MEMBRANE REACTOR FOR THE ELECTROCATALYTIC MINIMIZATION OF ORGANIC MATTER IN WATER AND EFFLUENTS

Report to the
WATER RESEARCH COMMISSION

by

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EXECUTIVE SUMMARY

There is an ever-increasing demand to improve the quality of potable wastewater in our surroundings. The nature of pollution and extreme threat to human and aquatic life caused by organic pollutants, especially aromatic compounds, has led to research being conducted on developing new methods fro the treatment and management of organic pollutants in water.

In this report, the sources and effect that aqueous phenol has on the environment are discussed. Different methods that are currently being used or commercialized, for the degradation of phenol in water are also discussed and the advantages as well as disadvantages of such processes are outlined.

The research discussed in this report is based on the development of a novel method for the degradation of organic compounds in water. The process is based on a flow-through system, which uses the combination of electrochemistry and membrane technology. Ceramic-based membranes were modified to exhibit properties for conducting electricity by deposition of various kinds of electroconductive layers on the membranes' surfaces. Electrocatalytic layers were also deposited on the electromembranes, which did not posses enough catalytic properties for the anodic decomposition of organic compounds in water.

Electromembrane reactors based on tubular ceramic membranes and flat sheet type ceramic membranes were designed and constructed. These purification units were used to study the electrochemical oxidation of aqueous phenol under different pH conditions, applied potential, flow rate and different types of materials that were coated on the membranes.

The electrochemical oxidation of phenol is also associated with the production of various types of intermediates. Among these are aromatic compounds, aliphatic acids and oligomers. It was, therefore, an important part of the research to develop fast and reliable analytical methods to monitor the disappearance of phenol in the feed solution as well as determine the type and concentration of all the by-products that would be formed. Three methods based on the measure of total phenol index, GC-MS and HPLC were developed. HPLC was found to be the quickest and reliable method for the qualitative and quantitative analysis of all the organic compounds. Measurements to determine the oxygen demand in the samples that had already passed through the electromembrane reactor were also carried out.

Aims of the contract

According to the contract, the objectives of the research project were as follows:

- Development of laboratory prototypes of novel high efficiency installations for the decomposition and total combustion of organic pollutants present in industrial effluent and potable water.
- Determination of optimum properties of ceramic-based membranes for the preparation of electrocatalytic composite membranes active in the direct electrochemical oxidation of organic pollutants.
- Development of synthetic procedures for the preparation of electrocatalytic membranes.
- Designing and development of optimal electromebrane reactors for the decomposition of organic pollutants.
- Manufacture of laboratory-scale as well as bench scale catalytic reactors for organic decomposition.
- Evaluation of reactor performance and determining decomposition efficiencies for selected effluents.

Findings

Tubular electromembrane units

The use of the tubular electromembrane, in general, for the electrochemical oxidation of organic pollutants in water was successful for the following reasons:

- A novel type of water purification unit was developed whereby, the organic pollutant (phenol) could be rapidly degraded by simply flowing through an electrically charged membrane.
- Methods for the preparation of electroconductive materials and electrocatalysts on the ceramic membranes' surface and matrix were developed.
- Apart form the material science and engineering involved with the development of these purification units, analytical methods and procedures based on spectrometry, GC-MS and HPLC for the determination of phenol concentration and its oxidation products were developed.
- The energy requirements for the complete oxidation of phenol in the electromembrane units, equipped with tubular ceramic membranes, were low (between 1.3 and 6.0 Wh/g).

Flat-sheet type electromembrane reactor

Flat-sheet type electromembrane reactor was designed and constructed.

- The bench-scale purification unit was used successfully for the electrochemical oxidation of phenol under different pH conditions and various types of electrolyte solutions.
- Complete degradation of phenol in phenolic effluent from the SAPREF (Durban, RSA) oil refinery was achieved over the entire pH range.
- In the bench-scale purification unit, COD could be reduced to less that 50 mg/L when treating the SAPREF (Durban, RSA) effluent.
- Apart from the immense technological advantage for oil refineries situated along the coast, the energy requirements for the degradation of phenol are very low.
- Under acidic conditions, when either acid mine drainage or H_2SO_4, is used as an electrolyte source, phenol is readily decomposed to p-benzoquinone and other hydrophilic, low molecular weight products, viz. the organic acids. These acids belong to non-hazardous solutes that have maximum permissible concentrations (MPC).
- In contrast, the maximum permissible concentrations of phenol and p-benzoquinone are at levels of 0.01 to 0.001 mg/L. The concentration of p-benzoquinone in most of the experiments that were conducted under acidic conditions was greater than 13 mg/L. From an electrosynthesis point of view p-benzoquinone is an interesting product since it has many important uses. It is used in the manufacture of unsaturated polyesters, as a polymerization inhibitor and raw material for hydroquinone. 1,4-Benzoquinone reacts with trialkylboranes to produce alkyl-substituted hydroquinones and so on.

Research Beneficiaries

The research is aimed at developing novel technology for the treatment of water polluted with organic compounds that will in turn be comparative with existing methods of treatment. The technology can be applied in the following industries:

ESKOM, Water Treatment Industry, Chemical Industry, Refineries, Food and Wine Industry, Textile Industry, Communities and Local Authorities.

Application areas

- Industrial feeds and waters with excessive total organic carbon (TOC)
- Natural draft wet cooling systems (for re-entry into the system)
- Industrial blowdown and raffinate waters - especially biorefractory organics

- Pretreatment for bio-degradation streams
- Treatment of groundwater

List of potential effluents

- Phenolic effluent from SAPREF oil refinery in Durban
- High COD organic effluent from wine makers such as KWV
- Phenolic effluent for the Cape Olives farm in Hugenot
- Organic effluent from fisheries, such as, I&J
- Phenolic and other simple effluents from the Pulp and Paper industry e.g. Sappi and Mondi
- Effluent resulting from the development of phenolic resins
- Chlorophenol-containg effluent in leather tanning and finishing industries

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GLOSSARY OF TERMS

Acid Mine Drainage

Drainage of water from areas that have been mined for coal or other mineral ores; the water has low pH, sometimes less than 2.0 (is acid), because of its contact with sulfur-bearing material.

Acid drainage is harmful because it often kills aquatic organisms

Anode

The electrode where oxidation occurs in an electrochemical cell. It is the positive electrode in an electrolytic cell, while it is the negative electrode in a galvanic cell. The current on the anode is considered a positive current according to international convention; however, in electroanalytical chemistry the anodic current is often considered negative.

Anion

A negatively charged ion.

Adsorption

An increase of the concentration of a solute in the vicinity of a solid surface, over that in the bulk of the solution, due to the attractive interaction between the solid immersed into the solution and the solute. Adsorption on a solid from a gaseous phase also occurs. It is a surface process, not to be confused with absorption.

Brackish water

Water containing dissolved solids in the range of 1,000 to less than 15,000 parts per million.

Biological oxygen demand (BOD)

(1) The amount of oxygen required to stabilize decomposable matter by aerobic action. (2) (Water Quality) An indirect measure of the concentration of biologically degradable material present in organic wastes. It usually reflects the amount of oxygen consumed in five days by biological processes breaking down organic waste.

Cation

A positively charged ion.

Cathode

The electrode where reduction occurs in an electrochemical cell. It is the negative electrode in an electrolytic cell, while it is the positive electrode in a galvanic cell. The current on the cathode is considered a negative current according to international convention; however, in electroanalytical chemistry the cathodic current is often considered positive.

Chemical oxygen demand (COD)

(Water Quality) (1) A measure of the chemically oxidizable material in the water, which provides an approximation of the amount of organic and reducing material present. The determined value may correlate with *Biochemical Oxygen Demand (BOD)* or with carbonaceous organic pollution from sewage or industrial wastes. (2) A chemical measure of the amount of organic substances in water or wastewater. A strong oxidizing agent together with acid and heat are used to oxidize all carbon compounds in a water sample. Nonbiodegradable and recalcitrant (slowly degrading) compounds, which are not detected by the test for BOD, are included in the analysis. The actual measurement involves a determination of the amount of oxidizing agent (typically, potassium dichromate) that is reduced during the reaction.

Desorption

The opposite process of adsorption. The removal of the excess concentration of the adsorbate from the vicinity of the solid surface.

Dissolved Organic Carbon

Carbon-based substances dissolved in water.

Effluent

(1) Something that flows out or forth, especially a stream flowing out of a body of water. (2) (Water Quality) Discharged wastewater such as the treated wastes from municipal sewage plants, brine wastewater from desalting operations, and coolant waters from a nuclear power plant.

Electrochemical cell

A device that converts chemical energy into electrical energy or vice versa when a chemical reaction is occurring in the cell. Typically, it consists of two metal electrodes immersed into an aqueous solution (electrolyte) with electrode reactions occurring at the electrode-solution surfaces.

Electrochemistry

A science concerned with the properties of solutions of electrolytes and with processes occurring when electrodes are immersed in these solutions.

Electrolysis

A method by which chemical reactions are carried out by passage of electric current through a solution of an electrolyte or through a molten salt.

Electrolyte

A chemical compound (salt, acid, or base) that dissociates into electrically charged ions when dissolved in a solvent. The resulting electrolyte (or electrolytic) solution is an ionic conductor of electricity. Very often, the so formed solution itself is simply called an "electrolyte." Also, molten salts and molten salt solutions are often called "electrolyte" when used in electrochemical cells.

Electron

A stable elementary particle which is the negatively charged constituent of ordinary matter, having a mass of about 9.11 ✕10-28 gram (equivalent to 0.511 MeV), a charge of about -1.602 ✕10-19 coulomb, and a spin of ½.

Electrooxidation

Oxidation carried out with an electrochemical reaction.

Electrosorption

Adsorption at electrode surfaces. Generally, adsorption at electrically charged interfaces.

Electrosynthesis

A reaction in which synthesis occurs as the result of an electric current.

Feed water

The water to be treated that is fed into a given water treatment system

Flux

In cross flow filtration, the flow rate of product water through a reverse osmosis, electrodialysis, or ultrafiltration membrane.

The flow rate is usually given in terms of volume unit per time per membrane area, such as gallons per day per square foot or liters per hour per square meter.

Fouling

Irreversible deposition of material onto or into the membrane, causing loss of flux and altered rejection.

Ion

An electrically charged chemical particle (atom, molecule, or molecule fragment).

Membrane

A membrane can be defined as a thin film separating two phases and acting as a selective barrier to the transport of matter.

Membrane process

An operation where the feed stream is divided into two streams: a permeate containing the components which have passed through the membrane and a reject (or retentate) containing the retained species.

Permeability

The ability of a body, such as a reverse osmosis or ultrafiltration membrane, to pass a liquid under pressure or to pass ions under the influence of an electric current as an ion exchange membrane in electrodialysis

Permeate

That portion of the feedwater which passes through a membrane to become product water.

pH

A measure of the degree of the acidity or the alkalinity of a solution as measured on a scale ("pH scale") of 0 to 14.

Proton

An elementary particle that is the positively charged constituent of ordinary matter and, together with the neutron, is a building block of all atomic nuclei; its mass is approximately 938 megaelectronvolts and spin 1/2.

Reverse Osmosis

A water treatment process that removes undesirable materials from water by using pressure to force the water molecules through a semipermeable membrane.

This process is called "reverse" osmosis because the pressure forces the water to flow in the reverse direction (from the concentrated solution to the dilute solution) to the flow direction (from the dilute to the concentrated) in the process of natural osmosis.

RO removes ionized salts, colloids, and organic molecules down to a molecular weight of 100.

May be called hyperfiltration.

1. INTRODUCTION

The destruction of hazardous organic wastes that are produced and discharged in water and wastewater during most chemical and industrial processes has become a worldwide problem that needs further study and monitoring. Existing methods for treatment of environmentally unfriendly waste, such as incineration and ozonation, have come with a lot of shortcomings, such as the use of high temperature, high costs and the formation of harmful by-products. The aim of this study was to develop an electrochemical unit for the detoxification of water and industrial effluent contaminated with harmful organic waste. The electrochemical unit would have to overcome drawbacks such as cost, ease of use and absence of costly reagents for water purification. In order to improve the efficiency of this electrochemical system, electromembranes were used as anodes in the electrochemical unit.

1.1 Water Scarcity

Water is one of the most essential natural resources needed for, not only human survival, but all other living organisms as well. It will be more appropriate to say, " Where there is water there is life". The total volume of water is estimated to be 1.36 X 10^{+9} Km^3 distributed in eight major sources as illustrated in the Table 1.1[1].

As can be seen from the data tabulated in Table 1.1, the total volume of water is quite high but the quality of water need for survival is limited. Most of the earth's water is contained in the oceans but it is useless for human consumption due to the high salt content (approx. 35000 $mg.L^{-1}$). Of the fresh water available for the earth's population, most of it is either heavily polluted due to human activity or geographically unavailable for certain communities such as arid regions. Membrane processes are currently playing a key role in alleviating water scarcity by processes such as the desalination of seawater.

Table1.1: Total volume of water from eight major sources.

Water source	Water volume (km^3)	Proportion of total water (%)
Oceans	$1.32 \times 10^{+9}$	97.24
Icecaps, glaciers	$2.92 \times 10^{+9}$	2.14
Groundwater	$2.0 \times 10^{+6}$	0.61
Freshwater lakes	$1.25 \times 10^{+5}$	0.009
Inland seas	$1.04 \times 10^{+5}$	0.008
Soil moisture	$6.67 \times 10^{+4}$	0.005
Atmosphere	$1.29 \times 10^{+4}$	0.001
Rivers	$1.25 \times 10^{+3}$	0.0001
Total Water Volume	$1.36 \times 10^{+9}$	100 %

1.2 Membrane Processes

A membrane can broadly be described as a semi permeable thin layer of material that is capable of allowing certain entities to pass through while retaining others. A membrane can be homogeneous or heterogeneous, symmetric or asymmetric in structure, and it may be either neutral, or may carry positive or negative charges, or both [2]. The successful use of membrane processes depends on a proper selection of membrane material. Ideally, a membrane should have high permeate flux, high contaminant rejection, great durability, good chemical resistance, and low cost [3]. The transport rate of materials through the membrane is determined by a driving force or forces acting on the individual components and their mobility and concentration within the interface [4]. Hence, membrane processes are classified by the range of materials separated and the driving forces employed [5]. These processes include reverse osmosis (RO), nanofiltration (NF), ultrafiltration (UF), microfiltration (MF) and electrodialysis (ED).

Due to the need for production and reusage of clean water, membrane technology has emerged as one of the processes that offer a number of advantages over existing methods for water treatment. Membrane processes in water treatment have mainly been applied for desalination of seawater, however, over the years, membrane technology has been employed for removal of a variety of pollutants. In this section we are going to describe the major membrane processes and some hybrid processes in their use for removal of organic compounds.

1.2.1 Reverse Osmosis (RO)

Along with nanofiltration, RO is one of the most commonly used membrane processes for water treatment. RO is capable of rejecting contaminants or particles with diameters as small as 0.001 μm [6]. Only solutions with low molecular weight components, which often have a significant osmotic

pressure, are processed at pressures up to 100 bars [7]. The use of RO for desalination of brackish and seawater is well documented in literature [8,9]. Comprehensive studies on the use of RO to investigate organic removal have been conducted, both on a full-scale (20 000 m^3/d) and pilot scale, using cellulose acetate and polyamide membranes [10,11]. Final analysis of the work showed that the use of RO for organic removal was associated with shortcomings relating to treatment of certain compounds, for example chlorophenol retention was up to 86 % in some cases, while other organic pollutants like chlorobenze were not retained.

1.2.2 Nanofiltration (NF)

Nanofiltration membranes are similar to RO membranes only the network structure is more open. The membranes are composite with pore sizes less than 2 nm. NF can also be described as a membrane process with separation characteristics between RO and ultrafiltration [12]. Application of NF membranes to treatment of drinking water has increased since they can separate hazardous organic pollutants such as pesticides [13-15]. The effect of solute molecular size in rejection properties of NF membranes was studied, and it was found that phenol rejection ranging between 14.6 and 31.8 % could be achieved in four different membranes [16]. Molecular width, shape and steric hindrance play a role in solute permeation. The performance of NF membranes has also been shown in many cases to be negatively influenced by the presence of foulants in the water to be treated [17].

1.2.3 Ultrafiltration (UF)

Ultrafiltration is a membrane process whose nature lies between NF and microfiltration [2]. The pore sizes of the membranes used range from 0.05 μm to 1 nm. UF is typically used to retain macromolecules and colloids from a solution [6]. Applications of UF membranes can be found in fields such as food and dairy industry, pharmaceutical industry, textile industry, chemical industry, metallurgy, paper industry, and leather industry [18]. UF is also applied as a pretreatment of process water before RO as a way to sustain membrane life and maintain an economical operation of the RO plant [19]. UF as a process is not particularly suitable for removal of organic compounds in water and it has been used in combination with other processes. An example would be the combination of UF with powered activated carbon (PAC) for the removal of organics. The PAC-UF process has been used to successfully predict and measure the removal of total organic carbon (TOC) and 2,4,6-trichlorophenol from natural water [20].

1.2.4 Microfiltration (MF)

Microfiltration is oldest of the four pressure-driven membrane technologies, three of which have already been discussed in Section 1.2.1 to 1.2.3. MF membranes are permeable to species up to 0.5 μm in diameter and are capable of relatively high flux under a small pressure difference across the membrane. This process is mostly applied in industrial and water treatment processes where particles of a size > 0.1 μm, have to be separated from the liquid. These applications include, among others, sterilization of beverages and pharmaceuticals, wastewater treatment and separation of oil-water emulsions [21]. In general, MF and UF by themselves are not effective in removing dissolved organic compounds (DOC) in surface water treatment, with typical removal efficiency of less than 15 % [22]. Massoud Pirbazari and co-workers have combined MF with PAC adsorption to treat waters contaminated with organic compounds [23].

1.2.5 Membrane Bioreactors

The technology of membrane bioreactors usually combine two processes, one being biological degradation and the other being membrane separation. In this process, suspended solids and microorganisms are responsible for biodegradation and the membrane separates the suspended solids and microorganisms from the treated water [19]. The oxidizing capability, white rot fungi enzymes, laccase and manganese-dependant peroxidase can be extended to xenobiotics such as aromatic organic pollutants, and hence UF in combination with immobilized enzymes appears to an attractive approach for the treatment of industrial wastewater [24]. Membrane bioreactors have been applied for the removal of phenols in wastewater [25-27]. The disadvantage, however, in enzymatic methods for treatment of phenol is that large amounts of enzyme are required to achieve high removal efficiency due to enzyme deactivation [28].

1.2.6 Electromembranes

The main electrochemical techniques applied for wastewater treatment are electrolysis and electrodialysis. Membrane processes in which an electrical potential difference acts as the driving force use the ability of charged ions or molecules to conduct an electrical current. There are four main membrane processes where ions are involved and ionic membranes are used. Theses are:

- Electrodialysis
- Membrane electrolysis
- Bipolar membranes
- Fuel cells

Electrodialysis (ED) is an operation by which ions are driven through ion-selective membranes under the influence of an electrical potential. Electrodialysis, the most commonly used electromembrane technology, uses a combination of two physical mechanisms: dialysis and electrolysis [29]. The most important application of electrodialysis is the production of potable water form brackish water [30]. Although the application of electrodialysis for the treatment of water containing organic pollutants is not common, Aldaz and co-workers have applied electrodialysis for recovery of aromatic amino acid from a solution with high concentration of sulphates and phosphates [31].

The membrane electrolysis process is also a combination of two phenomena, an electrolysis process and a membrane separation process. The chloro-alkali process [32], whereby sodium chloride is converted to chlorine and caustic soda, is a classical example of membrane electrolysis. Studies based on the use of membrane electrolysis for removal or degradation of organic compounds is very limited.

Bipolar membranes, as the name suggests, exhibit both cation and anion exchange properties. An example of the application of a bipolar membrane is in the production of sulfuric acid and sodium hydroxide [32].

Fuel cells are different from the three membrane processes discussed above. The other processes require an electrical potential difference as driving cells, which means they are electrolytic cells. Conversely, fuel cells, convert chemical energy into electrical energy, which means that they are galvanic cells. Hydrogen or methanol is oxidized and oxygen is reduced and water is produced:

Anode reaction: $2H_2 \rightarrow 4H^+ + 4e^-$

The electrons are transported through the external circuit from the anode to the cathode. The hydrogen ions diffuse through the ion exchange membrane to the cathode where they react with oxygen to form water.
Cathode reaction: $4H^+ + O_2 + 4e^- \rightarrow 2H_2O$

The overall cell reaction is: $2H_2 + O_2 \rightarrow 2\ H_2O$ with an electromotive force $E^o = 1.2$ V [6]. This value is obtained from the electrode potentials.

1.3 The Area of Research

Removal of hazardous organic waste products from industrial wastewater and the management of organic effluent, in general, has become a noticeable problem. Regulations on the amount of such pollutants discharged by most chemical industries have become more stern. Although there isn't a universal process for successfully treating all hazardous waste, electrochemical processes promise to alleviate most problems associated with conventional methods for dealing with hazardous waste in industrial wastewater.

Industrial electrochemical processes such as storage battery manufacturing [33] and fuel cells [34], organic electrosynthesis [35], metal extraction and refining, chloroalkali electrolysis [32] and removal of impurities from process liquids, air and soil [36] have been operating for more than a century. There has been an growing interest of a special field of research called environmental electrochemistry, which basically involves the use of electrochemical technology for prevention of environmental pollution [37].

Applying electrochemical techniques for waste treatment presents a challenge in that treatment of low concentrations of impurities is difficult. While industrial processes operate at high concentrations, typically more that one mole per liter, waste processing operations require treatment to concentrations down to ppm or even ppb levels. Working at low concentrations is challenging because of the thermodynamic and kinetic factors [38]. The thermodynamics of electrochemical reactions are governed by the Nernst equation [39]:

$$E = E^{\circ}_{f} + \frac{RT}{zF} \ln \frac{C_{ox}}{C_{red}}$$

where E is the electrode potential, E°_{f} is a formal thermodynamic reaction potential, C_{ox} and C_{red} denote the concentrations of reacting species, T is the temperature in Kelvins, z is the number of electrons involved in the electrode reaction, R is the gas constant and F is the Faraday constant. The cell potential is represented by the difference between the cathode and anode potentials. There is a voltage threshold at which an electrode reaction can thermodynamically begin at a given concentration. In the case of water electrolysis, these voltages in neutral solutions are:

$2H_2O \rightarrow 4H^+ + O_2 + 4e^-$, $\quad E = 0.87V$;

$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$, $\quad E = -0.42V$

When reaction potentials are higher than the ones required for water electrolysis, hydrogen and oxygen are produced in addition to the desired products. When applying electrochemical techniques for waste treatment, conditions must be found under which water electrolysis will be minimized. This can be done by using different electrode materials for different treatment processes or incorporating electrocatalysts, which would increase the overpotential of some reactions.

Phenols are among the most abundant pollutants that form components of mixed wastes. The main challenge in applying electrochemical techniques for treatment of phenols is the amount of by-products formed during the electrode reaction. This is brought about by the electrogeneration of three unstable species (ArO^+ $^{\bullet}H$, $ArO^{\bullet}$, ArO^+), whereby each exhibit chemical reactivity [40]. Hence it is imperative that the optimum conditions be found by changing reaction parameters such as oxidation potential, current density, electrode material, supporting electrolyte and others. Comninellis et.al. have proposed a general mechanism (Figure 1.1) of the electrochemical conversion/combustion of organics, with simultaneous oxygen evolution in order to select candidate oxide anodes which favour electrochemical conversion or combustion of organics for wastewater treatment [41].

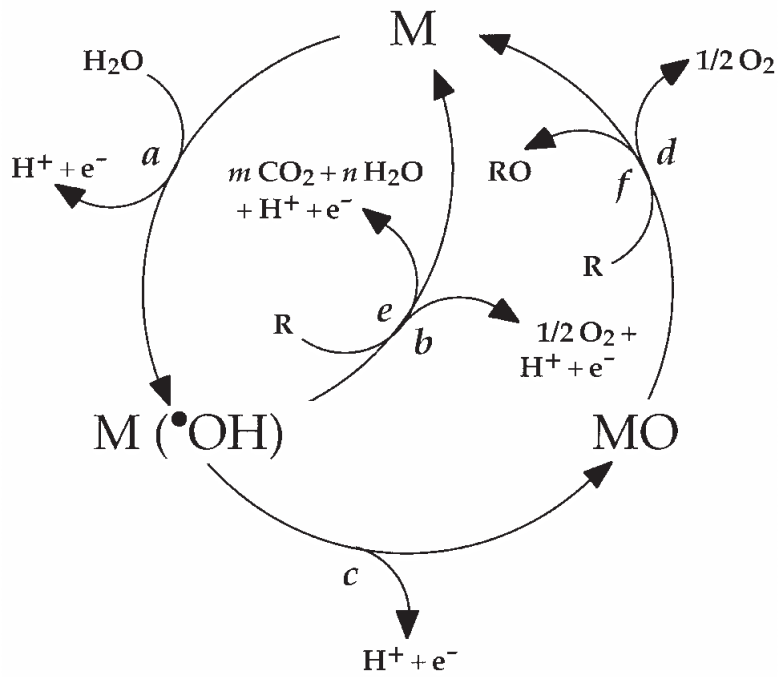

Figure 1.1: General scheme of the electrochemical conversion/combustion of organics with simultaneous oxygen evolution [41].

Electrochemical conversion transforms only the toxic non-biodegradable pollutants into biodegradable organics whereby biological treatment is the subsequent stage after electrochemical treatment. Electrochemical combustion, however, yields water and CO_2 and no further treatment is required. Experimental results indicate that the accumulation of $^{\bullet}OH$ radicals favours the combustion reaction, while introduction of oxygen into the electrode's lattice favours conversion [42]. In terms of phenol degradation, electrochemical oxidation is mediated by the physisorbed ($^{\bullet}OH$) radicals and the phenol molecule is either oxidized to its corresponding aromatic intermediates (for example, pbenzoquinone and hydroquinone) or further broken down to aliphatic acids such oxalic and maleic acid.

1.3.1 Discussions

Suitable conditions for the electrochemical treatment of wastes containing organic pollutants have been extensively studied by many research groups and sufficient knowledge has been gathered for further advancement in developing efficient systems to deal with such pollutants. The availability of new electrode materials, novel reactor types and advancement in the electrochemical engineering of cell designs will further develop the field of environmental electrochemistry.

Depending on the electrode material, organics can effectively be converted to less hazardous compounds or destroyed to carbon dioxide depending on the surface characteristics of the anode material. It should be noted that, compounds that are more hazardous than the starting material can be produced when the unsuitable electrode materials are used. For selective oxidation or conversion of organics, the concentration of adsorbed hydroxyl radicals on the anode surface must be almost zero. This would mean that, the rate of transition of oxygen into the oxide lattice (MO, figure 1.1) must be much more faster than the rate of hydroxyl radicals formation (M ($^{\bullet}OH$), figure1.1) [42]:

rate of hydroxyl radical formation = k_1 [MO]

rate of transition of oxygen in the oxide lattice = k_2 [ ],

$$k_2 [\ ] >> k_1 [MO]$$

where, k_1 is the electrochemical rate constant for H_2O discharge, k_2 the electrochemical rate constant for the transition of oxygen into oxide lattice, [MO] is the concentration of active sites on the oxide anode, and [ ] is the concentration of "oxygen vacancies" in the oxide lattice.

Conversely, the electrochemical combustion of organics to carbon dioxide would require that high concentration of hydroxyl radicals on the anode surface be present. This would mean that the rate of hydroxyl radicals formation is much faster than the rate of oxygen transition into oxide lattice:

$$k_1 [MO] >> k_2 [\ ].$$

The process described in this report makes use of modified ceramic-based membranes, of tubular and flat form, for the electrochemical oxidation of phenol. The results discussed in later chapters will give a clear picture of the kind of electrode material is exhibited by these electromembranes.

1.4 Objectives

The objective of this study was to develop a novel purification system in which a feed solution containing organic compounds is passed through an electrochemically charged ceramic-based membrane whereby the organic compounds are decomposed on contact with the electromembrane surface. The electromembranes were coated with highly active electrocatalysts in order to enhance the electrochemical oxidation process and improve the reduction of chemical oxygen demand (COD). A simplified explanation of the process is illustrated in Figure 1.2.

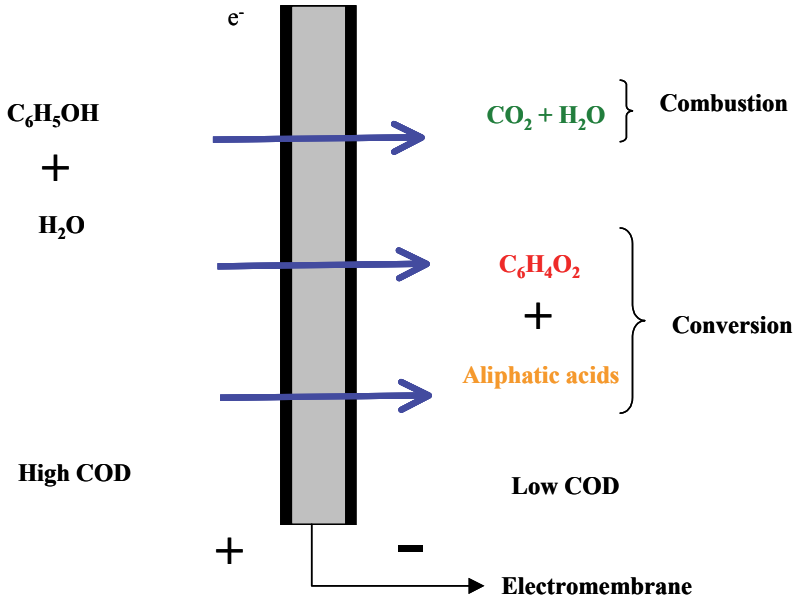

Figure 1.2: Schema of the ceramic-based electromembrane process for the oxidation of phenol.

This unit should be simple, practical and inexpensive and be efficient for the electrochemical oxidation of aqueous phenol. The unit will be further tested for the treatment of synthetic phenol solutions and then tested for the decomposition of phenol in real industrial effluent.

The above-mentioned electrochemical unit is expected to have intrinsic advantages over most treatment technologies. These advantages include:

- No harmful chemicals, such as ozone and hydrogen peroxide, will be used for the oxidation of harmful organics.
- Membrane separation processes are associated with formation of a reject stream and hence brine that needs disposal.
- The pressure needed for permeation through the membrane is very low compared to pressures associated with membrane processes such as reverse osmosis and nanofiltration.
- Unlike most electrochemical systems, expensive electrode material such as Pt and Ti are not required in this system.
- Because this is a flow-through system, one is not limited to a certain volume of water to be treated.

The disadvantages that are associated with electrochemical techniques include:

- Additional electrolyte solution is required to make it possible for electricity to flow between the electrodes of a cell.
- Careful choice of experimental conditions as well as electrode material is important.
- The intermediates that are formed during electrochemical oxidation can be more harmful than the starting material.
- Due to the complexity of the intermediates formed, good analytical methods need to be developed.

1.4.1 Realizing the Objectives

As mentioned in the set out objectives, this purification unit is based on the direct electrochemical oxidation of organic pollutants in water. The unit includes rigid ceramic-based membranes produced by e.g. slip-casting or moulding method, or ceramic felt, or ceramic paper or metal mesh coated with ceramic layers, or a similar material

Since the membranes are purely inorganic, modifications will be made to the membrane material in order for them to be adapted as anodic material. The porous ceramic membranes will be coated with a layer of suitable electrical conductivity or mixture of electroconductive layers. The suitable electrical conductive material will be selected from a group consisting of pyrolytic carbon, carbon black, or metals such as gold, platinum, platinum group metals, metal oxides or a mixture thereof. The electrical conductive materials may possess catalytic properties for the electrochemical degradation of organic compounds. In the case where the electrical conductive material does not exhibit sufficient catalytic properties for organic degradation, electrocatalytic material would have to be incorporated onto the electromembranes matrix.

For the process to be cost effective and be able to address some of the drawbacks associated with electrochemical oxidation processes, a flow-through system will be used. The phenol-containing water flows through the electrically charged membrane and the phenol molecules would be degraded at one pass through the electrocatalytic membrane.

1.5 The scope of the report

Two different systems for the electrochemical oxidation of phenol are examined in this report. Chapters 3 & 4 describe units based on tubular ceramic membranes coated with a combination of gold and platinum and pyrolytic carbon, respectively. The latter chapters in this report are based on flat ceramic-based electromembranes systems. The phenol degradation efficiencies as well as optimum conditions for the said processes are described fully. In Chapter 6 a bench scale model of the flat ceramic membrane system is tested for the electrochemical oxidation of phenol. Further tests were conducted, on the up-scaled system, for the efficiency of phenol degradation and COD removal in an industrial effluent. Overall conclusions and expected benefits of the electromembrane system are given in Chapter 8.

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2. ELECTROCHEMICAL OXIDATION METHODS FOR POTABLE AND WASTEWATER TREATMENT

Electrochemical processes have provided valuable contributions to the hygienic quality and protection of the environment through implementation of wastewater treatment and other processes for the minimization of waste and toxic compounds. This chapter reviews, mainly, direct electrochemical oxidation methods for potable and wastewater treatment. Although electrodialysis is the most common and commercialized electrochemical method for water treatment, electrochemical oxidation of organic pollutants has not yet gained enough attention. Different electrode materials have been tested for this process and in this chapter a critical evaluation of these electrode types is given. It is believed that the use of ceramic-based electromebranes will enhance the electrochemical oxidation process and address some of the drawbacks associated with the method.

