The investigation of alternative processes for the oxidation of phenol

By

Basanda Pongoma

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Supervisors: Dr Ernst E Ferg
Dr S. Gouws

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SUMMARY

The electrochemical oxidation of phenol can be considered as an important process for either producing value added products such as hydroquinone and catechol or for the removal of the phenol from waste water streams to form carbon dioxide. This process had been extensively studied with the main focus on type of anode material used. Even though the anode material could be made from a range of materials, this study focused on using PbO$_2$ as anode material that was made by using Pb-acid battery principles in designing a microporous electrode.

In this study, the focus was on using lead dioxide as an anode material that was made by using the formation principles used in the manufacturing of Pb-acid batteries. This allowed for the construction of an electrochemical flow-through micro-porous reactor that contained PbO$_2$ as the anode and Pb as the cathode, allowing for a solution containing phenol to flow through the cell continuously. By applying a suitable potential across the cell, the almost complete oxidation of phenol would occur to form benzoquinone, which was followed by the sequential reduction to other products such as hydroquinone and catechol. The system was shown to be made up of tightly packed micro-porous material that had a very high surface area-to-volume ratio.

The study showed that between 80 to 90% successful conversion of a 50 mM solution of phenol could be achieved by optimizing the continuous flow process of up to 500 minutes. The main reaction product from this process was hydroquinone, of up to 60% with a number of the minor products of which not all could be identified. In order to utilize the characteristics of this reactor system, its design and reaction conditions such as applied potential, phenol concentration, co-solvent concentration and support electrolyte concentration were investigated to optimize the convection of phenol and the yield of hydroquinone.
**Keywords:** Phenol, hydroquinone, electrochemical oxidation, lead dioxide, micro-porous cell.

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B. Pongoma, “Electrochemical Oxidation of Phenol on continuous micro-flow reactor”,

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My mother and the rest of my family for all their endless love and support.

The staff and fellow students at the Chemistry department for their assistance and friendship.

To the one who makes it all possible in my life, Christ my Saviour.
Declaration

I declare that this dissertation is my own, unaided work. It is being submitted for the degree of Master of Technology at the Nelson Mandela Metropolitan University, Port Elizabeth. It has not been submitted before for any degree or examination in any other Institution.

B. Pongoma
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Chapter 1

1. Introduction
Phenol is an important starting material in industrial applications as it plays a major role in producing other important chemicals for production of common consumer chemicals. It can be transformed chemically to a variety of compounds by routes that generally include alkylation, carbonylation, oxidation and acylation (Fig 1.1).\(^1\)

![Figure 1.1: Phenol Chemistry to Other Compounds](image)

The oxidation of phenol is one of the important routes in converting it to some valuable products that include hydroquinone and its isomers catechol and resorcinol. Hydroquinone and its isomers are widely used in the chemical industry ranging from photographic developer, pharmaceuticals, agrochemicals, and antioxidants. The oxidation of phenol to these products can be done either catalytically or electrochemically. The catalytic oxidation route is currently used as the preferred industrial route for the production of hydroquinone and catechol
and depending on the reaction conditions, this route can form different ratios of hydroquinone to catechol.\textsuperscript{2}

The electrochemical oxidation of phenol is widely investigated and especially in the removal of phenol from waste water treatments. In these studies the focus was usually on the anode material as it is the one that produces the intermediate species benzoquinone which can be further converted to aliphatic organic acids (maleic acid, oxalic acid, furmaric acid) and finally to the decomposition product carbon dioxide. The anode materials can range from graphite, boron, tin oxide, lead dioxide and platinum.\textsuperscript{3,4}

However, the electrochemical oxidation of phenol to produce benzoquinone can also under controlled conditions form hydroquinone and catechol. The use of lead dioxide as anode is widely investigated in the literature and had shown positive results for not only the degradation of phenol from water waste treatments \textsuperscript{3,4} but as a further reduction of the benzoquinone to hydroquinone or catechol on a cathode material such as lead or any other conductive metal (Fig 1.2).\textsuperscript{3,5,6}

\[
\text{OH} + \text{H}_2\text{O} \xrightarrow{\text{PbO}_2, \text{oxidation}} \text{C}_\text{O} + 4\text{H}^+ + 4\text{e}^- \xrightarrow{\text{Pb, reduction}} \text{OH} + \text{H}_2
\]

\textbf{FIGURE 1.2: ELECTROCHEMICAL OXIDATION OF PHENOL AND FURTHER REDUCTION OF BENZOQUINONE.}\textsuperscript{5}

However, some of the drawbacks of the electrochemical process are the multiple side reactions that can occur on the electrodes, ultimately poisoning the active surface with various polyphenols, reducing the effective use of such techniques commercially.
The following study considered the combination of a continuous micro-flow system using micro-porous electrodes that provide a high surface area to volume ratio providing a reduction in reaction time of the reactants at the working electrode but still allowing for effective conversion to the desired products.

1.1 Chemistry of phenol

1.1.1 Phenol
Phenol (hydroxybenzene, carbolic acid, C₆H₅O) is the parent compound of a homologous series of compounds where the hydroxyl group is directly bonded to the aromatic ring. It occurs as free a component or in addition to others in natural products and organisms. The compound was discovered by F. Runge in 1834, when he acidified a lime solution from steam-distilled light oil that he obtained coal tar. He named it a carbolic acid and it was later named as phenol by C. Gerhardt in 1842.

Large quantities of phenol were traditionally recovered from coke oven tars, coal gasification liquors and spent refinery caustics. The phenol from material resources (tars and wood) is obtained by fractional distillation from the crude phenols mixture. The rise in demand in phenol consumption led to the investigation of its synthetic production and various routes were discovered such as forming phenol from benzesulfonic acid, chlorobenzene, oxidation of toluene or cumene. The cumene oxidation known as Hock process produces large quantities of phenol and has replaced the other routes as the preferred industrial production for phenol. Its major advantage over the others is its formation of acetone as by-product which has an economical value.

Phenol is a colourless, crystalline solid at room temperature which melts at 40.9 °C. It is completely miscible with water at temperatures above 68.4 °C. It is also readily soluble in many organic solvents such as ketones, aromatic hydrocarbons, ethers and halogenated hydrocarbons, but less soluble in aliphatic hydrocarbons. Phenol is a weak acid which dissociates to form H₃O⁺ and the
phenoxide anion (ArO⁻) in aqueous solution. Its acidity is due to the fact that when the phenol molecule loses its proton, it can stabilize the negative charge on the molecule through forming \(\sigma\)- and \(\pi\)-quinoid resonance structures.

This property of forming the \(\sigma\)- and \(\pi\)-quinoid resonance structures allows the phenol molecule to easily undergo electrophilic substitution reactions. Under oxidative conditions, the phenol molecule can form a free radical, which can undergo dimerization or can be further oxidized to form dihydroxybenzenes and quinones (Fig 1.3). Phenol can be used as radical scavengers and also as an oxidation inhibitor since the radicals formed are relatively stable.

**Figure 1.3:** Phenoxyl-radical resonance structures.

Phenol is mainly used as a starting material in the production of a wide range of consumer goods and other process materials. It is extensively used in the production of phenol-formaldehyde resins, as a starting material in manufacture of laminated wood boards. Other phenol and phenol derivative products include household adhesives, agrochemicals, dyes, insecticides, herbicides, preservatives, antioxidants and flavourants for foods, impregnating resins, antiseptics and disinfectants, etc.

### 1.1.2. Phenol Products formed during the electrochemical oxidation

During the electrochemical oxidation of phenol, possible products that are formed are dihydroxybenzenes and benzoquinone. The dihydroxybenzenes can occur as
three isomeric forms that include hydroquinone, catechol and resorcinol (Fig 1.4) and their products have various industrial importance and consumer uses (Table 1.1). However during electrochemical oxidation of phenol the resorcinol isomer is not formed, as shown in (Fig 1.3) phenol prefers to undergo reaction on ortho- and para- positions that form hydroquinone and catechol respectively but not resorcinol which requires meta- position.

**Figure 1.4:** Products formed from electrochemical oxidation of phenol.
### TABLE 1.1: SOME MAJOR USES OF HYDROQUINONE, CATECHOL AND BENZOQUINONE

<table>
<thead>
<tr>
<th></th>
<th><strong>Used for production</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydroquinone</td>
<td>Photographic developer in photography films</td>
</tr>
<tr>
<td></td>
<td>Antioxidants and antiozonats in rubber industry</td>
</tr>
<tr>
<td></td>
<td>2-\textit{tert}-butylhydroquinone and 2-\textit{tert}-butyl-4-methoxyphenol for food-grade antioxidants</td>
</tr>
<tr>
<td></td>
<td>Hydroquinone, hydroquinone monomethyl ether and benzoquinone for vinyl monomer industry as polymerization inhibitor during production and storage of products.</td>
</tr>
<tr>
<td></td>
<td>Hydroquinone dimethyl ether as starting material for production of variety of dyes and pigments.</td>
</tr>
<tr>
<td></td>
<td>It also used for synthesis intermediates and water treatment.</td>
</tr>
<tr>
<td>Catechol</td>
<td>Photographic developer in photography</td>
</tr>
<tr>
<td></td>
<td>Eugonol (clove), safrole and piperonal (cherry and vanilla) used for fragrances in perfumery.</td>
</tr>
<tr>
<td></td>
<td>Vanillin (4-hydroxy-3-methoxybenzaldehyde) as flavouring agent and ethylvanillin (3-ethoxy-4-hydroxybenzaldehyde) not found in nature is 3-4 times stronger than vanillin as a flavouring agent.</td>
</tr>
<tr>
<td>Benzoquinone</td>
<td>Hydroquinone used in photographic and dye industries.</td>
</tr>
<tr>
<td></td>
<td>Oxidants, bactericides.</td>
</tr>
</tbody>
</table>

**Hydroquinone** (1,4-dihydroxybenzene, 1,4-benzenediol, \(\rho\)-dihydroxybenzene):  
This chemical occurs in nature as hydroquinone \(\beta\)-D-glucopyranoside (arbutin) in leaves of several plants and fruits. It was first described by Woehler in 1844 when it was made by adding hydrogen to 1,4-benzoquinone.\(^2\) It is a colourless crystalline solid that exists in three forms. The \(\alpha\)-form (hexagonal needles), \(\gamma\)-form (monoclinic prisms) and the \(\beta\)-form (as needles or prisms). Solutions of
hydroquinone are easily discoloured by oxidation when exposed to air. It easily dissolves in water and most organic solvents such as ethanol, acetone, and benzene. 

The hydroquinone has similar reaction behaviour to phenol as its hydroxyl group can be converted to an ether or ester. The important characteristic of hydroquinone is its easily reduction to benzoquinone in the presence of oxidizing agent, especially radicals, and that makes it an important antioxidant, (Fig 1.5).

\[ \text{OH} \quad -e^- \quad -H^+ \quad \text{OH} \quad -e^- \quad -H^+ \]

**Figure 1.5:** Oxidation of hydroquinone to benzoquinone.

**Catechol** (1,2-dihydroxybenzene, 1,2-benzediol, pyrocatechol), this chemical was first obtained by dry distillation of catechin by Reinsch in 1839. It is widely distributed in nature and found in plants (onion, eucalyptus, crude beetsugar), coal and tobacco smoke. It is a colourless crystalline solid (monoclinic crystals) and discolours when in contact with air and light. It readily dissolves in water and hydrophobic organic solvents (ethanol and acetone). It undergoes similar reactions to that of phenol when it reacts with acyl halides to form mono- and di-esters. It is also a weak acid as it forms mono- and di-salts with alkali hydroxides or carbonates. Of all three dihydroxybenzenes isomers, it is the strongest reducing agent as it can form heavy metal salts when reacting in solutions with elemental metals.

