Pathway Analysis of Phenol Degradation by UV/TiO$_2$ Photocatalysis Utilising the C-13 Isotopic Labelling Technique

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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 several intermediate compounds, some of which are feared to be more toxic than the original compound being treated. 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 (20mg/L) in ultrapure water in a batch system. Catalyst concentration was constant at 8mg/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 hydroquinone, benzoquinone catechol and resorcinol. The concentration of phenol was determined from the calibration curve of standards of phenol. Photocatalysis is a promising technology for the complete mineralization 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 cycling 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

Due to the toxicity effects and endocrine disrupting properties of phenolic compounds, their removal from water and wastewater has gained widespread global attention. This has led to the advancement of new methods and adoption of improved methods for the removal of pollutants from water. Numerous studies have been carried out to find a suitable technology for wastewater treatment. Advanced oxidation processes (AOP) have led the way in the treatment of aqueous waste. Photocatalysis is a proven and green technology available for the degradation of several persistent organic compounds in water (Tshuto et al., 2017). Photocatalysis is termed as a photoinduced reaction, which is accelerated by the presence of a semiconductor. The semiconductor commonly used is TiO$_2$. This reaction is activated by absorption of a photon with sufficient energy (equals or higher than the band-gap energy (E$_{bg}$) of the catalyst, as shown in the Figure 1. The absorption leads to a charge separation due to promotion of an electron (e$^-$) from the valence band of the semiconductor catalyst to the conduction band, thus generating a hole (h$^+$) in the valence band. The photogenerated electrons can reduce the pollutant or react with electron acceptors such as oxygen (O$_2$) adsorbed on the Ti(III)-surface or dissolved in water, reducing O$_2$ to superoxide radical anion (O$_2^{-\bullet}$) (Fujishima et al., 2008).

The photogenerated holes can oxidize the organic molecule to form R$^+$, or react with OH$^-$ or H$_2$O oxidizing them into OH$^\bullet$ radicals. Effective treatment is expected to mineralise the parent pollutant and degradation intermediates formed during the treatment process, or reduce the pollutant and intermediates to environmentally insignificant concentrations. Degradation is often accompanied by formation of intermediate compounds which may be more harmful than the original pollutant (Bamuza-Pemu and Chirwa, 2013). This study aims to identify and investigate the intermediates formed during the UV/TiO$_2$ photocatalytic degradation of phenol in a batch

system. The reaction mechanism will be tracked using the Carbon-13 isotopic labelling technique. The labelled compound (phenol-1-^{13}C) contained a single C-13 atom on position 1 (Figure 2).
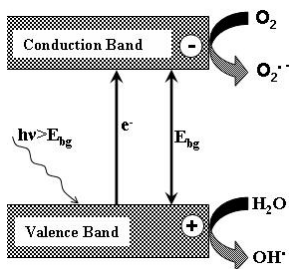

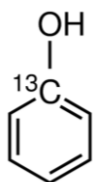Figure 1: Redox reactions occurring at the semiconductor (TiO$_2$) surface

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

2. 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. 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 minutes. 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).
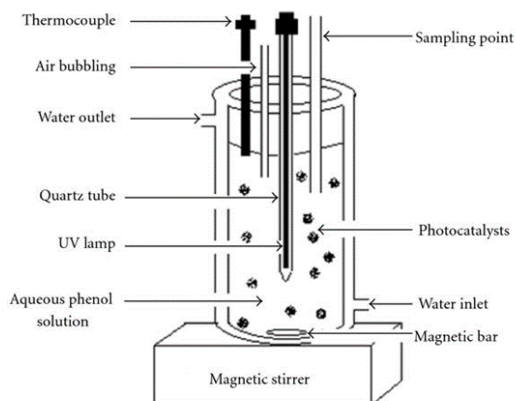

Figure 3: Experimental set-up of photocatalytic fed-batch reactor (Wang et al, 2004)

2.2 Batch studies

Experiments were run in triplicates and average values are reported. Carbon-12 phenol degradation experiments and Carbon-13 labelled phenol degradation experiments were run 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 Titanium dioxide (TiO₂) characterisation