2.1 Introduction

Human activities have contributed to the introduction of a wide variety of synthetic organic compounds into the environment, and many are causing significant pollution of ground and surface waters. Of all the organic pollutants causing problems around the world, the most harmful are aromatic hydrocarbons (mostly from gasoline, diesel, and other fuels), chlorinated hydrocarbons (used in various industrial processes, mostly as solvents) and pesticides [1-3]. Among a wide variety of properties, aromatic and chlorinated hydrocarbons are relatively resistant to biodegradation [4]. There are several methods of treating industrial wastewater containing organic pollutants. These include incineration, adsorption, biological treatment and chemical or electrochemical oxidation [2].

The US Environmental Protection Agency lists phenol, defined as a hydroxy derivative of benzene and its condensed nuclei, as a priority pollutant. It is also considered to be one of the major water pollutants that need recovery, removal or destruction [5]. Many industries are characteristic sources of phenolic waste and these include oil refineries, coke plants, plastic plants and chemical industries. Present Swiss guidelines limit phenol concentration to 0.05 $mg.L^{-1}$ and lower concentration limits are in discussion [2]. Numerous chemical treatment processes do exist to degrade phenols, but most of them do not lead to the complete mineralization of phenols, or are either expensive or time-consuming. Among these methods, are the following:

- UV photocatalytic oxidation [6], with or without an oxidizing agent such as hydrogen peroxide (H_2O_2) or ozone (O_3) [7]
- Photochemical oxidation with a semi- conductor, most often TiO_2 [8,9];

- Microbial degradation, which works well at low contaminant concentrations. However, the biodegradation process is very sensitive to shock loads and requires long hydraulic retention time [10];
- Activated carbon adsorption. This process requires low phenol concentration and high retention time in the reactor;
- Wet oxidation techniques (WOT) can be used for a wide range of contaminant concentrations and require low retention time in the reactor. However the process usually takes place at 453 K and 2.6 MPa, which makes the process costly and unpractical for industrial application [11];
- Chemical oxidation by H_2O_2 with Fe^{2+} ions as a catalyst (Fenton method) [12], by ozone [13], or super chlorination, chlorine dioxide [14] or chloramine treatment, and ozonation. Chlorination of phenol-containing water may result in formation of chlorophenols, which are carcinogernic [15], have a foul smell and do not have a desirable taste.
- Decomposition of phenols and removal of total organic carbon (TOC) with ultrasonic amplitude 120 μm and H_2O_2 (200 $mg.L^{-1}$) [16].
- Electrosorption methods for removal of organic compounds [17-19].

The choice of treatment depends on economics as well as ease of control, reliability and treatment efficiency. There is an increasing interest in the use of electrochemical methods for the treatment of waste streams [20]. The use of high oxygen overvoltage anodes for the direct oxidation of refactory organic chemicals [21] and the use of potent oxidants such as ozone, chlorine and H_2O_2 (in the presence of Fe^{2+} catalyst) [22] are of great importance in wastewater treatment. However, the more costly oxidants are of interest mostly where concentrations are too high or too variable for treatment by biological processes.

Apart from these well-known techniques, the electrochemical treatment of industrial wastes seems to be an interesting process [23]. The electrochemical method for wastewater treatment has attracted a great deal of attention recently, mainly because of the ease of control and the increased efficiencies provided by the use of compact bipolar electrochemical reactors and by the large surface area of three dimensional electrodes [2]. Furthermore, the electrochemical technologies offer the prospect of relatively simple equipment, environmental friendliness, because the main reagent is the electron and the possibility of high efficiency by comparison with thermal treatment that has a negative public image [24]. This work describes the electrochemical oxidation of low concentrations of organic pollutants at low currents and voltages.

2.2 Electrochemical Oxidation of phenol

The first papers dealing with the electrochemical degradation of phenols were published in the late 50's. But it was only around 1980 that the first electrochemical reactors were used [25] and that the influence of the nature of the electrodes on the degradation yields began to be studied [26].

Phenol oxidation can be used as a model reaction for methods for treatment of aqueous organic wastes. It represents a large family of compounds and is a good test compound because of its well-known electrode fouling properties. The tarry or resinous deposit formed on electrodes during phenol oxidation is attributed to polymerization products. The electrolysis of high concentrations of phenol, under controlled environments, is also a possible route for synthesis of quinones [27], a process that can add value to various effluents.

The general reaction pathways for phenol are shown in Figure 2.1 depicting the routes to various desired products: carbon dioxide for wastewater treatment, quinones for electrosynthesis, and the polymeric products for metal coating [28]. Formation of the yellow brown polymeric material at the anode surface is strongly dependent on experimental conditions such as alkaline media (pH > 9), low current density (< 30 $mA.cm^{-2}$), high temperature (>50ºC) and high phenol concentration (50 mM) [29]. The further reactions of the quinones and the ether and quinone type polymer structures are slow reactions with the main products being organic acids (i.e. aliphatic acids) such as maleic and oxalic acid.

The production of quinones is of great concern from a toxicity point of view due to the fact that these reaction intermediates are more hazardous than phenol. Among these quinones there is 1,4-benzoquinone, which represents one of the most toxic xenobiotics [30]. Accordingly, complete oxidation of phenol to CO_2 should be achieved to ensure environmentally safe discharges.

However, from an electrosynthesis point of view, hydroquinone has its principal use in the manufacture of black and white film developers. Other uses include the manufacture of antioxidants and polymerization inhibitors; as a chemical intermediate in the manufacture of pharmaceutical, agrochemicals and dyes; in the production of cosmetics and topical creams; and as a laboratory reagent [31].

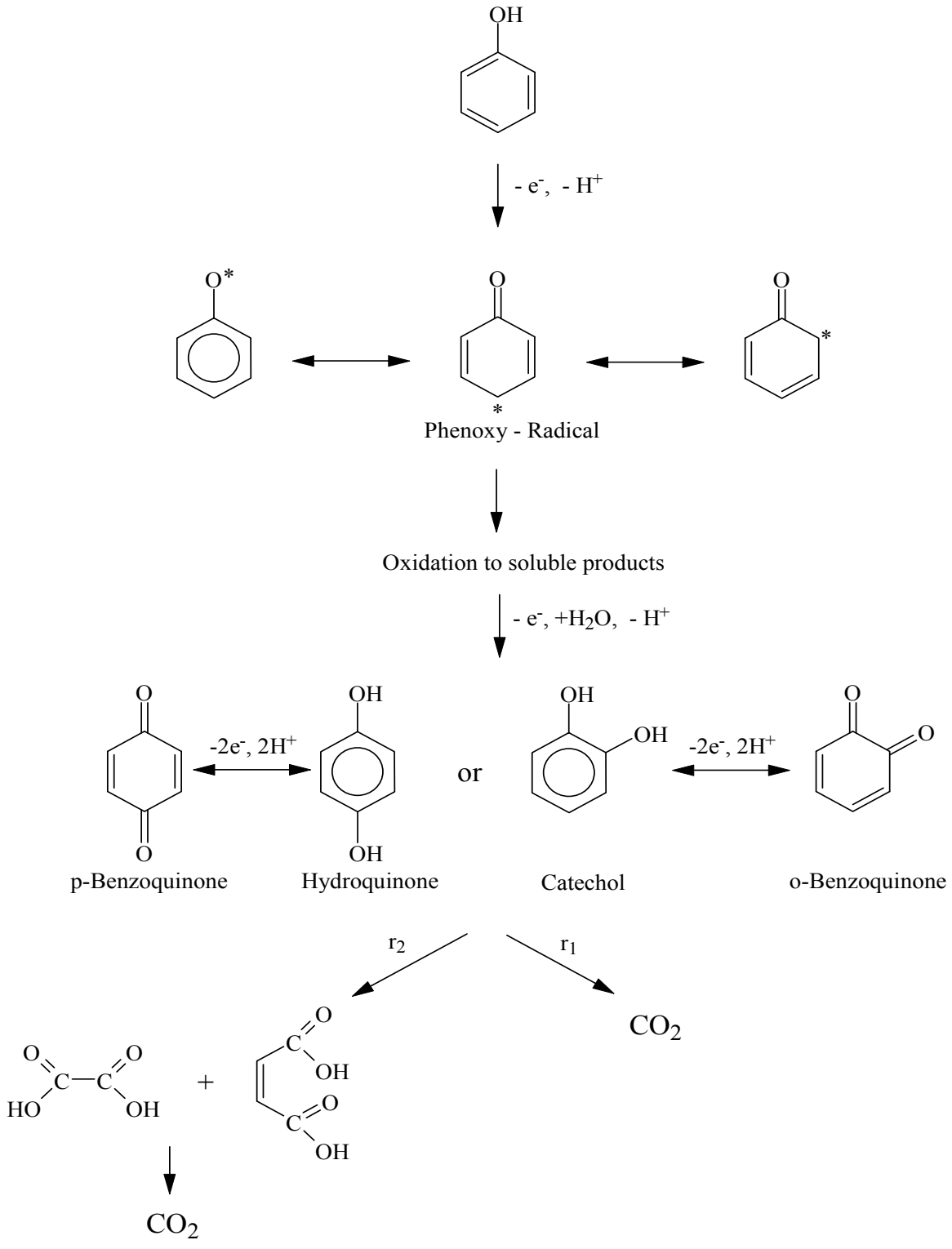

Figure 2.1. Phenol oxidation mechanism to simple organic compounds and carbon dioxide.

2.3 Anode Materials

The removal of undesirable impurities from liquid (usually aqueous) phases through electrochemical processes is based on the possibility of choosing suitable electrodes and potential/current conditions selectively to destroy these impurities [32]. This is due to the dependency of the mechanisms and products of some anodic reactions on the anode material [33]. The dependency of anodic reactions on the anode material can also be illustrated by, for example, formation of hydroquinone and benzoquinone at Ti/IrO_2 anode and carbon dioxide at a Ti/SnO_2-Sb_2O_5 anode by the anodic oxidation of phenol [34].

Oxidation of organic material is governed by two distinguishable mechanisms. That is, direct oxidation on electro catalytic electrodes such as platinum or indirect electrochemical oxidation, which can occur via surface mediators that remain fixed on the anode surface, where they are continuously generated [35]. Even though organic waste can, in general, be oxidized at numerous electrode materials [36], phenols cause inactivation of the anode through deposition of oligomers that form when the phenoxy radical attacks the unreacted substrate.

The possible oligomers that can be formed are illustrated in Figure 2.2. These deposit in the form of a yellow brown film at the surface of the anode. The formation of this anodic film is dependant on experimental conditions and it has been reported that, alkaline media (pH >9), low current density (<30 mA.cm^{-2}), high temperature (≥ 50°C) and high phenol concentration (50 mmol.L^{-1}) favour film formation [37].

Oxide-based anodes such as PtO_2 are generally not as affected by fouling as metals. It has been reported that phenol is oxidized faster at PtO_2 than Pt, graphite or nickel with less adsorption of products onto the electrode surface [38]. However, electrochemically active oxides such as RuO_2 and IrO_2, represent, in general, the most expensive element of coating. When used in severe conditions, losses of active material caused by chemical or electrochemical corrosion can make the process expensive for technological application.

Platinum has proved to be one of the most favoured anodic materials because it shows minimum degradation or corrosion in acid or when used as an anodic or cathodic electrocatalyst [39]. The electrochemical oxidation has also been studied at dimensionally stable anodes (DSA). DSA electrodes are characterized by a thin active coating (usually few micrometers) deposited on a base metal, usually a valve metal: Ti, Zr, Ta, Nb [40].

Comninellis et.al. have studied the electrochemical oxidation of phenol at various anodic materials and their reaction intermediates as well as the measurement of the current efficiency have shown that conventional anodes (Pt, Ti/IrO_2, Ti/RuO_2, Ti/PbO_2) give relatively low current efficiencies [41]. This was in contrast to the Ti/SnO_2 anode, which not only gives high current efficiencies, but allows quasi-complete total organic carbon (TOC) removal. The electrochemical oxidation of phenol has also been studied at alloy electrodes such as platinum/gold alloys (at 60/40 atom %), which effectively prevent the electrode surface fouling, and this is attributed to the presence of the α_2-phase rich in Au [42]. Flow-through graphite electrodes show phenol removal efficiency of 70 % at a current of 2.2 A with the production of a high ratio of quinones that are more harmful than phenol [43].

Amorphous alloys have also been studied as electrode materials, with the analogy that, due to their metastable nature, the amorphous alloys should be more reactive than their crystalline counterparts. Amorphous Ni-Nb based alloys, with different amounts of platinum and tin, have been used for electro oxidation of phenol at room temperature, with the main oxidation products being benzoquinone and hydroquinone [44]. A high rate of phenol removal is also achieved at lead oxide (PbO_2) using a packed-bed cell [45]. Complete phenol oxidation was achieved at optimum conditions of pH and temperature by employing this anode. The main by-products identified were CO_2, benzoquinone and maleic acid. A wide variety of materials can be used as anodes for electrochemical decomposition of organics, however, two main properties are required for a suitable anode: high oxygen overvoltage and corrosion stability. Generally, noble metals are fouled at phenol concentrations > 1 mM and films of polymer material are observed [46].

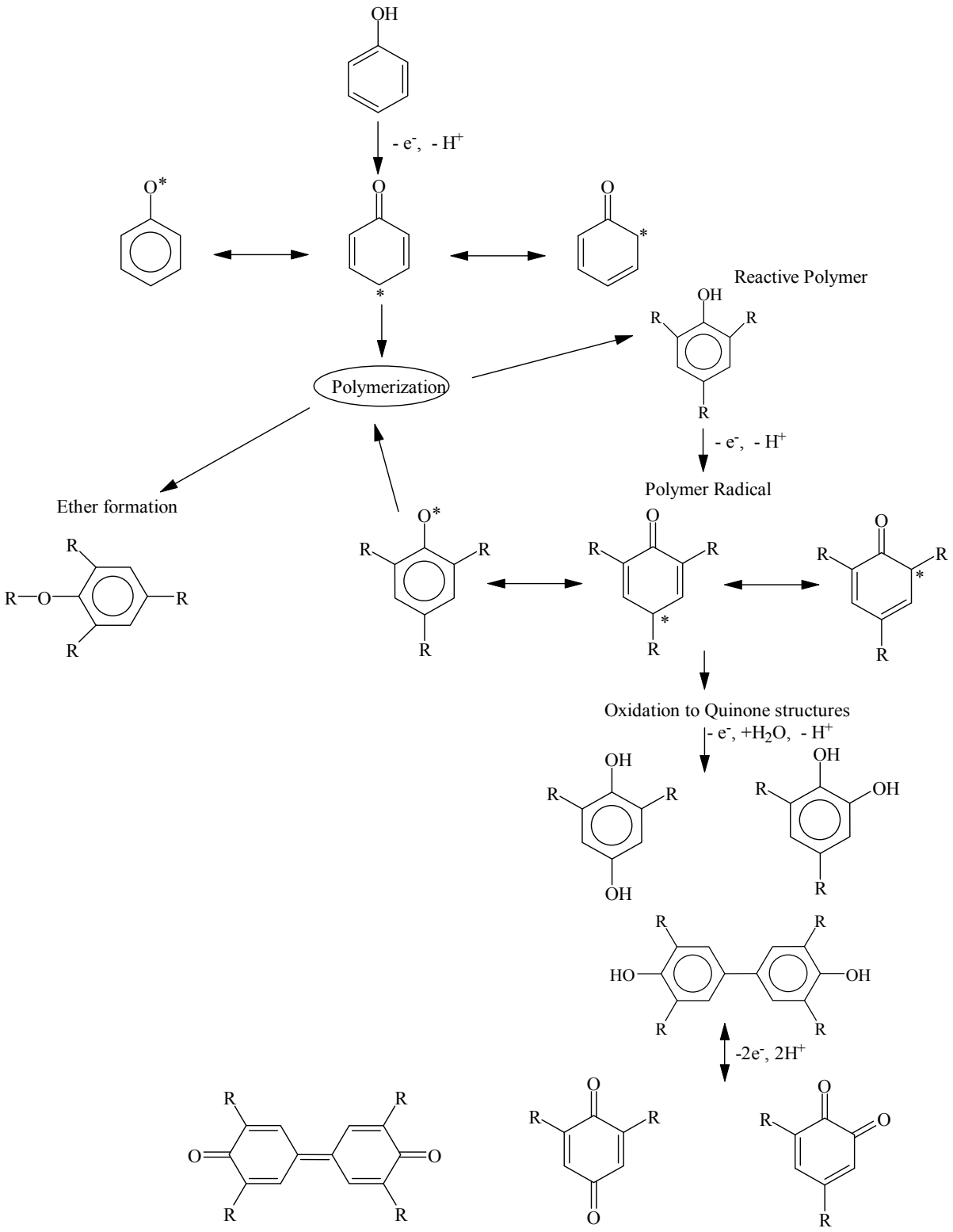

Figure 2.2: Electrochemical oxidation of phenol to oligomers by radical coupling.

2.4 Inorganic Ceramic Membranes for the Electrochemical Oxidation of Phenol

The use of inorganic materials as membrane material is limited although a sudden growth in interest has been observed. Four different types of inorganic materials frequently used may be classified as ceramic, glass membranes, metallic membranes and membranes made from zeolites. In the past, ceramic membranes were applied for the enrichment of uranium hexafluoride (^{235}U) by Knudsen flow [47]. Recently, however, ceramic membranes have been mainly used in water purification processes such as microfiltration and ultrafiltration

In the past few decades, the use of inorganic membranes for various industrial processes, including food, biotechnology, environmental control, electronics and petrochemical industries has grown substantially [48]. Inorganic membranes, such as ceramic and carbon membranes, are thermally stable, chemically inert and are mechanically stable when compared to organic polymeric membranes. Ceramic membranes made out of inorganic materials, such as Al_2O_3 and TiO_2, have been modified into electrodes by deposition of electroconductive materials such as carbon by pyrolysis of methane [49].

Ebonex® ceramic (Ti_4O_7) the most common of ceramic-based anode materials is reported to exhibit electrical conductivity similar to that of graphite (6.3×10^{-4}) [50]. The Ebonex® ceramic anode has been used to study the electrolytic oxidation of trichloroethylene to CO_2, CO, Cl^- and ClO_3^- [51]. Ebonex® and PbO_2-coated Ebonex® electrodes have been used for the electrochemical treatment of phenolic pollutants in water [52]. This work investigates the electrochemical oxidation of phenols, using Al_2O_3 and Al_2O_3/ZrO_2 ceramic membranes as supports for electrocatalysts.

2.4.1 Properties of base material

The inorganic ceramic membranes are composed of a metal (e.g. aluminum, titanium, silicium or zirconium) with a non-metal in the form of an oxide, nitride, or carbide. The membranes that were chosen for this work are made of Al_2O_3 or a mixture of Al_2O_3 (70%) and Yttrium stabilized ZrO_2 (30%) or pure ZrO_2. These include rigid ceramics produced by, for example, slip-casting or moulding method, or ceramic felt, or ceramic paper of metal mesh coated with ceramic layers, or a similar material. The membranes are either in the tubular form or flat form and possess the following properties:

- High mechanical and chemical stability
- Relatively high surface area
- Pore size suitable for microfiltration process
- Inexpensive
- Modifiable

2.4.2 Electroconductive layers

The development of porous electrodes is of importance for various types of industrial applications. Most processes require electrodes with high electrochemical stability, large surface area and good electrocatalytic properties. Such porous electrodes can be applied in the fields of water treatment by electrosorption of undesired compounds such as metal ions [53] and organics [19]. Porous electrodes can be further used in fuel cell applications and this work reports on the applications of ceramic-based porous electrodes for the anodic oxidation of phenol-containing wastewater.

The preparation of electrodes form an integral part of the project on the electrochemical decomposition of organic pollutants. Modifications to the ceramic substrates have to be made in order to adapt the ceramic membranes as porous electrodes. Various electroconductive films, such as pyrolytic carbon, gold and carbon black have been deposited on the ceramic membrane substrate. The desired porous electrode had to meet the following requirements [54]:

- The conductive coating should have low electrical resistance to minimize the potential drop over the axial length of the electrode during the electrolytic process
- The coated substrate must be permeable and the pores of the substrate must remain accessible for the sorption phase that will subsequently be incorporated.
- The porous electrode must exhibit high catalytic activity towards water electrolysis
- The conductive coating should have high chemical stability under anodic and cathodic conditions

2.4.3 Electrochemical reactor design

In this report, Chapters 3 & 4 discuss results obtained from using three dimensional electrode structures. As will be seen in these chapters, the configurations of these electromembrane systems

would be difficult to apply for water treatment purposes. Hence it was decided adopt electromembrane systems that resemble that of fuel cell technology.

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3. THE ELECTROCHEMICAL OXIDATION OF PHENOL IN AQUEOUS MEDIA AT A TUBULAR CERAMIC-BASED MEMBRANE COATED WITH PYROLYTIC CARBON

Abstract

Phenol was used as a model compound for the electrochemical treatment of aqueous organic wastes. Parameters such as applied potential, feed concentration, and pyrolysis time, were studied. The pyrolytic carbon was deposited throughout the ceramic membrane matrix by pyrolysis of LPG gas in a tube furnace at 900°C. To enhance the electrochemical oxidation process, inorganic proton conducting materials were impregnated into the ceramic membrane porous structure. The electrochemical oxidation of phenol was carried out under acidic and neutral conditions by means of a flow-through electromembrane reactor. The specific energy consumption for phenol degradation was calculated in terms of kWh per gram of phenol destroyed. The concentration of phenol as well as its electrolysis products was monitored by HPLC analysis.

3.1 Introduction

Highly electrochemically active surfaces can be prepared onto suitable substrates by pyrolysis of a carbonaceous gas. Materials such as glassy carbon, graphite [1], porcelain ceramics [2], machinable glass ceramic [3] and quartz [4,5] have previously been used as the substrate. Solid electrodes based on carbon have found widespread use in electroanalytical chemistry when mercury electrodes are not suitable [6]. Due to their applicability to oxidation of organic compounds over an extended potential range, carbon electrodes have been mainly applied in voltammetry and in amperometric detectors [7].

This section of the report discusses the use of tubular ceramic-based membranes as substrates for the deposition of carbon films by pyrolisis of natural gas. It has previously been reported that deposition parameters such as pyrolysis time, temperature, partial pressure and flow rate of the carbonaceous gas have an effect on the properties of the carbon film [7]. Pyrolysis times a short as few minutes have been reported [4], however, longer periods are more common. In this work, pyrolysis time range from 30 to 120 minutes.

Although literature on the electrochemical oxidation of phenol on electrodes prepared from pyrolytic carbon is scares, other carbon electrodes have been employed in the electrochemical treatment of phenols in aqueous solutions [8]. Graphite electrodes have been employed for the electrochemical oxidation of phenol under acidic conditions with current efficiency (CO_2) reaching a maximum value

in the current range of 1.0 to 1.2 A [9]. Kirk and Gattrell also studied the electrochemical oxidation of phenol at glassy carbon electrodes [10] while Comninellis et al have studied the electrochemical oxidation of phenol at boron-doped diamond (BDD) thin film coating on a p-Silicon substrate [11]. Ceramic membranes coated with pyrolytic carbon have also been reported to be highly effective electrodes for the anodic oxidation of phenol in wastewater [12].

A new class of materials, namely, inorganic-based proton conducting materials such as phosphates of polyvalent metals, for example, titanium and zirconium, has been developed. Their use results in significant improvements in various electrochemical processes. Inorganic proton conductive membranes have been previously tested for separating hydrogen from a mixture of gases. Since the purification from organic substances also depends upon high organic adsorption capacity on the membrane, it is believed that impregnation with proton conductors would enhance adsorption due to the increased surface area of the membrane.

3.2 Experimental

3.2.1 Materials

Tubular ceramic membranes made from Al_2O_3 (Inorcermic, Germany) were chosen for this study. The main properties of these ceramic membranes are given in Table 3.1.

Table 3.1: Properties of unmodified tubular ceramic membranes from Inorcermic

Base material	Al_2O_3	
Parameter	Units	Value
Outer diameter	mm	10
Inner Diameter	mm	7
Average Pore Size	μm	0.9
Porosity	%	40 – 45
Permeability	$m^3.m^{-2}.bar^{-1}.h^{-1}$	105

(a) Carbon coating

The preparation of the carbon film on the ceramic membrane matrix was carried out by pyrolysis of LPG gas (AFROX) at a predetermined temperature and flow rate. The ceramic substrate was placed inside a quartz tube in a tube furnace. The LPG gas was introduced into the tube from one side at a flow rate of 50 ml/min. Pyrolysis temperature was varied between 700 and 900 ºC and the pyrolysis time ranged between 30 and 120 min. The resulting carbon-coated membranes were removed immediately after switching off the gas feed in order to avoid the carbon coating being burnt off in

air. After deposition was complete, the carbon material deposited on the wall of the quartz tube was burned off at 800 ºC in an oxygen atmosphere.

(b) Anodic oxidation

The experimental electromembrane reactor used in this study is shown in Figure 3.1. The principle features of the cell are the electromembrane, which is used as the anode and the cathode placed inside the ceramic tube. The cathode, which can be any conducting metal, such as stainless steel or titanium rod, protrudes from the reactor and connected to an external power source. The anode, which is prevented from touching the cathode by placing o-rings around the cathode, is connected to the external power source via a stainless steel coil. The feed water is pumped into the electromembrane reactor and comes into contact with the electrocatalytic ceramic membrane and passes through the membrane and the "phenol free" water is collected as permeate.

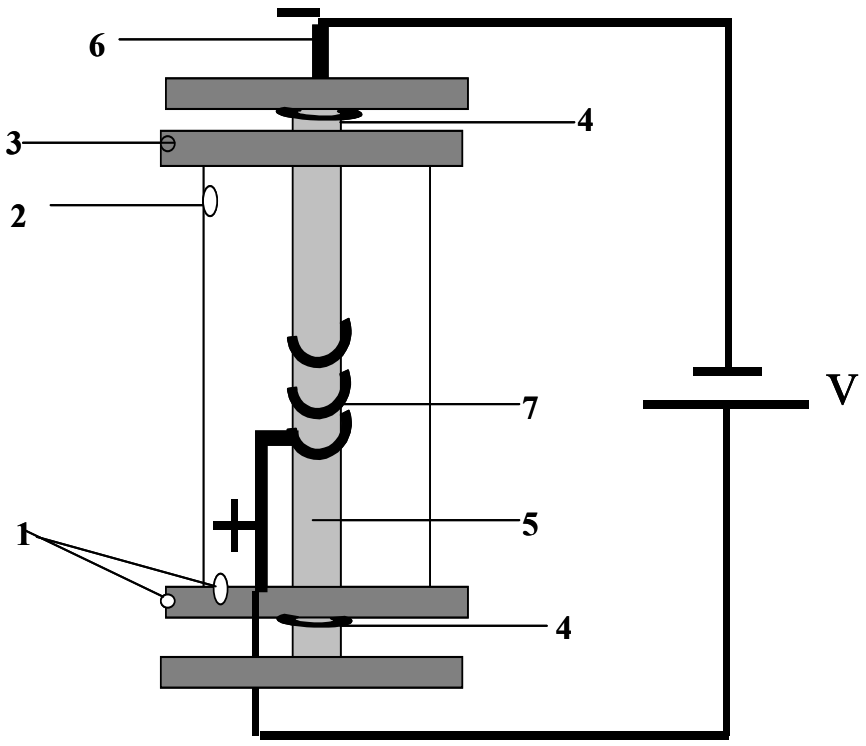

Figure. 3.1 Schematic representation for the tubular electrombrane reactor used in the electrochemical oxidation of phenol in aqueous media and its features are (1) feed inlet, (2) reject outlet, (3) permeate outlet, (4) o-rings to prevent leakages in the reactor, (5) electroconductive ceramic membrane, (6) the cathode and (7) the conductive coil that connects the anode and the external power source.

(c) Proton conductors

Zirconium phosphate was used as the proton conducting material in this work. The preparation of the zirconia phosphate starts with the preparation of a zirconia sol from the zirconium oxychloride salt ($ZrOCl_2.8H_2O$).

1 M $ZrOCl_2.8H_2O$ (Alfa Aesar) was prepared by adding 32.2 g of the zirconium salt in 100 ml water. The pH of the 1 M $ZrOCl_2$ solution was adjusted to pH 4 by adding ammonia solution (drop-wise). The resulting precipitate was filtered through and washed with ultra pure water. An equal weight of water was added to the filtrate and stirred until a slurry was formed. The slurry was refluxed for 120 hours.

The membranes are impregnated with the zirconia sol by dipping the membrane into the sol and heating to temperatures ranging between 80 and 90˚C. The membrane is removed from the heat and allowed to cool to room temperature and then dried at 80˚C. The phosphate groups are incorporated by treating the membrane with 25% phosphoric acid (H_3PO_4) at 90 ˚C followed by washing of the membrane with distilled water and drying in the oven.

3.2.2 Analysis

Analysis of phenol and its oxidation products were carried out on a high-performance liquid chromatography (Spectra physics, SP 8450). Samples of 20 µL were injected via an autosampler (Spectra physics, SP 8780). The mobile phase was methanol/water (v/v) 40/60 with trymethylamine buffer. The column that was used for separation in the phenol and aromatic intermediates analysis was a HAISIL 100 C18 reversed phase column (Higgins Analytical) at a flow rate of 0.8 $ml.min^{-1}$ and column temperature of 30°C. The UV detector was set at 254 nm. An ICSep ICE-ORH-801 (Transgenomic) column was used for the analysis of organic acids. A flow rate of 0.8 $ml.min^{-1}$ was maintained with a 0.01N sulphuric acid mobile phase at column temperature of 40°C. The detector was set at 214 nm.

3.2.3 Method

All the experiments were carried out at room temperature and ultra pure water (Milli-Q, ρ=18 M Ω cm^{-1}) was used throughout the work. The feed solutions (0,1$g.L^{-1}$ phenol) were prepared from reagent grade phenol (Aldrich puris. > 99%).

3.3 Results and Discussions

This section of the chapter is divided into two separate sections, whereby the one section discusses the results that were obtained by varying different pyrolysis conditions for the deposition of carbon on the ceramic substrate. The other section discusses the effectiveness of our carbon-coated electromembranes in the electrochemical decomposition of phenol as well as present the different intermediates obtained under different conditions.

3.3.1 Carbon Deposition

A homogenous black carbon coating was deposited on the ceramic membrane surface and matrix by pyrolysis of LPG. Figure 3.2 shows a comparison of the SEM pictures of the blank support and the coated supports. Although the differences in the characteristics of the blank and the carbon-coated membranes are not clearly visible under SEM, small carbon particles can be seen on the surface of the ceramic membrane supports.

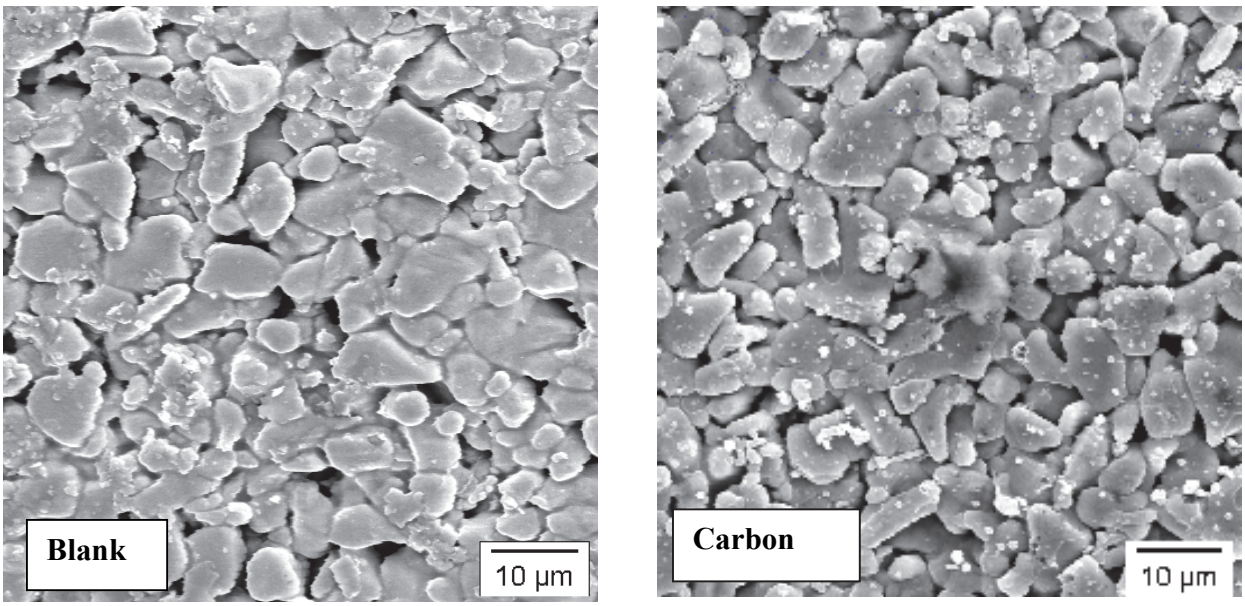

Figure 3.2: SEM images of the blank and the carbon-coated ceramic membranes.

Shorter pyrolysis times resulted in less carbon being deposited on the ceramic surface. The period of pyrolysis also had an adverse effect on other properties of the membrane. Table 3.2 shows the different properties of the membranes as a result of the amount of time taken for carbon deposition.