**Benzoquinone:** There are two isomers forms of this chemical. The ortho isomer which forms a yellow crystalline solid (monoclinic prisms) when crystallised from alcohol. When it sublimed to form the para-isomer which is a red crystalline solid
with typical plate like or prism shaped crystals. The ortho isomer is less stable than the para-isomer and decomposes in water. It is soluble and stable in ether, acetone and benzene but insoluble in petroleum ether. The para-isomer is soluble in most oxygenated organic solvents (ether, alcohol), and slightly soluble in petroleum ether and insoluble in water.\textsuperscript{10}

The world wide industrial production of dihydroxybenzenes in countries like USA, China, Japan and Europe are obtained from a variety of synthetic routes (Table 2).\textsuperscript{2,9,12} There are many other synthetic routes described in the literature towards forming the dihydroxybenzenes but are either not commercially available or are viable only at the lab scale level such as carbonylation of acetylene to produce hydroquinone, catechol can be produced from hydrolysis of aminophenol using a hydrogen halide and electrochemical oxidation of phenol or benzene to benzoquinone which followed by reduction to form both hydroquinone and catechol.\textsuperscript{2,9}
### TABLE 1.2: INDUSTRIAL PRODUCTION PROCESSES FOR DIHYDROXYBENZENES

<table>
<thead>
<tr>
<th>Dihydoxybenzenes</th>
<th>World capacities, Ton</th>
<th>Process</th>
<th>Companies</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydroquinone</td>
<td>50 000</td>
<td>$p$-Diisopropylbenzene oxidation</td>
<td>Eastman chemical company, Rhodia, Yancheng Fengyang chemical industry co., LTD</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Hydroxylation of phenol</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Aniline oxidation</td>
<td></td>
</tr>
<tr>
<td>Catechol</td>
<td>25 000</td>
<td>Hydroxylation of phenol</td>
<td>Rhodia</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Coal-tar distillation</td>
<td></td>
</tr>
<tr>
<td>Benzoquinone</td>
<td>1000&lt;sup&gt;a&lt;/sup&gt;</td>
<td>Aniline oxidation</td>
<td>Yancheng Fengyang chemical industry co., LTD</td>
</tr>
</tbody>
</table>

<sup>a</sup>: annual output from Yancheng Fengyang chemical industry co., LTD.

1.1.3 **Hydroxylation of phenol**: This process is the most common and mostly widely used method to produce a mixture of catechol and hydroquinone. There are two typical routes used in a stirred batch reactor, one using iron (II) salt and the other one uses a strong mineral acid such as sulphuric acid, perchloric acid or trifluoromethanesulphonic acid as catalysts in the presence of hydrogen peroxide. The one route that uses iron as catalyst with 60% hydrogen peroxide at 40 °C can achieve a ratio of hydroquinone to catechol that is between 40:60 and 20:80 with overall selectivity of over 90% and phenol conversion of about 20%. The mineral acids catalyzed route at 90 °C, with $\text{H}_2\text{O}_2$ achieves relatively low phenol conversion of less than 10% with an overall selectivity of 90%. The
hydroquinone to catechol ratios can vary between 60 to 40 molar ratios, depending on the reaction conditions. This molar ratio variation can be tailored according to the demand in the consumer market for catechol or hydroquinone by simply varying the temperature, concentration of peroxide and catalyst type. Reactions with selectivity of 99% towards the hydroquinone are achieved by using shape-selective zeolite such as titanium silicate (TS-1) as a catalyst. The reaction mechanism is shown in (Fig 1.6) and purification is usually achieved by a series of extractions and solvent separations procedures.  

![Reaction mechanism](image)

**FIGURE 1.6: HYDROXYLATION OF PHENOL**

**Benzoquinone:** This process involves the oxidation of aniline using manganese oxide in an acidic medium (Fig 1.7). The product is obtained in relatively high yields and the purity improved by steam distillation and chilling the product mixture.

![Chemical reaction](image)

**FIGURE 1.7: ANILINE OXIDATION TO BENZOQUINONE**

### 1.2 Electrochemistry

Electrochemical synthesis is a process whereby a chemical process takes place in conductive medium and an applied current becomes the driving force to allow
a chemical reaction to take place. It is considered as a non-conventional reaction technique, whereby radical ions at various oxidation states are formed as typical intermediates. It is the discipline that has wide applications such as the organic synthesis of electrohydrodimerization of acrylonitrile to adiponitrile. An example of typical inorganic synthesis is brine electrolysis where chlorine and sodium hydroxide is produced from aqueous sodium chloride solution. Other applications include energy storage devices (batteries and fuel cells) and electro-analytical processes (cyclic voltammetry, electro-sensors and or pH testing). Reactions occurring in electrochemical processes can be considered as heterogeneous chemical reactions that involve electrodes that are generally a metal, conductive carbon or semiconductors in a medium (liquid or solid) where the charge transfers to or from the electrodes occur via charged ion transport. These reactions are referred to as redox mechanisms where the reduction occurs at the cathode (negative electrode) and the oxidation reaction at the anode (positive electrode).

Organic electrosynthesis reactions are usually classified as either direct electron transfer reactions or indirect electron transfer reactions. The direct electron transfer reactions takes place by electron transfer between the electrode and the solution. Oxidation occurs on the anodes and reduction on cathodes. The indirect electron transfer reactions take place by using a redox species where the electrons transfer between the redox species and the solution.

Typical reactions occur in specially designed reactors that are either constructed as divided, undivided, or continuous flow cells. However there are some specialized cells that are made for specific purposes such as a flow-through cell, packed bed cell, fluidized-bed cell, Swiss-role cell, capillary gap cell, and recently new developments in reactor design have emerged by the construction of electrochemical micro-reactors. The reactors designs depend mainly on the electrode configuration where the shape, size or types of electrode are considered. For example, a commercial Retec cell contains 6 to 50 three-
dimensional cathodes made of flow-through metal sponge electrodes that are used mainly in the electroplating industry.\textsuperscript{17} Another example is the capillary gap cell that consists of circular disk electrodes with gaps between the each other used mainly for electro-organic synthesis.\textsuperscript{17}

Most of the electrochemical reactions studied take place either in a divided or an undivided cell. The divided cells have two compartments separated by a cell divider made usually from a porous or an ion-exchange membrane. This helps to prevent the two compartment’s solutions from mixing and to maintain the current flow (ionic) between them. The one compartment contains the anolyte (anodic reaction) and the catholyte (reduction reaction). The undivided cell on the other hand has both the oxidation and the reduction reactions occurring in one compartment without any separator. When considering a cell design, the undivided cell is less complex as it needs only one compartment when compared to the divided cell. However, reactions done in divided cell are usually better as they prevent the occurrence of side reactions which can take place on the counter electrodes and then interfere with the desire reaction process and product.\textsuperscript{15,19}

In recent years, many commercial chemical product reactions are done using electrochemical processes. There has also been an increase in related research which is due to the advantages over convectional industrial processes that are large volume organic solvent based or require large amount of thermal energy, that then impact on the cost of the production. The electrochemical processes have potential of removing or lessening some of these factors affecting the conventional processes especially in the field of electro-organic synthesis. The main advantage of this type of synthesis processes are that they have a wide range of oxidation and reduction reactions that require less energy and often minimize the production of by-products, when compared to the multi-step of conventional routes.\textsuperscript{15}
There are also a number of limitations in organic electrochemical processes such as the use of particular solvents to solubilise the reactants and products. Also the use of co-solvents is often needed to increase the solubility of the reactants where there is always a need for a supporting electrolyte to carry current in the reactions. The electrolytic cells also need stable components such as electrodes and separators which may have limited lifetimes and can affect economic viability.\textsuperscript{15}

Electrochemical process with its various advantages have been used for producing different materials with great success such as the famous and largest commercial electrochemical process known as the Monsanto Process which involves the production of adiponitrile from electrohydrodimerization of acrylonitrile and has an estimated total production worldwide of about 340 000 metric tons/year. The Table 1.3 show some of the commercial and pilot processes.\textsuperscript{15}
Table 1.3: Commercial and pilot processes using Electro-organic synthesis (2002).

<table>
<thead>
<tr>
<th>Starting material</th>
<th>Product</th>
<th>Status^a</th>
<th>Company</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acrylonitrile</td>
<td>Adiponitrile</td>
<td>C</td>
<td>Monsato (Solutia), BASF, Asahi Chemical</td>
</tr>
<tr>
<td>p-Methoxytoluene</td>
<td>p-Methoxybenzaldehyde</td>
<td>C</td>
<td>BASF</td>
</tr>
<tr>
<td>Glucose</td>
<td>Calcium Gluconate</td>
<td>C</td>
<td>Sandoz, India</td>
</tr>
<tr>
<td>Anthracene</td>
<td>Anthraquinone</td>
<td>C</td>
<td>L. B. Holliday, ECRC</td>
</tr>
<tr>
<td>Chlorosilanes</td>
<td>Polysilanes</td>
<td>C</td>
<td>Osaka Gas</td>
</tr>
<tr>
<td>Naphthalene</td>
<td>1-Acetoxynaphthalene</td>
<td>P</td>
<td>BASF</td>
</tr>
<tr>
<td>Cephalosporin C</td>
<td>Ceftibuten</td>
<td>P</td>
<td>Electrosynthesis Co., Schering Plough</td>
</tr>
<tr>
<td>Formaldehyde</td>
<td>Ethylene glycol</td>
<td>P</td>
<td>Electrosynthesis Co.</td>
</tr>
<tr>
<td>Acetone</td>
<td>Pinacol</td>
<td>P</td>
<td>BASF, Diamond Shamrock</td>
</tr>
<tr>
<td>Propylene</td>
<td>Propylene oxide</td>
<td>P</td>
<td>Kellog, Shell</td>
</tr>
</tbody>
</table>

^a: C = commercial, P = pilot.

1.2.2. Electrochemical oxidation and reduction of phenol

The summary mechanism of the electrochemical oxidation of phenol on an anode material and the reduction of its intermediates on a cathode in an acid medium is shown in (Fig 1.8 and 1.9) respectively.
Oxidation of phenol mechanism:

**Figure 1.8: Electrochemical Oxidation of Phenol**
During the anodic oxidation of phenol, it electro-generates a phenoxy radical by losing one electron. This phenoxy radical has three resonance structures which can exhibit its own chemical activity during the reaction. In the presence of water, hydroquinone and its isomer catechol are formed with the loss of one electron. These are further oxidised to form $p$-benzoquinone and $o$-benzoquinone with the loss of 2 electrons. Benzoquinone can further oxidised by ring opening to form aliphatic organic acids which can further decompose to carbon dioxide. This decomposition to carbon dioxide has been reported by A. Savall et al.\textsuperscript{4} to have two pathways, first one is via the stable organic acids, maleic acid or its isomer furmaric acid. The second pathway is via the relatively unstable acids such as (oxalic acid, formic acid, glyoxal and glyoxalic acid). Existing large amounts of phenoxy radicals during phenol oxidation allows the reaction to take another route where these phenoxy radicals can either react together or attack the phenol to form phenolic dimers which later form polymeric phenols.\textsuperscript{3,20,21,22}

Reduction mechanism:

\textbf{Figure 1.9: Electrochemical reduction of $o$-benzoquinone and $p$-benzoquinone.}
Both \( p \)-benzoquinone and \( o \)-benzoquinone when subjected to cathodic reduction, can readily reduce simultaneously to form hydroquinone and catechol respectively (Fig 1.9). This takes place by addition of 2 electrons and 2 hydrogen cations to \( p \)-benzoquinone and on the \( o \)-benzoquinone. 

