic Acid, and Hydrogen Peroxide, Environmental Science and Technology, 35, 1771-1778.

Kilic M, Cinar Z, (2008) Hydroxyl radical reactions with 4-chlorophenol as a model for heterogeneous photocatalysis, Journal of Molecular Structure, 851,263-270.

Pandiyan T, Rivas OM, Mart´ınez JO, Amezcua GB, Mart´ınez-Carrillo MA (2001) Comparison of methods for the photochemical degradation of chlorophenols, Journal of Photochemistry and Photobiology A: Chemistry, 146, 149–155.

Zhang C, Zhou M, Ren G, Yu X, Ma L, Yang J, Yu F (2015) Heterogeneous electro-Fenton using modified iron–carbon as catalyst for 2.4-dichlorophenol degradation: Influence factors, mechanism and degradation pathway, Water Research, 70, 414-424.

Zhao Y, Anichina J, Lu X, Bull RJ, Krasner SW, Hrudey SE, Li X (2012) Occurrence and formation of chloro- and bromo-benzoquinones during drinking water disinfection, Water Research, 46, 4351-4360.

Zimbron JA, Reardon KF (2009) Fenton's oxidation of pentachlorophenol, Water Research, 43, 1831-1840.