As pyrolysis time increases, more carbon is deposited and hence resistance decreases and the membranes become less permeable (Table 3.2). The results obtained also show that, for our applications, pyrolysis temperature of 900º C and pyrolysis time of 60 minutes produced the best results. Under these conditions, the required permeability as well as conductivity suitable for the electrochemical oxidation of phenol was achieved. At temperatures below 900º C LPG gas was not completely pyrolysed and products that resemble tar were formed. The subsequent deposition of such products onto the ceramic support resulted in severe loss of permeability and the conductivity of the membranes was not improved. Above 900º C other forms of carbon are produced which would not be suitable for our applications. Impregnation with inorganic proton conducting materials results in both loss of permeability and conductivity.

Table 3.2: The properties of carbon coated ceramic membranes with respect to pyrolysis time.

Membrane Type	Pyrolysis Time (min)	Permeability ($m^3.m^{-2}.bar^{-1}.h^{-1}$)	Resistance ($\Omega.cm^{-1}$)
1	30	1.61	2.4
2	60	1.03	2.0
3	90	0.64	1.3
4	120	0.58	0.7
*5	60	0.55	2.9

*Membrane impregnated with inorganic proton conductors.

The electrical stability of the carbon-coated membranes was studied by voltammetry. This can be illustrated by means of cyclic voltammograms (Figure 3.3).

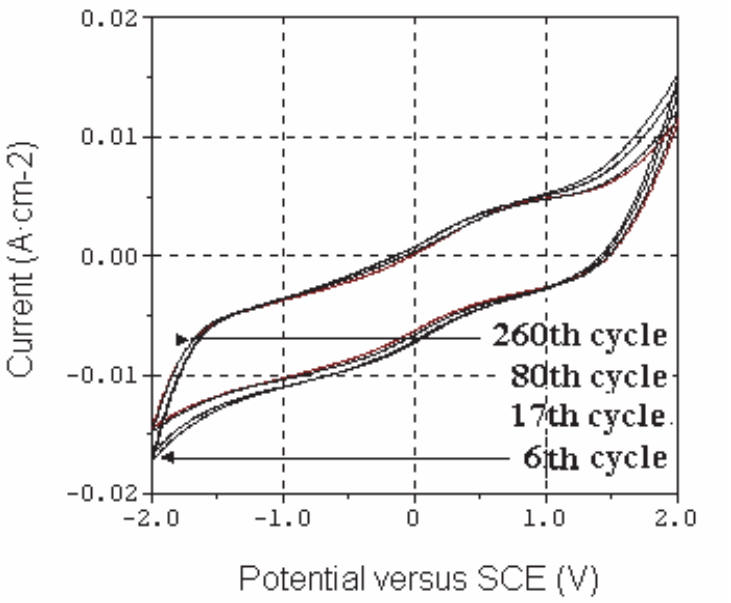

Figure 3.3: The electrical stability of membrane coated with pyrolytic carbon.

3.3.2 Electrochemical Oxidation

This section of the chapter stets out to illustrate and discuss the results obtained by using the carbon-coated tubular ceramic membranes as anode material for the electrochemical oxidation of aqueous phenol. Several sets of experiments were conducted, in triplicate, and the ones that are reported upon are listed in Table 3.3 (details of experiments are listed in appendix H).

It is also noteworthy to mention that permeability through the membrane was lost by impregnation with proton conducting materials. These membranes could, however still be used be used for the electrochemical oxidation of aqueous phenol, as reported in the sections to come.

Table 3.3: Experimental variables in the electrochemical oxidation of phenol at ceramic based tubular membranes coated with pyrolytic carbon.

Experiment	Applied potential (V)	Flux ($L.m^{-2}.h^{-1}$)	Electrolyte	Electroconductive coating	Proton conductors
1	2.5	240 ± 10	Na_2SO_4	Carbon	No
2*	2.5	240 ± 10	Na_2SO_4	Carbon	No
3**	2.5	240 ± 10	Na_2SO_4	Carbon	No
4	2.5	120 ± 3	Na_2SO_4	Carbon	Yes
5	2.5	240 ± 10	H_2SO_4	Carbon	No
6	2.5	115 ± 5	H_2SO_4	Carbon	Yes

*Regenerated membrane **The membrane was regenerated twice

(i) Experiment 1

In this experiment a feed solution of 100 mg.L^{-1} phenol in 0.1 M Na_2SO_4 was pumped into the tubular electromembrane reactor at an applied potential of 2.5 V. The total volume of the feed solution was 1 liter. A constant flow rate was maintained and samples were collected from the permeate side at certain time intervals. Each sample was tested for the disappearance of phenol using the 4-aminoantipyrine and HPLC methods. Identification of the different intermediate species that were produced during the experiment was done by the use of GC-MS and HPLC.

Although phenol was continuously degraded to 100 %, further anaylis by GC=MS and HPLC shows that most of the phenol was converted to its corresponding aromatic intermediates (p-benzoquinone and hydroquinone) as shown in figure 3.4. The concentration of p-benzoquinone went up as high as 12.7 to 14.0 mg.L^{-1}. The concentration of hydroquinone, which is a resonance structure of p-benzoquinone, was even higher (>30 mg.L^{-1}). The chromatogram also showed that two other unidentified products of high molecular weight were produced during the experiment.

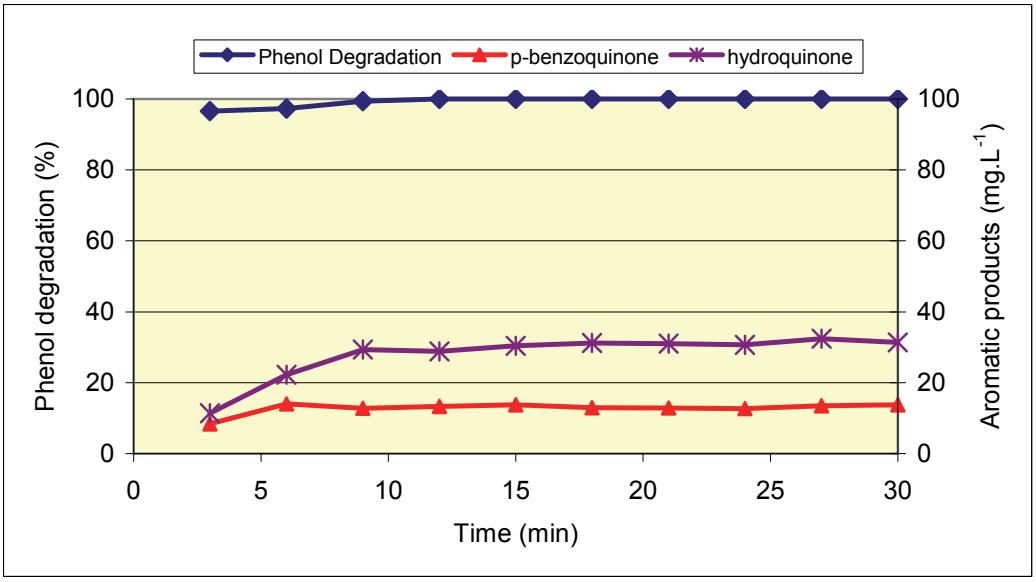

Figure 3.4: Electrochemical oxidation of phenol at a ceramic-based electromembrane coated with pyrolytic carbon.

(ii) Experiment 2 & 3

Experiments 2 and 3 (Table 3.3) are based on electromembranes that have been regenerated. Regenerated membranes, in this case, are membranes that had been coated with pyrolytic carbon and used in several experiments until significant phenol degradation could not be achieved on the membranes. Approximately 5 liters of liquid would have been passed through the membranes prior to loss of activity. After the experiment, the membrane is then heated in the furnace at 800 ºC under oxygen. The pyrolytic carbon and organic residues that might have been deposited on the membrane surface and pores during the experiment are burnt off. The membrane is then recoated with pyrolytic carbon and reused for the electrochemical oxidation of phenol.

Even though the regenerated membranes posses sufficient electrical conductivity to be used as electrodes, they did not exhibit same kind of electrical stability as the original membrane. In the original membrane, current density stays almost constant for more than 30 min whereas it (current density) decreases faster with the regenerated membranes (Figure 3.5).

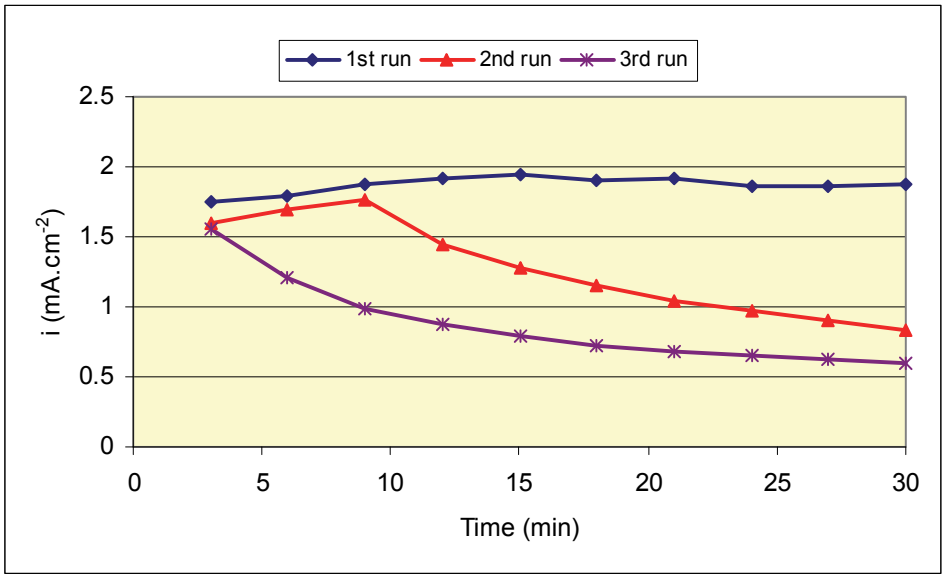

Figure 3.5: The effect of membrane regeneration on its electrical stability

As with the membranes' electrical stability, the electrocatalytic activity for the degradation of phenol was also decreased at regenerated membranes, as illustrated in Figure 3.6. As previously explained, phenol degradation was reduced (from 100 % to less than 40 %) by regenerating the membrane and further electrocatalytic "inactivation" was noticed with more membrane regenerations.

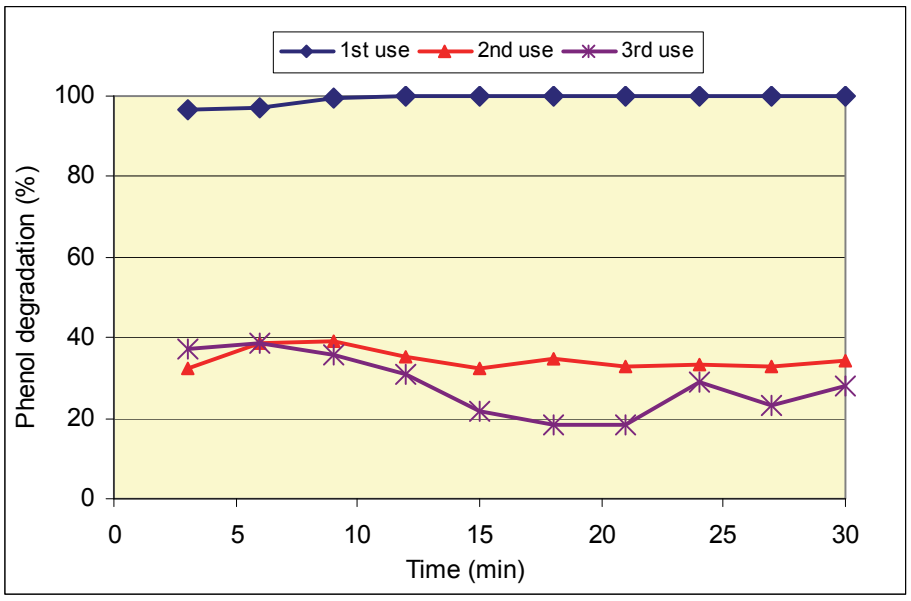

Figure 3.6: The effect of membrane regeneration on the electrochemical oxidation of phenol (100 $mg.L^{-1}$).

(iii) Experiment 4

It is believed that inorganic proton conducting materials would enhance the electrochemical degradation of phenol by speeding up the rate of diffusion of protons from the anode side to the cathode. In this experiment, a membrane was coated with pyrolytic carbon and then impregnated once with zirconium phosphate (Section 3.2.1 c). Figure 3.7 illustrates the results obtained from the said experiment.

An interesting observation was that, although phenol was not completely degraded during the experiment (60 to 82 %), the concentration of detected aromatic intermediates was zero in some samples and only 10 $mg.L^{-1}$ in some samples. The incomplete degradation of phenol could be brought about by the fact that impregnating the membrane with proton conductors increased the resistance of the membrane and hence the current generated during the experiment was very low (0.8 $mA.cm^{-2}$)

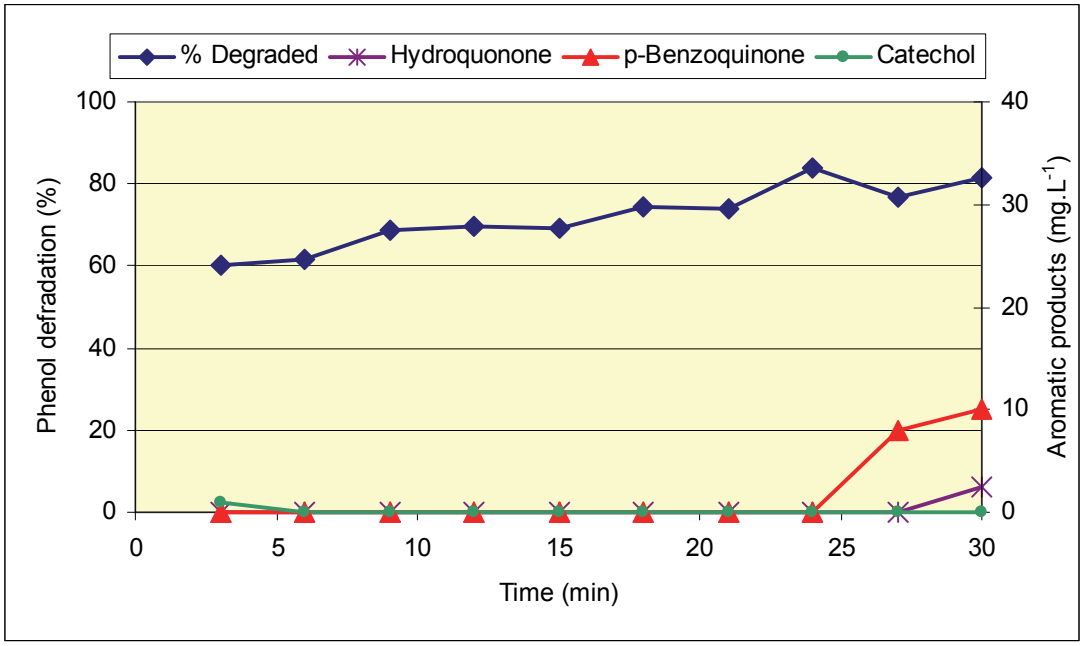

Figure 3.7: Electrochemical oxidation of phenol (100 $mg.L^{-1}$) at a carbon-coated electromebrane impregnated with proton conductors.

(iv) Experiment 5

This experiment was carried out under acid conditions. 0.05 M sulfuric acid was used as the background electrolyte and a potential of 2.5 V. The flux was kept constant at 240 $L.m^{-2}.h^{-1}$ and no flux decline was noticed during the entire duration of the experiment. Degradation of phenol proceeds faster under acid conditions, with no trace of phenol in all the samples that were collected.

Even though phenol was completely degraded in just a single pass through the electrocatalytic membrane, the concentration of the aromatic intermediates formed was still very high. The aromatic intermediates that were formed are p-benzoquinone (16.6 $mg.L^{-1}$) and hydroquinone (9.96 to 14.79 $mg.L^{-1}$) as shown in Figure 3.8.

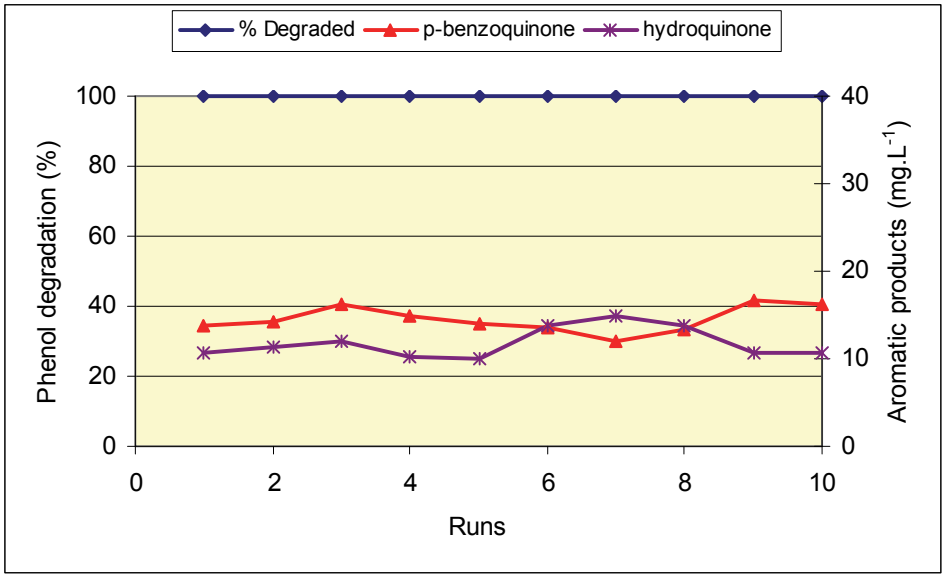

Figure 3.8: Electrochemical oxidation of phenol and emergence of aromatic intermediates a carbon-coated electromembrane under acidic conditions.

(v) Experiment 6

Figure 3.7 has shown that the introduction of inorganic proton conductors onto the carbon-coated ceramic matrix had a positive outcome in terms of the concentration of the aromatic intermediates that are formed during the electrochemical oxidation of phenol.

Although phenol was not completely degraded in all the collected samples, the concentration of the aromatic intermediates that were produced (p-benzoquinone and hydroquinone) had been reduced (Figure 3.9) compared to the results illustrated in Figure 3.8. The concentration of p-benzoquinone ranged between 0.19 and 0.41 $mg.L^{-1}$ and that of hydroquinone between 0.071 and 0.18 $mg.L^{-1}$. All the results that were discussed are summarized in Table 3.4.

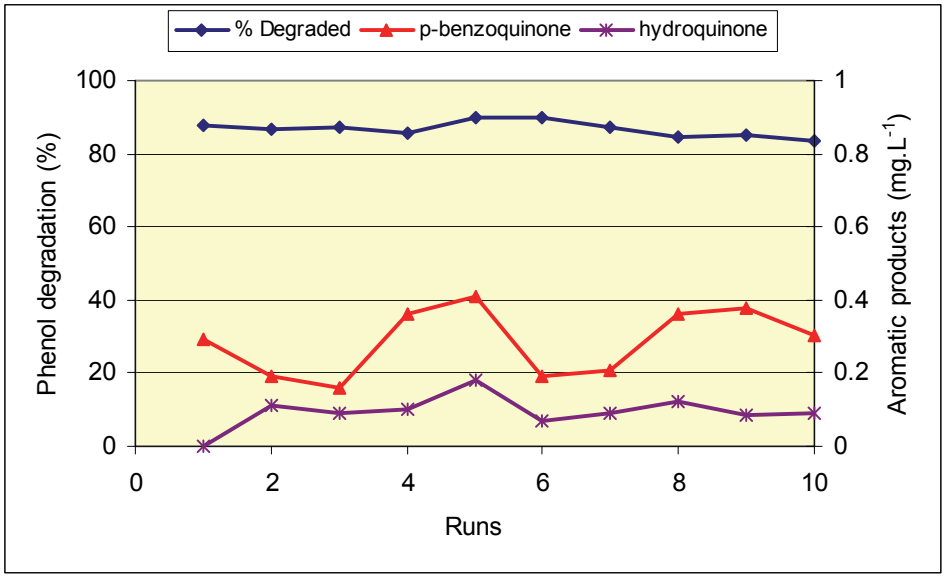

Figure 3.9: Electrochemical oxidation of phenol at a carbon-coated electromebrane impregnated with proton conductors, under acid conditions.

Table 3.4: Summary of results from the electrochemical oxidation of phenol at electromembranes coated with pyrolytic carbon.

Experiment	Phenol degradation (%)	Energy consumption (kWh/g)	Benzoquinone (mg/L)	Hydroquinone (mg/L)	Other intermediates
1	97 - 100	0.0019	14	37	2 peaks
2	34 - 40	0.0039	6.7	14.3	2 peaks
3	18 -24	0.0060	4.8	13.6	2 peaks
4	60 - 82	0.0031	0 - 10	0.59	No peaks
5	100	0.0013	4.7	9.96 – 14.79	2 peaks
6	81 - 86	0.0030	0.9	0.31	No peaks

Here, “other intermediates”, refers to those products that were not identified with HPLC and GC-MS but whose peaks were present on the chromatograms. It must also be noted that due the reactions with the cathode (stainless steel), the resulting permeate, from all the experiments were above a pH value of 11. This is an indication of current inefficiency due to the steel corrosion.

3.4 Conclusions

Coating ceramic-based membranes with pyrolytic carbon could produce electrodes of high conductivity. By adjusting the pyrolysis time, the electrical conductivity and permeability through the membrane could be regulated with some reproducibility. Apart from being stable electrodes, carbon

coated ceramic membranes also exhibit very good electrocatalytic activities for the electrochemical oxidation of phenol.

Phenol was readily oxidized to p-benzoquinone and hydroquinone. Hydroquinone is formed as a result of the partial reduction of p-benzoquinone at the cathode. Our studies also show that after the membranes had been used for several times, electrical and catalytic properties were gradually lost. The membranes could, however, be regenerated but although the regenerated membranes had good electrical conductivity, their catalytic properties had been reduced.

The concentration of the aromatic intermediates that were formed was extremely high for environmental purposes. Introducing the resulting feed into another reactor, which could be arranged in series with the first, could solve this problem. The problem in this case is that, the resulting permeate already has a pH of 11 or greater (from initial pH ranging between high acidity to neutral). At highly alkaline pH, the phenol molecule is said to ionize to form phenoxy radicals which then couple to form polyphenols and other high molecular weight products. Studies to analyze the extent to which polyphenols are formed were not conducted in the work reported here. It is, however, possible that such compounds could be deposited on the electromembrane and further contribute to loss in activity.

Impregnating the carbonized membranes with inorganic proton conductors (zirconium phosphate) slightly reduced the electrical conductivity and the flux through the membrane. Although the electrocatalytic properties of the proton conductive membranes were slightly reduced in terms of complete degradation of phenol, aromatic intermediates were formed at very low concentrations. Hence the introduction of proton conductors improved the efficiency of the process from a by-product formation point of view. The concentration of both phenol and its corresponding aromatic intermediates was low enough (< 5 mg.L^{-1}) to be treated biologically.

3.5 References

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4. THE ELECTROCHEMICAL OXIDATION OF PHENOL IN AQUEOUS MEDIA AT A TUBULAR CERAMIC-BASED MEMBRANE COATED WITH GOLD-PLATINUM FILM

Abstract

The electrochemical oxidation of aqueous phenol was studied at ceramic membranes coated with a gold layer and impregnated with a platinum-based catalyst. A thin gold film was deposited by sputtering in order to enhance the ceramic membranes electroconductive properties. The platinum catalyst was impregnated by thermal decomposition of H_2PtCl_6 at 450 ºC. The electrochemical stability and electrocatalytic efficiency of the Au/Pt electromembranes were also studied by voltametric techniques. The electrooxidation of phenol was carried out under room temperature at a constant potential difference. The effect of the gold-platinum membranes on the production of intermediate products from phenol electrooxidation was studied. The efficiency of the electromembranes, with respect to aromatic intermediates formed, was improved by impregnating with inorganic proton conductors.

4.1 Introduction

Gold is generally considered as a poor electrocatalyst, particularly under acidic conditions [1]. A considerable amount of research has been conducted in the past few decades to improve the catalytic activity of existing electrocatalysts and to develop new, better ones. Gold-supported platinum catalysts have been shown to have excellent catalytic activity for the 4-electron reduction of O_2 in acidic medium [2]. The electrochemical oxidation of simple organic compounds such as oxalic acid [3] and formaldehyde [4] have already been studied at gold electrodes.

Since the electro-oxidation of phenol has been reported to involve polymerization steps due to electrode pretreatment and other experimental conditions [5], gold has been used in the electrochemical quartz crystal microbalance (EQCM) to give information on changes in the interface and the occurrence of polymerization [6].

Literature on the electrochemical oxidation of phenol on gold is scarce. Ureta-Zanartu et al. studied the electrochemical oxidation of chlorophenols at a gold electrode and found that the electro-oxidation of phenol depended on pH, the phenol concentration, the number of chlorine atoms in the aromatic ring, and the position of the Cl atoms with respect to the phenolic OH [5]. A mechanism for the electrochemical oxidation of phenol at a platinum/gold electrode in acid medium, was proposed

by Iotov and Kalcheva [6]. They also reported that due to the presence of the α_2-phase in the Pt/Au alloy catalyst, the electrode surface fouling is effectively removed. The electrochemical oxidation of phenol on ceramic-based membranes coated with gold and platinum has also been investigated [7]. This section of the study reports more work that have been conducted on the electrochemical oxidation of phenol on ceramic membranes coated with a gold layer and impregnated with a platinum-based catalyst.

4.2 Experimental

4.2.1 Materials

Similar ceramic supports and electromembrane reactor that were discussed in Chapter 3 (Section 3.2.1) were also used in the studies that are discussed in this chapter.

4.2.2 Gold Coating

A thin layer of gold was deposited on the surface of the ceramic substrate by using an Edwards S 150B sputter coater. In order to achieve sufficient conductivity, the deposition time was 10 min on each side of the tubular ceramic membrane.

4.2.3 Analysis

High performance liquid chromatography (HPLC) was used to monitor the disappearence of phenol and the emergence of its oxidation products. This was done on a Spectra physics, SP 8450 HPLC. Samples of 20μL were injected via an autosampler (Spectra physics, SP 8780) running with a mobile phase of methanol/water (v/v) 40/60 with trymethylamine buffer. The column that was used for separation in the phenol and aromatic intermediates analysis was a HAISIL 100 C18 reversed phase column (Higgins Analytical) at a flow rate of 0.8 $mL.min^{-1}$ and column temperature of 30°C. The UV detector was set at 254 nm. An An ICSep ICE-ORH-801 (Transgenomic) column was used for the analysis of organic acids. A flow rate of 0.8 $mL.min^{-1}$ was maintained with a 0.01N sulphuric acid mobile phase at column temperature of 40°C. The detector was set at 214 nm.

4.3 Results and Discussions

4.3.1 Gold and Platinum Deposition

Any specimen that is to be viewed by means of the scanning electron microscope (SEM) has to be coated with electroconductive material first. In general, most samples are gold sputtered before being

viewed by SEM. In our case, the blank sample in Figure 4.1 is coated with gold. A thin homogenous gold layer was deposited on the ceramic membrane surfaces and this resulted in very low membrane resistance (0.2 to 0.3 Ω/cm). The entire membranes surface was coated with Pt after impregnation with a solution of H_2PtCl_6 and heating up at 450 ºC.

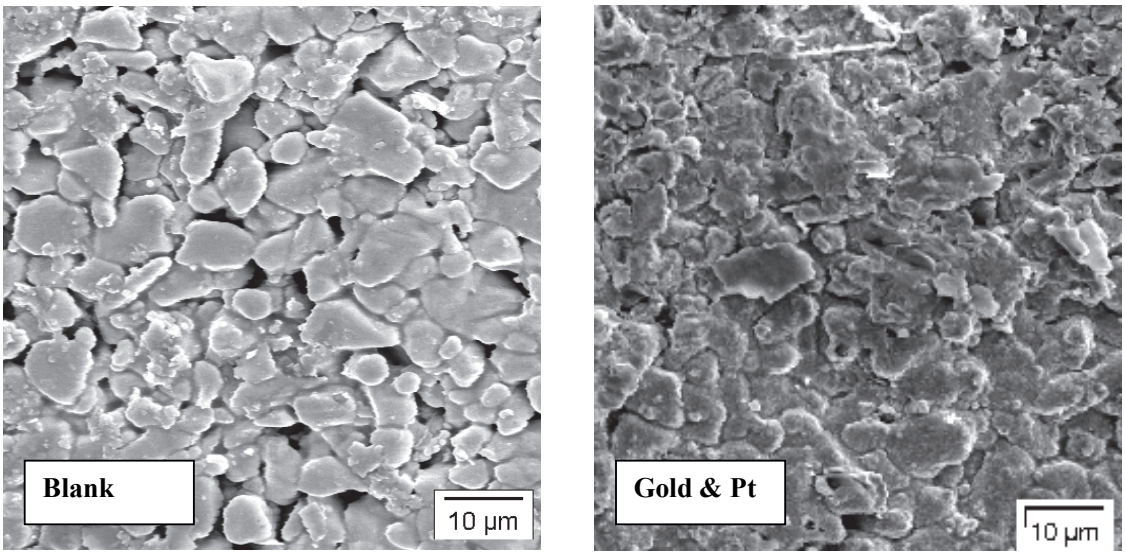

Figure 4.1: SEM images of the blank and the Au/Pt coated ceramic membranes

4.3.2 Electrochemical Oxidation

In this section, the usefulness of gold as electroconductive material is discussed. However, as discussed below, unlike carbon, which could be used as electroconductive and electrocatalytic material, the gold coating does not exhibit good catalytic properties for the electrochemical degradation of phenol. The experiments that were carried out are listed in Table 4.1 below.

Table 4.1: Experimental variables in the electrochemical oxidation of phenol at ceramic based tubular membranes coated with gold and gold/platinum.

Experiment	Applied potential (V)	Flux ($L.m^{-2}.h^{-1}$)	Electrolyte	Electroconductive coating	Proton conductors
1	2.0	240 ± 10	Na_2SO_4	Au	No
2	2.0	240 ± 10	Na_2SO_4	Au/Pt	No
3*	2.0	240 ± 10	Na_2SO_4	Au/Pt	No
4	2.0	2 10	Na_2SO_4	Au/Pt	Yes
5	2.0	240 ± 10	H_2SO_4	Au/Pt	No

*Regenerated membrane

(vi) Experiment 1

The gold-coated membranes were tested for the electrochemical oxidation by voltammetric techniques at phenol concentration of 50 mM and electrolyte solution of 0.5M H_2SO_4. Figures 4.2 and 4.3 show linear voltamograms of sweeps carried out in the absence and in the presence of phenol from 0 to 2.3 V.

In the presence of phenol the resulting voltamogram shows that the gold coating ahs some catalytic activity for the oxidation of phenol (Figure 4.3). Oxidation peaks can be seen when phenol is present in the electrolyte solution. Another observation was that the gold layer on the ceramic membrane started coming off in the acidic solution and a passivative film was formed at surface of the gold-coated ceramic membrane. This film could be the result of the high phenol concentration but it had negative outcomes on the stability of the electromembrane.

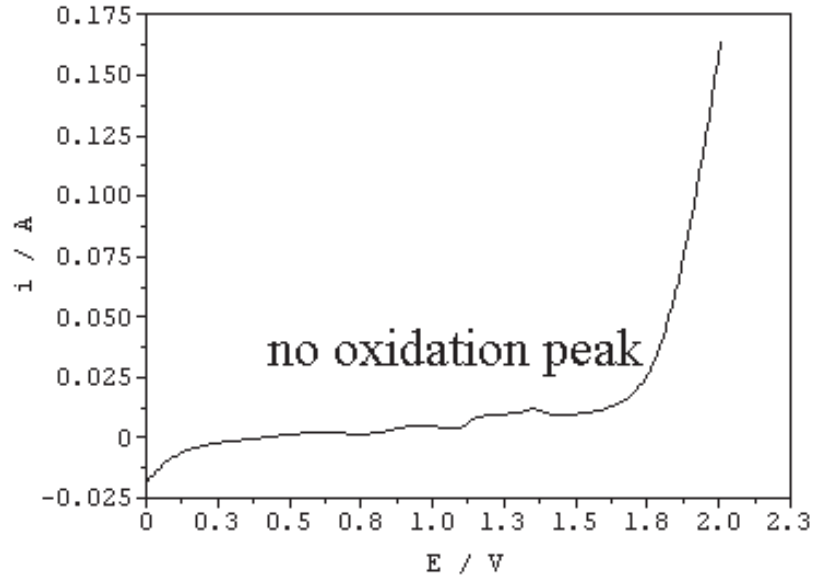

Figure 4.2: Linear voltamogram of a gold-coated electromembrane in acidic solution.