1.2.3 Electrochemical micro-reactor

1.2.3.1. Micro-channelled reactor

The principles of electrochemical micro-reactors can be explained by the use of an interconnecting planar micro-channelled surface that is embedded between a working and a counter electrode. The reactants are introduced by pumping the solution into the micro-channels (channel diameter of 50-500 microns and channel lengths of 1-10 mm) that are engineered into one of the electrodes. The advantage of having micro-channels is that it provides small reaction volume with a high surface area for the interacting of the reactants with the working electrode.

Other advantages of such systems are the fact that there is a very small gap between working and auxiliary electrode allowing for reactions to be conducted with little or no electrolyte salts. Some of the limitations that are observed in using micro-reactors are the possibility of mixing of the oxidation and reduction products in an uncontrolled manner where possible products formed can be further converted to by products or reversed at the auxiliary electrode. Also, the presence of small particulates or the formation of precipitation products may end up blocking the micro-channels. Also, the current density distribution in the reactor should be uniform across the electrode surface combined with a uniform distribution of the electrolyte / reactant flow in the micro-channels.

1.2.3.2 Micro-flow process on porous electrodes

One way of eliminating the problem of the reactants and products being simultaneously exposed to both cathode and anode, is to design the micro-
reactor using a flow-through system where the two porous electrodes placed in series allowing for the reactant / products to be exposed to the respective electrodes sequentially as the supporting electrolyte moves through the cell. The micro-pores in the electrodes then act as micro-channels with a high surface area to volume ratio for the reactants to move through (Fig 1.10).

**FIGURE 1.10: CROSS-SECTION OF MICRO-FLOW PROCESS**

Some examples of such electrochemical flow-through reactors are the ceramic based electro-membrane (SnO$_2$-Sb anode) reactor used by V.M. Linkon *et al.*,\textsuperscript{21} a flow-through porous graphite anode by Abuzaid *et al.*,\textsuperscript{25} and the electrochemical flow-through reactor (SnO$_2$-Sb porous anode) by Henuset *et al.*,\textsuperscript{26} all for the oxidation of phenol in wastewater treatment.

### 1.3 Lead dioxide

Lead dioxide (PbO$_2$) is a brownish-black crystalline powder which exhibits two different crystallographic morphological forms of orthorhombic (α) and tetragonal (β). It is an electrically conductive material that is used as an electrode in lead-acid batteries and also in many processes of electrosynthesis.\textsuperscript{3,27} The material has many good characteristics ranging from its stability under aggressive conditions such as high anode potentials, strong acids, vigorous oxidizing agent and is relatively low cost material when compared to other electrode type materials such as Pt, Ni or stainless steel. PbO$_2$ can be produced chemically, or electrochemically.\textsuperscript{3,27,28}
Depending on the required morphology, it has been produced by starting with red lead (Pb₃O₄) which is oxidised in an alkaline slurry with chlorine to form the β-PbO₂. It can also be made by starting from lead tetra-acetate dissolved in acetic acid and water producing the β-PbO₂ form that precipitates out of solution.²⁷,²⁸ Different routes are applied depending on the application where for most electro-synthesis, the lead dioxide is produced by electro-deposition on another anode material such as lead, titanium, platinum or platinum-coated titanium. Lead is not normally used as a support for the anode material because it suffers from excessive corrosion when the lead dioxide is regenerated.³,²⁹

PbO₂ made by the electrochemical route is the most common one for its production in Pb-acid battery. In the lead–acid battery, PbO₂ is produced from a mixture of lead oxide and various lead sulphate phases that are converted in a sulphuric solution by a process known as formation. In a Pb-acid battery, the PbO₂ is the cathode and Pb, the anode immersed in a sulphuric acid solution. It has a cell potential of about 2 V / cell. The Pb-acid battery system was discovered by Planté in 1859, where he combined two lead strips dipped in sulphuric acid to produce electricity.³,²⁹,³⁰,³¹

The lead acid battery is versatile in its use when compared to other commercial batteries. It is cheaper to manufacture because it’s readily available raw material is fully recycled and relatively easy to produce. The battery can be made to various sizes for various applications with a long cycle life. It does have some limitations as it suffers from poor charge retention (shelf life) and limited energy density per battery mass.³¹

1.3.1 Chemistry of lead-acid battery
A completely charged lead-acid cell consists of a negative electrode made from sponge lead and a lead dioxide (PbO₂) as the positive electrode. The electrodes are immersed in a sulphuric acid solution of specific gravity that ranges between 1.25-1.28 (32-37% by weight). The two lead-acid battery electrodes have high
surface area and porosity depending on the formation conditions. The PbO$_2$ can have an average porosity of 40% to 60% with a surface area between 4 to 11 m$^2$.g$^{-1}$. The negative electrode can have an average porosity of 57% to 74% with a surface area between 0.5 to 0.9 m$^2$.g$^{-1}$. $^{32}$

The cell chemistry can undergo a reversible discharge / charge reaction, where the active material on both electrodes discharge to form lead sulphate and charge back to their respective forms. These characteristics include high reversible electrochemical reactions, low solubility of the active material in the aqueous solution and the high electronic conductivity of the major components. However, on both electrodes, the formation of an insulating product of lead sulphate is formed which can lead to a condition of irreversible sulphation. The discharge reaction mechanisms can be explained as follows. $^{28,30,31}$

At the positive electrode:

$$\text{PbO}_2 + 4\text{H}^+ + \text{SO}_4^{2-} + 2\text{e}^- \rightarrow \text{PbSO}_4 + 2\text{H}_2\text{O}$$  \hspace{1cm} (5)

At the negative electrode:

$$\text{Pb} + \text{SO}_4^{2-} \rightarrow \text{PbSO}_4 + 2\text{e}^-$$  \hspace{1cm} (6)

Overall discharge reaction:

$$\text{Pb} + \text{PbO}_2 + 2\text{H}_2\text{SO}_4 \rightarrow 2\text{PbSO}_4 + 2\text{H}_2\text{O}$$  \hspace{1cm} (7)

During the charging process, the cell voltage usually increases above the water gassing potential (ca. 2.39 V). Typical overcharge reactions in commercial cells result in the electrolysis of water to hydrogen and oxygen, corroding of the positive electrode grid and if any organic materials are present, they would undergo oxidation.

1.3.2 Manufacturing process of lead-acid battery electrodes

The production of lead dioxide electrodes for lead-acid battery can be done in different ways and forms, depending on the battery type and application. The most common are either as flat plates or tubular electrodes. The process is by
making a paste that will be electrochemically formed to the lead dioxide and lead respectively.  

**1.3.2.1 Preparation of β-PbO₂**  
**Paste and Curing:**  
The paste is made by mixing a low concentration acid (1.1 S.G) to a fine powder consisting of PbO and residual Pb. This paste is then applied to a Pb grid for flat plate types or filled into porous tubes for tubular types. Through the subsequent curing process, a number of mono-, tri- and sometime tetrabasic sulphates are formed as described below. The plates are placed in a high humidity curing chamber where the paste cures into a porous material that is made up primarily of tribasic lead sulphate (T3) and depending on the curing temperature, in some cases some tetrabasic lead sulphate (T4). Any free lead will be converted to lead oxide. The curing process also hardens the plate and usually takes two days to complete.

\[
PbO + H_2SO_4 \rightarrow PbSO_4  \]  
\[
PbSO_4 + 3PbO \rightarrow 3PbO . PbSO_4  \]  
\[
PbSO_4 + 4PbO \rightarrow 4PbO . PbSO_4  \]  
\[
2Pb + O_2 \rightarrow PbO  \]  
3PbO . PbSO_4 = Tribasic lead sulphate (T3)  
4PbO. PbSO_4 = Tetra-basic lead sulphate (T4)

The T4 phase is usually not favoured when compared to T3 because of its difficulty to convert to lead dioxide during the subsequent formation process.  

The cured electrodes can contain up to 50% of the mono- and tribasic lead sulphates that are then converted to PbO₂ through a formation process. However, since the initial lead sulphate phases present act as insulating material sometimes Pb₃O₄ (red lead) is added to aid the subsequent formation process.
A short pickling or soaking step is used to initiate the formation of PbO\textsubscript{2} seed crystals from the Pb\textsubscript{3}O\textsubscript{4}. This is usually done for the manufacturing of tubular electrodes.

\[ \text{Pb}_3\text{O}_4 + 2 \text{H}_2\text{SO}_4 \rightarrow 2 \text{PbSO}_4 + \text{PbO}_2 + 2\text{H}_2\text{O} \quad (18) \]

This process involves the submerging of the tubular plates filled with dry oxide mixture in a low-density sulphuric acid solution.\textsuperscript{28,31,33}

**Formation of Positive electrode:**

The formation process is preceded by a short acid soaking step that converts the mono- and tribasic sulphates to PbSO\textsubscript{4}. The formation process involves the oxidation of the PbSO\textsubscript{4} crystals to PbO\textsubscript{2} on the cathode and depending on the acid concentration, the formation of different ratios of the $\alpha$- and $\beta$-PbO\textsubscript{2} phases would change: \textsuperscript{28,35}

\[ \text{PbSO}_4 + 2\text{H}_2\text{O} \rightarrow \text{PbO}_2 + \text{H}_2\text{SO}_4 + 2\text{e}^- + 2\text{H}^+ \quad (19) \]

On the anode, the PbSO\textsubscript{4} would reduce to form sponge Pb:

\[ \text{PbSO}_4 + 2\text{e}^- \rightarrow \text{Pb} + \text{SO}_4^{2-} \quad (20) \]

**1.4 Objectives**

The aim of this study was to investigate the development of a continuous flow-through micro-porous PbO\textsubscript{2} / Pb electrochemical cell for the oxidation of phenol followed by the sequential reduction of its oxidation products. This was done by constructing an electrochemical cell containing both micro-porous PbO\textsubscript{2} as anode and Pb as cathode in series. The novelty of the study was to create the micro-porous PbO\textsubscript{2} electrode with a very high surface area which was developed from the Pb-acid battery principles. By then using the continuous flow of an electrolyte solution containing dissolved phenol through the two electrodes, the
effective formation of desirable products of hydroquinone and catechol would be investigated in terms of flow rates, cell design and phenol concentrations.
Chapter 2

2. Experimental

2.1 Cyclic Voltammetry (CV)
CV studies were done on a BAS CV50 cyclic voltammetry system. A personal computer running CV50 software was used for both instrumental control and data acquisition. The electrochemical cell was equipped with lead and lead dioxide as working electrodes, a platinum wire as auxiliary electrode and Hg/Hg$_2$SO$_4$ (sat K$_2$SO$_4$) reference electrode. The potential of the working electrode was scanned over potential ranges permitted by the working electrode. The scan rates used ranged from 5-100 mV.s$^{-1}$ and sensitivities were carried as needed according to the sample concentrations and scan rate. The same solvent/supporting electrolyte system used for the reactions was used for as the analysis medium.