XRD measurements were performed on a Bruker D8 Advance diffractometer with 2.2 kW CuKα radiation (λ=1.54 nm) fitted with a LynxEye detector with a 3.7 º active area. Samples were scanned in reflection mode in the angular range 2 ° to 70 ° 2 θ at a rate of 0.01 ° s−1. The generator settings were 40 kV and 40 mA. Data processing and analysis were carried out using the Bruker DiffracPlus EVA evaluation program. Quantitative XRD analyses were performed according to the Rietveld method using DiffracPlus TOPAS software.
The samples were roasted at 1,000 °C to determine Loss on Ignition (LOI). 1 g roasted sample was then placed together with 6 g of Li2B4O7 into a Pt/Au crucible and fused The ARL Perform'X Sequential XRF instrument was used for the analyses. Analyses were executed using the Quantas software. The software analysed for all elements in the periodic table between Na and U, but only elements found above the detection limits were reported. The results were also monitored and filtered to eliminate the presence of some of the flux, wetting and oxidising agents' elements. Blank and certified reference materials were analysed with each batch of samples.

2.3.2 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.

2.3.3 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.

3. Results and discussion

3.1 X-ray diffraction (XRD)

The sharp diffraction peaks in the XRD patterns as well as the low impurity peaks indicate that the synthesised compound has high crystallinity and purity (Figure4). The small peak intensities in the XRD pattern are attributed to the presence of fine grains (Moore and Reynolds, 1997).
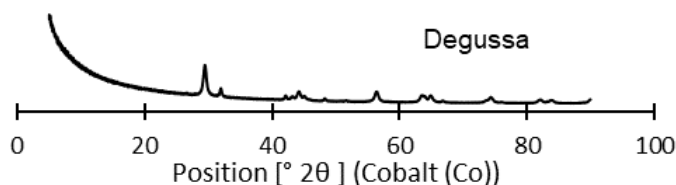

Figure 4: An x-ray diffraction pattern for TiO₂ in the P-25 Degussa form

3.2 X-ray fluorescence (XRF)

Table 1 shows the chemical composition of P-25 Degussa. The chemical composition of a certified standard and the analysed standard are shown in column 2 and column 3, respectively. The P-25 Degussa powder was found to contain 96.7 % TiO₂ and the rest being contaminants as reported in the table. These contaminants may or may not contribute to the photoactivity of the catalyst.

Table1: Chemical composition of P-25 Degussa

	Certified Standard	Analysed Standard	Degussa
SiO_2	99.6	99.40	0.02
TiO_2	0.01	0.00	96.70
Fe_2O_3	0.05	0.01	0.05
Na_2O	0.05	0.02	<0.01
Cr_2O_3	0	0.00	<0.01

3.2 A comparison of phenol-C-12 and phenol-C-13 degradation kinetics

The degradation profile of phenol C-12 and the C-13 labelled phenol can be seen in Figure 5. An initial phenol concentration of 20 mg/L and 8 mg/L TiO_2 was used for all experiments. It is evident that there was greater phenol removal with phenol C-12 than that of phenol C-13 under the same photocatalytic conditions, this can be attributed to kinetic isotope effects (KIE). KIE are rate changes due to isotopic substitution at a site of bond breaking in the rate determining step of a reaction (Simmons et al., 2012). KIE was calculated according to Eq(1). It is understood that C-13 contains a neutron more than C-12 and is considerably heavier than C-12. This results in slower reaction rate. KIE was calculated using Eq(1), where kC-12 and kC-13 are the rate constants of C-12 phenol and C-13 labelled phenol, respectively.