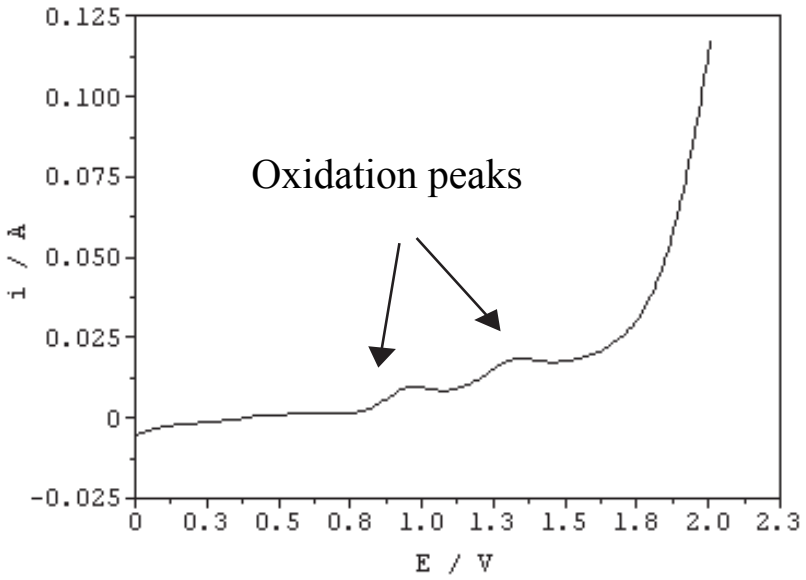

Figure 4.3: Linear voltamogram of a gold electromembrane in a phenolic solution.

The voltamogram in Figure 4.4 shows that the gold-coated electromembrane became less stable with number of scans carried out.

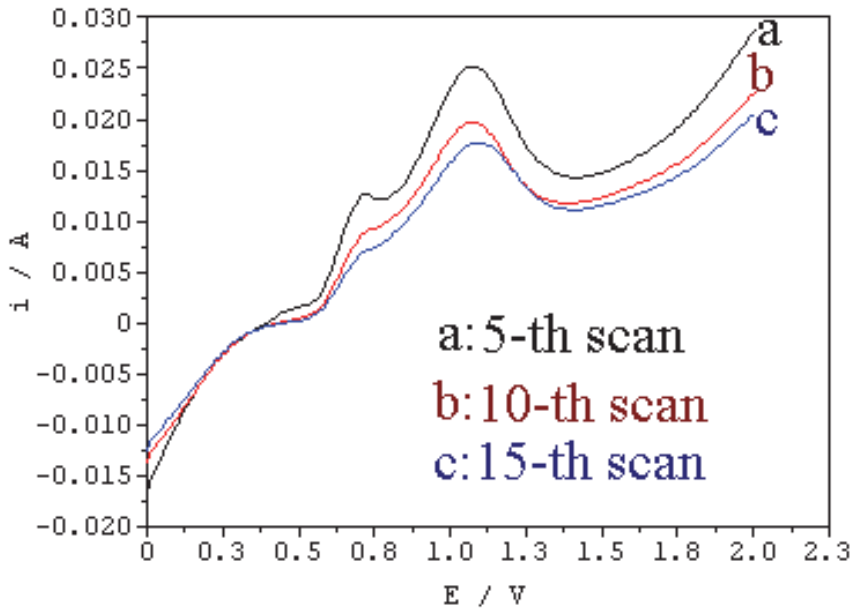

Figure 4.4: Stability of the gold-coated electromembrane in 0.5 M phenol and 0.5 M sulfuric acid solution.

Experiments carried out in an electromembrane reactor show that the catalytic activity of the gold electromembranes is not good even at neutral pH (i.e. using Na_2SO_4 as electrolyte) containing a solution of 100 $mg.L^{-1}$ phenol.

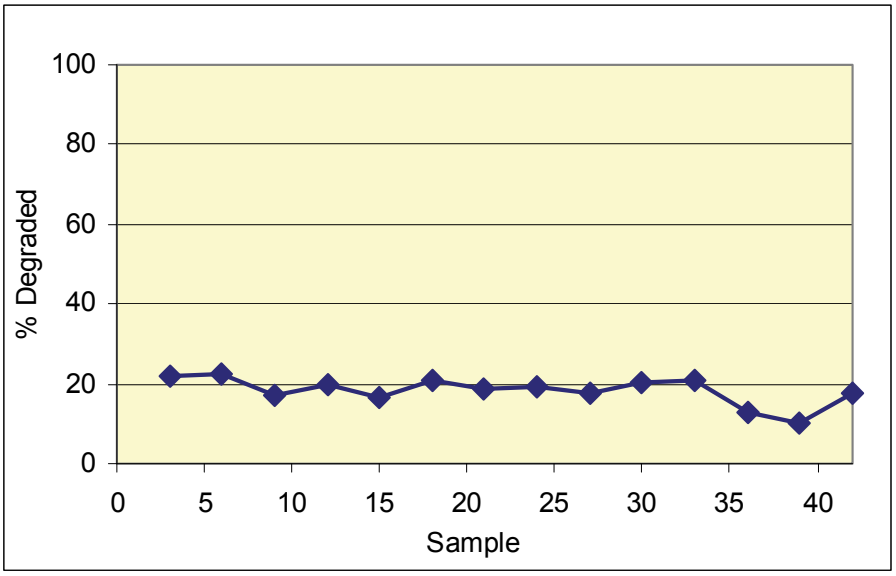

Figure 4.5: Electrochemical oxidation of phenol at a gold-coated electromembrane

The degradation of phenol ranged between 11 and 23 % at the gold-coated electromembrane.

(vii) Experiment 2

Pt and PtO_2 are well known catalysts for most electrochemical processes and, hence it was decided to introduce the platinum catalyst to the gold-coated ceramic membranes. As expected, the activity of the Au/Pt coated membranes for the electrochemical degradation of phenol was very high (Figure 4.6). Solution containing 100 $mg.L^{-1}$ phenol in 0.1 M Na_2SO_4 was introduced in the electromembrane reactor at 2.5 V and a flux of 240 $L.m^{-2}.h^{-1}$.

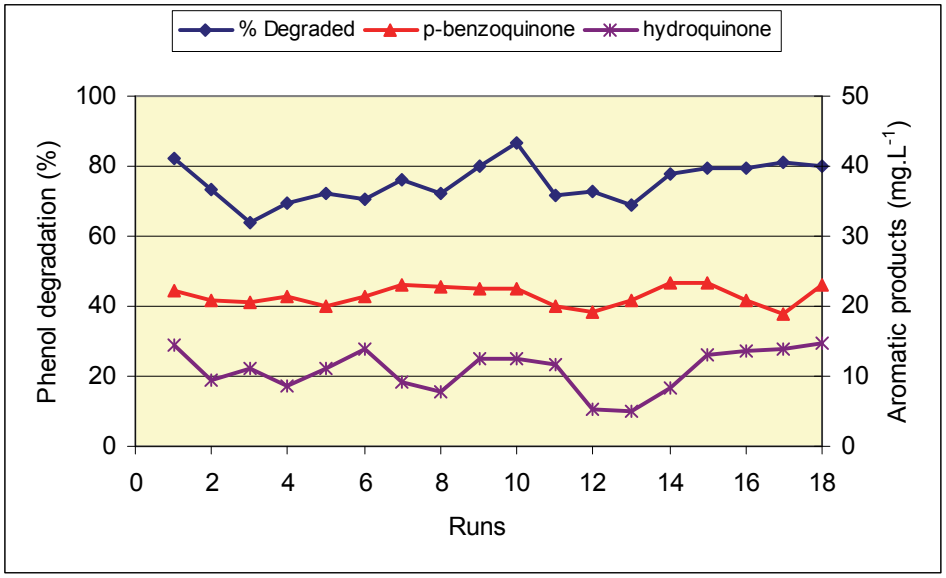

Figure 4.6: The electrochemical oxidation of phenol at an Au/Pt electromembrane.

Phenol was readily oxidized to p-benzoquinone, hydroquinone and several other unidentified aromatic intermediates. The degradation of phenol was at range of 64 to 83 % and the concentration of p-benzoquinone (> 20 $mg.L^{-1}$) and hydroquinone (> 10 $mg.L^{-1}$) were very high.

(viii) Experiment 3

Attempts were made to regenerate membranes that were used for several experiments and had lost most of their activity for phenol degradation. This was done by first heating the membranes under air and re-depositing the platinum catalyst. The regenerated membrane, however, does not retain its high activity for phenol degradation as illustrated in Figure 4.7.

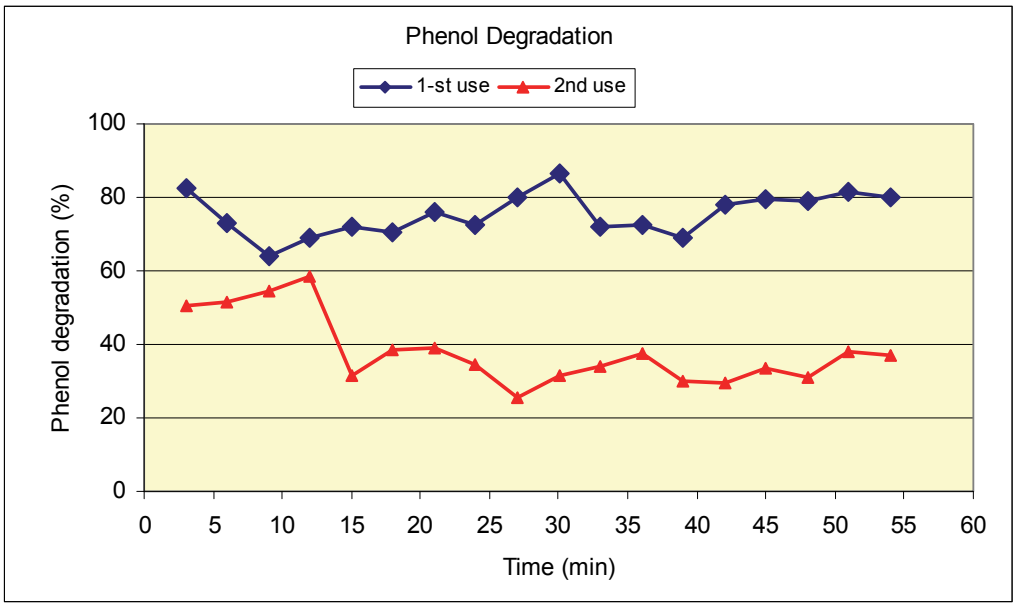

Figure 4.7: Effect of membrane regeneration on the electrochemical oxidation of phenol.

Other than loss of activity of phenol degradation, the regenerated electromembranes become more electrically unstable with time (Figure 4.8).

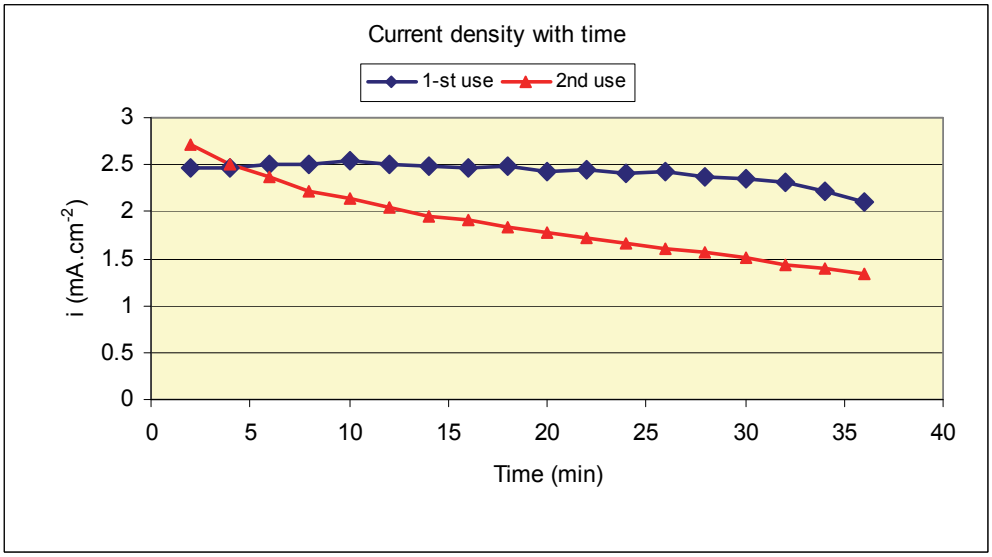

Figure 4.8: Electrical stability of Au/Pt membranes during the electrochemical oxidation of phenol.

(ix) Experiment 4

In Chapter 3 we illustrated that the introduction of inorganic proton conductors enhanced the electrochemical oxidation of with respect to the number aromatic intermediates formed and their respective concentration. The same trend was noticed for membranes coated with gold and platinum. Due to the high conductivity of the gold layer, as compared to carbon, impregnating with proton conductors did not have big influence on the resistance of the membrane. This will probably explain why phenol degradation was also improved at such membranes.

A phenolic solution of 100 $mg.L^{-1}$ in 0.1 M Na_2SO_4 was introduced into the electromembrane reactor at applied potential of 2.5 V and a flux of approximately 210 $L.m^{-2}.h^{-1}$. The reduced flux is due to the impregnation with zirconium phosphate. The results thereof are discussed in Figures 4.9 and 4.10.

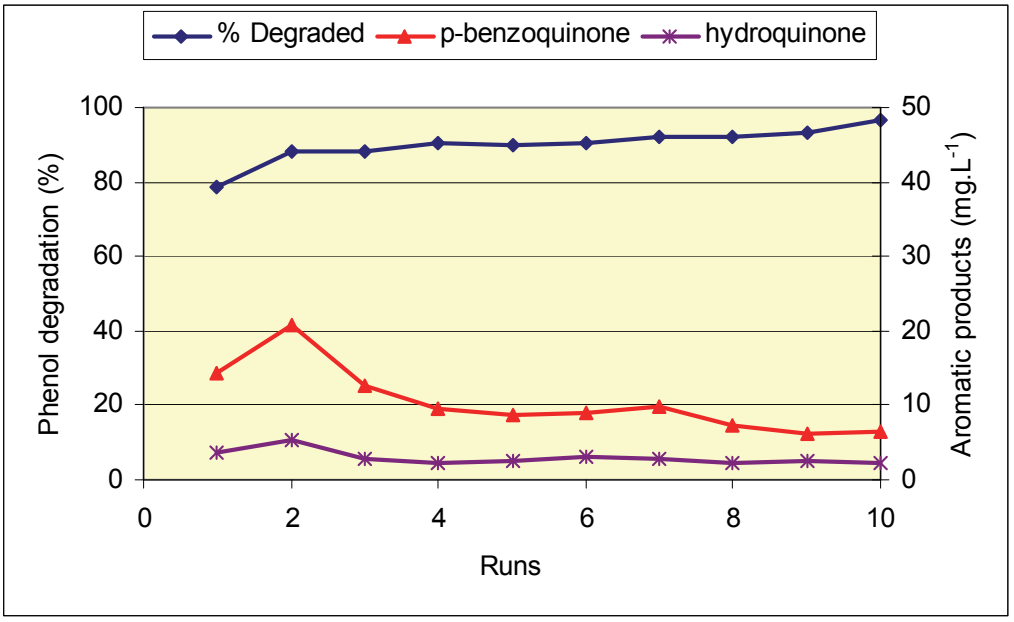

Figure 4.9: Electrochemical oxidation of phenol at an Au/Pt electromembrane impregnated with proton conductors.

Apart from improved degradation of phenol (79 to 97 %), p-benzoquinone (ranging between 6.4 and 21 $mg.L^{-1}$) and hydroquinone (2 to 5 $mg.L^{-1}$) are formed in lower concentrations when compared to Au/Pt membranes without proton conductors. Although the concentrations of p-benzoquinone and hydroquinone were lower when membranes impregnated with zirconium phosphate were used, there were still some unidentified products whose peaks were present in all the samples tested.

A further observation that was made was the decline in permeate flux of the membrane as the experiment progressed (Figure 4.10). It was also difficult to reverse the fouling process by regenerating the membrane. In all the work that has been discussed so far, the membranes were regenerated by heating at temperatures exceeding 500 ºC. Unfortunately, these temperatures are too high for zirconium phosphate.

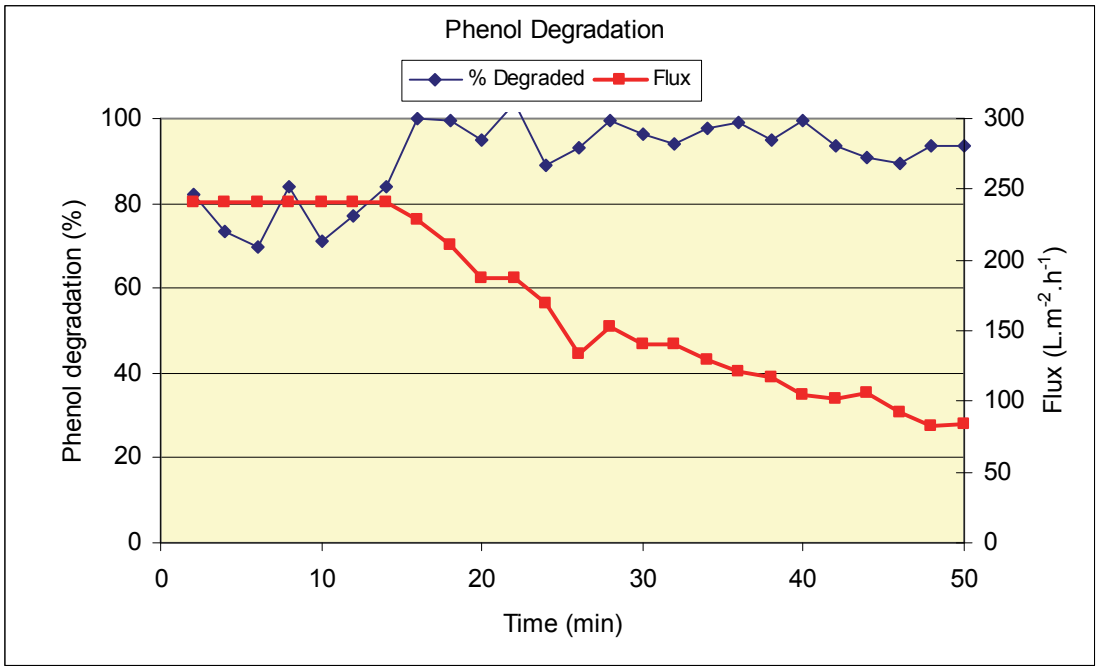

Figure 4.10: The influence of inorganic proton conductors on the flux through the electromembrane.

(x) Experiment 5

The experiment discussed in Figure 4.11 was conducted under acidic conditions on a membrane coated with gold and platinum. The feed solution was made of 100 $mg.L^{-1}$ phenol in 0.05 M H_2SO_4.

The resulting permeate turned yellowish/gold and current dropped rapidly. This was the result of the gold layer being washed of the ceramic membrane surface under acidic conditions. The degradation of phenol decreased with time, due to the loss of electrical conductivity.

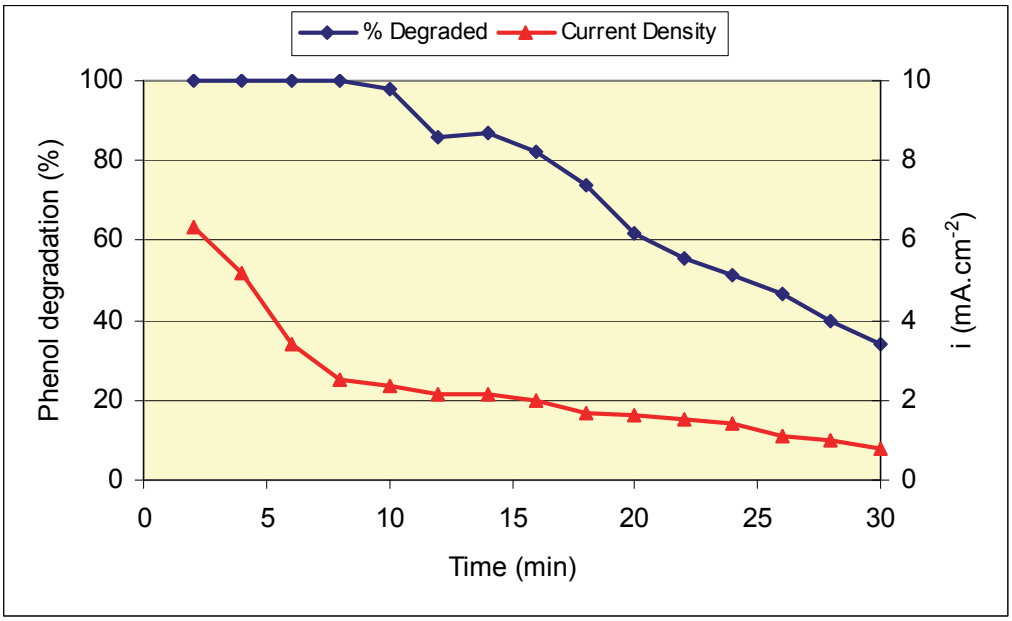

Figure 4.11: Electrochemical oxidation of phenol at an Au/Pt electromembrane under acidic conditions.

4.4 Conclusions

Gold-coated electromembranes have excellent conducting properties for electricity. The gold layer did not have any negative effect on permeability through the membrane. The gold electromembranes also exhibited good electrical stability when used under neutral and alkaline conditions. When used as an anode, under acidic conditions, the gold layer was washed off the membrane surface. This also meant that current decreased rapidly as there was a huge potential drop on the surface of the membrane. Although phenol was rapidly degraded under acidic conditions, the degree of degradation decreased very fast due to a drop in current.

The gold layer, on its own, wasn't enough to have a significant effect on the electrochemical oxidation of phenol. The efficiency of the gold electromembranes on the degradation of phenol was improved dramatically by introducing platinum as an electrocatalyst. Although the degree of phenol degradation was relatively high at the Au/Pt electromembranes, aromatic intermediates were also formed in unacceptably high concentrations. A number of unidentified products with high molecular weight were also formed during the experiments. Regenerating the membranes that had lost both their electroconductive and electrocatalytic properties did not restore the membrane electrocatalytic properties to what they used to be.

As it was the case with membranes coated with pyrolytic carbon (Chapter 3), impregnation with inorganic proton conductors had a huge advantage for the process efficiency. The degree of phenol degradation was improved and p-benzoquinone and hydroquinone were formed at relatively low concentrations. The drawbacks of introducing the proton conductors included the loss of permeability through the membrane with time and the fact that there was still some formation of unidentified by-products of high molecular weight.

4.5 References

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5. PARTIAL ELECTROCHEMICAL OXIDATION OF PHENOL ON CERAMIC-BASED FLAT-SHEET TYPE ELECTROMEMBRANE REACTORS

Abstract

The partial electrochemical oxidation of aqueous phenol, as a model organic pollutant, has been studied using a flow-through electromembrane reactor with a novel flat-type ceramic-based membrane as the anode material. The ceramic-based membranes were modified to exhibit electrocatalytic properties by depositing nano-sized electrocatalytic inks on the membrane surfaces. The electrocatalytic ink was prepared from carbon black-supported antimony doped tin oxide. Comparisons were made between the commercially available Sb doped SnO_2 as well as the Sb doped SnO_2 prepared by a sol-gel method. The effects of pH, and electrolyte type are also reported in this section. Phenol concentration, intermediate products and COD of the oxidized solution was monitored during the experiments. It was found that phenol is readily oxidized to 1,4-benzoquinone and organic acids.

5.1 Introduction

In chapters 3 and 4 we have reported on the use of tubular ceramic membranes as anode materials for the electrochemical oxidation of phenol. The results show that phenol was completely degraded in a single pass through the tubular system at flow rates ranging between 200 – 250 $L.m^{-2}.h^{-1}$ with energy consumption of 0.002 – 0.006 $kWh.g^{-1}$.

For industrial purposes, however, several drawbacks associated with the use of tubular systems have led to the need to replace the tubular membranes with flat sheet-type ceramic membranes. Some of the difficulties that were experienced while trying to upscale the tubular electromembrane systems for industrial use included the breaking of the membranes while trying to assemble the reactor. Other drawbacks are listed in chapter 8 as part of overall conclusions.

This section discusses work that has been conducted using flat sheet-type ceramic membranes as anode material for the electrochemical oxidation of aqueous phenol. Flat ceramic membranes have become an industrial reality. TAMI industries has developed and commercialized flat ceramic membranes since 1996 [1]. They have compared the flat with tubular membranes in the treatment of diary products and found flat membranes easy to use for sanitation and lead to reduction in energy consumption and equipment cost.

Many studies have been conducted on the influence of electrode material and electrocatalysts on the electrochemical oxidation of phenol. It was also found that the reaction pathway of oxidation by electrochemical methods is highly influenced by the type of electrode/electrocatalys used. Comninellis and his co-workers reported that anodes with high oxygen-overpotential such as Ti/SnO_2, Ti/PbO_2 and graphite-felt favoured the electrochemical oxidation of phenol to CO_2 [2-4].

In this work, the electrochemical oxidation of phenol is carried out at a ceramic membrane surface coated with carbon black-supported Sb doped SnO_2 electrocatalysts. Usually electrodes such as Ti are used as support material, but other researchers have used Ebonex® ceramic (Ti_4O_7), the most common of ceramic-based anode materials with electrical conductivity similar to that of graphite (6.3×10^{-4} $\Omega.cm^{-1}$) [5], as support of electrocatalytic coating [6].

The use of carbon black (Vulcan XC 72) as support for catalytic metal/metal oxide particles has been mainly associated with fuel-cell technology [**7**], however, this catalyst also works well in the electrochemical oxidation of phenol as will be discussed in this section. The partial oxidation of phenol on flat-sheet type electromembranes coated with carbon black-supported Sb doped SnO_2 electrocatalysts ahs been reported [8].

5.2 Experimental

5.2.1 Materials

Commercially available composite ceramic sheets (Lydall, USA), with properties listed in table 5.1, were used as the catalyst support.

Table 5.1: Properties of unmodified composite ceramic sheets

Property/Variation	1P-397 – 2 (40 % glass)
Basis Weight (kg/m^2)	0.267
Caliper @ 4 PSF (mils)	64
Density ($kg.m^{-3}$)	164.20
Caliper @ 8 PSI (mils)	46.9
MD Tensile (kg/m)	124.68
CD Tensile (kg/m)	95.47
Resistance @ 32 $L.min.m^{-2}$ (mm H_2O)	284
Estimated Composition (wt %):	
Al_2O_3	23.6
SiO_2	51.2
Other Metal Oxides	25.2

(a) Preparation of carbon black-supported Sb-doped SnO_2 electrocatalyst

The Sb-doped SnO_2 solutions were prepared from two alkoxides [8] obtained directly from chlorides. 8.37 g of $SnCl_2$ $2H_2O$ was dissolved in 100 ml of absolute ethanol. The antimony solution was simultaneously prepared from a given amount of $SbCl_3$ dissolved in 20 mL of absolute ethanol. Both mixtures were separately stirred and heated in a closed vessel. The vessels were then opened and the solvent completely evaporated to yield two powders. The resulting powders were mixed together in 50 mL of ethanol. The doped mixture was finally stirred and heated at 50ºC for 2 h.

For the preparation of the electrocatalyst or catalytic ink, a predetermined amount of carbon black (VULCAN XC 72) was added to the Sb doped SnO_2 sol and stirred at room temperature for several hours. The carbon black was then washed thoroughly with water and dried at 100ºC for 1 h followed by further drying at 500ºC under nitrogen for 30 min.

(b) Preparation of the anode

The ceramic membranes are cut into the correct size for the electromemrane reactor and then impregnated with the electrocatalyst. A slurry or ink of the carbon black-supported Sb doped SnO_2 was prepared in an appropriate solvent and a few drops of Liquion-1100 5 wt% Nafion® solution (Ion Power Inc, USA) followed by ultrasonic treatment for 30 to 60 min. The resulting ink was sprayed onto the ceramic membrane surface by using commercially available spray guns. The membranes were then dried at room temperature overnight. The basic properties of the electromembranes used in this section are listed in Table 5.2.

Table 5.2 Basic properties of the electromembrane for the electrochemical decomposition of phenol.

Parameter	Value
Diammeter	50 mm
Thickness	1.5 mm
Catalyst loading	1.8 $mg.cm^{-2}$
Surface area	12.5 cm^2

5.2.2 Electrochemical Oxidation

The electromembrane reactor that was used in this section is shown in Figure 5.1. This reactor is a flow-through undivided electrocatalytic cell. The principal feature of the cell is the ceramic-based membrane, which was coated with the carbon-supported catalyst on one side. The coated side was used as the anode and the cathodic side was not coated with any electroconductive substance or catalyst. Current is supplied to the anode and cathode by means of backing layers, which are connected, to the external power source by means of a conducting wire. The backing layers that were used in this study are carbon cloths 6100-200 purchased from Lydal, USA.

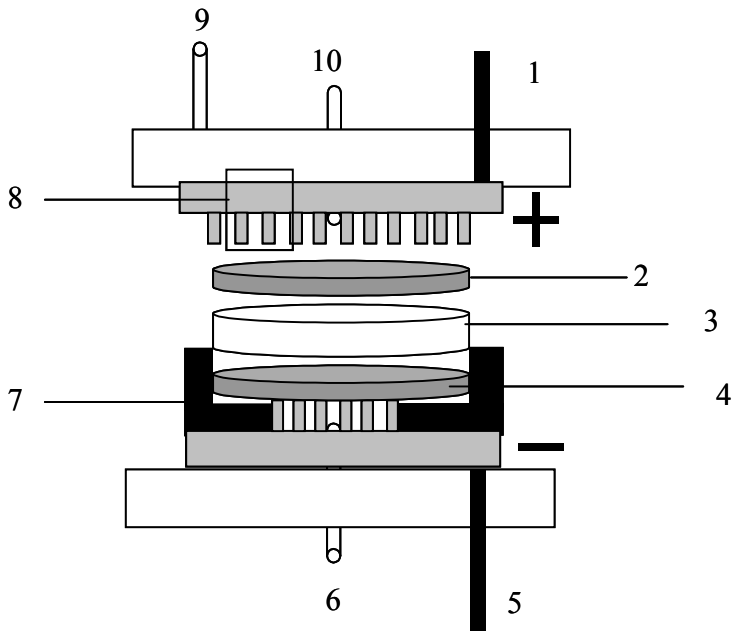

Figure 5.1. Schematic representation for the flat sheet type electrombrane reactor used in the electrochemical oxidation of phenol in aqueous media and its features are (1) current collector (anode), (2) anodic carbon paper, (3) ceramic support, (4) cathodic carbon paper, (5) current collector (cathode), (6) permeate outlet (7) rubber seal, (8) stainless steel flow channel, (9) reject outlet and (10) feed inlet.

The untreated water was pumped into the electromebrane reactor through the inlet (10) where the feed is guided by means of a stainless steel flow channel. The water came into contact, first, with the carbon cloth on the anodic side and then with the electrocatalyst on the surface of the ceramic support. The feed is subsequently pumped through the membrane and the oxidized or "treated" water is collected as permeate and analyzed. After collection of the entire batch, the collected water is reintroduced into the reactor and, depending on the nature of the catalyst and experimental conditions, a number of runs are carried out and phenol concentration, oxidation products and COD were monitored with each run.

5.2.3 Analysis

Oxidation intermediates produced during the electrochemical oxidation of phenol belong to a number of different chemical families including quinines, biphenols, aliphatic alcohols and organic acids having widely varying solubilities, polarities and dissociation constants [9]. Hence phenol concentration and the emergence of 1,4-benzoquinone, hydroquinone and catechol were monitored by HPLC (Spectra physics, SP 8450) on an HAISIL 100 C18 reversed phase column (Higgins Analytical). A flow rate of 0.8 ml/min, a mobile phase of methanol/water (v/v) 40/60 with trimethyamine buffer and a column temperature of 30ºC were used. A diode array UV detector set at 254 nm was used. With this method, the concentration of phenol and its aromatic derivatives could be detected down to 0.01 $mg.L^{-1}$. Organic acids were analyzed by using an ICE-ORH-801 (Transgenomic) column. A flow rate of 0.8 $ml.min^{-1}$, a mobile phase of 0.01N sulphuric acid and column temperature of 40ºC was used. The UV detector was set at 214 nm. The progress of the electrochemical oxidation was also monitored by measuring the chemical oxygen demand (COD).

5.2.4 Method

All test solutions were prepared from reagent grade phenol (Aldrich puris. > 99%) in ultrapure water (Milli-Q, ρ = 18 M Ω cm^{-1}). Sulfuric acid (H_2SO_4), sodium chloride (NaCl), sodium sulphate (Na_2SO_4) and sodium hydroxide (NaOH) were used as background electrolytes in different experiments. A preset potential difference was applied to the electrochemical cell by means of a BSA CV 27 external power source and current was recorded in mA.

The proportion of phenol converted to aromatic intermediates, relative to the amount of phenol converted, was defined by J. Iniesta et al [10] as:

$$\% \text{ Aromatics} = \frac{[\text{Aromatics}]}{[\text{Ph}]_0 - [\text{Ph}]_t} \times 100$$

where [Aromatics] is the concentration of aromatic intermediates (p-benzoquinone, hydroquinone and catechol) in $mg.L^{-1}$, $[Ph]_0$ the initial phenol concentration and $[Ph]_t$ the final phenol concentration in $mg.L^{-1}$.

5.3 Results and Discussion

5.3.1 The influence of Sb doped SnO_2 catalyst on the electrochemical oxidation of phenol.

This section sets out to illustrate the influence of the Sb doped SnO_2 electrocatalyst on the electrochemical oxidation of phenol. Comparison were also made between the Sb doped SnO_2 that we prepared by sol-gel techniques and commercial Sb doped SnO_2 nanoparticles that were purchased from Nanotek, USA. Four different experiments were conducted and a list of experimental conditions and variables is shown in Table 5.3. The feed was 100 $mg.L^{-1}$ phenol and 0.01 $mol.L^{-1}$ sulfuric acid (chosen randomly) solution was used as the background electrolyte in these set of experiments. The feed was pumped into the electrocatalytic cell at a constant flow rate.