2.2 Electrode Preparation and cell construction

2.2.1 Pickling, curing and formation of lead dioxide electrodes
The preparation of lead dioxide was carried in three steps. Firstly tubular electrode holder was prepared consisting of two lead strips as current collectors in a tubular polypropylene mesh (40 mm length and 20 mm diameter). The electrode holder was then filled with a homogeneous mixture of lead oxide (80%) and red lead (20%) until an approximate density of 4 g.cm$^{-3}$ of the material was achieved. The packed electrode was then placed into a solution of 1.1 SG sulphuric acid for an hour, for the pickling process. After pickling, the electrode was then removed and sparingly washed with de-ionised water. This was followed with a curing step by placing it into a high humidity chamber at 50 ºC for an hour. This was followed by leaving it at room temperature for 24 hours before further use. After curing, formation was done by soaking the cured electrode in a sulphuric acid solution of 1.24 SG for an hour. The formation process was done by connecting to a DC power supply with a constant current of about 1 A and
took between 5-7 days to complete the conversion of lead sulphate to lead dioxide. The material was then characterised using powder X-ray diffraction for its phase composition, BET surface area by nitrogen adsorption and Hg porosimetry pore size distribution.

2.2.2 Continuous electrochemical micro-flow cell
The experimental apparatus consisted of the following (Fig 2.1) and laboratory set-up of the electrochemical reactor system (Fig 2.2):

- A tubular polypropylene reactor inserted with (approximately 40 mm in height and 20 mm diameter) tubular micro-porous lead dioxide electrode as an anode and a micro-porous lead electrode (1 mm thick and 20 mm diameter) as a cathode in series.
- Hg/Hg₂SO₄ (sat K₂SO₄) reference electrode fitted in between the lead dioxide and lead electrodes.
- An inlet port and metering pump for the liquid solution feed.
- A product port for the solution containing the product from which regular samples are taken for further analysis by HPLC.
- A DC power (P) supply where a constant potential was applied across the anode and cathode electrodes.
- An ammeter (A) to monitor the current flow across the cell.
- A voltmeter (V1) to monitor the cell voltage and a voltmeter (V2) to monitor the potential across the lead dioxide electrode versus the reference electrode.
**Figure 2.1:** Experimental apparatus flow diagram

**Figure 2.2:** Laboratory set-up of the electrochemical reactor system.
The phenol solution was pumped through the reactor by using a higher pressure liquid chromatography (HPLC) pump set at various low flow rates. At regular intervals, samples from the product stream were collected in sample vials, which were then further prepared for HPLC analysis.

### 2.3 Analytical techniques

Several analytical procedures were used for the analysis of the electrode materials and of the starting, intermediates and products of the main aqueous solutions.

#### 2.3.1 High Pressure Liquid Chromatography (HPLC)

HPLC analysis were carried out on a Hewlett Packard 1100 series HPLC chromatograph with a dual pump system, equipped with a variable UV-Vis detector and an auto sampler unit. Data analysis was done with HP Chemstation for LC software (version A.06.03). All solvents were HPLC grade and were degassed prior to analysis with a Millipore vacuum-degassed unit. A 3.9 x 300 mm Waters Bondpak C\textsubscript{18} (serial no. WAT027324) column fitted with a Supelco Discovery C\textsubscript{18} guard column was used for the analysis of reaction samples.

An external calibration method was done in order to quantify starting materials and final products in the study. An aliquot sample of 0.5 cm\textsuperscript{3} was taken and diluted with 2 cm\textsuperscript{3} of methanol before HPLC analysis.
**TABLE 2.1: HPLC CONDITIONS**

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Specification</th>
</tr>
</thead>
<tbody>
<tr>
<td>Injector Volume</td>
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</tr>
<tr>
<td>Column</td>
<td>µBondpack C\textsubscript{18} 3.9 x 300 mm (Waters)</td>
</tr>
<tr>
<td>Wavelength</td>
<td>280 nm</td>
</tr>
<tr>
<td>Initial flow rate</td>
<td>0.8 cm\textsuperscript{3}.min\textsuperscript{-1}</td>
</tr>
<tr>
<td>Final flow rate</td>
<td>1.0 cm\textsuperscript{3}.min\textsuperscript{-1}</td>
</tr>
<tr>
<td>Initial mobile phase ratio</td>
<td>20% methanol : 80% water buffered to pH3 by phosphoric acid.</td>
</tr>
<tr>
<td>Final mobile phase ratio</td>
<td>30% methanol : 70% water buffered to pH3 by phosphoric acid.</td>
</tr>
</tbody>
</table>

**2.3.2 Gas Liquid Chromatography-Mass Spectrometry (GC-MS)**

Selected samples were analyzed by GC-MS in order to qualify some unknown products formed during the electrochemical reaction. The GC-MS analysis carried out on a Thermo-Finnigan Trace GC coupled to Quadrople Trace MS plus detector. Separation of the analytes was achieved with the aid of a Restek-RTX 5 MS column (15 m x 0.25 mm i.d.). Helium was used the carrier gas, with the flow rate of 40 cm\textsuperscript{3}.min\textsuperscript{-1}.

**TABLE 2.2: GC-MS ANALYSIS CONDITIONS**

<table>
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<th>Parameter</th>
<th>Specification</th>
</tr>
</thead>
<tbody>
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<td>Initial column temperature</td>
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</tr>
<tr>
<td>Initial column hold time</td>
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</tr>
<tr>
<td>Heating rate</td>
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</tr>
<tr>
<td>Final column temperature</td>
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<tr>
<td>Final Column hold time</td>
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</tr>
<tr>
<td>Injector temperature</td>
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</tr>
<tr>
<td>Detector temperature</td>
<td>300 °C</td>
</tr>
<tr>
<td>Detector solvent delay</td>
<td>2 min</td>
</tr>
</tbody>
</table>
2.3.3 Powder X-Ray Diffraction (PXRD)
PXRD analysis of the electrode material was done on a Brucker D8 Advanced powder diffractometer. The diffractograms were scanned from 5º to 60º 2θ at 0.02 increments with 1 second per increment. Standard Bruker search and match software were used to identify the phases using the ICDD PDF2 data base. 35

2.3.4 BET surface area and porosity analysis
A standard 5 point BET surface area analysis was done by nitrogen adsorption on a Micromeretics Gemini III 2375. Samples were degassed with N₂ gas at 140 °C for 4hrs before analysis. Hg porosimetry was done on a Micromeretics Autopore II 9215.

2.4 Electrochemical oxidation of phenol
2.4.1 Reactions conditions
After evaluating the CV results of various acetonitrile / water solutions containing the phenol, a mixture of 60 / 40 acetonitrile / water solution was used for all subsequent experiments. Different phenol solutions concentrations (25 mM; 50 mM; 100 mM) were pumped at different flow-rates (0.5; 1; 2) cm³.min⁻¹. At different time intervals, a volume of 40 cm³ of the liquid product from the reactor was collected for analysis.

2.4.2 Sample preparation
Some samples were further analyzed by GC-MS. The rest of the liquid product was then placed into a separating funnel for extraction twice with 50 cm³ of ethylacetate and the organic phase was separated. The organic phase was then neutralised with a sodium bicarbonate salt. Then neutralised organic phased was washed twice with 50 cm³ of water to remove salts formed. The neutralised organic phase was the dried with anhydrous magnesium sulphate. The dried organic phase liquid sample was taken for GC-MS analysis.
3.1 Cyclic Voltammetry (CV)

3.1.1 Lead electrode CV

The investigation of cyclic voltammetric studies were done to establish the influence of the reaction medium (supporting electrolyte: acetonitrile and aqueous sulphuric acid) with the phenol and its reaction products during the oxidation and reduction on the working electrodes. A pure lead electrode was used as working electrode vs Hg/Hg$_2$SO$_4$ (sat K$_2$SO$_4$) as the reference electrode.

**Figure 3.1:** CYCLIC VOLTAMMOGRAM: SULPHURIC ACID ONLY

(reaction medium: 3% v/v sulphuric acid, 37% v/v water) on Pb working electrode vs Hg/Hg$_2$SO$_4$ reference electrode.

During the anodic sweep, a first peak appeared at -900 mV vs Hg/Hg$_2$SO$_4$ due to the oxidation of Pb to PbSO$_4$. Later the peak of oxygen evolution from water splitting was observed over 1400 mV vs Hg/Hg$_2$SO$_4$. On the reverse sweep, i.e.
cathodic sweep, a peak of PbO$_2$ reducing to PbSO$_4$, appeared at 900 mV vs Hg/Hg$_2$SO$_4$. Lastly the reduction peak of PbSO$_4$ to Pb, appeared at -1000 mV vs Hg/Hg$_2$SO$_4$.

**Figure 3.2:** Cyclic voltammograms: Supporting electrolyte solution (reaction medium: 3% v/v sulphuric acid, 37% v/v water and 60% acetonitrile) on Pb working electrode vs Hg/Hg$_2$SO$_4$ reference electrode.

Fig 3.3 shows the anodic and cathode sweeps with the addition of various amounts of acetonitrile to the electrolyte solution. Similar to the previous results, the oxidation and reduction peaks of Pb and PbO$_2$ were clearly visible with a noticeable positive shift in the reduction peak PbO$_2$ to PbSO$_4$. Also, a slight positive increase in the oxygen overpotential was observed. In all the oxidation and reduction peaks, it shows a decrease in peak height (current) from lower concentration to higher concentrations of acetonitrile. Both the oxidation and reduction peaks showed a gradually decrease as the supporting electrolyte concentration increased.
**Figure 3.3:** *Cyclic voltammograms: supporting electrolyte solutions* [three different reaction mediums: 3% sulphuric acid constant; 37% water constant; acetonitrile 10%, 30% and 60%] on Pb working electrode vs Hg/Hg\(_2\)SO\(_4\) reference electrode.

In the presence of phenol (Fig 3.4) without any acetonitrile, the anodic sweep showed the typical first peak of oxidation of Pb to PbSO\(_4\) at 900 mV. However, the typical phenol oxidation peak was not observed and might be overshadowed by the high intensity of the oxygen evolution peak. There was also no change in oxygen evolution at above 1400 mV vs Hg/Hg\(_2\)SO\(_4\). On the cathodic return sweep, the reduction peak of PbO\(_2\) to PbSO\(_4\) at 900 mV was not observed. This might be due to that PbO\(_2\) formed on the anodic sweep underwent passivation in the presence of phenol to form polyphenols.\(^3\)\(^,\)\(^36\) However, at further negative potentials, the typical reduction of PbSO\(_4\) to Pb peak was again observed at -1000 mV. This shows that the presence of phenol only in a sulphuric acid electrolyte, does not influence the oxidation and reduction of Pb and PbSO\(_4\), but does influence the respective oxidation and reduction of the PbO\(_2\) electrode.
**Figure 3.4: Cyclic Voltammograms: Phenol**

(reaction medium: 3% v/v sulphuric acid in water with 50 mM phenol) on Pb working electrode vs Hg/Hg$_2$SO$_4$ reference electrode.

Fig 3.5 and 3.6 shows the cyclic voltammetric results with the addition of benzoquinone and hydroquinone respectively.
In the presence of benzoquinone; the anodic sweep showed no influence on the oxidation and reduction of the compound on the Pb in the reaction medium as shown in (Fig 3.5). The oxidation of Pb to PbSO₄ appeared at the same potential of -900 mV and also oxygen evolution around 1400 mV. On the cathodic sweep, the reduction peak of PbO₂ to PbSO₄ was still clearly there, showing that the benzoquinone does not influence the cathode reduction and oxidation. Noticeably, the reduction peak of the PbSO₄ to Pb, was relatively broad which would be due to the reduction to hydroquinone.