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

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. Note 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.
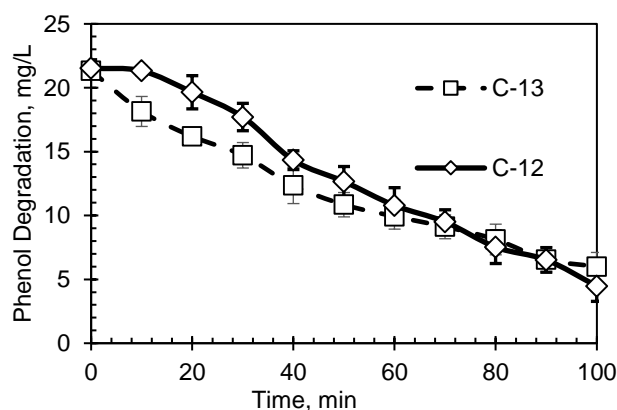

Figure 5: The degradation profile of phenol-C-12 and phenol-C-13 over 100 min

3.3 The evolution of degradation intermediates during photocatalysis

As degradation proceeded, other peaks were observed on the chromatogram from HPLC analysis. These intermediates could not be identified. It can be concluded that these are degradation intermediates.
To investigate the reaction mechanism of phenol degradation, the evolution of intermediates during phenol degradation was followed by GC-MS analysis. When TiO_2 was irradiated, the phenol concentration decreased significantly. Several hydroxylation products were detected within the first 10 min as indicated by (x) in Table 2. Hydroquinone, benzoquinone, catechol, benzene-1.2.3-triol and resorcinol were all detected within the first 10 min of irradiation.
Intermediates appeared and disappeared during the course of reaction. Photocatalysis is a complex reaction, one that consists of competing reactions where the starting material is converted to something other than the desired products. Photocatalysis is further complicated by the fact that it occurs in stages in which intermediate products are formed and then converted by further reactions to the final products. This explains the appearance and disappearance of intermediates throughout the photocatalytic reaction. There is an observed difference in the evolution of intermediates for C-12 phenol and the C-13 labelled phenol. The 2-propylphenol intermediate

was only detected in C-13 phenol experiments. The C-13 isotope labelled phenol seems to have undergone a slightly different reaction pathway than that of C-12 phenol. This can be attributed to a kinetic isotope effect. Many reactions including photocatalysis can proceed by more than one reaction path, therefore the knowledge of the reaction mechanisms involved may make it possible to choose reaction conditions favouring one path over another, thereby giving maximum amounts of desired products and minimum amounts of undesired products (Maitra and Chandrasekhar, 1997).

Table 2: Intermediates detected during the course of phenol C-12 and phenol-C-13 degradation by UV/TiO$_2$ Photocatalysis over a period of 100 min

Intermediate	Phenol C-12 Time, min									
	10	20	30	40	50	60	70	80	90	100
Maleic acid	x		x	x	x	x		x		x
Benzoquinone	x		x	x	x			x		x
Resorcinol	x	x		x	x	x		x	x	x
2-Hydroxybenzophenone				x				x		
Catechol	x	x	x	x	x	x		x		x
Hydroquinone	x	x	x	x	x	x		x	x	
Benzene-1.2.3-triol	x		x	x	x	x		x		x
Intermediate	Phenol C-13 Time, min									
	10	20	30	40	50	60	70	80	90	100
Maleic acid	x			x	x	x		x		x
Benzoquinone	x			x	x	x		x		x
Resorcinol	x		x	x	x	x		x		x
Catechol	x		x	x	x	x		x		x
Hydroquinone	x		x	x	x	x		x		x
Benzene-1,2,3-triol	x			x	x	x		x		x
2-Propylphenol	x		x	x	x			x		x
2-Hydroxyphenone	x		x	x	x	x		x		x

3.4 Carbon-13 isotope tracking

The movement of the carbon-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 4 was therefore postulated based on these findings.

Table3: Intermediates detected from C-13 tracking results by UV/TiO$_2$.