Table 5.3: Summary of the experimental conditions and variables during the electrochemical oxidation of phenol.

Experiment	Membrane coating	Applied potential (V)	Flux ($L.m^{-2}.h^{-1}$)
1	Blank	2.5	300
2	Carbon black	2.5	300
3	Commercial Sb doped SnO_2 on carbon black	2.5	300
4	Carbon black supported Sb doped SnO_2	2.5	300

A total of five (5) runs were carried out through the electromembrane reactor and the results are discussed below. In the experiments discussed in this chapter, the number of runs represent the number of times the resulting permeate has passed through the electromebrane reactor.

Experiment 1,2 and 3

Figure 5.2 illustrates the effect of coating the membranes with carbon black and the influence the Sb doped SnO_2 has on the degree of phenol degradation . "Runs", as labeled on the x-axis of the figures, represents the number of cycles through which the feed solution was pumped into the electromembrane reactor.

As expected, no significant degradation of phenol was noticed at blank ceramic membranes. Spraying the surface of the membrane carbon black improved the degree of degradation from 34 to 72 % under the conditions and number of runs through the reactor. The commercial Sb doped SnO_2 catalyst proved to be highly effective for phenol degradation with 82 % of the initial phenol in the feed solution being degraded after 5 runs.

The removal of chemical oxygen demand (COD) was also measured in the experiments discussed above. Again, the introduction of the commercial Sb-SnO_2 electrocatalyst improved the efficiency of COD removal when compared to the blank and the carbon black-coated membrane (Figure 5.3).

Although the removal of COD was not sufficient for environmental purposes, better COD removal was possible when the Sb-SnO_2 coated membrane was used. The removal of COD only improved by 15 % between the membranes coated with carbon black only and the ones where carbon black used as support for the commercial Sb-SnO_2 electrocatalyst.

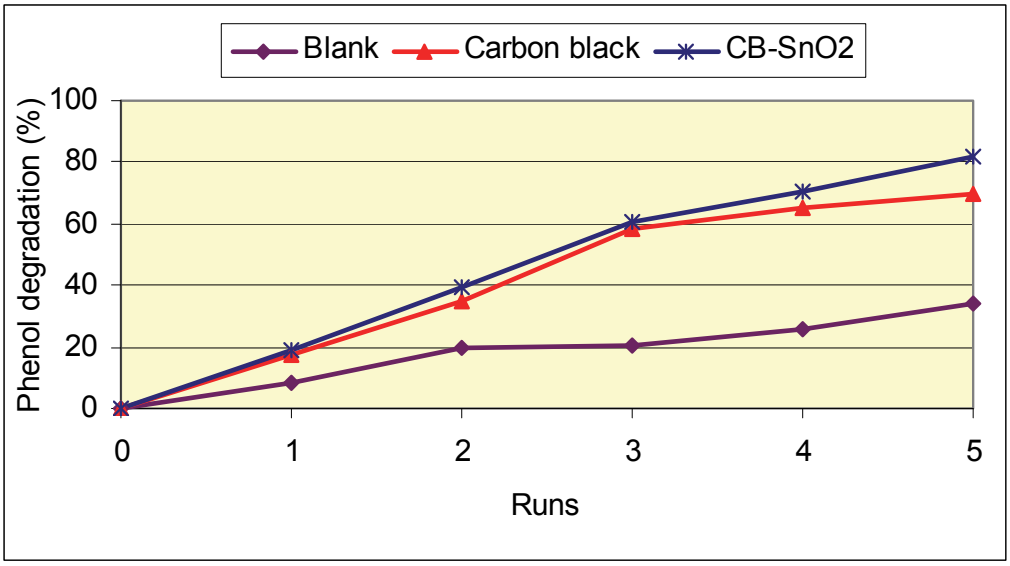

Figure 5.2: Trend of phenol degradation at the electromembrane reactor to compare the efficiency of the commercial electrocatalysts loaded on carbon black.

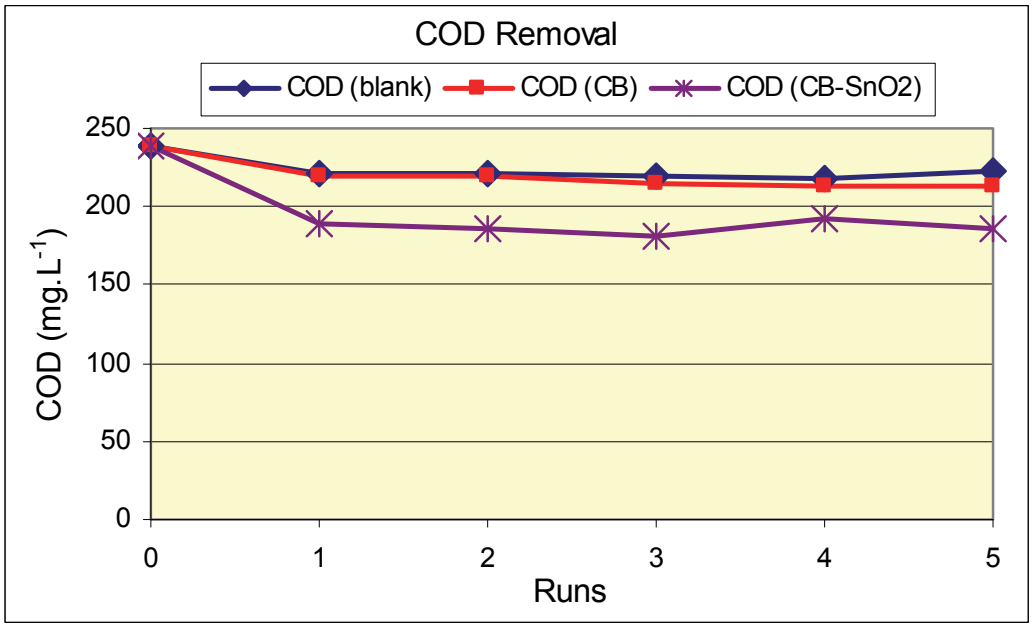

Figure 5.3: Trend of COD removal at the electromembrane reactor to compare the efficiency of the commercial electrocatalysts loaded on carbon black.

Experiment 3 and 4

Comparisons between the commercial Sb doped SnO2 nanophase catalyst and the Sb doped SnO_2 catalyst that was prepared by sol-gel techniques in our lab were also made. Results show that the synthesized Sb-SnO_2 electrocatalyst had better efficiency for phenol degradation (Figure 5.4).

There was quite a significant difference between the commercially available Sb-SnO_2 and the Sb-SnO_2 that was synthesized in our laboratory by sol-gel techniques. Figure 5.4 shows that the degradation of phenol improved from 82 to 97 % (nearly complete phenol degradation) when using the synthesized Sb-SnO_2 electrocatalyst under the same conditions and number of runs through the electromembrane.

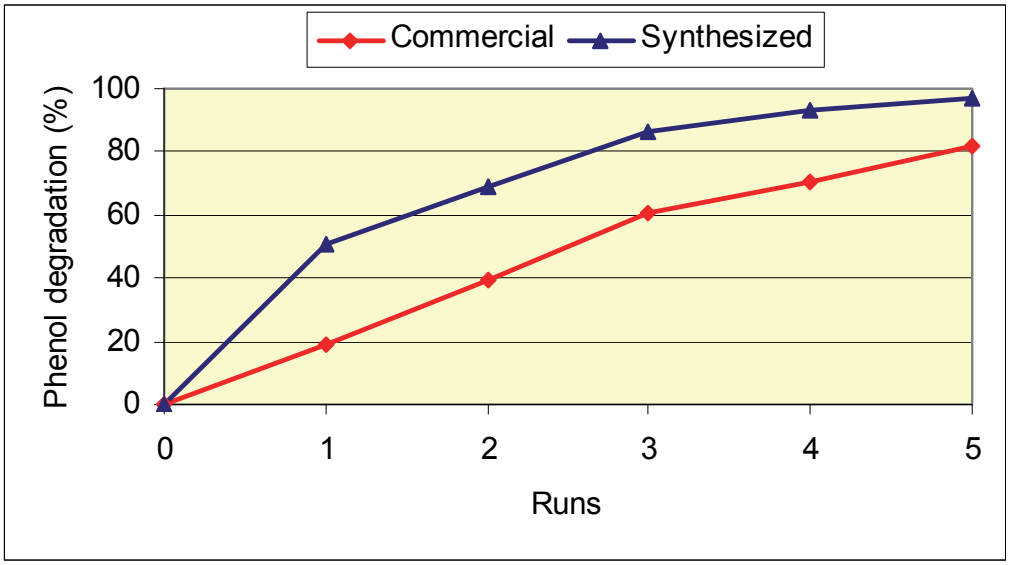

Figure 5.4: Comparison of electrocatalyst efficiency for phenol degradation in an electromembrane reactor.

There was no significant difference in the trend of COD removal between the two electrocatalyst. COD removal in both instances was approximately 24 –26 % (Figure 5.5).

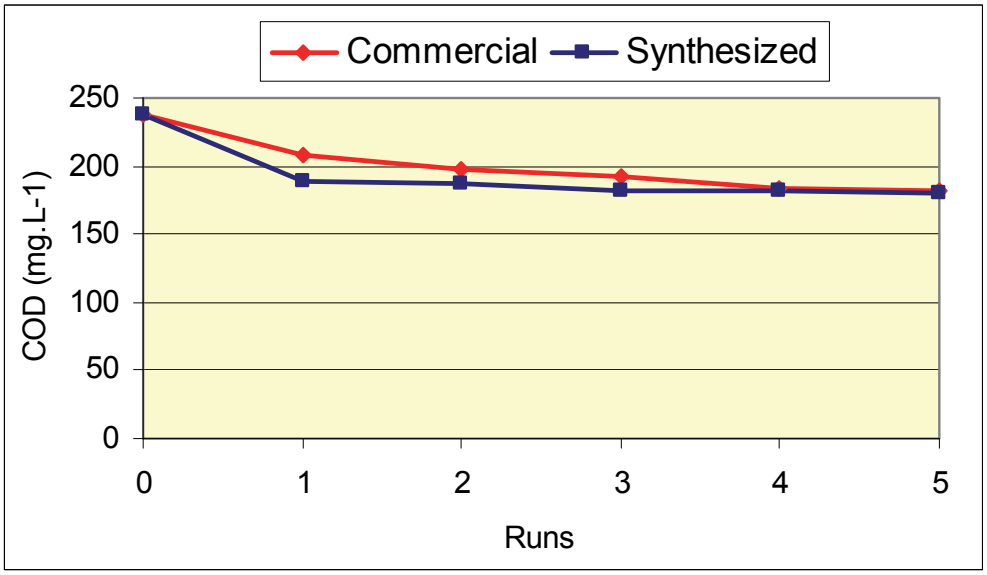

Figure 5.5: Comparisons between commercial and synthesized Sb-SnO_2 electrocatalyst with respect to COD removal in the electrochemical oxidation of phenol.

As mentioned above, the COD levels in both experiments were still very high even though most of the phenol had been degraded. This would suggest that phenol had been converted to other products instead of being combusted to CO_2. The intermediates that were detected are p-benzoquinone, and hydroquinone. The concentrations of these intermediates as well as the percentage of aromatics relative to phenol degradation are listed in table 5.4.

Table 5.4: The comparison between the commercial and synthesized Sb-SnO_2 electrocatalysts.

SnO_2 catalyst	Phenol degradation (%)	COD removal (%)	Benzoquinone ($mg.L^{-1}$)	Hydroquinone ($mg.L^{-1}$)	Aromatics (%)
Commercial	82	24	9.4	37	76
Synthesized	97	26	6.2	65	74

The proportion of aromatic compounds relative to phenol degradation clearly shows that most of the phenol was converted to its corresponding aromatic intermediates. Hence COD was still very high at the end of the experiments.

5.3.2 Influence of electrolyte solution on the electrochemical oxidation of phenol at a flat-sheet type electromembrane reactor.

A number of experiments were conducted in order to investigate the effect of background electrolyte on the electrochemical oxidation of phenol. As it will be seen later, the type of electrolyte added can affect the outcome of each experiment positively or negatively. The different conditions under which the experiments were performed are listed in Table 5.5.

Table 5.5: List of experimental conditions to evaluate the effect of background electrolyte on the electrochemical oxidation process.

Experiment	Membrane coating	Electrolyte solution	Electrolyte concentration	Flux ($L.m^{-2}.h^{-1}$)
A	Carbon black supported Sb doped SnO_2	H_2SO_4	0.1 M	300
B	Carbon black supported Sb doped SnO_2	Na_2SO_4	0.1 M	300
C	Carbon black supported Sb doped SnO_2	NaOH	0.1 M	300
D	Carbon black supported Sb doped SnO_2	NaCl	0.1 M	300

Experiment A: Influence of sulfuric acid (H_2SO_4) as an electrolyte

A feed solution containing 100 $mg.L^{-1}$ phenol in 0.1M H_2SO_4 was introduced into the electromembrane at a flux 300 $L.m^{-2}.h^{-1}$ and applied potential of 2.5 V. The flux and current density remained constant throughout the experiment of 5 runs. The results obtained are illustrated by means of Figure 5.6.

The results are not very different to those discussed in the preceding sections where H_2SO_4 was used as the background electrolyte. Phenol was almost completely degraded and converted to its corresponding aromatic intermediates (p-benzoquinone and hydroquinone) and aliphatic acids (oxalic and maleic acid). The initial COD concentration was only reduced by 37 % and the recorded COD concentration was 150 $mg.L^{-1}$ at the end of the experiment.

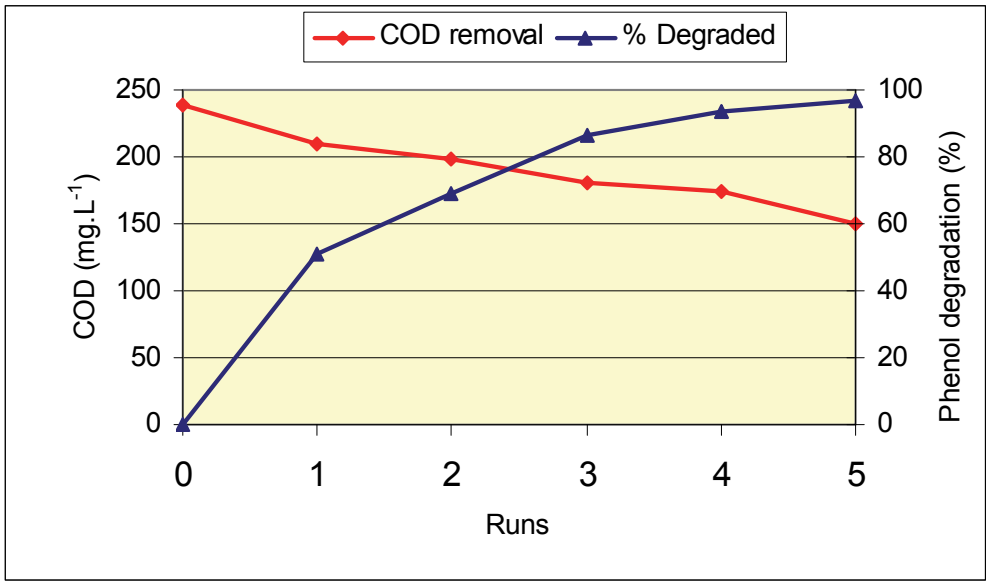

Figure 5.6: The degradation of phenol and removal of COD at flat-sheet electromembrane reactor with H_2SO_4 as the background electrolyte.

Experiment B: Influence of sodium sulphate (Na_2SO_4) as an electrolyte

Sodium sulphate is a weaker electrolyte than sulfuric acid, hence less current was generated under the similar conditions as with experiment A. As a result, it took ten (10) runs to get close similar phenol degradation as in experiment A. However, although phenol degradation was only 70 % after 5 runs, the concentration of COD after a similar number of runs was 156 $mg.L^{-1}$ (Figure 5.7).

Under neutral conditions (Na_2SO_4 as electrolyte), the concentration of the aromatic intermediates is relatively lower than previously observed. The only aliphatic acid detected was oxalic acid, which would explain why COD concentration was relatively lower.

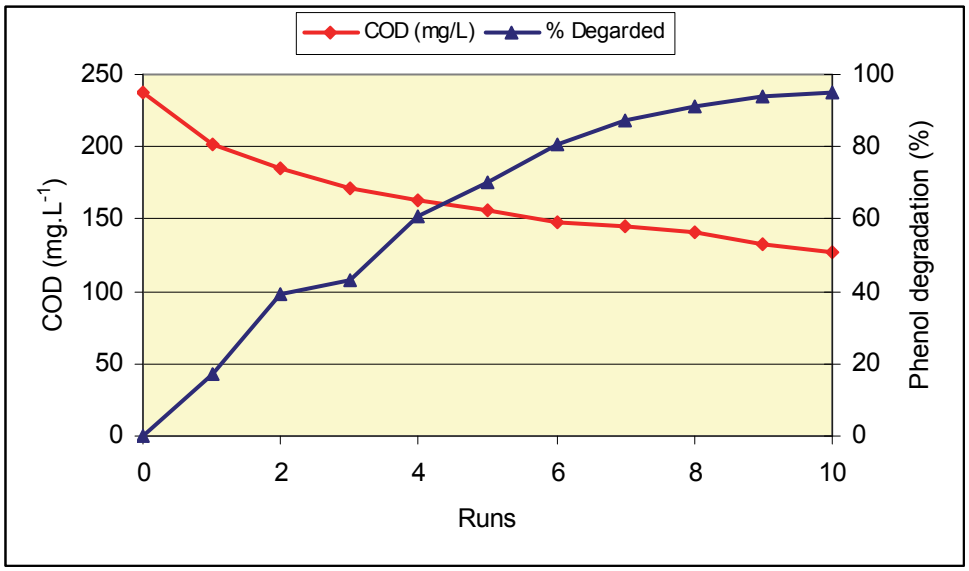

Figure 5.7: The effect of Na_2SO_4 on the degradation of phenol and COD removal

Experiment C: Influence of sodium hydroxide (NaOH) as an electrolyte

Although it has been previously reported that under alkaline media a yellow brown polymeric product is formed during the electrochemical oxidation of phenol [12], we have decided to conduct experiments using NaOH as a background electrolyte.

A feed solution of 100 $mg.L^{-1}$ phenol in 0.1M NaOH was pumped into the electromembrane reactor at 300 $L.m^{-2}.h^{-1}$ and 2.5V. The results are illustrated in Figure 5.8.

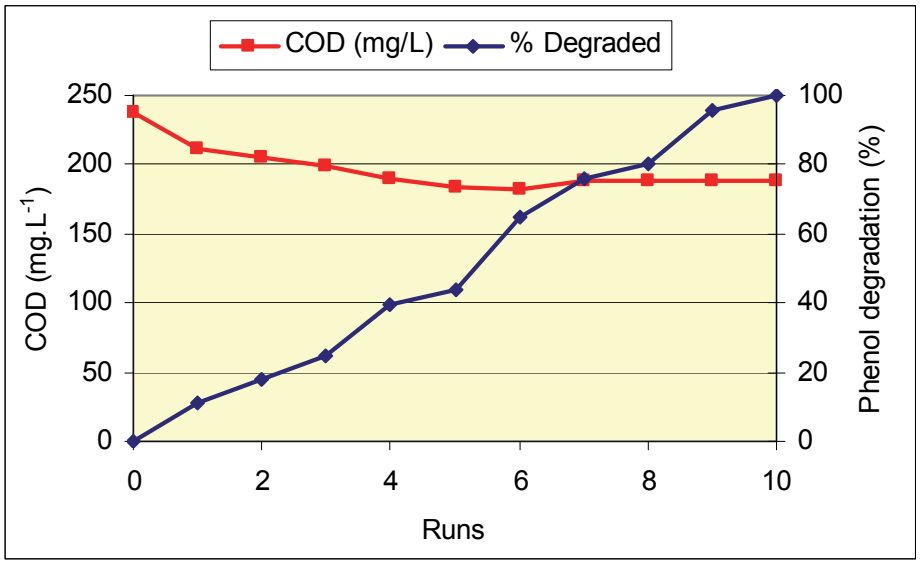

Figure 5.8: The effect of NaOH on the degradation of phenol and COD removal

Electrolysis in alkaline media yielded neither p-benzoquinone nor hydroquinone. Benzoquinone itself is reported to be unstable in alkaline solution. The concentration of COD decreased in the initial stages of the experiment but remained constant (179 to 189 $mg.L^{-1}$). As the experiment progressed, the resulting permeate turned yellowish brown as illustrated in Figure 5.9.

Apart from the yellowish brown solution being formed during the electrochemical oxidation of phenol in alkaline media, a yellowish brown film was deposited on the surfaces of the membranes (Figure 5.10). This film resulted in a flux decline of 50 % after ten (10) runs.

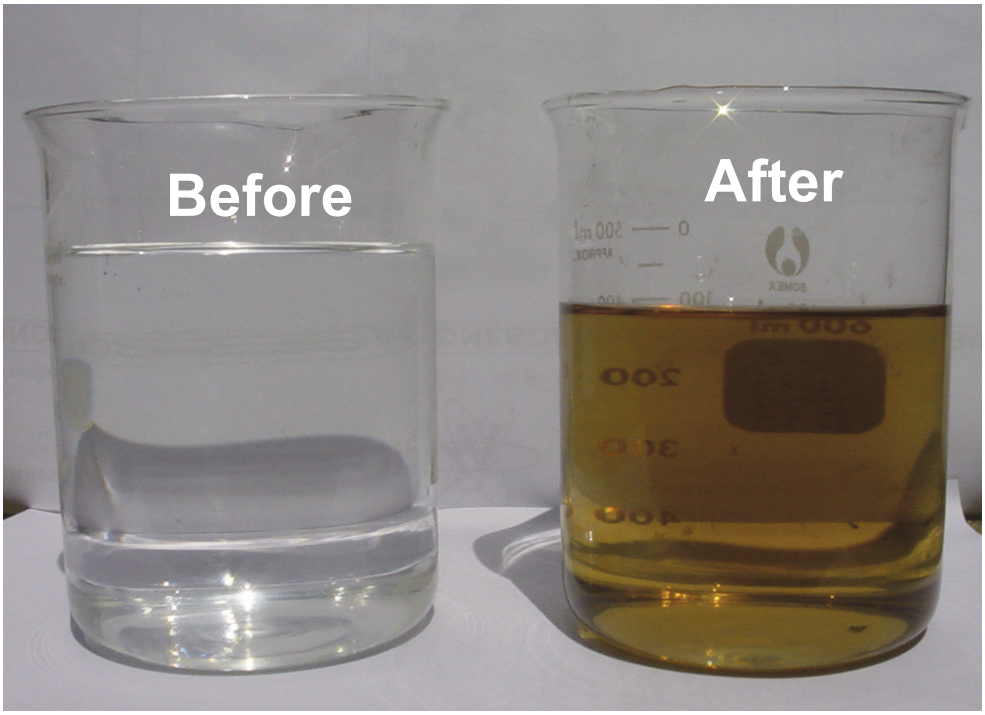

Figure 5.9: Formation a yellowish brown solution during the electrochemical oxidation of phenol in alkaline media.

In the electrochemical oxidation of phenol, the first reaction to occur is the formation of phenoxy radicals. If the lifetime of these radicals, in solution, is too long, radical coupling occurs and polymeric products are formed. Radical lifetime is prolonged under alkaline media. This would explain why the polymeric film, which could not be dissolved in acetone, was formed on the surface of the electromembrane.

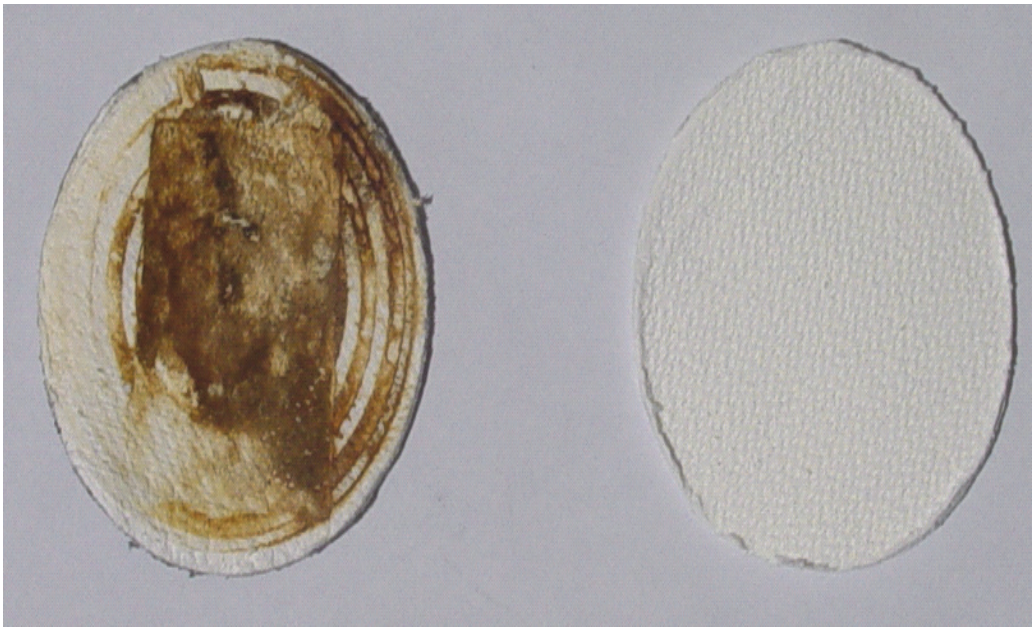

Figure 5.10: Formation of a yellowish brown film on the surface of the electromembrane during the electrochemical oxidation of phenol in alkaline media.

Experiment D: Influence of sodium chloride (NaCl) as an electrolyte

Most industrial effluents or wastewaters contain chlorides in significantly high concentrations; it was, therefore, necessary to investigate the influence of the chloride anion on the electrochemical oxidation of phenols and COD removal. Hence in this experiment, NaCl was used as an electrolyte.

The picture illustrated in Figure 5.11 shows that the resulting permeate changes rapidly in colour and a brown precipitate is formed. This is due to the reaction between the chloride ions with the stainless steel flow-channel at the anode.

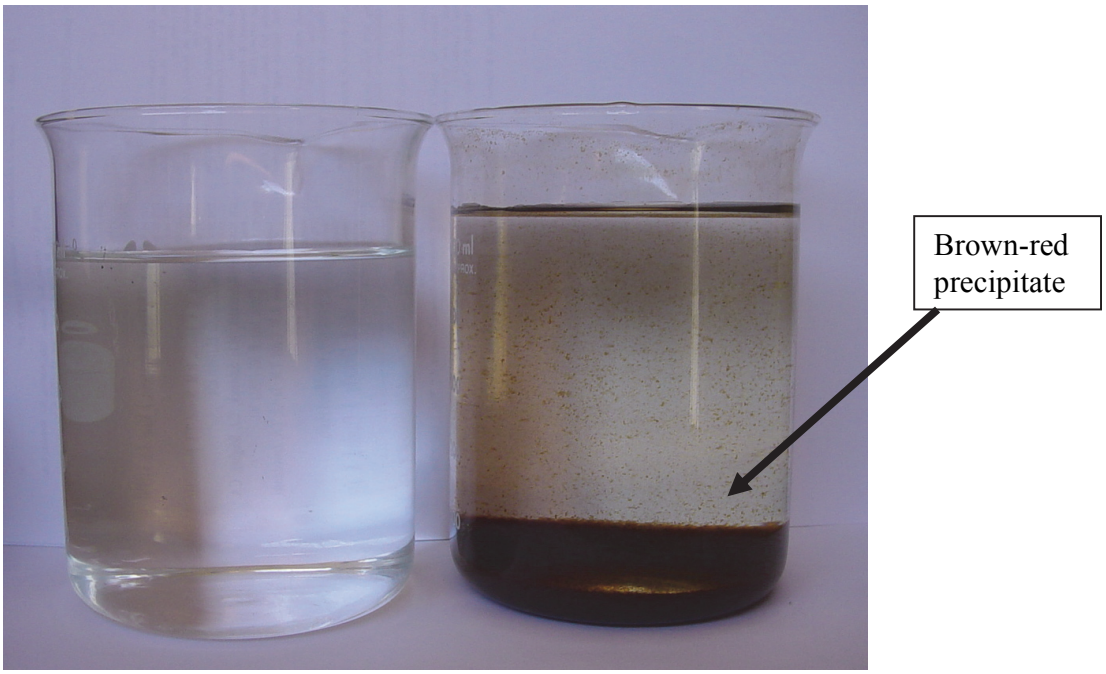

Figure 5.11: The effect of NaCl on the electrochemical oxidation of phenol.

Figure 5.12 shows the process that is likely to be going on in the electrochemical cell, the dissolution reaction of iron in sodium chloride (NaCl) water solution as electrolyte. The result of electrolytic dissociation

$$H_2O \longrightarrow H^+ + (OH)^- \qquad \text{and} \qquad NaCl \longrightarrow Na^+ + Cl^-$$

are negatively charged anions: $(OH)^-$ and Cl^- towards the anode, and positively charged cations: H^+ and Na^+ towards the cathode.

At the Anode:

$$Fe \longrightarrow Fe^{2+} + 2e^-$$

At the cathode, the reaction is likely to be generation of hydrogen gas and the hydroxyl ions:

$$2H_2O + 2e^- \longrightarrow H_2 + 2OH^-$$

The outcome of these electrochemical reactions is that the iron ions combine with other ions to precipitate out as iron hydroxide Fe $(OH)_2$ (Figure 5.12 adopted from: www.unl.edu/nmrc/ecm1/ecm1.htm).

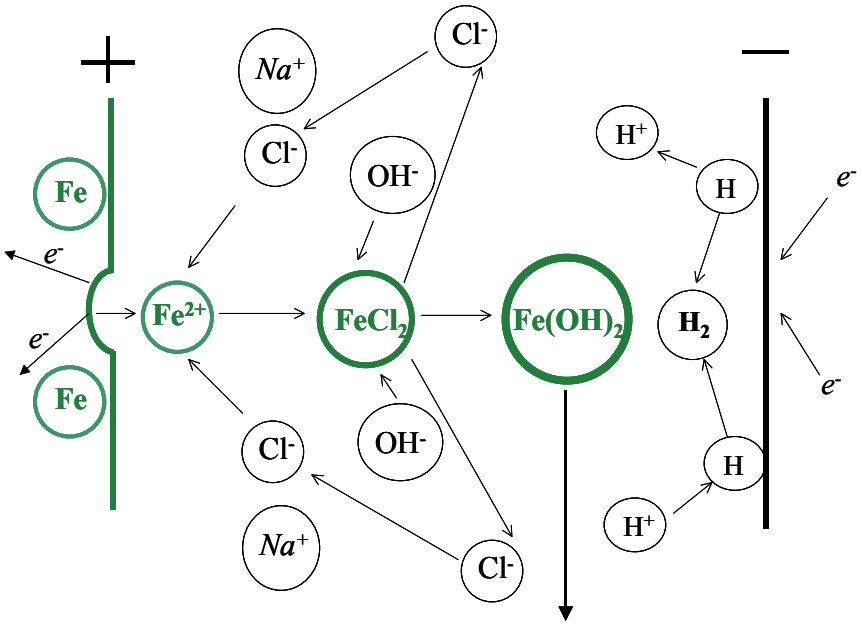

Figure 5.12: Diagram of electrochemical reactions during electrochemical machining of iron in sodium chloride (NaCl) electrolyte

Based on the observations discussed in this section modifications to the bench-scale electrochemical cell were made and further studies on the influence of chloride ions were conducted. Experimental conditions as well as the findings will be discussed in detail in Chapter 6.

5.4 Conclusions

Nanosized electrocatalysts based on Sb-doped SnO_2 supported on carbon black have been synthesized and successfully coated on the surfaces of flat sheet ceramic membranes. The electromebranes were then tested for their catalytic potential as oxidation catalysts for aqueous phenol. Comparisons were also made between the commercially available Sb-doped electrocatalyst and the synthesized electrocatalysts. The degradation of phenol and removal of COD progressed much faster when using the synthesized Sb-doped SnO_2 electrocatalyst supported on carbon black.

The efficiency of the phenol degradation process in the electromembrane reactor was highly affected by the type of electrolyte used (pH conditions). The degradation of phenol progresses much faster under highly acidic media and phenol was converted to its corresponding aromatic intermediates and aliphatic acids. Under neutral conditions, phenol was degraded much slower but the number of intermediates produced was relatively lower. The concentration of COD in both instances, however, was higher than 100 $mg.L^{-1}$, which is still quite high for environmental purposes.

Under alkaline conditions, none of the intermediates resulting from phenol degradation were detected. The water that passed through the electromembrane reactor, however, turned yellowish brown and the measured COD was still very high (> 170 $mg.L^{-1}$). A polymeric film was also formed on the surface of the electromembrane under alkaline conditions and this resulted in the membrane losing 50 % its permeability.

The General Standard as set by the Government Gazette No. 9225, Regulation No. 0991 of 18 May 1984, for COD concentration is 75 $mg.L^{-1}$ after applying the chlorine correction. Therefore it is quite important that, apart from complete phenol degradation, the concentration of COD be reduced to less than 75 $mg.L^{-1}$. Modifications were made to the electromembrane reactor in order to improve such parameters and the results are discussed in chapter 6 and 7.