**FIGURE 3.5: CYCLIC VOLTAMMOGRAMS: BENZOQUINONE**

(reaction medium: 3% v/v sulphuric acid in water with 50 mM benzoquinone) on Pb working electrode vs Hg/Hg₂SO₄ reference electrode.
**Figure 3.6:** Cyclic Voltammograms: Hydroquinone
(reaction medium: 3% v/v sulphuric acid in water with 50 mM hydroquinone) on Pb working electrode vs Hg/Hg\(_2\)SO\(_4\) reference electrode.

In the presence of hydroquinone, almost the same trend was observed as with benzoquinone with a slightly lower reduction peak of the PbSO\(_4\) to Pb near -1200 mV.

### 3.1.2 Lead dioxide electrode CV
The following investigation of cyclic voltammetric studies were done to establish the influence of the reaction medium (supporting electrolyte: acetonitrile and sulphuric acid) with the phenol and its products during reaction on the lead dioxide electrode only. This was done in order to confirm the trend observed in literature that indicated possible passivation effects of the phenol on the lead oxide surface and how to overcome it.\(^\text{3,36,37}\)
**Figure 3.7:** Cyclic voltammograms: Sulphuric acid only

(reaction medium: 3% v/v sulphuric acid in water) on PbO₂ working electrode vs Hg/Hg₂SO₄ reference electrode.

The lead dioxide electrode in the presence of water with sulphuric acid, during the anodic sweep showed a broad peak of PbSO₄ to PbO₂ at 1600 mV vs Hg/Hg₂SO₄. This is due to some passivation of lead dioxide electrode in the solution before the start of cyclic sweep. Oxygen evolution peak was observed at 1800 mV. On the reverse sweep, there was a well defined PbO₂ to PbSO₄ peak appeared at 1250 mV.
The investigation of different concentrations of the supporting electrolyte showed that the higher acetonitrile shifted both the oxidation and reduction peaks more negatively.
The addition of the phenol to the aqueous H₂SO₄ solution only showed Oxygen evolution peak that was observed at 1800 mV (Fig 3.9). There were peaks, PbSO₄ to PbO₂ at 1600 mV from cathodic sweep and PbO₂ to PbSO₄ at 1250 mV from the reversed sweep were not observed as the case of no phenol presence (Fig 3.7). The results show the typical complete passivation effect of the phenol only on the surface of the working lead dioxide electrode. This is due to the formation of polyphenols that deposit on the surface of the electrode preventing further reactions to take place.³⁶,³⁷ When adding the phenol to the acetonitrile mixtures, the following results were observed (Fig 3.10).
**Figure 3.10:** Cyclic voltammograms: Phenol concentrations in different acetonitrile solutions

[reaction medium for solutions: (3% v/v sulphuric acid in water with acetonitrile at 10%, 30% and 60%) and 50 mM phenol on PbO₂ working electrode vs Hg/Hg₂SO₄ reference electrode.]

The anodic sweep showed the oxidation peak of PbSO₄ to PbO₂ to increase slightly with the increase in acetonitrile concentration. Similarly, the reduction peak showed the typical reverse reaction with small peaks showing typical reduction to PbSO₄. This indicates that the phenol does not form a complete passivation layer on the surface allowing for both oxidation and reduction reactions to take place. The phenol oxidation is not clearly observed due to the high intensity of the oxygen evolution overshadowing the phenol oxidation peak. The solution concentration of 60% acetonitrile was subsequently decided on as the suitable solution for all subsequent experiments in the microflow reactor.
3.2 Physical Characteristics of the electrodes

(Fig 3.11) shown the schematical sketch of the micro flow-through electrochemical cell. The cross-sectional outline of the positive electrode is shown in (Fig 3.11) where suitable strips of Pb grid were used as current collectors. Sections from a standard 5 mm thick pasted plate was used in typical manufacturing of negative flat plate industrial Pb-acid batteries for the formation of the sponge Pb negative electrode.

FIGURE 3.11: A meshed polypropylene cylinder filled with porous PbO$_2$ and Pb disc shaped current collectors.

The cylindrical formed PbO$_2$ anode was then further assembled into a larger solid polypropylene cell ensuring that the Pb current collectors protruded sufficiently for connecting to an external power supply and potentiostat. Care was taken to ensure that no electrolyte would be able to flow around the outer edges of the cell assembly and be kept within the length of the porous active material.

Similarly, two of the 5 mm thick sections of the porous sponge Pb as cathode were moulded in series with the anode into the cylindrical polypropylene cell housing allowing sufficient sections of the current collector to protrude for connections to a potentiostat. The typical flow diagram of the cell is shown in
(Fig 2.1) where the cell is connected in series with a suitable HPLC pump that allows for careful flow control of the solutions containing the starting material. A sampling outlet and an Hg/Hg₂SO₄ reference electrode were inserted in the section between the two electrodes. The sampling outlet was used occasionally during the experiment to determine the intermediate products formed between the two electrodes and the reference electrode was used to control the applied potential versus the working electrode.

The BET surface area determined for the lead dioxide formed electrode was 2.708 m².g⁻¹. The micro pore volume distribution determined by Hg porosimetry is shown in (Fig 3.12). The porosity was 51.57% with an average pore diameter 0.1770 µm. The apparent and bulk densities as determined by Hg porosity were 7.236 g.cm⁻³ and 3.505 g.cm⁻³ respectively. The intrusion volume determined for the cathode material was 0.1471 cm³.g⁻¹.

**Figure 3.12:** Micro pore volume distribution determined by Hg porosimetry.
The surface area to volume ratio (SA:V) is an important parameter of solid materials that are used in chemical reactions. It is a parameter commonly used in micro-reactor systems and an indication of the possible rate at which a reaction can proceed. Typical micro-reactors are reported to have a ratio of 100 to 200 cm$^{-1}$ when compared to a conventional batch type reaction in a 100 cm$^3$ flask would have a ratio of 0.06 to 1 cm$^{-1}$. 39

The main advantages of microreactor systems are primarily with regards to temperature control of highly exothermic systems and effective mixing. In this particular system under study, heat transfer is not a problem, but there is a need for good mixing and effective contact of the reagent (in this case phenol) with the electrode surface to allow for the electro-reaction to take place.

Considering the surface area determined by BET analysis and the porosity as determined by Hg porosimetry, the following calculations for a SA:V can be made that will show a very high ratio. One can consider a cylindrical electrode (2 cm diameter by 4 cm) with a volume of approximately 12.57 cm$^3$ and an active mass of 39.55 g (excluding the current collectors). With a porosity of 51.57%, the SA:V for the cathode material would be 184 092 cm$^{-1}$. One could also consider the intrusion volume that was determined by Hg porosimetry of 0.1471 cm$^3$.g$^{-1}$ and the BET surface area, then a SA:V of 165 269 cm$^{-1}$ would be calculated. Either way, this shows that the two methods of calculating the effective SA:V results in values that are similar in magnitude and by a significant order of magnitude larger than conventional micro-flow systems. This large ratio is due to the three directional porous structure of the active material acting as effective sites for electro reactivity to take place.

The following powder X-ray diffraction patterns in (Fig 3.13 and 3.14) showed that the both the cathode and anode material were effectively converted to the correct phases during the formation process.
**Figure 3.13:** Lead cathode (Pb) powder X-ray diffraction pattern.

**Figure 3.14:** Lead dioxide anode (PbO$_2$) powder X-ray diffraction pattern.
The results showed that the predominant phase in the cathode material was $\beta$-PbO$_2$ with some $\alpha$-PbO$_2$. The anode material was predominantly Pb with some unconverted PbSO$_4$. This small amount of PbSO$_4$ would not be a problem during the cell operation, since it could easily convert to the Pb phase during the applied charge process. The PbO observed in the diffraction pattern comes from the reactive pure Pb being exposed to air during drying of the sample for the analysis.

3.3 Electrochemical oxidation of phenol

The initial stage of the study was to investigate the performance of the micro reactor in terms of converting the phenol found in a solution of a certain concentration in one continuous flow over a certain time period of about 500 minutes. In these initial investigations variables such as reactor configuration, applied potential and current, phenol concentrations of the flow stream, and supporting electrolyte concentration were considered at a constant flow rate of 0.5 cm$^3$.min$^{-1}$. This was equivalent to about 250 cm$^3$ of total product stream having flowed through the electrochemical micro reactor. The flow rate was kept constant at a relatively low rate and variation in the other parameters only. This was done in order to ensure that there was enough reaction time for the phenol in the flow stream to react with the “porous” electrodes and to allow for sufficient sampling time at various intervals to be done on the HPLC instrument. In this initial study, only approximate quantities of the primary products of hydroquinone (HQ), benzoquinone (BQ), catechol (CAT) and the remaining unreacted phenol that were in the flow through stream are reported relative to the initial amount of phenol in the starting solution. It was of interest to observe if the complete conversion of the phenol could be achieved and maintained in a continuous flowing product stream through the micro reactor cell, under certain conditions. The other minor products that were observed in the final product stream by HPLC are grouped together as OTHERS and will be discussed in more detail at a later stage.
3.3.1 Reactor stability

In this study, two reactors were constructed and its ability to ensure that the product stream flowed effectively through the porous PbO$_2$ anode was investigated. A second reactor unit had to be built after a number of problems occurred after the first set of studies. By considering a number of parameters, it was not possible to obtain complete conversion of the phenol that came out of the reactor unit (Table 3.1). The concentration of the phenol in the solution before entering the reactor was 50 mM and the % remaining (mM/mM) was calculated by considering the amount of phenol in the final product flow through stream that came out of the reactor after 80 minutes (40 cm$^3$ of total reaction product), of which, 0.5 cm$^3$ of this sample was taken for HPLC analysis. The % (mM/mM) of the phenol was determined from a suitable calibration graph which will be discussed later. The other main products were similarly determined from a suitable calibration graph which will be discussed later.

The results for the first reactor were poor, and it was assumed that the problem might have been in the reactor assembly, where some of the solution could have been moving around the outer sections of the porous cathode cell without actually having had the opportunity to react in the micro porous channels within the PbO$_2$ active material. The second reactor that was assembled was done by ensuring proper sealing of the outer sections of both the electrodes, thereby forcing the product flow stream to go through the bulk microporous active material. This reactor did show better conversion of the phenol, where the final product stream that was collected after about 80 minutes of continuously flowing through the reactor indicated that almost no phenol remained when compared to the phenol in the starting solution (Table 3.1).
**TABLE 3.1:** Comparison of the phenol remaining in a product stream that had flowed through the reactor for 80 minutes. The other products indicated are approximate values.