	Phenol C-13
Intermediates	Hydroquinone
	Maleic acid
	Resorcinol

Different regioisomeric hydroxylated products were detected because phenol is a substituted aromatic ring. The phenol structure consists of a hydroxyl (-OH) group substituent on a benzene ring. The –OH substituent is an electron donating group (EDG) and therefore results in electrophilic substitution at the ortho (-o) and para (-para) positions (Palmisano et al., 2006). This was confirmed by the detection degradation of intermediates; hydroquinone, benzoquinone, catechol and benzene-1,2,3-triol. Subsequent oxidation of hydroxylation products is reported to lead to ring open products (Bui et al., 2010). This was confirmed by the detection of maleic acid. Based on this knowledge, the phenol degradation mechanism over UV/TiO$_2$ was postulated as depicted in Figure 6.

The observed initial ring-opening products of aromatic compounds in aerated aqueous solutions are always carboxylic acids or carboxylic acid derivatives. Thus, decarboxylation of these carboxylic acids is one of the most important steps for complete mineralization of organic pollutants (Pang et al., 2014). Further degradation by decarboxylation is reported (Pang et al., 2014) to lead to further ring breaking into smaller hydrocarbon chains until the compound reaches full mineralisation. However, these hydrocarbon chains were not detected during experiments because of short reaction times. The reaction did not reach full mineralisation.
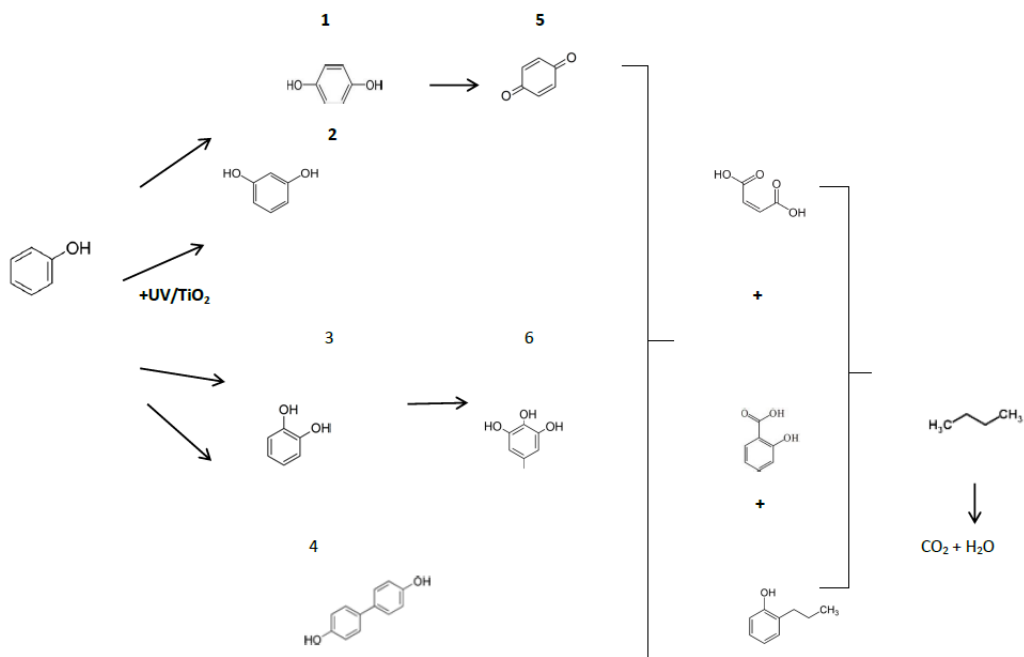
Figure 6: The postulated reaction pathway for the UV/TiO₂ photocatalytic degradation of phenol.

4. Conclusion

Carbon-13 tracking results showed that hydroquinone, resorcinol and maleic acid were the main degradation intermediates. Phenol degradation undergoes aromatic dihydroxy substitution followed by aromatic ring cleavage and decarboxylation of organic chain until mineralisation. The dominant degradation pathway is via hydroxyl radical mechanism, shown by distribution of intermediates formed. Photocatalysis is a promising technology for complete mineralization of aromatic organic pollutants as demonstrated by removal of phenol and its intermediates. Therefore, combined UV/TiO₂ process may be applied as an effective method for the removal of phenol from aquatic solutions such as industrial wastewaters and polluted water resources.

5. References

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