5.5 References

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6. BENCH-SCALE REACTOR FOR THE ELECTROCHEMICAL OXIDATION OF PHENOL IN AQUEOUS MEDIA

Abstract

Results from a bench-scale study on the performance of the ceramic-based electromembranes in treating phenolic waters are presented. The effect of acid content, applied potential as well as the presence of chloride ions in the feed water were also studied. The permeate flux was varied in the range of 50 to 250 $L.m^{-2}.h^{-1}$ and the influence thereof was reported. It is worth noting that COD removals between 80 to 84 % are possible when chloride ions are present in the feed solution. The emergence of aromatic intermediates in the resulting permeate was also not evident in the presence of chloride ions.

6.1 Introduction

Most industries produce effluent that contains toxic and/or non-biodegradable organic substances. Biological degradation processes are obviously not efficient in this case and hence the need to develop industrial scale electrochemical methods for degradation of hazardous organic pollutants.

Although ceramic membranes have been evaluated on a pilot or even industrial scale, for the treatment of high turbid water [1], it has also been previously reported that direct electrochemical oxidation methods are industrially of very little or no interest [2]. The reasons listed by the authors for the apparent uselessness of electrochemical methods included the unavailability of cheap and inert electrode material, the fact that charge per molecule organic species is very high and that processes such as adsorption followed by burning and chemical oxidation are cheap alternatives.

Recently, however, it has been reported that the destruction of hazardous organic waste produced as waste products in chemical processes has actually become an industry in itself, regulated by environmental agencies and government bodies [3]. The CerOx^{TM} [4] is one such process, which is used to treat most organic waste materials. Compared to a hazardous waste incinerator destroying the same amount of waste materials, the CerOx Process is said to release about 25 % less carbon dioxide. Although, the CerOx Process shows impressive results, it still makes use of titanium electrodes plated with platinum.

In the work report in this section, we aim to alleviate the drawbacks listed above by using the, already mentioned, ceramic-based flat sheets coated with inexpensive electrocatalytic material capable of

decomposing organic compounds. The process is an upscaled version of the one discussed in Chapter 5 with the membrane surface increased from 12.5 to 320 cm^2.

6.2 Experimental

6.2.1 Materials

The same materials that were used in Chapter 5 were also used in this section but the properties of the electromembranes were altered. The basic properties of the electromembranes used in this section are listed in Table 6.1.

Table 6.1: Basic properties of the electromembrane for the electrochemical decomposition of phenol.

Parameter	Value
Thickness	1.5 mm
Catalyst loading	1.8 ± 0.2 $mg.cm^{-2}$
Surface area	320 cm^2

6.2.2 Electrochemical Oxidation

The electromembrane reactor discussed in Chapter 5 had a feed flow-channel made from stainless steel and as we have seen in Section 5.3.2, upon coming into contact with the feed solution, the stainless steel reacts with the compounds that make the feed solution and this can lead to undesirable results. It was decided to use non-conducting material as the flow-channel as this would have no effect on the outcome of the results.

The electromembrane reactor that was used in this section is shown in Figure 6.1. The reactor design is similar to the one discussed in Section 5.2.2 with the only modification being the flow channel.

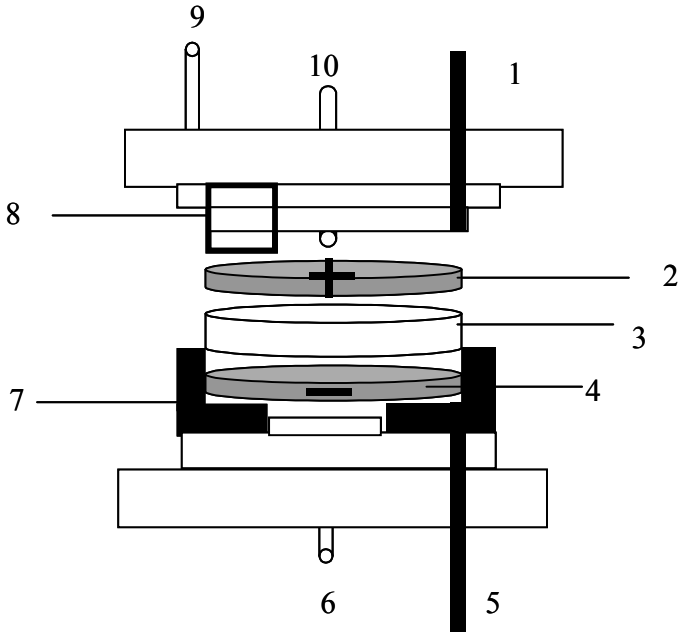


Figure 6.1. Schematic representation for the flat sheet type electrombrane reactor used in the electrochemical oxidation of phenol in aqueous media and its features are (1) current collector (anode), (2) anodic carbon paper, (3) ceramic support, (4) cathodic carbon paper, (5) current collector (cathode), (6) permeate outlet (7) rubber seal, (8) non-conducting flow channel, (9) reject outlet and (10) feed inlet.

The current work is based on a bench-scale pilot plant reactor (320 cm^2) that we have designed and had it constructed by a local technician. An illustration in the difference between the laboratory-scale and the bench-scale reactor is shown by means of the picture in Figure 6.2.

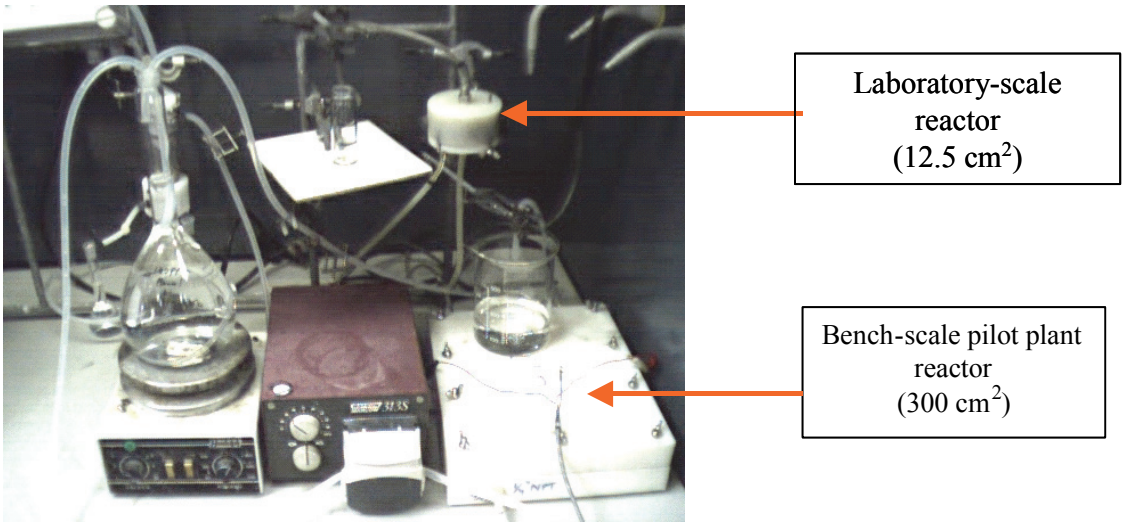


Figure 6.2: Picture of the laboratory-scale and bench-scale electromembrane reactors

6.3 Results and Discussion

6.3.1 The influence of sulfuric acid (H_2SO_4) concentration on the electrochemical oxidation process

Literature as well as results from the preceding chapter suggest that the electrochemical oxidation of phenol is mostly favoured under acidic conditions. Abuzaid and Awad [5] have reported that the percentage of complete phenol oxidation is higher at pH 0.2 than at pH 0.5. This section discusses the results obtained at different acid concentrations and the experimental variables are summarized in Table 6.2.

Table 6.2: Summary of the experimental conditions and variables during the electrochemical oxidation of phenol.

Experiment	Phenol concentration ($mg.L^{-1}$)	H_2SO_4 concentration ($g.L^{-1}$)	Applied potential (V)	Flux ($L.m^{-2}.h^{-1}$)
A	100	1 (10 mM)	2.0	150 ± 5
B	100	5 (50 mM)	2.0	150 ± 5
C	100	10 (100 mM)	2.0	150 ± 5
D	100	50 (500 mM)	2.0	150 ± 5

On each of these experiments, a total of fourteen (14) runs were carried out through the electromembrane reactor and the results are discussed below. The electrochemical oxidation of phenol progresses faster at high acid concentration or low pH (Figure 6.3). Complete phenol degradation was achieved after six (6) runs through the electromembrane reactor when an electrolyte (H_2SO_4) concentration of 50 $g.L^{-1}$ was added to the feed solution.

The results obtained also show that phenol was readily oxidized to p-benzoquinone. The concentration of the p-benzoquinone formed during the experiment was also influenced by the concentration of sulfuric acid in the feed solution.

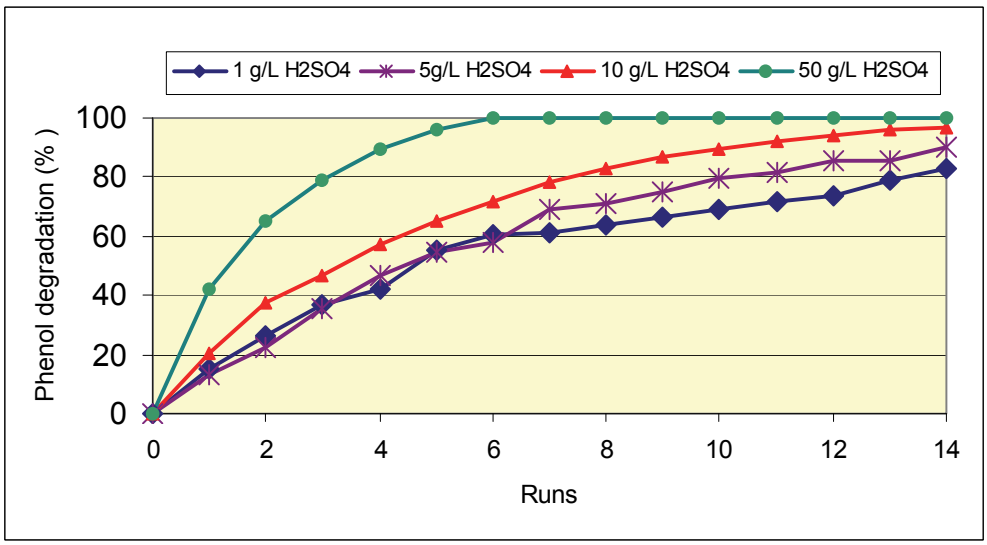


Figure 6.3: Trend of phenol degradation in an electromembrare reactor to compare the influence of sulfuric acid concentration.

At sulfuric acid concentration of 1 $g.L^{-1}$ (1 mM), p-benzoquinone concentration could go as high as 20 $mg.L^{-1}$ as illustrated in Figure 6.4. The trend is such that, p-benzoquinone concentration decreases with increasing sulfuric acid concentration.

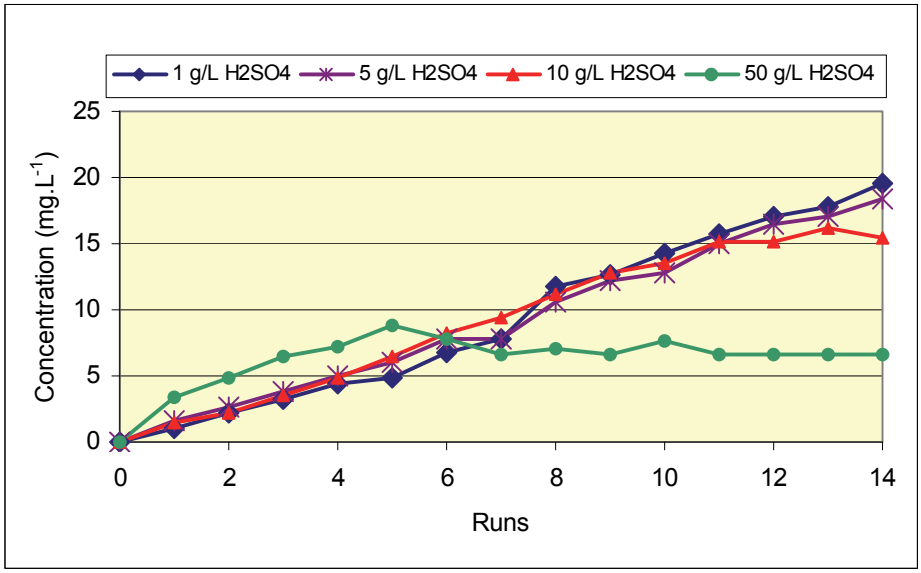


Figure 6.4: Trend of p-benzoquinone formation in an electromebrane reactor at varying sulfuric acid concentration.

The removal of COD followed a similar trend to that of the results illustrated in Figures 6.3 and 6.4. When the concentration of sulfuric acid was increased COD removal could be increased from 39 % to 80 % at 1 $g.L^{-1}$ and 50 $g.L^{-1}$, respectively (Figure 6.5).

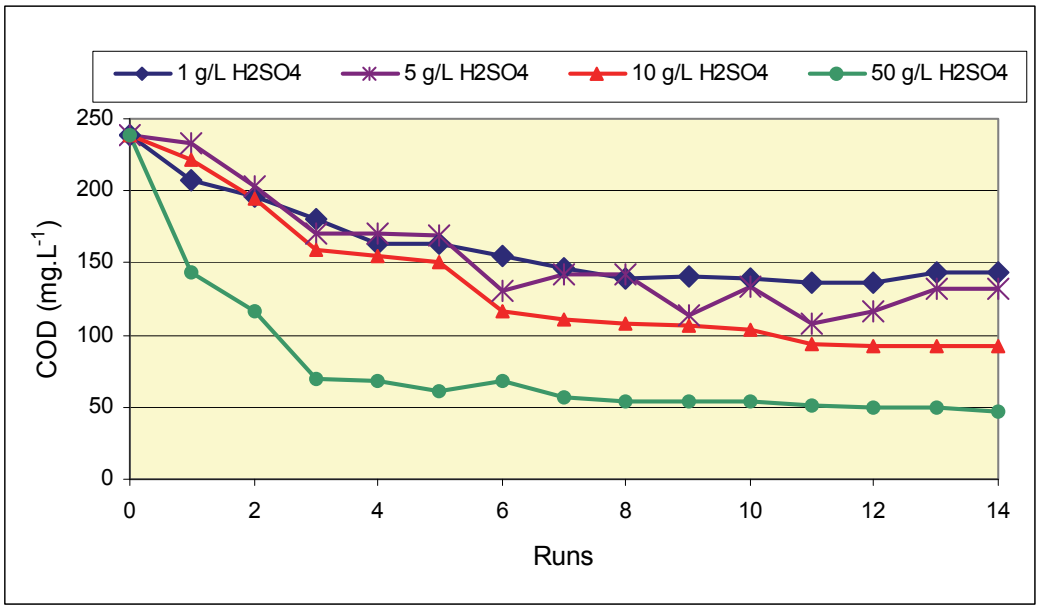


Figure 6.5: Trend of COD removal in an electromembrane reactor.

A summary of all the results obtained in Section 6.3.1 is tabulated below.

Table 6.3: Summary of the experimental results obtained in Section 6.3.1

Experiment	Phenol Degradation (%)	E. Consumption (kWh/g)	p-benzoquinone (mg/L)	COD removal (%)
A	82.6	0.66	19.6	39.7
B	90.4	0.31	18.4	44.6
C	96.6	0.38	15.5	61.2
D	100	0.32	6.6	80.0

6.3.2 The influence of higher applied potential and lower sulfuric acid concentration on the electrochemical oxidation of phenol.

For production of clean water, acid concentration of greater than 1$g.L^{-1}$ in the feed water would result in very high levels of totally dissolved solutes (TDS) and hence water
recovery would still be a major problem. In the experiment illustrated in Figure 6.6 it was decided to keep the sulfuric acid concentration at or below 1 $g.L^{-1}$ but increase the applied potential to 2.5 V.

When potentials above 2.5 V are used, water electrolysis becomes the most dominant process thus resulting in very low phenol degradation.

As it had been seen with all the other results discussed in Section 6.3.1, p-benzoquinone was the sole aromatic intermediate detected in the collected samples. The degradation of phenol was improved by applying a higher voltage with phenol completely degraded in nine (9) runs through the electromembrane reactor. The concentration of p-benzoquinone increases as the concentration of phenol decreases but since phenol is oxidized simultaneously with its intermediates, p-benzoquinone concentration also decreases with time and stays constant after a while (Figure 6.6).

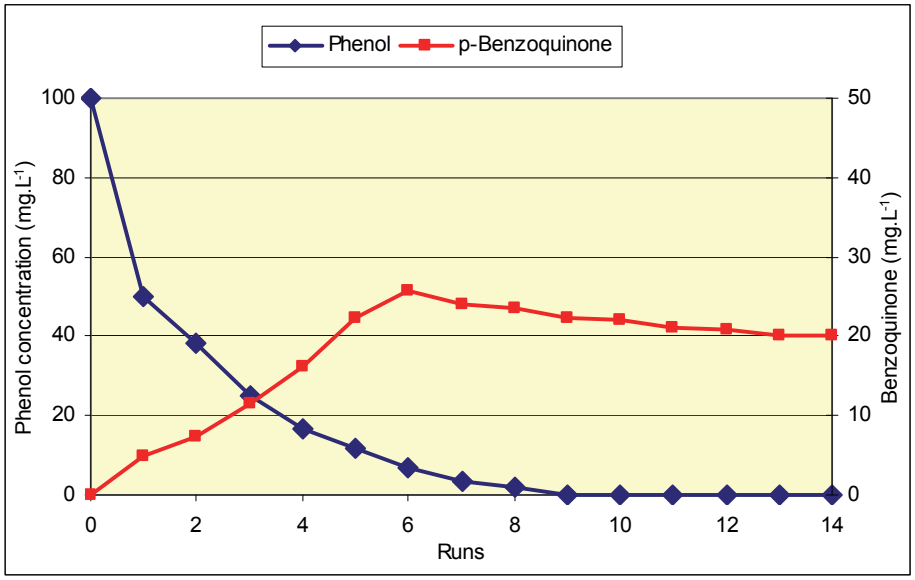


Figure 6.6: Trend of phenol degradation and the emergence of p-benzoquinone in an electromebrane reactor.

Although phenol degradation has improved by applying a potential of 2.5 V, the concentration of p-benzoquinone is still very high (20 $mg.L^{-1}$). The removal of chemical oxygen demand, however, was also improved to 60 % (Figure 6.7).

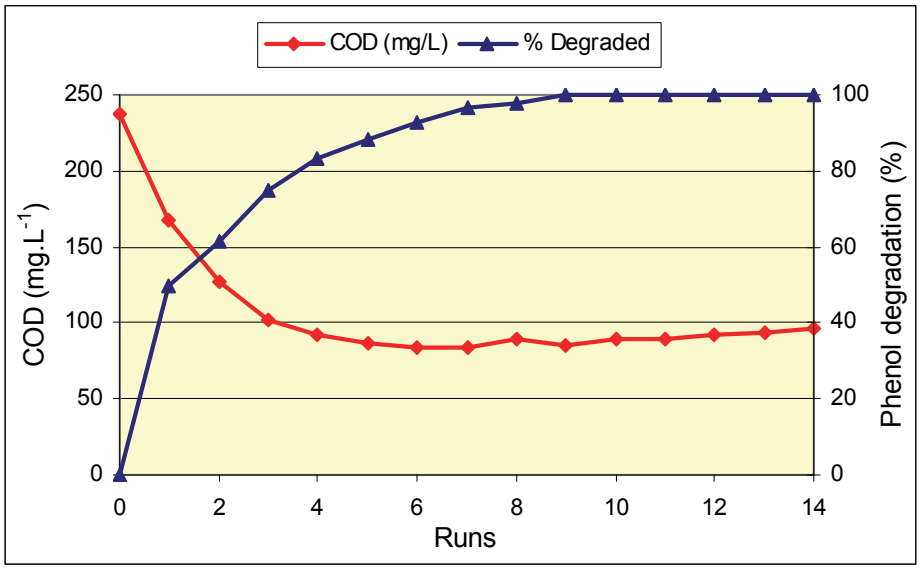


Figure 6.7: Trend of phenol degradation and COD removal in an electromembrane reactor.

6.3.3 Study of the influence of membrane feed flux through the membrane on phenol degradation, the formation of intermediates and COD removal.

Several experiment were conducted in order to study the influence of feed flux through the electromembrane reactor. The fluxes were varied in the region of 50 to 200 $L.m^{-2}.h^{-1}$ and Figures 6.8 to 6.10 show that difference in the flow rate of the feed solution through the electromembrane reactor has had a significant effect on the phenol degradation, formation of intermediates and COD removal. In all the experiments discussed in this section, sulfuric acid (10 mM or 1 $g.L^{-1}$) was used as the electrolyte and a potential difference of 2.5 V was applied.

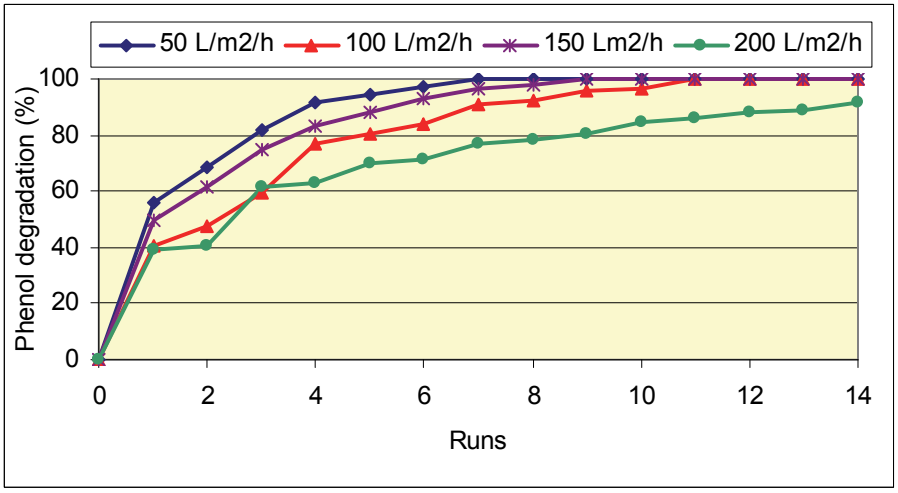


Figure 6.8: Trend of phenol degradation in an electromembrare reactor to study the effect of feed flux through the electromembrane reactor.

At fluxes less than 180 $L.m^2.h^{-1}$ phenol is degraded faster (i.e. in less number of runs) than at higher fluxes. At 200 $L.m^{-2}h^{-1}$ complete degradation of phenol was not achieved even after fourteen (14) runs. This might be attributed to residence time near the surface of the anode as the organic compounds are allowed ample time to be electrooxidized at lower fluxes.

It was also noticed, however, that p-benzoquinone is not necessarily oxidized faster or to completion at lower flow rates. In all the instances, the concentration of p-benzoquinone increases then decreases slightly after a while (Figure 6.9). The concentration of p-benzoquinone was higher than 20 $mg.L^{-1}$ in all the experiments and went as high as 27.2 $mg.L^{-1}$ at a flux of 50 $L.m^{-2}h^{-1}$.

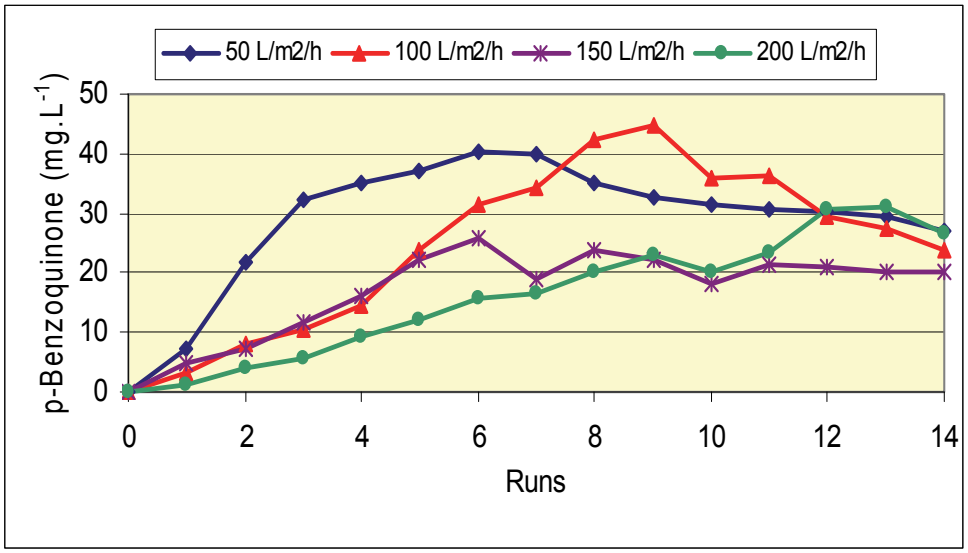


Figure 6.9: The formation of p-benzoquinone during the electrochemical oxidation of phenol at different membrane fluxes.

Better results were achieved at fluxes of 150 ± 20 $L.m^{-2}h^{-1}$ for phenol degradation (complete) degradation and formation of aromatic intermediates (p-benzoquinone = 20.0 $mg.L^{-1}$). Better COD removal was also achieved at that same range of permeate flux (Figure 6.10). All the parameters discussed in this section, together with the energy consumption at different fluxes, are summarized in Table 6.4.

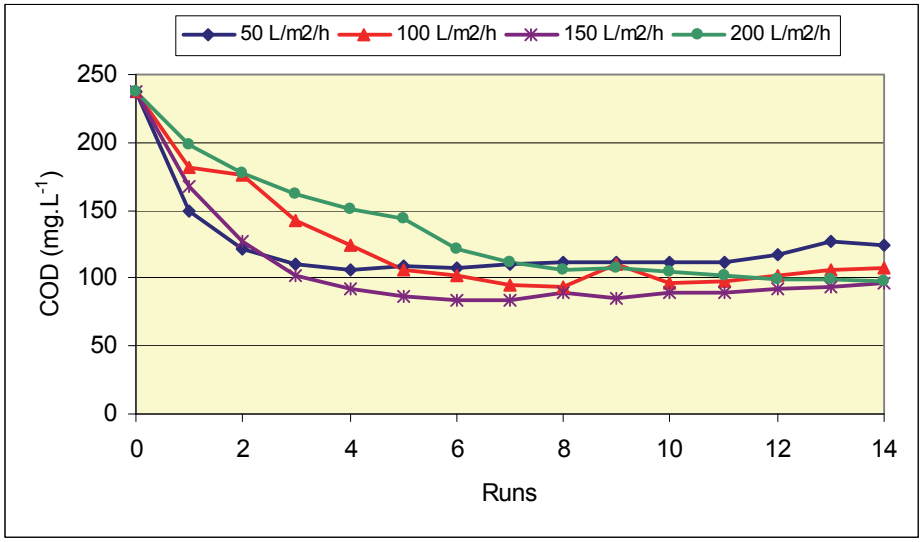


Figure 6.10: The removal of COD during the electrochemical oxidation of phenol at different membrane fluxes.

Table 6.4: Summary of the experimental results obtained in Section 6.3.3.

Flux ($L.m^{-2}.h^{-1}$)	Phenol Degradation (%)	Energy Consumption (kWh/g)	COD Removal (%)	p-benzoquinone ($mg.L^{-1}$)
50	100	2.01	47.8	27.2
100	100	1.42	54.8	23.8
150	100	1.03	60.0	20.0
200	91.6	1.28	58.9	26.6

6.3.4 The influence of chloride ion on the electrochemical oxidation of phenol in a ceramic based electromembrane reactor.

The need to study the influence of chloride ions on the electrochemical oxidation of phenol was necessitated by the fact that real (industrial) effluents contained chlorides in significantly high concentrations. Chloride ions, in solution, have the ability to produce chlorinated organic products, especially in acidic media. Halocompounds are usually more harmful to the environment than the organic compounds they result from. It has been reported that under certain conditions, electrogenerated chlorine converts to hypochlorite, which is a powerful oxidant but weak chlorinating agent [6].

The lowest sodium chloride (NaCl) concentration we could use in our experiments was 0.1 M (5.8 $g.L^{-1}$). NaCl concentrations less than 0.1 M resulted in low conductivity water and, therefore, the electrical current necessary for the electrochemical oxidation of phenol could not be achieved as the

experiment progressed. Furthermore, electrolyte concentrations higher than 0.1 M (5.8 $g.L^{-1}$) would result in very high TDS, as mentioned earlier. This is not only important for environmental purposes but for industry as well; because high chloride levels cause corrosion and shorten the life of pipes, pumps, hot water heaters and fixtures.

For the results shown in Figure 6.11, an experiment was conducted using a feed solution of 0.1 $g.L^{-1}$ phenol in 0.1 M NaCl electrolyte at flux of 150 $L.m^{-2}.h^{-1}$ and applied potential of 2.5 V.

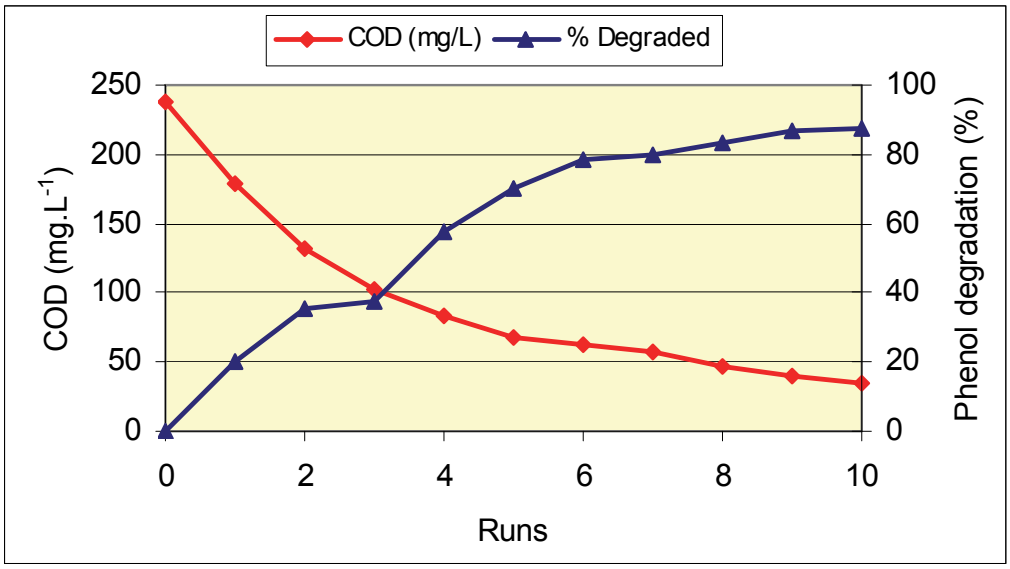
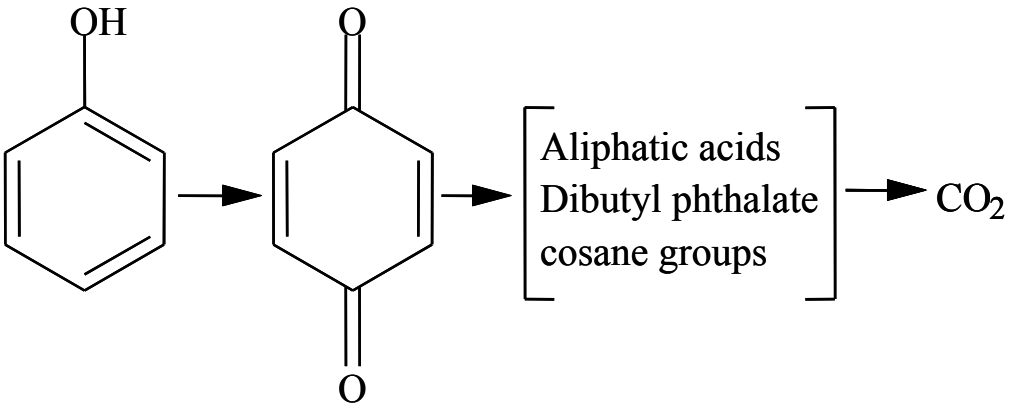


Figure 6.11: The degradation of phenol and removal of COD in the presence of chloride ions.

Figure 6.10 shows that 87 % degradation of phenol could be achieved but what is worth noting and of extreme importance is that there were no aromatic intermediates detected in the resulting permeate. This can also be supported by the fact that 85 % of the initial COD was removed.

6.4 Conclusions

The electrochemical oxidation of aqueous phenol in the ceramic-based electromembrane reactor progresses at a faster rate in highly acidic conditions. In weakly acidic media, oxidation proceeds in stages:



Addition of high concentrations of sulfuric acid is not desirable for the environment. The acid itself is extremely harmful to aquatic life and streamside plants. But the problem is compounded because sulfuric acid also dissolves other metals, causing further contamination to water, soil, and plant communities. When streambank soils are so toxic they cannot grow plants, severe bank erosion follows, and that only puts more contaminants into the river to be ingested by aquatic life.

Improved results, in terms of phenol degradation, were obtained by increasing the applied potential and decreasing the acid concentration to 0.01 M (1 $g.L^{-1}$). Phenol degradation, however, still follows a conversion (to aromatic and aliphatic intermediates) pathway instead of a combustion (to CO_2) pathway. Although complete phenol degradation was achieved, the concentration of p-benzoquinone, which is more harmful than phenol itself, was extremely high (20 $mg.L^{-1}$). p-Benzoquinone formation followed by it is degradation is evidence that the electrochemical oxidation of phenol was successful and provide guarantee for the conversion to more biodegradable products. The reduction of COD is one of the most challenging tasks for any water treatment process. The electrochemical is no exception, even though phenol might be completely degraded, COD might have decreased by 39.7 %. This also suggests that the oxidation of follows a conversion route rather than combustion to CO_2.