<table>
<thead>
<tr>
<th>Reactor No.</th>
<th>HQ (%mM/mM)</th>
<th>BQ (%mM/mM)</th>
<th>CAT (%mM/mM)</th>
<th>Others (%mM/mM)</th>
<th>Phenol (%mM/mM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>~37</td>
<td>0</td>
<td>~5</td>
<td>~39</td>
<td>~9.1</td>
</tr>
<tr>
<td>2</td>
<td>~65</td>
<td>0</td>
<td>~5</td>
<td>~30</td>
<td>0.0</td>
</tr>
</tbody>
</table>

The stability of converting the phenol in the solution mixture on a continuous basis as it flows through the “micro reactor” over a longer period of time was done by taking samples of 40 cm$^3$ of the product stream at regular time intervals and determining the amount of phenol remaining (Fig 3.15). An amount of 0.5 cm$^3$ of the product sample would then be taken for HPLC analysis and be an average representation of the amount of phenol that was collected in the 80 minute intervals. The applied cell potential (3.2 V), flow rate (0.5 cm$^3$.min$^{-1}$) and initial phenol concentration in a 60 / 40 acetonitrile solution were kept constant for the duration of the experiment.
The results showed that with time, most of the phenol in the solution being pumped through the electrochemical porous micro-reactor reacted as the solution continuously flowed through the reactor design 2. The amount of unreacted phenol in the product stream started to increase slightly after 250 minutes where, after 500 minutes (total flow through volume of 240 cm$^3$) the phenol in the sample taken was less than 10%. Note, that the concentration reported is that of the 0.5 cm$^3$ sample from a 40 cm$^3$ sample taken at that specific time and not of the total product obtained up to that point. This slight drop in the phenol conversion could be due to some loss in cell integrity with time, where some “pathways” through the cells become sulphated causing the formation of so-called dead spots to occur within the three dimensional porous cell matrix. By comparison, the phenol that remained in the product stream from reactor 1...
showed significant lack of phenol conversion over the 500 minutes of continuous product flow.

This observed decrease in reactor activity can be reversed by “flushing” the reactor on a continuous basis for about 2 to 4 hrs with a 3% sulphuric acid water solution. Simultaneously, a sufficiently high voltage (above 2.7 V) is applied to convert the sulphated areas of the anode and cathode micro reactor back to their respective active material. This is similar to the charging step taken in a lead acid battery where the corresponding electrodes are converted back to their starting product, with excess energy usually used to electrolyse water. For all subsequent studies, only reactor 2 was used, and it was always “charged” and “flushed” with a 3% sulphuric acid solution before commencing to the next set of experiments.

3.3.2 Varying Applied Potential
The following study was done to investigate the effect of varying the applied cell potential on the conversion of the phenol. It must be remembered, that if a too high applied cell potential is used, water electrolysis will dominate the reactions at the electrodes, reducing the efficiency and increasing the “gassing” of products in the process. In addition, higher applied potential would favour the conversion of phenol to organic acids and the final decomposition product of CO₂ (Fig 1.8). The initial results after 80 minutes of reaction time are shown in Table 3.2 and over a 500 minute continuous reaction time in (Fig 3.16).

**Table 3.2:** Determining the effect of applied potential in phenol conversion.

<table>
<thead>
<tr>
<th>Potential</th>
<th>HQ</th>
<th>BQ</th>
<th>CAT</th>
<th>Others</th>
<th>Phenol</th>
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</thead>
<tbody>
<tr>
<td>2.8</td>
<td>~14</td>
<td>~23</td>
<td>~4</td>
<td>~43.6</td>
<td>~15.4</td>
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<tr>
<td>3.0</td>
<td>~68</td>
<td>0</td>
<td>~6</td>
<td>~21.2</td>
<td>~4.8</td>
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<tr>
<td>3.2</td>
<td>~65</td>
<td>0</td>
<td>~5</td>
<td>~30</td>
<td>0</td>
</tr>
<tr>
<td>3.4</td>
<td>~53</td>
<td>0</td>
<td>~5</td>
<td>~39</td>
<td>~3.1</td>
</tr>
</tbody>
</table>
The results show that the phenol remaining in the continuous flow through solution mixture indicated a decrease from almost 15% to 0% as the cell potential increased from 2.8 V to 3.2 V and a slight increase to about 3% at the higher cell potential of 3.4 V. (Fig 3.16) also shows that there was a considerable increase in phenol remaining in the continuous flow through solution mixture at the lower cell potentials over time. Some reasons for the increase in phenol in the product stream could be due to gassing, PbO$_2$ electrode deactivation forming PbSO$_4$ due to sulphation or just deactivation from absorbed polyphenols, and experimental error.

**FIGURE 3.16:** Determining the effect of applied potential in phenol conversion.

This increase in the phenol remaining at the lower potential may be due to deactivation of lead dioxide electrode to lead sulphate. It must be remembered that the oxidation of the phenol to benzoquinone at the electrode surface results in a reduction of the electrically conductive PbO$_2$ to an insulating PbSO$_4$. By
maintaining a certain applied potential across the cell, the PbSO$_4$ is converted back to the active PbO$_2$. If a suitable potential and accompanying current is set to flow through the electrochemical cell, eventually equilibrium is reached between the reduction of the PbO$_2$ and the accompanying oxidation of phenol and the subsequent oxidation of PbSO$_4$. Note, that the reactions at the Pb counter electrode at the other end of the cell are exactly the opposite, where the Pb is oxidized to PbSO$_4$ and the benzoquinone formed in between the two electrodes as the solution flows through, is reduced to hydroquinone, catechol and other products (Fig 1.8). Hence, a suitable higher applied potential is required in order to ensure that the electrodes active material are converted back to their initial starting material and to ensure that limited sulphation would occur on the surface of the electrode surface and pores. Sulphation in terms of lead acid batteries is described as the process where the PbSO$_4$ crystals that form on both electrodes become so large that they cannot convert back to their starting material and end up blocking the porous structure of the active material.

### 3.3.3 Phenol concentration

The aim of the next set of experiments was to see if it was possible by using the existing cell configuration to increase the phenol concentration of the starting solution thereby optimizing the product formation in terms of solution concentration. The results are shown in Table 3.3 and (Fig 3.17) respectively.

**Table 3.3: Determining the effect of phenol concentration in phenol conversion.**

<table>
<thead>
<tr>
<th>PhOH</th>
<th>HQ</th>
<th>BQ</th>
<th>CAT</th>
<th>Others</th>
<th>Phenol</th>
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<tbody>
<tr>
<td>mM</td>
<td>%(mM/mM)</td>
<td>%(mM/mM)</td>
<td>%(mM/mM)</td>
<td>%(mM/mM)</td>
<td>%(mM/mM)</td>
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<tr>
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<td>~33</td>
<td>~38</td>
<td>~6</td>
<td>~17.8</td>
<td>~5.2</td>
</tr>
<tr>
<td>25</td>
<td>~32</td>
<td>~33</td>
<td>~7</td>
<td>~21</td>
<td>~6.8</td>
</tr>
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<td>50</td>
<td>~65</td>
<td>0</td>
<td>~5</td>
<td>~30</td>
<td>0</td>
</tr>
<tr>
<td>100</td>
<td>~19</td>
<td>~21</td>
<td>~3</td>
<td>~32.6</td>
<td>~24.4</td>
</tr>
</tbody>
</table>
The various phenol concentrations were 10, 25, 50 and 100 mM respectively in 60% acetonitrile concentration, 3% sulphuric acid and 37% water. The other cell setting was 3.2 V with 0.5 cm$^3$.min$^{-1}$ flow rate. Analysis of the solution product within the first 80 minutes showed that the phenol remaining in the continuous flow through solution mixture for the 10, 20 and 50 mM solutions were relatively similar between 7 to 0%. However, an increase of 15% phenol was observed for the 100 mM solution. The increase in phenol of the higher concentrated solution was more prominent with time where an amount of about 60% of phenol remained after 500 minutes. The lower concentrated solutions showed relatively similar phenol conversion after 500 minutes which all showed to be less than 20% of phenol remaining.

**Figure 3.17:** Determining the effect of phenol concentration in phenol conversion.
At a flow rate of 0.5 cm$^3$.min$^{-1}$, a total solution volume of 240 cm$^3$ passed through the reactor. At a concentration of 50 mM an amount of 12 mmol or 1129.3 mg of phenol were converted within approximately 8.3 hrs.

### 3.3.4 Co-solvent concentration

In part, the effect of the acetonitrile concentration (10, 30 and 60%) on the phenol conversion was already studied by cyclic voltametry (CV) in Chapter 3.1.2 (Table 3.4). The influence of the acetonitrile solution concentration over time is shown in (Fig 3.18). The applied potential was 3.2 V with a flow rate of 0.5 cm$^3$.min$^{-1}$ and a phenol concentration of 50 mM phenol. The sulphuric acid concentration was kept at 3%.

#### TABLE 3.4: Determining the Effect of Co-solvent Concentration in Phenol Conversion.

<table>
<thead>
<tr>
<th>Acetonitrile</th>
<th>HQ (mM/mM)</th>
<th>BQ (mM/mM)</th>
<th>CAT (mM/mM)</th>
<th>Others (mM/mM)</th>
<th>Phenol (mM/mM)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10% (v/v)</td>
<td>~26</td>
<td>~5</td>
<td>~2</td>
<td>~38</td>
<td>~29.4</td>
</tr>
<tr>
<td>30% (v/v)</td>
<td>~42</td>
<td>~7</td>
<td>~4</td>
<td>~35</td>
<td>~12.2</td>
</tr>
<tr>
<td>60% (v/v)</td>
<td>~65</td>
<td>0</td>
<td>~5</td>
<td>~30</td>
<td>0</td>
</tr>
</tbody>
</table>

The results supported the previous CV studies in that the higher acetonitrile concentration supports phenol conversion. After 80 minutes, the phenol remaining in a continuous flow through solution mixture in the 10% acetonitrile was 29%, which increased to 55% over 500 minutes (Fig 3.18). This can be largely ascribed to the formation of polyphenols where the acetonitrile effectively reduces this phenomenon, and it is known that using acetonitrile as a co-solvent reduces tar formation on the catalyst or electrode by dissolving those materials that are not soluble in water.  

Note, that after each experiment, where possible polyphenols or excessive sulphation was formed during the reaction, regeneration of the electrodes and cell was done by flushing the cell with a 3% sulphuric acid water solution over 2.7
V for 2 to 4 hrs. This would effectively remove the passivation layer and regenerate the active material back to its starting material of PbO$_2$ and Pb on the cathode and anode respectively.

![Graph showing the effect of co-solvent concentration in phenol conversion](image)

**Figure 3.18**: Determining the effect of co-solvent concentration in phenol conversion.

3.3.5 Support electrolyte concentration

In order to show the effect of increasing the sulphuric acid concentration on the conversion of the phenol, the acid concentration was increased from 3 to 6%. The results are shown in Table 3.5 and (Fig 3.19) respectively. The acid concentration influences the conductivity of the solution, but would also increase the sulphate concentration.
**TABLE 3.5: Determining the effect of support electrolyte concentration in phenol conversion.**

<table>
<thead>
<tr>
<th></th>
<th>H$_2$SO$_4$</th>
<th>HQ</th>
<th>BQ</th>
<th>CAT</th>
<th>Others</th>
<th>Phenol</th>
</tr>
</thead>
<tbody>
<tr>
<td>% (v/v)</td>
<td>% (mM/mM)</td>
<td>% (mM/mM)</td>
<td>% (mM/mM)</td>
<td>% (mM/mM)</td>
<td>% (mM/mM)</td>
<td></td>
</tr>
<tr>
<td>3.0</td>
<td>~65</td>
<td>0</td>
<td>~5</td>
<td>~30</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>6.0</td>
<td>~36</td>
<td>~21</td>
<td>~6</td>
<td>~9</td>
<td>~27.8</td>
<td></td>
</tr>
</tbody>
</table>

The results show that the increase in the sulphuric acid concentration detrimentally influences the conversion of the phenol. This is primarily due to the possible formation of more PbSO$_4$ at the electrodes active sites. In order to alleviate this problem, one would have to increase the cell potential. However, this would subsequently increase the water electrolysis and the formation of organic acids and CO$_2$.\textsuperscript{3,41} Within the present experimental conditions, there would not be a problem with the conductivity of the electrolyte solutions, since the currents were always relatively small. However, if such a system was considered to be scaled up to accommodate larger volumes and concentrations, one might have to reconsider the optimal acid concentration.
In order to show the stability of electrical parameters of the reactor configuration with time, the variation in the current flowing through the cell was studied by connecting an ammeter in series between the anode and cathode. The applied potential between the anode and cathode was 3.2 V with a 60% acetonitrile solution containing 50 mM phenol solution at a flow rate of 0.5 cm$^3$.min$^{-1}$ and an acid concentration of 3%. The results are summarized in figure 3.20 and 3.21.

**FIGURE 3.19:** Determining the effect of support electrolyte concentration in phenol conversion.

**3.3.6 Study of cell current, cell potential versus phenol conversion**

In order to show the stability of electrical parameters of the reactor configuration with time, the variation in the current flowing through the cell was studied by connecting an ammeter in series between the anode and cathode. The applied potential between the anode and cathode was 3.2 V with a 60% acetonitrile solution containing 50 mM phenol solution at a flow rate of 0.5 cm$^3$.min$^{-1}$ and an acid concentration of 3%. The results are summarized in figure 3.20 and 3.21.
The initial introduction of phenol showed a corresponding higher current of about 53 mA, which decreased to an average of about 31 mA as a reactor system stabilized after 50 minutes. Over the 498 minutes of experimental time, the current fluctuated between 25 and 35 mA. In terms of the coulombic energy of the 498 minute experiment, a total of 916.28 C was consumed.

With an average of 95% phenol conversion over the 498 minutes, a total of 11.7 mmol (95% of 12.3 mmol) of phenol would be equivalent to 282 C. Since the coulombs consumed over the time period was 916.28 C, a fair amount of the current was used for other side reactions not considered besides the phenol oxidation and benzoquinone reduction. These include water electrolysis, formation of larger biphenols and other reactions products besides the basic considerations of hydroquinone and catechol formation. Also, there could be some organic acid formed, which decompose further to carbon dioxide.

**Figure 3.20: Study of Cell Current Versus Phenol Conversion.**
FIGURE 3.21: COMPARISON OF THE CURRENT CONSUMED AND THE RESPECTIVE CELL VOLTAGES OVER A CONTINUOUS FLOW REACTION TIME OF 500 MINUTES. The anode vs a Hg/Hg$_2$SO$_4$ (sat K$_2$SO$_4$) reference electrode is also shown.

The results (Fig 3.21) also show some initial slight fluctuations in the anode potential vs the reference electrode at the start of the continuous flow process. This stabilized and remained relatively constant over the duration of the experiment showing that a dynamic equilibrium of the system was achieved between the conversion of phenol and that of the energy input.

### 3.4 Intermediate products analyzed on HPLC

In general, the electrolysis of a solution containing phenol, results in intermediate products such as aromatic compounds (benzoquinone, hydroquinone, catechol), aliphatic organic acids (maleic acid, furmaric acid, formic acid, glyoxal) and carbon dioxide. In order to qualify and quantify the reaction products, HPLC
proved to be the most suitable analytical technique for the experiment. A suitable wavelength for the UV-Vis detector was chosen that would detect a wide range of phenol type compounds and its derivatives. There could be however some other products formed that are not observed by the detector or co-elute on the HPLC column with one of the main products. The aim of the study was not to identify all possible reaction products, but to rather show that the principle of a continuous flow cell can be constructed to convert most of the phenol in a solution to some well known commercial products.

The qualification of the main observed peaks in a HPLC chromatogram was done by “spiking” a standard solution containing the three dominant products namely phenol, hydroquinone and benzoquinone in suitable concentration ranges. All possible reaction products would then be added to observe their elution relative to the main product peaks. Once all the main peaks on an HPLC chromatogram were identified, their quantification would be done by preparing suitable standards of the pure products in the right concentration ranges.

The standard solution of 0.02 % (m/v) containing main products of the studied reaction was prepared. Each spiked sample had 2 cm$^3$ of the standard solution and added approximately between 1 to 5 mg of spiked material.

3.4.1 Aliphatic Organic Acids

From literature, a number of organic acids can be formed due to the further decomposition of hydroquinone or cathecol under high cell potential conditions.$^{3,4,41,42}$ These include maleic acid, oxalic acid, glyoxal, acetic acid and formic acid.

(Fig 3.22) shows the HPLC chromatograms of hydroquinone, benzoquinone and phenol only to which the spiked compounds were added. There elution relative to these four main compounds were then compared. (Fig 3.23 to Fig 3.29) show the respective HPLC chromatograms spiked with the various organic acids.
**Figure 3.22:** Standard solution containing hydroquinone at 4.590 minutes, benzoquinone at 6.267 minutes, catechol at 8.259 minutes and phenol 14.138 minutes.
**Figure 3.23:** Standard solution and spiked with maleic acid eluting at 3.300 minutes.

**Figure 3.24:** Standard solution and spiked with oxalic acid eluting at 3.136 minutes.
**Figure 3.25:** STANDARD SOLUTION AND SPIKED WITH GLYOXAL ELUTING AT 3.099 MINUTES.

**Figure 3.26:** STANDARD SOLUTION AND SPIKED WITH FORMIC ACID ELUTING AT 3.374 MINUTES.
**Figure 3.27:** Standard solution and spiked with acetic acid, acetic acid was not detected.

**Figure 3.28:** Standard solution and spiked with malonic acid eluting at 3.433 minutes.
The results show that HPLC is a suitable technique for the qualification of maleic acid, oxalic acid, malonic acid, glyoxal and formic acid in a reaction product mixture that could result from the electrochemical oxidation of phenol. However, the presence of formic acid and acetic acid show a decrease in the area of hydroquinone compared to the original standard solution. This maybe due to a reaction involve in hydroquinone and these two compounds. Acetic acid and succinic acid were not observed under these analysis conditions. A different wavelength in the detector would have to be selected or a different experimental technique suitable for the analysis of acetic acid and succinic acid would have to be studied.

3.4.2 Phenolic based products
The following qualification of reaction products that could form from the electrochemical oxidation of phenol include the cathecol, resorcinol, 2,2-biphenol, 4,4-biphenol and 1,2,3-trihydroxybenzene. These possible products were primarily sourced from the literature that discussed similar oxidation and reduction experiments.\textsuperscript{3,4,21,42}
**Figure 3.30:** Standard solution and spiked with resorcinol eluting with benzoquinone at 6.332 minutes.

**Figure 3.31:** Standard solution and spiked with 4,4-biphenol eluting at 22.951 minutes.
Figure 3.32: Standard solution and spiked with 2,2-biphenol was not detected.

Figure 3.33: Standard solution and spiked with 1,2,3-trihydroxybenzene eluting with hydroquinone at 4.599 minutes.

The results showed that HPLC is a suitable technique for the qualification of resorcinol, 4,4-bi-phenol, 1,2,3-trihydrobenzene in a reaction product mixture that could result from the electrochemical oxidation of phenol but both resorcinol and
1,2,3-trihydroxybenzene co-elute with benzoquinone and hydroquinone respectively. However, 2,2-biphenol was not detected under these analysis conditions and that maybe it elutes beyond the 25 minutes analysis time or not detectable at the UV wavelength or UV detector used.

3.5 Qualification and quantification of reaction products from the micro-flow reactor

3.5.1 Qualification of the phenol conversion products

The qualification of the reaction products that results from the 50 mM phenol flowing through the micro reactor is shown in (Fig 3.34). The elution products were identified as hydroquinone at 4.579 minutes, benzoquinone at 6.204 minutes, catechol at 8.259 minutes, an unknown species at 8.823 minutes, phenol at 14.130 minutes and 4,4-biphenol at 22.112 minutes.

**FIGURE 3.34:** TYPICAL HPLC CHROMATOGRAM OF REACTION PRODUCTS AFTER 50 MINUTES USING REACTOR 1

These reaction products in (Fig 3.34) were typical of the ones identified in all the analysis done. There were some minor peaks around 17 and 23 minutes that were not identified since they only occurred occasionally in very low amounts.
One of the main product peaks at around 8.823 minutes did not correspond to any of the known reaction products discussed previously (Chapter 3.41 and 3.4.2 respectively).

Further investigations to identify the unknown product, GC-MS analysis was done for a standard solution containing known compounds common to the reaction mixture of this study (phenol, hydroquinone, catechol and benzoquinone). The GC-MS trace of this standard solution showed the peak at 1.59 min corresponded to benzoquinone. Phenol was observed to the peak at 2.27 min, catechol at 8.72 min. and hydroquinone at 11.43 min. (Fig 3.35). The standard solution and reaction mixtures with their respective mass spectra are shown in appendix A.

**Figure 3.35:** GC-MS Trace of Standard Solution.

In the GC-MS trace of a typical reaction mixture that contained the unknown compound observed from the HPLC at 8.823 minutes (Fig 3.36). The distinctive peak of hydroquinone was observed at 11.41 min and small peak of catechol at 8.85 min and phenol at 2.27 min. The GC peak for benzoquinone was very small,
and was due to being present in small quantities in the sample used. However there were other peaks observed besides the desired products at retention times of 1.08, 3.09 and 12.78 min respectively. Using the available MS library, (Appendix A, Fig 3.8 to 3.10) to identify the other observed GC peaks at 1.08 min with a mass fraction pattern (Fig 3.37), peak at 3.09 min with a mass fraction pattern (Fig 3.38) and the peak at 12.79 min with a mass fraction pattern (Fig 3.39), it was not possible to clearly characterize the unknown as a compound that could occur under the reaction conditions and as a derivative of phenol.

**Figure 3.36:** GC-MS Trace of Reaction Mixture

**Figure 3.37:** MS Mass Fraction of Unknown Compound at 1.08 min
In trying to identify the peak that was observed in the HPLC analysis at 8.823 min (Fig 3.34), further work was done to isolate, concentrate the product and to possibly qualify it in order to confirm its mass fragment observed by the GC-MS.

This illusive peak at 8.823 min in the HPLC was close to catechol and an assumption was made that it might be structurally similar to catechol or one of the other isomers such as benzoquinone. One compound that was considered was benzosemiquinone which was made and analysed by the same HPLC method in order to confirm if it would elute at the same time as the unknown at 8.823 min. A method by R. E. Richards et. al.\textsuperscript{43} was used to make the
benzosemiquinone by mild oxidation of hydroquinone or catechol in an alkaline solution and the proposed reaction mechanism is as follows in (Fig 3.40).

Figure 3.40: Reaction mechanism of mild oxidation of hydroquinone or catechol in an alkaline medium to form benzosemiquinone.

The precipitated product which was assumed to be \( p \)-benzosemiquinone was added to a standard reaction mixture solution that contained the unknown and the HPLC peak appeared at 9.660 min (Fig 3.41). This peak eluted just after the peak of interest which had shifted from 8.823 to 8.938 min in this example due to column ageing.
Similarly, the o-benzosemiquinone was prepared from catechol by the same method used described previously by R. E. Richards et. al.\textsuperscript{43} The solid product formed was then dissolved and added to a reaction mixture (Fig 3.42). In this case, the HPLC results showed that the peak due to the o-benzosemiquinone added would elute at 9.737 min, just after the peak of interest at 9.003 min.
3.42: HPLC CHROMATOGRAM OF REACTION PRODUCTS MIXTURE SPIKED WITH O-BENZOSEMIQUINONE.