The best results were obtained by using NaCl as an electrolyte solution in the place of H_2SO_4. No aromatic intermediates were detected at the end of the treatment process. The removal of COD by 87 % shows that most of the phenol was degraded to CO_2. The presence of Cl^- improved COD removal, proving that phenol degradation is also carried out near the surface [7] by the hypochlorite formed through oxidation of chloride.

6.5 References

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7. BENCH-SCALE REACTOR FOR THE ELECTROCHEMICAL OXIDATION OF PHENOL IN AQUEOUS MEDIA: INFLUENCE OF DIFFERENT ELECTROLYTE SOURCES ON THE DECOMPOSITION OF SYNTHETIC PHENOL AND PHENOL IN INDUSTRIAL EFFLUENT

Abstract

In this section, the ceramic-based electromembrane system was tested for the electrooxidation of synthetic phenol and real (industrial) phenolic effluent. Commercial chemicals, acid mine drainage and seawater (Houtbay Beach, Cape Town) were used as electrolyte solutions. Phenol-containing effluent from the Sapref (Durban) refinery was tested. As it was already established in Chapter 6, the experiments were conducted at 2.5 V with a permeate flux of 150 ± 30 $L.m^{-2}.h^{-1}$.

7.1 Introduction

Industrial effluents are known to contain toxic and/or non-biodegradable organic substances [1]. In South Africa oil refineries such as SAPREF (Durban, RSA), Caltex (Cape Town, RSA) and SASOL are the most common sources of phenolic waste, which needs to be treated before the effluent is introduced to our watercourses or reused for industrial purposes. Regulations set out by environmental groups and government bodies are becoming more strict on the manner in which waste should be managed. In the USA, the Environmental Protection Agency (EPA) monitors and advices industry and individuals about the safe disposal of hazardous waste, and a system of laws and regulations are in place for tackling waste produced [2].

From industrial point of view though, the management, destruction or disposal of waste is burden and often not considered as part of any process. This is due to the fact that, waste treatment can be expensive and does not generate any profit. Thus, for waste treatment process to be accepted by industry, it has to simple and cheap to operate. We have designed the electromembrane reactor based on inexpensive material and in this chapter we discuss operation conditions that might solve most of the problems faced by organic waste-producing industries.

7.2 Experimental

The materials, experimental procedure and electromembrane reactor that were employed in this chapter is similar to those discussed in Chapter 6 and hence, will not be repeated in this chapter.

7.2.1 Electrochemical oxidation

The characteristics of the SAPREF effluent that was used in the experiment discussed in this chapter are listed in Table 7.1.

Table 7.1: The characteristics of the BP phenolic effluent.

Type of effluent	Phenol content (mg/L)	pH
Caustic	300 – 390	8.5 – 9.0
Phenolic	120 – 220	8.5 – 9.0

The phenol content in the feed solution that was pumped into the electromembrane reactor was always 100 $mg.L^{-1}$. Therefore, the effluent was diluted to 100 $mg.L^{-1}$ in a suitable electrolyte solution. The applied potential in all the experiments discussed in this chapter was 2.5 V and constant flux of 150 ± 30 $L.m^{-2}h^{-1}$ was also maintained.

7.3 Results and Discussions

A list of experiments that were performed is given in Table 7.2. In some experiments, synthetic phenol was used as the test solution while in other cases, real effluent was used as the test solution. Sulfuric acid (H_2SO_4), acid mine drainage (AMD), sodium chloride (NaCl) and seawater were used as electrolyte solutions.

Table 7.2: List of experimental variables

Experiment	Potential (V)	Flux ($L.m^{-2}.h^{-1}$)	Electrolyte	Phenol source	Conductivity (mS/cm)	pH
1	2.5	150 ± 30	AMD	Synthetic phenol	5.38	3.02
2	2.5	150 ± 30	H_2SO_4	SAPREF effluent	6.38	2.01
3	2.5	150 ± 30	AMD	SAPREF effluent	2.25	6.67
4	2.5	150 ± 30	NaCl	SAPREF effluent	2.18	7.64
5	2.5	150 ± 30	Seawater	Synthetic phenol	> 20	7.36
6	2.5	150 ± 30	Seawater	SAPREF effluent	> 20	7.45

The acid mine drainage (AMD) samples that were used in our applications were collected from ARNOT mines in Gauteng. There are different chemical species in the AMD samples and theses are listed in Table 7.3.

Table 7.3: Composition of the acid mine drainage (AMD) samples from ARNOT

Parameter		Value	Units
pH		3.22	
EC		1.41	mS/cm
Acidity		200	
Majors	SO_4	1051	mg/L
	Na	54	mg/L
	Cl	11	mg/L
	NH_4	1	mg/L
	NO_3	4	mg/L
	Fe	16	mg/L
	Al	2	mg/L
	Ca	115	mg/L
	Mg	92	mg/L
	K	17	mg/L
	B	1	mg/L
Minors	Zn	694	µg/L
	Sr	550	µg/L
	As	2	µg/L
	Ba	6	µg/L
	Pb	11	µg/L
	Se	6	µg/L
	U	1	µg/L

(i) Experiment 1

Depending on the geographic site, some areas in South Africa have industries experience problems with either AMD or organic pollutants in close proximity.

Companies such as SASOL are faced with problems of managing and treating organic waste while the surrounding mines have problems with the disposal of fly ash and AMD. Chapter 6 already discussed the effect acidic conditions have on the degradation of phenol. In this experiment we investigate whether AMD would be a suitable electrolyte in the electrochemical oxidation of phenol or not. A synthetic phenol solution (100 $mg.L^{-1}$) was diluted with AMD as received and the results are shown in Figure 7.1.

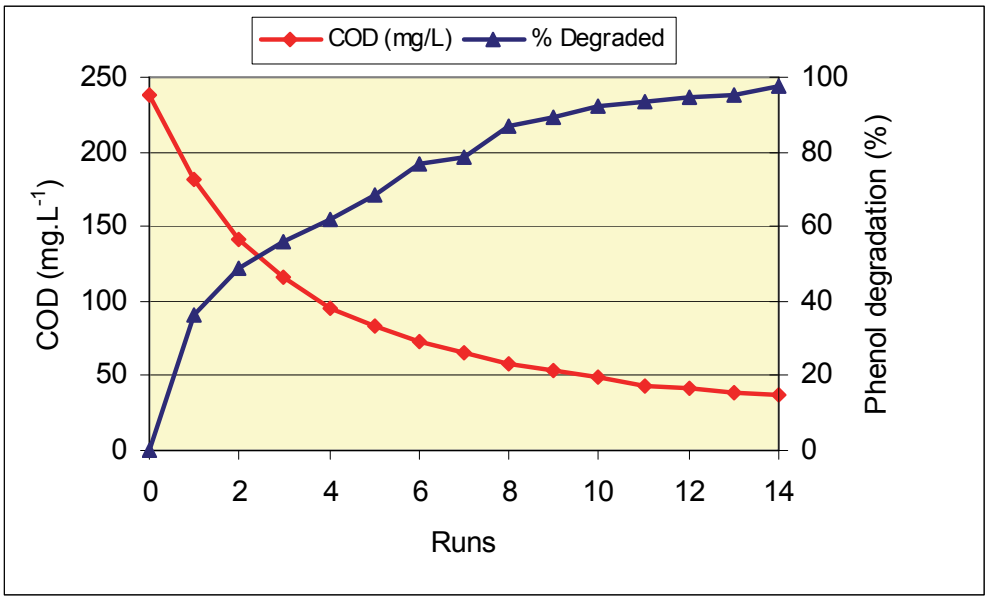

Figure 7.1: The effect of AMD on the electrochemical oxidation of synthetic phenol.

97 % of the initial phenol concentration had been depleted at an energy consumption of 660 $Wh.g^{-1}$. An interesting observation was the reduction of COD by 84 %. Further analysis of the samples show that the only aromatic product formed was p-benzoquinone (7.0 $mg.L^{-1}$). Maleic acid (0.54 $mg.L^{-1}$) and oxalic acid (12.6 $mg.L^{-1}$) could also be detected in the samples. The concentration of the intermediates that resulted from phenol degradation in this experiment was quite low. We can, therefore, assume that most of the phenol was degraded to CO_2.

(ii) Experiment 2

Although the results shown in experiment 1 are impressive in terms of phenol degradation, COD removal as well as the concentration of intermediates formed, a synthetic phenol solution was used. The results could be completely different when the test solution is real industrial effluent. In this experiment, the BP effluent was tested and commercial H_2SO_4 (0.01 M; $1g.L^{-1}$) was used as the electrolyte solution (Figure 7.2).

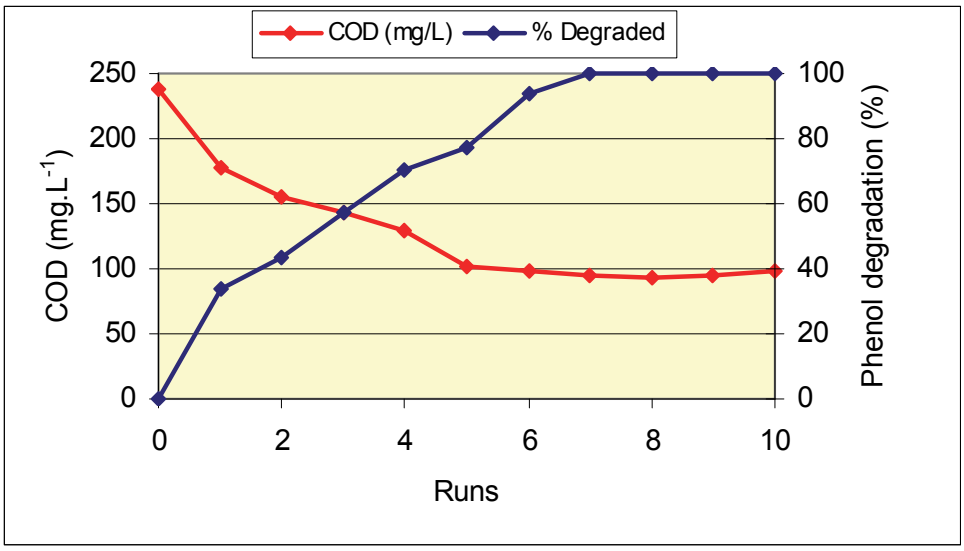

Figure 7.2: Influence of H_2SO_4 on the electrochemical oxidation of phenol in SAPREF effluent.

Phenol was completely degraded and COD was reduced by 59 %. The removal of COD remained almost constant after 5 runs and there was not any significant change in COD concentration after that. p-Benzoquinone was detected as the sole aromatic intermediate formed with a concentration as high as 23 $mg.L^{-1}$. Aliphatic acids (maleic, fumaric and oxalic acid) were also detected in very low concentrations. COD was still high (approx. 97.6 $mg.L^{-1}$) and above the permissible concentration. The high COD concentration can be attributed to the formation many reaction intermediates and the high concentration of such intermediates. This means that there were a lot of products that could be easily oxidized by dichromate.

(iii) Experiment 3

We suspected that the presence of chloride ions in the AMD might have had a positive influence on the degradation phenol and the removal of COD, as previously observed. Hence, in experiment 3, the SAPREF effluent was diluted to 0.1 $g.L^{-1}$ phenol concentration with AMD as the electrolyte source. The results obtained had improved from the ones discussed in experiment 2, where pure H_2SO_4 was used (Figure 7.3).

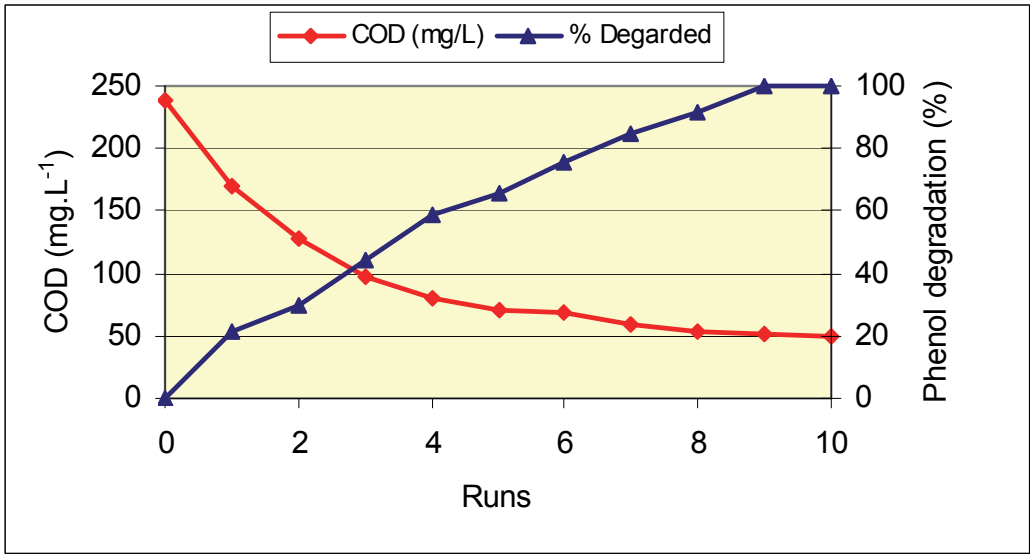

Figure 7.3: The effect of AMD on the electrochemical oxidation of phenol in a phenolic effluent from SAPREF.

No phenol could be detected in the samples after ten (10) runs, and COD was reduced to 49 $mg.L^{-1}$. The concentration of p-benzoquinone (the sole aromatic product) in the samples was 13 $mg.L^{-1}$ and only trace amounts of oxalic acid and maleic could be detected.

(iv) Experiment 4

The use of NaCl solution as an electrolyte was reported to improve the efficiency of phenol degradation and COD removal (Chapter 6, Figure 6.10). That experiment was conducted using synthetic phenol solutions though. In the experiment illustrated in Figure 7.4, the effect of NaCl on the degradation of phenol and removal of COD was studied on the phenolic effluent from the SAPREF oil refinery.

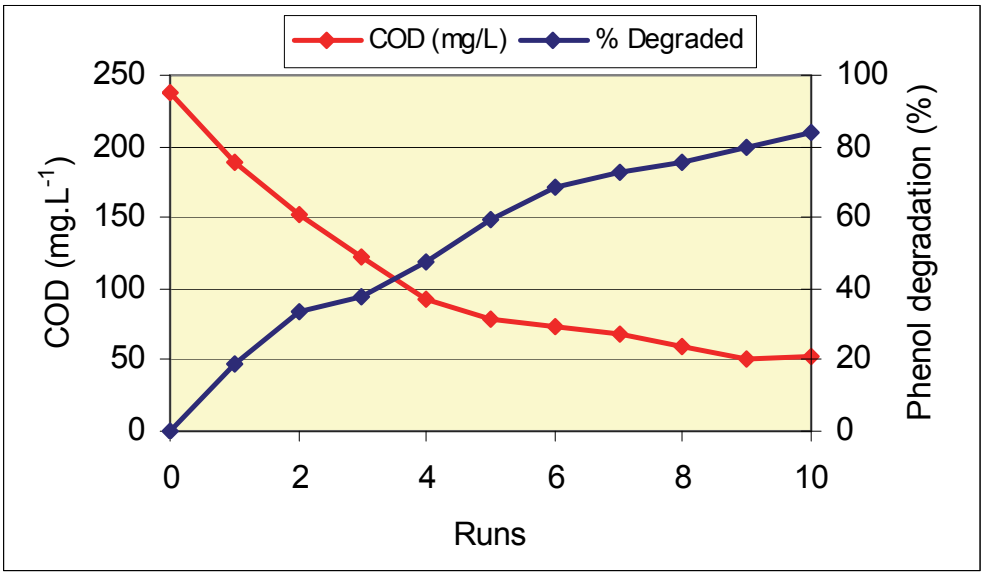

Figure 7.4: The effect of NaCl on the electrochemical oxidation of phenol in a phenolic effluent from SAPREF.

As with the previous experiments, NaCl had a positive effect on COD removal ((78.31 %) and the concentration of p-benzoquinone was found to be lower (7.8 $mg.L^{-1}$). Phenol concentration, however, was only reduced to 16 mg/L after ten (10) runs through the electromebrane reactor (Figure 7.4). Oxalic acid was the only aliphatic acid detected and the other aliphatic acids were below our detection limit (0.5 $mg.L^{-1}$).

(v) Experiment 5

Chlorine-containing salts are in abundance in seawater and, from an economic point of view, it would make sense to use seawater as a chloride source instead of buying commercial chemicals. Experiments were conducted, whereby a 100 $mg.L^{-1}$ solution of synthetic phenol, prepared with seawater was passed through the electromembrane reactor and the phenol concentration and COD removal measured after that (Figure 7.5). The seawater was also diluted with pure water due to the high salt content in the seawater.

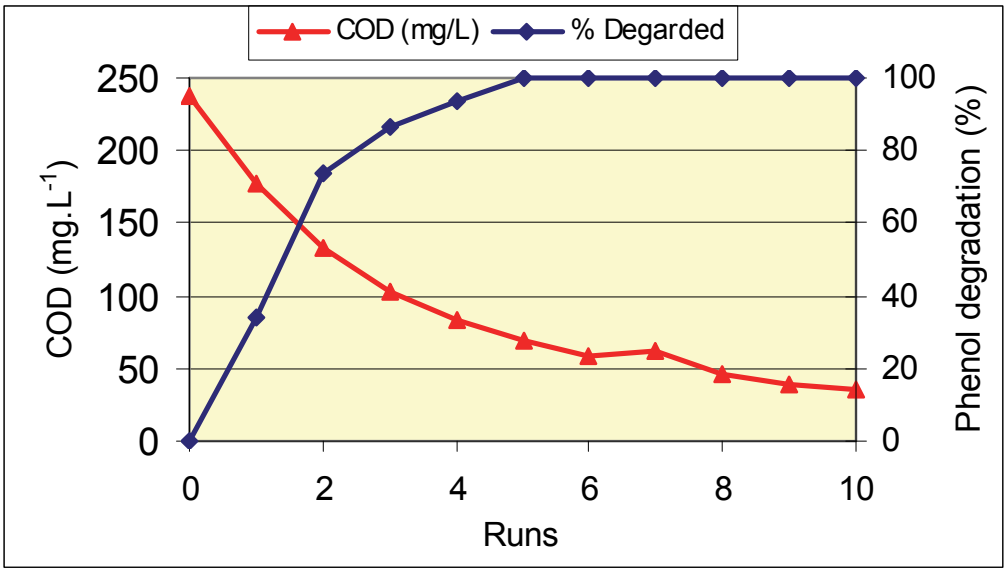

Figure 7.5: The effect of seawater as an electrolyte for the electrochemical oxidation of synthetic phenol.

Total phenol degradation was achieved after five (5) runs through the electromembrane reactor. The concentration of p-benzoquinone was lower than 3.0 $mg.L^{-1}$ and no other intermediates were detected in the collected samples. 85 % of the initial COD concentration had been removed from the resulting water.

(vi) Experiment 6

The SAPREF oil refinery in Durban (South Africa) is situated in along the coast and most of its wastewater is disposed by means of a pipeline into the ocean. Regulations have been put in place to manage the amount of waste that is dumped into the ocean and wastewater with high phenol concentrations would have to be treated before being disposed of. In the experiment discussed below (Figure 7.6) the BP effluent was diluted to a phenol concentration of 100 $mg.L^{-1}$ with seawater.

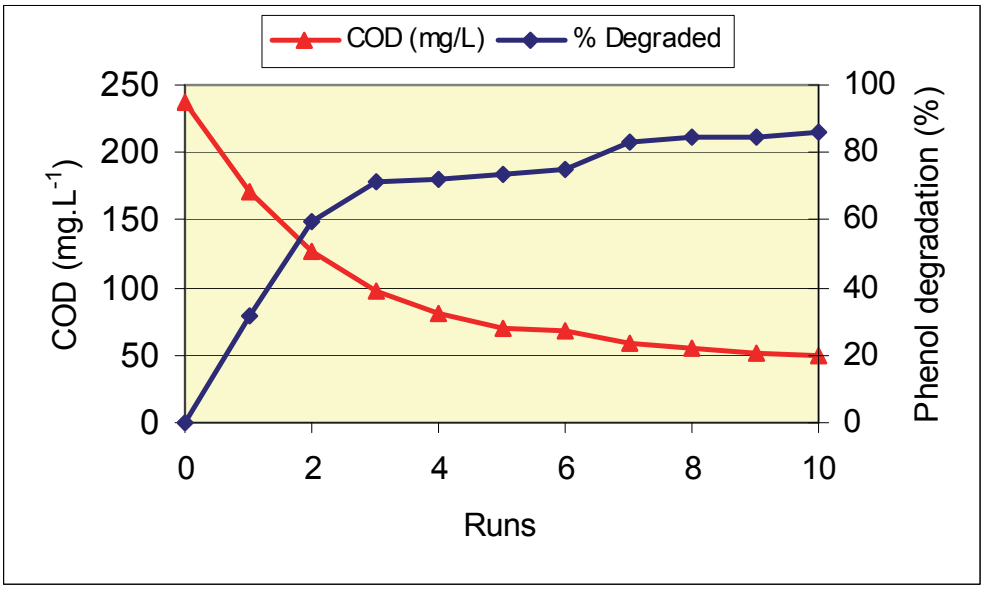

Figure 7.6: The effect of seawater as an electrolyte for the electrochemical oxidation of phenol in a phenolic effluent from SAPREF.

The concentration of phenol was only reduced from 100 to 13.0 $mg.L^{-1}$. The concentration of p-benzoquinone was also low (6.2 $mg.L^{-1}$) and COD was reduced by 79.42 %. Aliphatic acids such as maleic, oxalic and fumaric were also produced during the experiment, hence COD removal is relatively low compared to the results discussed in experiment 5.

A summary of all the results discussed in this chapter is listed in Table 7.4 below.

Table 7.4: Summary of results obtained from the electrochemical oxidation of phenol at a bench-scale electromembrane reactor.

Experiment	Electrolyte	Phenol source	Phenol Degraded (%)	E. Cons. ($Wh.g^{-1}$)	COD Removal (%)	Benzoquinone (mg/L)
1	AMD	Synthetic phenol	97	660	84	7.0
2	H_2SO_4	SAPREF effluent	100	190	59	23.0
3	AMD	SAPREF effluent	100	210	79	13.0
4	NaCl	SAPREF effluent	84	740	78	7.8
5	Seawater	Synthetic phenol	100	200	85	2.8
6	Seawater	SAPREF effluent	87	840	79	6.2

7.4 Conclusions

The conditions for the electrochemical oxidation of phenol in the bench-scale flat-sheet type electromembrane reactor had been improved quite substantially. Acid mine drainage was used to replace commercial sulfuric acid solution as the electrolyte. Better results in terms of COD removal and the number of intermediates formed had been achieved when using acid mine drainage instead of H_2SO_4. Due to the complex nature of the chemical composition of the acid mine drainage, it is quite difficult to deduce which of the compounds present might "assist" in the electrochemical oxidation process.

Among all the compounds present in the acid mine drainage, chloride ions are most likely to be the reason for improved results. We suspect that chloride ions are activated to hypochloride at the surface of the anode and thus also assist in the electrochemical oxidation of organics.

Sodium chloride solution was also used as an electrolyte in order to support the statement mentioned earlier on. The effect of NaCl on the degradation of phenol in the SAPREF effluent was then investigated and it was found that a high degree of phenol degradation could be achieved and an even higher COD removal efficiency was possible.

The use of seawater instead of commercial Cl^- ion sources as electrolyte would be more advantageous for coastal industries, which are faced with the task of treating and managing organic waste. Oil refineries such as Caltex (Milnerton, Cape Town) and the SAPREF refinery in Durban are a perfect example of industries, which would make use of seawater for the treatment process. Our results show that seawater was a suitable electrolyte for the electrochemical oxidation of phenol and the removal of COD in the phenolic water.

7.5 References

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8. OVERALL CONCLUSIONS AND RECOMMENDATIONS

As a source of life, water is one of the most precious commodities for all living organisms. Although water resources are reported to be declining in numbers or the amount of water present, the existing ones are being polluted as a result negligent human activities and intense industrialization. This means that the treatment, management and usage of polluted water has become an important part of industrial practices.

There are many treatment methods that exist for polluted water. Electrochemistry is proving to be a tool with which current purification systems can be improved upon. Anodic oxidation, as a water purification system, is already being used commercially (AEG, Electrosythesis), but there is a very high cost associated with the purification units. The availability of new electrode and reactor materials and the development of electrocatalysts with good efficiency for phenol degradation will further develop and improve these water purification units.

The data obtained using the flow-through ceramic-based electromembrane reactor verify the improvements that can be made on the anodic oxidation purification systems in order to effectively destroy pollutants at lower cost. This chapter is set out to discuss the conclusions that were made based on the results that were obtained when using tubular ceramic membranes and flat-sheet type ceramic membranes as anode materials for the electrochemical oxidation of phenol.

8.1 Tubular ceramic membranes

Tubular ceramic membranes were used successfully as anode materials for the electrochemical oxidation of aqueous phenol. Section 8.1 is subdivided into two subsections 8.1.1 and 8.1.2, where conclusions were made on data obtained when using carbonized tubular ceramic membranes and data obtained when using the gold/platinum-coated ceramic membranes.

8.1.1 Carbon-coated tubular ceramic-based electromembranes

The following conclusion, based on the use of carbonized ceramic membranes for the electrochemical oxidation of aqueous phenol were made:

- The preparation of a hydrophilic carbon coating with suitable electron conducting properties on the ceramic matrix was successful. Suitable conditions for the carbon coating technique were optimized with respect to pyrolysis time and temperature. The influence of these parameters on membrane conductivity and permeability were studied and discussed.

- Apart from good electron conducting properties, the carbon coating exhibited good electrocatalytic properties for phenol degradation. Phenol could be degraded completely in just one pass through the carbonized ceramic substrate.
- Impregnation of the carbonized ceramic membranes with inorganic proton conducting materials (zirconium phosphate) had its some advantages as well as drawbacks on the electrolysis process. An advantage was the reduction in the number of by-products formed and the concentration of the aromatic intermediates. The drawback was that the carbonized membranes lost some of their surface conductivity as well as permeability. The loss in conductivity had a negative influence on the current density in that the subsequent electrical stability of the electromembranes was low.

8.1.2 Gold/platinum-coated tubular ceramic-based membranes

A thin layer of sputtered gold was coated on the surface of the ceramic substrate, followed by impregnation with a platinum-based catalyst. The following conclusions were made on the data obtained when using the Au/Pt electromembrames for phenol degradation in water:

- A thin, homogeneous layer of gold was successfully deposited on the ceramic surface by using a sputter coater. The gold layer had excellent properties for conducting electricity with very high stability as well. Unlike the carbon coating, the gold layer had poor properties for the electrochemical oxidation of aqueous phenol.
- A platinum-based catalyst was successfully loaded onto the ceramic membrane matrix by impregnation in a platinum salt solution, followed by thermal decomposition.
- By flowing through the Au/Pt-coated membranes, phenol (in solution) was rapidly degraded to its corresponding aromatic intermediates.
- Unlike the situation experienced with carbonized membranes, impregnating the Au/Pt-coated membranes with zirconium phosphate did not have an adverse effect on the electrical stability or conducting properties of the Au/Pt electrodes.
- The number of intermediates formed during the electrochemical oxidation of phenol was also reduced when employing membranes impregnated with zirconium phosphate.
- The flux through the membrane decreased rapidly with time due to the reduced pore sizes as a result of impregnation with zirconium phosphate and formation of a polymeric film on the surface of the electromembrane.
- The Au/Pt membranes were poor electrodes under highly acidic conditions because the gold layer was washed off the surface of the membrane during electrolysis.

8.1.3 Overall conclusions of the tubular electromembrane units

The use of the tubular electromembrane, in general, for the electrochemical oxidation of organic pollutants in water was successful for the following reasons:

- A novel type of water purification unit was developed whereby, the organic pollutant (phenol) could be rapidly degraded by simply flowing through an electrically charged membrane.
- Methods for the preparation of electroconductive materials and electrocatalysts on the ceramic membranes' surface and matrix were developed.
- Apart form the material science and engineering involved with the development of these purification units, analytical methods and procedures based on spectrometry, GC-MS and HPLC for the determination of phenol concentration and its oxidation products were developed.
- The energy requirements for the complete oxidation of phenol in the electromembrane units, equipped with tubular ceramic membranes, were low (between 1.3 and 6.0 Wh/g).

Although the purification systems based on tubular membranes offer further improvement for a number of electrochemical processes and devices, which have been developed in the process industry, there were a number of drawbacks associated with the use of these units and these are:

(i) Carbon deposition

The deposition of pyrolytic carbon was done in a quartz tube, and several disadvantages can be listed with regards to deposition of carbon on the ceramic substrate.

- Very high temperatures (> 800 ºC) and dangerous conditions are associated with the deposition of pyrolytic carbon on the ceramic substrate. The use of high temperatures requires lots of electrical energy and this is an addition to the total cost of the process.
- In order to achieve reproducible results only one membrane can be coated at a time, regardless of size.
- Since one is limited to a certain membrane size, carbon coating would not be suitable on an industrial scale. The longer the membrane, the less homogenous or less consistent the coating is.

(ii) Gold/platinum coating

- Since gold deposition is carried out in the sputter coater, one is also limited to the size and number of membranes that can be coated at a time.

- The membranes were dipped in a solution of platinum salt, followed by heating at 450 ºC. Most of the platinum evaporated and was lost to the surrounding walls of the oven during heating. This proved to be a very costly experience due to the high value of platinum.
- A lot of platinum was required in order to achieve the required electrocatalytic activity. Therefore, several dip coating procedures had to be done for a single membrane.

(iii) Membrane assembly

The assembly of the tubular electromembrane reactor was also associated with certain drawbacks that might hamper the application of the tubular purification systems on a larger scale.

- On several occasions, the membranes break while being assembled into the reactor. Should the number of such membranes be high in one day, this would be a costly exercise as well.
- A conductive coil, made out of stainless steel or any conducting metal, was used to collect current from the external power source to the membrane. There have be adequate contact between the conductive coil and the ceramic surface. This close contact between the membrane and the conductive coil also lead to the conductive coating being scrapped off or, in other cases, the membrane breaking.
- Because we had to make sure that the conductive coil did not influence the outcome of the electrooxidation process, we had to make sure that it only made contact with a small portion of the membrane. This lead to a potential drop, from the point of contact along the length of the membrane. For industrial processes, where longer or multiple membranes would be required, it would be difficult to make sure that potential drop along the length of the membranes is minimized.

(iv) Electrochemical oxidation process

- One of the disadvantages associated with these purification systems was that the pH of the resulting permeate solution was very high (> 11) and would need further neutralization.
- The number and concentration of aromatic intermediates formed was very high, as a result of secondary cathode reactions that took place.

8.2 Flat-sheet type ceramic-based electromembrane reactors

Section 8.2 is divided into two subsections, 8.2.1 and 8.2.2, which highlight the conclusions that were made on the laboratory-scale electromembrane reactor and the bench-scale electromembrane reactor.

8.2.1 Lababoratory-scale flat-sheet type electromembrane reactor

The use of the flat-sheet type electromembranes for the electrochemical oxidation of aqueous phenol was successful in the following areas:

- A novel, flow-through, water purification system based flat-sheet type electromembranes was developed. The purification unit was easy to assemble and the problem of membranes breaking during reactor assembly was overcome by the use of flexible ceramic sheets.
- The flat unit's design is such that it is easy to upscale for industrial applications.
- Leakage was prevented by tightly pressing the compartments of the electrochemical cell against rubber seals.
- Problems associated with potential drop across the membrane surfaces, due to insufficient contact between the current collector and the membrane surface, were overcome by using carbon cloth as a current collector and pressing the carbon cloth against the surface of the electromembrane.
- The purification unit was designed in such a way that cathodic reactions were minimized so that there shouldn't be a difference in the salinity of the feed solution and that of the resulting permeate solution during the electrochemical oxidation process.
- Complete phenol degradation could be achieved over the entire pH range. Under basic conditions, however, phenol was converted to several unfavourable products, including polyphenols, which also resulted in the membrane being partially blocked and subsequently losing its permeability.

Apart from the development of a novel purification system, new types of materials and methods for the preparation of such materials were also developed. These are:

- A method for loading the Sb-doped SnO_2 catalyst on carbon black (Vulcan XC 72) was developed. Nanosized electrocatalysts were synthesized from the carbon black/Sb-SnO_2 mixture.
- Comparisons were made between the synthesized electrocatalysts and the commercially available nanoparticles from Nanotek (USA) and it was found that the synthesized electrocatalyst showed better efficiency for the electrochemical oxidation of phenol and COD removal. The major drawback of the lab-scale electromembrane units was mainly in the design. A stainless steel flow-channel was used to distribute the feed water, evenly throughout the entire membrane surface before it permeates through the membrane. The stainless steel on the anodic side had negative influences on the outcome of the results due to reactions that occurred between

the electrolyte solution and the stainless steel. When a solution of NaCl was used as an electrolyte, the iron on the stainless steel reacted with the chloride ions and was leached off resulting in a red/brown precipitate, which further polluted the water.

8.2.2 Bench-scale flat-sheet type electromembrane reactor

An upscaled version of the flat-sheet type electromembrane reactor was designed and constructed. Apart from making it bigger, several modifications were made to the bench-scale electromembrane reactor in order to address the problems that were encountered when applying the lab-scale unit for the electrochemical oxidation of phenol in water.