However this investigation was not able to confirm or match to the unknown peak observed in the HPLC analysis of the reaction product. Also, the GC-MS analysis of the two benzosemiquinone synthesized did not correspond to any of the mass fractions observed in (Fig 3.37 to Fig 3.39). Subsequently, no full quantification and mass balance of the reaction products obtained from the electrochemical continuous flow reactor could be done where only the following compounds were quantified by preparing suitable standards and obtaining calibration graphs by HPLC analysis.

3.5.2 Quantification of the phenol conversion products
Preparation of standards was done by adding known amounts of the main identified compounds and determining their eluted peak areas. (Fig 3.43), shows a typical chromatogram of the phenol standards prepared from lowest to the highest concentrations.
Figure 3.43: Variation in HPLC peak area elution for various phenol concentrations.

The respective calibrations graphs of all the main identified compounds are shown in (Fig 3.44 to Fig 3.48) by plotting the peak area with concentration (mmol/L). A suitable statistical regression analysis was done in order to determine the equation of the calibration graph and the lower level of detection for a particular compound (LoD).

For phenol, the best fit calibration curve was found to be linear and from the statistical data its high p-value for the intercept showed that it does not differ significantly from zero and that the intercept may be due to sampling and instrumental errors (Fig 3.44). The lower level of detection was determined to be 0.313 mmol/L.
FIGURE 3.44: CALIBRATION CURVE OF PHENOL

SUMMARY OUTPUT

Regression Statistics

<table>
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<th>Multiple R</th>
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<tr>
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ANOVA

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Coefficients

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<th>Upper 95%</th>
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<tr>
<td>Intercept</td>
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<td>Conc.</td>
<td>492.4938103</td>
<td>10.74868543</td>
<td>45.818981</td>
<td>0.000475991</td>
<td>446.2459496</td>
</tr>
</tbody>
</table>

LOD= 0.3130

However, for the other main products, the best fit calibration curves were found to be exponential and not linear as observed with phenol. Hence, the exponential curves ($y = b_0 e^{b_1 x}$) that can be expressed as a linear equation by plotting $\ln$.
(Area) versus the Concentration (Ln(Area) = b_0 + b_1 \text{ conc}) was then obtained (Fig 3.45 to 3.48).

The corresponding regression statistics shows a good fit and the respective p-value from the statistical data showed that the Y-intercept was significant. The lower limit of detection for hydroquinone was determined to be 0.225 mmol/L.

**FIGURE 3.45: CALIBRATION CURVE OF HYDROQUINONE**

**SUMMARY OUTPUT**

<table>
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<th>Regression Statistics</th>
</tr>
</thead>
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<tr>
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<tr>
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<th>P-value</th>
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<td>1.22135E-05</td>
<td>6.912400583</td>
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<tr>
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<td>54.40601</td>
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**LOD=** 0.2248
The corresponding regression statistics shows a good fit and the respective p-value from the statistical data showed that the Y-intercept was significant. The lower level of detection for catechol was determined to be 0.227 mmol/L.

**SUMMARY OUTPUT**

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**LOD= 0.2272**
The corresponding regression statistics shows a good fit and the respective p-value from the statistical data showed that the Y-intercept was significant. The lower level of detection for benzoquinone was determined to be = 0.224 mmol/L

**Figure 3.47: Calibration curve of Benzoquinone**

**Summary Output**

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**ANOVA**

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**LOD=** 0.2237
The corresponding regression statistics shows a good fit and the respective p-value from the statistical data showed that the Y-intercept was significant. The lower level of detection for 4,4-biphenol was determined to be 0.707 mmol/L.

**FIGURE 3.48: CALIBRATION CURVE OF 4,4-BIPHENOL**

**SUMMARY OUTPUT**

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<td>10.09317</td>
<td>0.009674</td>
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</table>

[LOD= 0.7065]
3.5.3 Quantification of the phenol for selected reactions
Since not all the reaction products observed for the reaction of phenol by the continuous flow micro reactor could be qualified, it was not possible to fully quantify the reactions products, except to give an indication of what the amounts of the main products were in relation to the phenol that was converted. Only an approximation of the amount of the unknown reaction product could be determined by considering all the quantified amounts of the main reaction products and assuming that the remaining products by % (mM/mM) comparison to the starting amount of phenol.

The distribution of the main product components with time that resulted from the continuous flow through of the electrochemical micro reactor is shown in (Fig 3.49). The samples were obtained from using reactor 2 described previously where the applied cell potential was 3.2 V, the flow rate was 0.5 cm$^3$.min$^{-1}$ and the initial phenol concentration in a 60 / 40 acetonitrile solution with a 3% acid solution were kept constant for the duration of the experiment.

![Figure 3.49: Phenol conversion and reaction products formed from the continuous flow micro reactor.](image)
The results showed that for each point of analysis of the reaction products obtained with time of flowing through the reactor, that there was an unaccounted for mass balance amount. One can make the assumption that the unaccounted amounts are mainly due to the unknown compound identified by the HPLC analysis near 8.823 min. Hence, one could assume that measured reactions products should all add up to 100% and the unknown could be estimated to be close to 20% over the range of analysis at the different times of flow through (Fig 3.50).

![Graph](image)

**Figure 3.50:** Phenol conversion and reaction products formed from the continuous flow micro reactor.

However, an assumption was made that all the unaccounted-for product would be due to the observed unknown at 8.823 min and that no other products could be present in the reaction product stream that was either not detected by the HPLC method. According to the reaction scheme in (Fig 1.8), a possible decomposition product of phenol could be CO$_2$. Even though none of the possible organic acids that could form were observed by HPLC analysis, however, significant amount of gassing was observed during the reaction.
process, which could be primarily due to water electrolysis. Further work would have to be done in order to clearly identify the unknown product observed from the HPLC method and to determine an accurate mass balance of the reaction mixture based on the starting solution. Analysis for CO$_2$ in the gasses observed would also have to be done.
Chapter 4

4. Conclusion

In the investigation of this work, the following aspects were looked at: (1) cyclic voltammetric studies influence of the reaction medium (supporting electrolyte: acetonitrile and aqueous sulphuric acid) with the phenol and its reaction products during the oxidation and reduction on the working electrodes, (2) cell design (micro-porous lead dioxide electrode preparation) using lead acid battery technology. And (3) the optimisation and performance of the continuous flow micro-reactor in conversion of phenol under different parameters such as applied potential, phenol concentration, co-solvent concentration and support electrolyte concentration.

1. Voltammetric studies

In investigating the behaviour of the lead electrode in the different supporting electrolyte solutions using 60% acetonitrile / water showed no significant difference in both the anodic and cathodic sweep direction with a slight decrease of oxidation and reduction peaks as the solution concentration increased. Similar trends were observed when phenol was added with a slight change observed in the disappearance the reduction peak of PbO$_2$ to PbSO$_4$ during cathodic sweep that was due to slight passivation of the electrode during phenol oxidation.

2. Cell design

Powder X-ray diffraction patterns results showed that the long tubular shaped lead dioxide electrode cell was successfully prepared. The BET surface area of the lead dioxide formed was 2.708 m$^2$.g$^{-1}$ with a porosity of 51.57%. The average pore diameter of 0.1770 $\mu$m and the apparent and bulk densities as determined by Hg porosity were 7.236 g.cm$^{-3}$ and 3.505 g.cm$^{-3}$ respectively. Commercial micro-reactors are distinguished by their surface area to volume ratio (SA:V) that
ranges from 100 to 200 cm\(^{-1}\) when compared to a conventional batch type reaction in a 100 cm\(^3\) flask would have a ratio of 0.06 to 1 cm\(^{-1}\). The lead dioxide electrodes prepared showed a higher SA:V compared to commercial micro-reactors with a SA:V ratio between 184 000 cm\(^{-1}\) and 165 000 cm\(^{-1}\). This is significantly high due to the packed microporous structure of the active PbO\(_2\) cathode material.

3. Reactor performance
This study showed that a continuous flowing micro reactor can be made by using Pb-acid battery principles in designing a bulk microporous electrode that would allow for the oxidation of phenol to compounds such as hydroquinone under a continuous flowing process. The study showed that on a relatively small scale, the electrochemical cell could be optimized to allow for the continuous oxidation of almost all of the phenol in the starting solution stream. This would allow for a continuous product stream to be obtained from a feed solution that would convert an unwanted material such as phenol to an industrial important product such as catechol and hydroquinone.

In theory, the desired products could be removed from the reaction product solution, allowing for the solvent to be reused in the initial reaction feed to which phenol can be added. A disadvantage of this system would the use of the solvent acetonitrile that would be an undesirable solvent for making pharmaceutical active products.

The concept of using the Pb-acid battery electrode materials for the conversion of phenol can be relatively easily scaled to a pilot scale to consider larger amounts of reactant in a process where large manufactured Pb-acid battery electrodes could be assembled in a continuous flowing reactor system. These electrodes could be easily obtained form a Pb-acid battery manufacturer or be custom made from material that is easily assembled into sealed cell units that are typically done in battery manufacturing.
The study did however highlight the fact that all reaction products need to be identified in order to accurately do a mass balance of the reaction products. This was important in optimizing such as system where the energy to obtain such products would be calculated.

Such reaction products would also have to be separated from each other which in this case proved to be difficult due to the limited sample amounts produced. Further work would be to increase the amounts of the reaction product obtained from such a reaction process and to concentrate the products to a level where all the compounds can be clearly identified.

GC-MS analysis showed that the potential by-products formed had a specific mass fraction that could not be identified with limited library data available. Other analysis work that was not reported in this study was proton and $^{13}$C NMR analysis of a partially concentrated solution containing the unknown material. However, no conclusive results could be reported to obtain a clear structure, since there were too many impurities present in the analysis sample. Further work in using NMR analysis would be proposed for a sample that could be increased in concentration by using preparative HPLC or a suitable TLC technique.
References


39. ChemFiles, Enabling Technologies Microreactor Technology; Vol 5 No 7; sigma-aldrich.com/chemicalsynthesis.


42. R. Alnaizy, A. Akgerman, Advance oxidation of phenolic compounds, Advances in Environmental Research, **4** (2004) 233-244.
Appendix

Appendix A:
Standard solution mass spectra

Appendix 3.1: MS fragmentation pattern of benzoquinone with retention time 1.59 min.

Appendix 3.2: MS fragmentation pattern of phenol with retention time 2.27 min.
Appendix 3.3: MS fragmentation pattern of catechol, retention time 1.59 min.

Appendix 3.4: MS fragmentation pattern of hydroquinone with retention time 11.43 min.
Appendix 3.5: MS fragmentation pattern of phenol with retention time 2.27 min.

Appendix 3.6: MS fragmentation pattern of catechol with retention time 8.85 min.

Appendix 3.7: MS fragmentation pattern of hydroquinone with retention time 11.41 min.
**Appendix 3.8:** GC-MS library predicted matches for MS fragmentation pattern of unknown compound at the retention time of 1.08 min.
### Appendix 3.9: GC-MS library predicted matches for MS fragmentation pattern of unknown retention time of 3.09 min.

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![Diagram of structure](image)
Appendix 3.10: GC-MS library predicted matches for MS fragmentation pattern of unknown at retention time of 12.78 min