- The bench-scale purification unit was used successfully for the electrochemical oxidation of phenol under different pH conditions and various types of electrolyte solutions.
- Complete degradation of phenol in phenolic effluent from the SAPREF (Durban, RSA) oil refinery was achieved over the entire pH range.
- According to the department of Water Affairs and Forestry (DWAF) specifications, COD levels must be 75 mg/L or lower when discharging wastewater into river streams. In the bench-scale purification unit, COD could be reduced to less that 50 mg/L when treating the SAPREF (Durban, RSA) effluent.
- Apart from the immense technological advantage for oil refineries situated along the coast, the energy requirements for the degradation of phenol are very low.
- Under acidic conditions, when either acid mine drainage or H_2SO_4, is used as an electrolyte source, phenol is readily decomposed to p-benzoquinone and other hydrophilic, low molecular weight products, viz. the organic acids. These acids belong to non-hazardous solutes that have maximum permissible concentrations (MPC).
- In contrast, the maximum permissible concentrations of phenol and p-benzoquinone are at levels of 0.01 to 0.001 $mg.L^{-1}$. The concentration of p-benzoquinone in most of the experiments that were conducted under acidic conditions was greater than 13 $mg.L^{-1}$. From an electrosynthesis point of view p-benzoquinone is an interesting product since it has many important uses. It is used in the manufacture of unsaturated polyesters, as a polymerization inhibitor and raw material for hydroquinone. 1,4-Benzoquinone reacts with trialkylboranes to produce alkyl-substituted hydroquinones and so on.

8.3 Recommendations and technological outcomes

At the begin of this research a problem statement was issued and the objective was to find a suitable technology for water treatment based on a combination of electrochemical techniques and membrane separation technology, without using high pressures. It was decided that the use of flow-through membrane electrode-based systems would be suitable and effective for water purification from organic pollutants. However, the success and implementation of such systems would also be based on the following material-related factors:

- electroconductivity,
- catalytic activity
- high COD removal capability
- ease of use and implementation
- affordability
- technological applicability and outputs

The following research questions were answered based on the research that was conducted:

1. *How can ceramic-based membranes be modified to posses electron conducting properties and be adopted as electrodes*?

   Suitable electroconductive materials were selected from an array of materials, with respect to their electrical stability, ease of preparation as well as deposition onto the ceramic substrate. A thin layer of the desired electroconductive material was deposited, either on the ceramic membranes' surface or throughout the ceramic membranes' matrix.

2. How can the ceramic-based electromembranes be optimized to exhibit high catalytic properties for the decomposition of organic pollutants?

   The electroconductive layer that is deposited on the ceramic membrane might possess catalytic properties for organic decomposition. Most of the electroconductive layers, however, show poor catalytic properties for the decomposition of organic compounds. In such cases, electrocatalytic materials are incorporated into the ceramic membrane, either with electroconductive material or after deposition of the electroconductive material.

3. *Can flow-though purification units be designed and constructed to provide for effective decomposition of organic pollutants*?

   Electromembrane reactors were designed and constructed to work as flow-through purification units. The ceramic-based electromembranes were adapted to work as anodes, whereby the feed water comes into contact with the electrocatalytic surface and the organic compounds are mineralized to CO_2 and biodegradable compounds.

4. *How difficult would it be to implement and operate such a device on a polluted site*?

   The purification units are easy to assemble onto a mobile pilot plant and can be used at any site where there is electricity. The flat-sheet type membrane purification units are designed in the form of cartridges whereby additional cells can be added on, depending on the nature of pollutants and the application.

5. Will the energy consumption and overall efficiency of the electromembrane reactor be sufficient to justify its upscaling to an industrial applicable prototype?

   The materials used for the purification systems, i.e. the ceramic membranes, conductive materials, electrocatalysts and reactor materials, are inexpensive materials. There has been a decrease in the price of ceramic membranes and other membranes, in general, due to the growing interest in membrane technology. Hence, downward trend in membrane price is expected in the future. The energy requirements for the electrooxidation process are very low. The efficiency of the process is such that the organic components are rapidly degraded by passing through the electrocatalytically active membrane at high flow rates. The laboratory-scale flat-sheet type electromembrane reactor was upscaled to the bench-scale version and treatment of industrial effluent polluted with phenols was possible.

6. *What will the technological outputs and advantages of such a system be*?

   The technological outputs expected from the system are:

   - Optimum properties and conditions of ceramic membranes for the preparation of electrocatalytic membranes suitable for the anodic degradation of organic pollutants in water.
   - Procedures for the synthesis, preparation and deposition of different types of electrocatalytic material onto the ceramic membranes.
   - Prototypes of the different purification units that were designed and constructed.
   - Optimum conditions and procedures for the application of the purification units in the electrochemical oxidation of organic pollutants under different conditions.

- The cost of the electricity consumed by the electromembrane reactor during the electrooxidation process.

The main advantage of the system is that, it is operated as a flow-through system and it is not limited to a certain volume of the water to be purified. The flat sheet-type electromembrane reactor can be assembled in a form of stacks of membranes or several reactors can be operated in series or in parallel.

The technology shows good potential for industrial application as a low energy intensive process. It can be operated under different conditions, depending on the feed water and the application. Apart from being used as a purification unit, it can also be used for selective electrosynthesis of other organic compounds by simple controlling the operating conditions. The successful development of this process could have significant impact on water treatment for oil refineries; plastic manufactures municipalities and South Africa as a whole, in the treatment of organic pollutants.

Appendix A: THE 4-AMINOANTIPYRINE METHOD FOR THE DETRMINATION OF PHENOL IN WATER.

Abstract

A colorimetric method was used for the measurement of phenol concentration during the experiment. The method is based on the reaction between phenol and 4-aminoantipyrine in the presence of an oxidant and a buffer solution having pH between 6.8 and 7.0.

Introduction

The determination of phenols in river and drinking water is of great importance around the world. Due to the toxicity of priority pollutant phenols (PPP), characterized by a variety of substituents such as chloro-, methyl-, and nitro- groups [1], the World Health Organization suggests different guide levels of concentrations for different phenols. New methods and studies are continuously searched for the determination of phenols in the environment. Due to the high number of various phenols with different toxicity levels, a sensitive, fast and selective analytical method for their detection and quantification must be developed [2].

A large number of analytical methods have been developed for the quantitative analysis of phenols in water. These include spectroscopic or colorimetric techniques [3] and several other methods that are discussed later. The use of 4-aminoantipyrine for determination of phenolic material promises ease of manipulation, speedy results and use of relatively stable reagents [4]. This procedure is applicable over a wide range of phenolic concentrations and has been incorporated into past "Standard Methods" editions. This method determines phenol, ortho- and meta-substituted phenols. Some para-substituted phenols, in which the substitution is a carboxyl, halogen, methoxyl, or sulphonic acid group, can be determined only under proper pH conditions [5]. Those para-substituted phenols where the substitution is an alkyl, aryl, nitro, benzoyl, nitroso, or aldehyde group, cannot be determined by the 4-aminoantipyrine method.

Phenolic compounds condense with 4-aminoantipyrine and, by subsequent alkaline oxidation, produce a colour that follows Beer's law [6]. Colour sensitivity is shown to be a function of ionization of phenolic species and steric hinderance for reaction with the 4-aminoantipyrine molecule. Hence, para-substituted phenols, such as 2,4-dinitrophenol [7], do not react adequately and no information concerning the presence of individual phenols is obtained because this method is base on

the measurement of the total phenol index. This method is also subject to interferences and lacks the specificity and sensitivity required by the recent laws.

Experimental

Due to the interferences and changes in pH that occur during the electrode reactions, it is impossible to measure the disappearance of phenol directly by means of UV/VIS spectroscopy. The absorption of UV light is influenced by the pH of the sample to be analyzed. The 4-aminoantipyrine method was used for the determination of the total phenol index in the samples collected. The method for preparation of samples was done according to the standard methods.

In a 100-ml volumetric flask, a 0,5N solution of ammonium hydroxide was added to 5-ml of each sample to reach pH 10. The pH of the solution was adjusted to 7,9 ± 0,1 with phosphate buffer after which 10-ml of a 4-aminoantipyrine solution (2.0g/100-ml) was added. 1-ml of $K_3Fe(CN)_6$ solution (8.0g/100-ml) was added and the flask filled to the mark with distilled water. It takes 15 minutes for a reproducible colour to develop. After the 15 minutes, the solutions are transferred to cuvettes and the absorbance of the standards and samples is read against the blank on a spectrophotometer at a wavelength of 500-nm.

Results and discussions

Figure A1 depicts the calibration curve of the 4-AA method for samples collected under highly basic conditions.

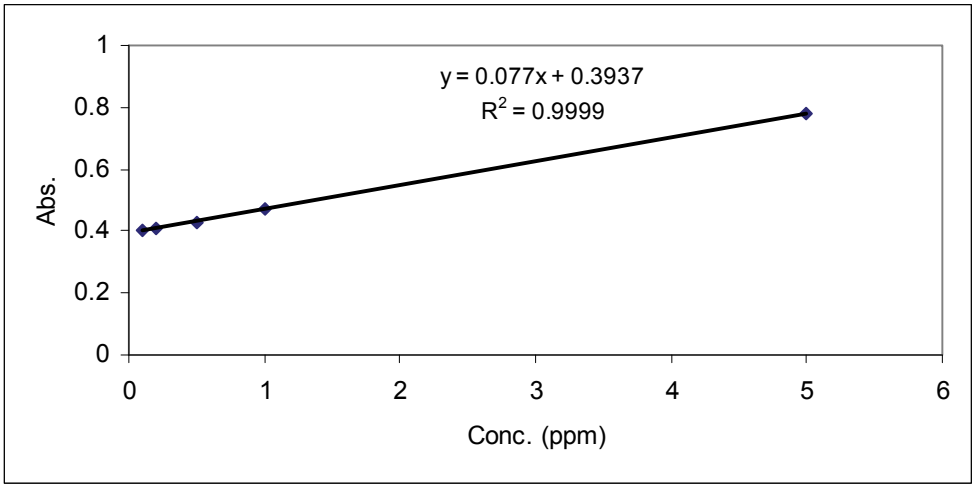

Figure A1: Calibration curve for the 4-AA method for phenol concentration determination.

The calibration curve showed excellent linearity at 500 nm. Problems were experienced when trying to use this method to measure phenol concentrations for extremely acidic (below pH 1) samples. A lot of NH_4OH solution had to be added to the test samples in order to get the required pH of pH 10, which would be further adjusted to 7.9 ± 0.1 with phosphate buffer.

A lot of modifications had to be made to the standard method for it to be suitable for analysis of samples at different pH levels. Another drawback with the method is that it only measures the total phenol index in a sample and doesn't give any information about the concentration of individual phenols or their oxidation products.

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6. R.D. Neufeld and S.B. Pladino, *Communication***, 57**, (1985) 1040-1044.
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Appendix B: DETERMINATION OF PHENOL BY GAS CHROMATOGRAPHY MASS SPECTROMETRIC (GC-MS) METHODS.

Abstract

Gas chromatography, coupled with mass spectrometry (GC-MS) was used for the qualitative determination of phenol and its oxidation intermediates. A liquid-liquid extraction method (LLE) was used to extract the organic phase from the water before injecting into GC-MS.

Introduction

Gas chromatography is one the methods that have always been used for the analysis of phenols [1]. Gas chromatographic methods for determination of phenols in water are sensitive (1ppb) [2] and have been accepted in routine analytical laboratories, although because of polar properties of phenols and low vapour pressure, GC methods require time-consuming derivatization steps [3].

Experimental

The emergence of different oxidation products of phenol was also studied by means of the GC-MS method. 1-ml of the collected sample was added to 3-ml distilled water together with 2 drops of sulfuric acid. The pH of the solution was controlled to be less than 2. Extraction of the organic species was performed with 2-ml diethyl ether. The layers were separated by centrifugation for 20 minutes at 1600g. 500µl of the supernatant was dried over 50-mg anhydrous sodium sulfate. 100-µl was transferred for manual injection into the GC-MS.

Results and discussions

Quantitative analysis of phenol and its aromatic products was difficult when using the GC-MS method for analysis. Liquid-liquid extractions had to be performed before analysis and it was impossible to make sure that all the organic contents had been extracted from the aqueous phase in each and every sample. Figure B1 depicts a calibration curve that was drawn from the peak area results that were obtained from the chromatograms.

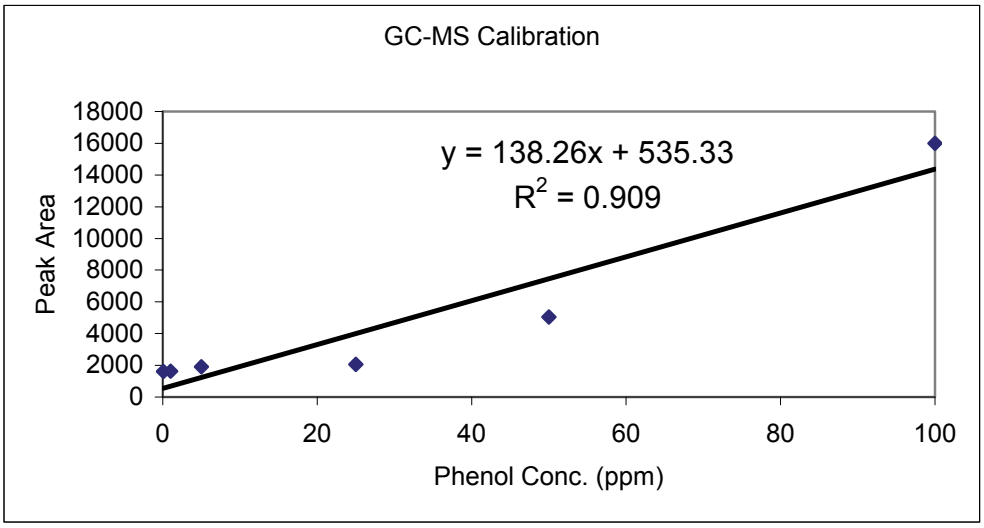

Figure B1: Calibration curve for the GC-MS method

Poor calibration curves were drawn when using the GC-MS method for quantitative analysis of aqueous phenol and its oxidation products.

Attempts to develop a reliable method for the measurement of phenol and its oxidation products could be made. This would be a time-consuming experience, however, because each and every sample would have to go through the LLE method before injecting into the GC.

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APPENDIX C: HIGH PERFORMANCE LIQUID CHROMATOGRAPHY FOR THE ANALYSIS OF PHENOL AND ITS OXIDATION INTERMEDIATES IN WATER.

Abstract

Introduction

Due to the time-consuming derivatization steps required in the GC analysis of aqueous samples, attention has been recently paid to the development of the HPLC methods. HPLC methods are suitable for determination of mono- and polyhydroxy, and their chloro-, nitro- and methyl phenols [1]. HPLC determinations of phenols are usually carried out in a reversed-phase system with C18 columns with UV detection at 254 nm. .

Although high-performance liquid chromatography is now considered to be a mature separation method, there are still a number areas in which problems are encountered [2]. HPLC analysis, as with other chromatographic analysis, still requires proper sample handling and this is the most determining step of errors. For the determination of different kinds or a combination of phenolic samples, the HPLC method becomes complicated due the need to use gradient elution whereby dual pumps are used as well as different kinds of eluents.

Experimental

High performance liquid chromatography (HPLC) analysis was used to follow the loss of phenol and the formation of by-products. During each experiment, samples were collected from the permeate solution, filtered through a 0.45-μm membrane, diluted with the mobile phase and analyzed. The intermediates produced during the anodic oxidation of phenol belong to a number of different compounds with varying solubilities, polarities and dissociation constants. Three columns were used for analysis of these intermediates: an Envirosep PP C_{18} column with water-methanol (50:50, v/v) isocratic elution and a flow rate of 1-ml.min^{-1} for the phenols, a Higgins Halsil C_{18} 5 micron column with water-methanol (50:50, v/v) isocratic elution and a flow rate of 0.8-ml.min^{-1} for quinines, and a Transgenomic ICSep ICE-ORH-801 packed bed transgenomic cation-exchange resin column with a mobile phase of 0.05N sulfuric acid and a flow rate of 0.5-ml.min^{-1}, for organic acids. The aromatics were detected at a wavelength of 254-nm and the organic acids at 210-nm.

Results and discussions

An HPLC method for the qualitative and quantitative analysis of phenols, its aromatic intermediates and aliphatic acids was developed. Figure C1 shows the reliability of the method in terms of precise measurements of phenol concentration and its intermediates.

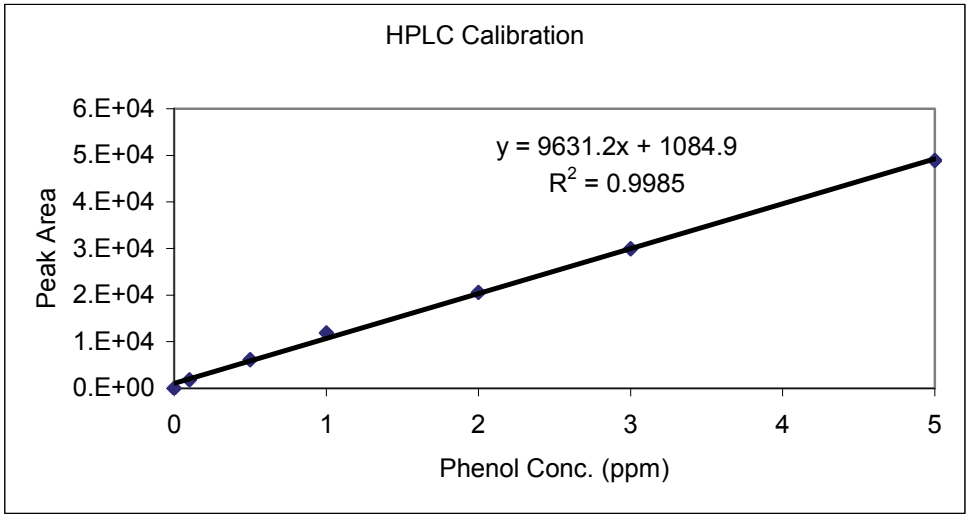

Figure C1: Phenol calibration curve by HPLC analysis.

Phenol and its aromatic intermediates (p-benzoquinone, hydroquinone and catechol) could be analyzed on the same chromatogram, as shown in figure C 2.

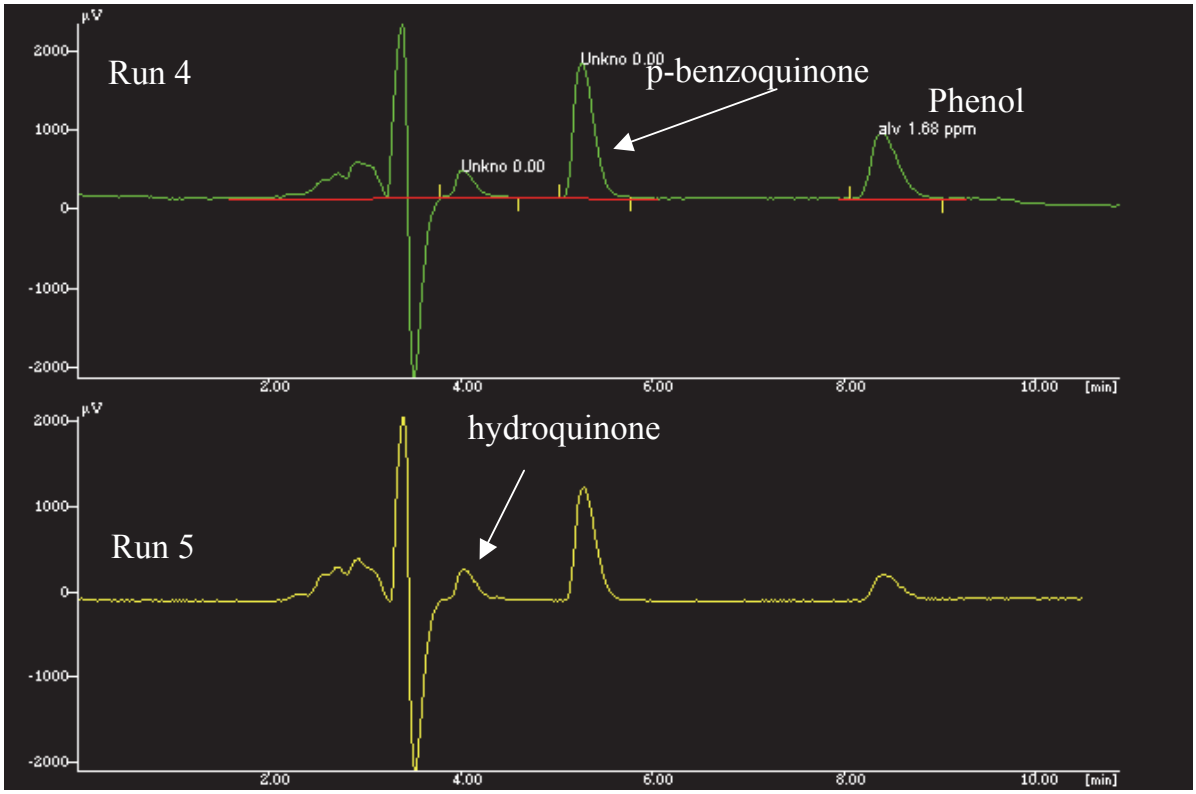

Figure C2: Chromatograms of phenol and its aromatic intermediates at different runs.

The peaks of phenol and the other intermediates are well separated and no peak tailing was experienced. HPLC analysis was fast and reliable due to the possibility of using one column for all the aromatic compounds and another column for all the aliphatic acids.

References

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APPENDIX D: CHEMICAL OXYGEN DEMAND IN WATER.

Abstract

After the phenol concentration measurements were carried out by HPLC, further analysis to estimate the organic content of the water were done by means of COD measurements. The COD measurements gave us an estimate of the amount of oxygen that will be needed to stabilize the organic content of the effluent. The COD test were carried out by using the dichromate method.

Introduction

Chemical oxidation demand (COD) measures the ability of hot chromic acid solution to oxidize matter. This analyzes both biodegradable and non-biodegradable (refractory) organic matter, expressed in mg/L of O_2. An advantage of the COD test over the biological oxygen demand (BOD) test is that a test time of 2 to 3 hours is required to complete the COD test while BOD tests require 5 days for completion.

Two methods are known, both based on the chemical oxidation of the matter present: one is the oxidation by means of permanganate (sometimes known as consumed oxygen) and oxidation by the dichromate ion. Oxidation by means of permanganate was the standard method until 1965 when it was replaced by the dichromate method [1]. The COD analysis, by the dichromate method, is more commonly used to control and continuously monitor wastewater treatment systems.

The results of the COD test are usually higher than those of the corresponding BOD tests. The reasons why this is the case are:

- Many organic compounds which are dichromate oxidizable are not biochemically oxidizable;
- Certain inorganic substances, such as sulfides, sulfites, thiosulfate, nitrites and ferrous ion are dichromate oxidizable, creating an inorganic COD.

The method of COD, which uses dichromate as oxidant is carried out by heating under total reflux a wastewater sample of known volume in an excess of potassium dichromate ($K_2Cr_2O_7$) in presence of sulphuric Acid (H_2SO_4) for a fixed period (usually two hours) in presence of silver sulphate (Ag_2SO_4) as catalyst. The organic matter present is oxidized and, as a result, the dichromate ion (orange colour) is consumed and replaced by the chromic ion (green colour):

$$Cr_2O_7^{2-} + 14H^+ + 6\ e^- \longrightarrow 2Cr^{3+} + 7H_2O$$

Experimental

(i) Equipment and reagents

- Oven at 150 ± 5 ºC
- Digestion tubes: Corning #99449 or equivalent; 25 x 200mm disposable. borosilicate glass tubes with Teflon liner caps.
- Blender or homogenizer.
- Tube rack.
- Sulfuric acid (95% H_2SO_4), for chloride pretreatment.
- $K_2Cr_2O_7$
- Distilled water. Precautions should be taken to insure that water used in the test be low in organic matter, preferably containing less than 0.3 ppm organic carbon.
- Phenol ACS primary standard grade

(ii) Preparation of reagents

- Digestion solution: Add 10.2 $K_2Cr_2O_7$, 167 ml of concentrated H_2SO_4, and 33.3 g of H_2SO_4 to 500 ml of distilled water. Cool to room temperature and dilute to one liter. Store at or above 20 ºC to avoid precipitation.
- Catalyst solution: Dissolve 22 g of Ag_2SO_4 in a 9 lb bottle of concentrated H_2SO_4.

For the titration method:

- Ferrous ammonium sulfate (FAS): $FeSO_4(NH_4)_2SO_4$ $6H_2O$ reagent grade. To prepare a stock concentrate solution with normality of about 0.10, weigh 39.0 g FAS and dissolve in deionized water, filling a 1000 ml volumetric flask 3/4 full. Then add 20 ml concentrated H_2SO_4 and fill to mark with water. Addition of H_2SO_4 causes the iron to remain in the ferrous state.

NOTE: If H_2SO_4 is not added, the solution will turn light brown indicating the presence of the ferric ion. In this case the solution will need to be prepared again.

- Dilute (as needed) this solution 1:1 with deionized water to obtain a 0.05 N titrant solution. This FAS solution is not stable and should be prepared weekly if usage rate is low.
- If Low Range vials are being analyzed or if greater precision is desired for Standard Range vials, a 0.025 N FAS titrant can be prepared by one of the following methods: (1) dilute the resulting solution in Section 6.7.1 (0.05 N FAS) with deionized water 1:1 or (2) dissolve 7.5 g FAS to 1000 ml with 20 ml $H_2 SO_4$ and deionized water to the mark.
- Ferroin Indicator Solution: This solution can be obtained already prepared as "Ferroin Indicator Solution." It can also be prepared by dissolving 1.485 g 1, 10-phenanthroline monohydrate and 0.695 g ferrous sulfate heptahydrate ($FeSO_4 7H_2O$) in a 100 ml volumetric flask with 40 ml deionized water. Dilute to the mark. This solution is stable and can be stored.

(iii) Procedure

- Preheat COD reactor to 150 degrees Celsius

(A). This section describes procedures for pretreatment of high chlorides (>2000 mg/L). If pretreatment is not necessary, skip this section.

NOTE: Samples should be diluted when possible to minimize chloride concentration. This procedure is preferred over the pretreatment method.

- Place 30 ml of the sample into an Erlenmeyer flask.
- Add 10 mg $HgSO_4$ for every milligram of chlorides present in the sample.
- Carefully add 5 ml of 95% H_2SO_4 with stirring to the contents of the flask and mix thoroughly.
- Remove screw cap from vial.
- Using an automatic pipet with disposable tips, rinse the tip with an aliquot of sample and then transfer 7.5 ml of sample into a screw top culture tube. Carefully add 4.5 ml of the digestion solution and 10.5 ml of catalyst solition. Cap tightly and shake the tube to mix the reagents. Blanks and standards should be prepared in the same manner.
- Place the tubes on a tube rack and into an over or that is capable of maintaining 150 ± 5 ºC for 2 hours. The 2-hour oxidation period is standard practice and is sufficient for complete oxidation of most compounds.
- Remove, then mix the contents of the tubes by shaking and cool down to room temperature.

(B) Standardization of FAS titrant

- Pipet 1.00 ml of potassium dichromate standard solution into a 125 ml Erlenmeyer flask, containing a magnetic stir bar.
- Add 20-50 ml distilled water and 2-3 drops of ferroin indicator.
- Add 5 ml of concentrated H_2SO_4 down the side of the flask.
- Place flask on magnetic stirrer directly under the buret valve.
- Start stirrer and rapidly titrate with FAS titrant to the end point (dark orange). (Color changes are typically yellow to green to blue to clear/gray to dark orange.)
- Record the amount of titrant used.

(C) Analyzing for COD

- Remove the screw cap
- Add stir bar and contents of the vial into a clean 125 ml Erlenmeyer flask. Rinse vial once or twice with distilled water into the flask
- Add approximately 40-50 ml distilled water and 2-3 drops of ferroin indicator
- Place flask on stirrer directly under buret valve. Start stirrer and quickly titrate to the end point (dark orange). Color changes are the same as before. (See Section 5.)
- Record titrant amounts for each vial

NOTE: Alternatively, analysis of the digested sample can be carried by UV-vis spectrometry. The peaks for the blanks and sample can be observed at 600 nm.

(D) Calculation for the titration method

- Calculate the mean and standard deviation of the normality of the FAS using the values obtained from the titration of 1.00 ml of $K_2Cr_2O_7$ standard.

$$N(FAS) = (N(K_2\ Cr_2\ O_7))/(FAS\ volume\ (ml))$$

- If a mathematical solution for the COD of samples is required, perform the following calculation:

$$COD\ (mg/L) = (D\ (a-b)N \times 8{,}000) / S$$

where,

D = Dilution factor = 1 if H_2SO_4 is not added for pretreatment = 35/30 = 1.1667 if 5 ml H_2SO_4 was added to a 30 ml sample

a = Milliliters of FAS required for titration of the blank

b = Milliliters of FAS required for titration of the sample

N = Normality of FAS

S = Milliliters of sample used

- As an alternative, a linear regression may be applied to standard data sets and sample COD values derived accordingly.

Results and discussions

The theoretical oxygen demand of a certain concentration of the compound of interest has to be determined first before drawing the calibration curve. This is done by using the following calculation:

For phenol:

$$C_6H_5OH + 7O_2 \longrightarrow 6CO_2 + 3H_2O$$

i.e. 7 moles of O_2 are required to oxidized 1 mole of phenol to CO_2

Therefore, for phenol concentration of 0.1 g/L, the ThOD = 238 mg/L O_2.

Figure D1 and D2 depict the calibration curves for the titration method and the UV-vis method, respectively.

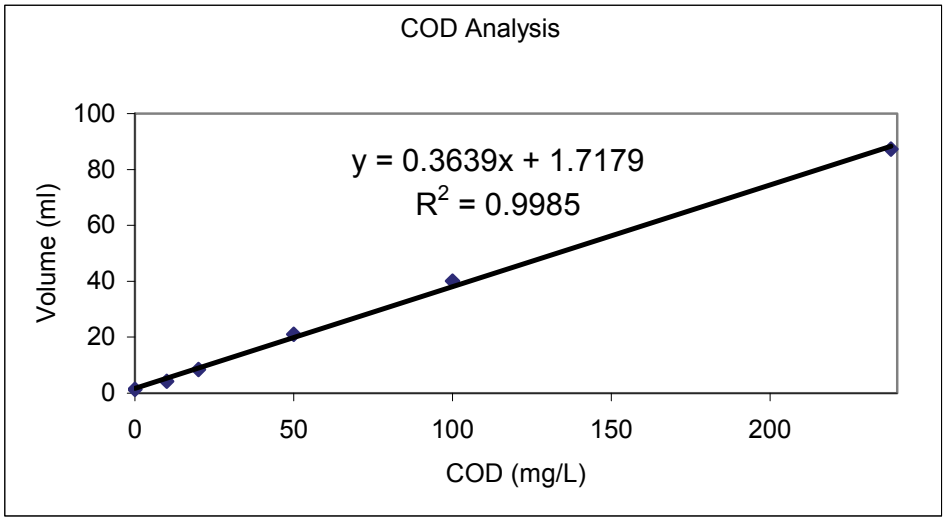

Figure D1: Calibration curve for the titration method COD measurements.

The calibration curves showed excellent linearity especially when using the UV-vis method for COD measurement (figure D2).

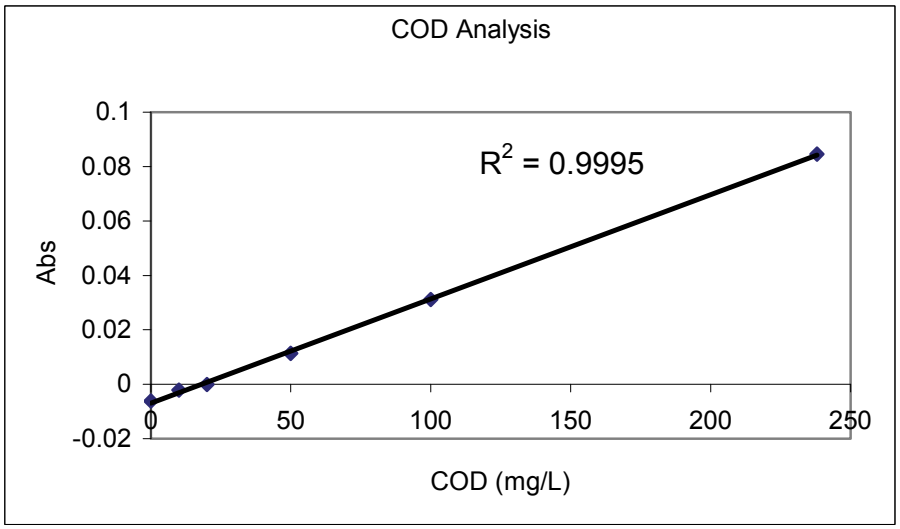

Figure D2: Calibration curve for the UV-vis method COD measurements

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APPENDIX E: EXPERIMENTAL SETUP FOR THE ELECTROCHEMICAL OXIDATION OF PHENOL IN THE ELECTROMEMBRANE REACTOR

(A) Tubular electromembrane reactor

The experimental setup for the tubular membrane reactor was different to the of the flat sheet type electromembranes reactors. The principle of membrane permeation in the tubular system was such that, the feed solution (1 liter) was pumped into the reactor, initially coming into contact with the electrocatalytic layer of the membrane, subsequently permeating through the membrane, and then passing through the cathodic compartment before being colleted (Figure E1).

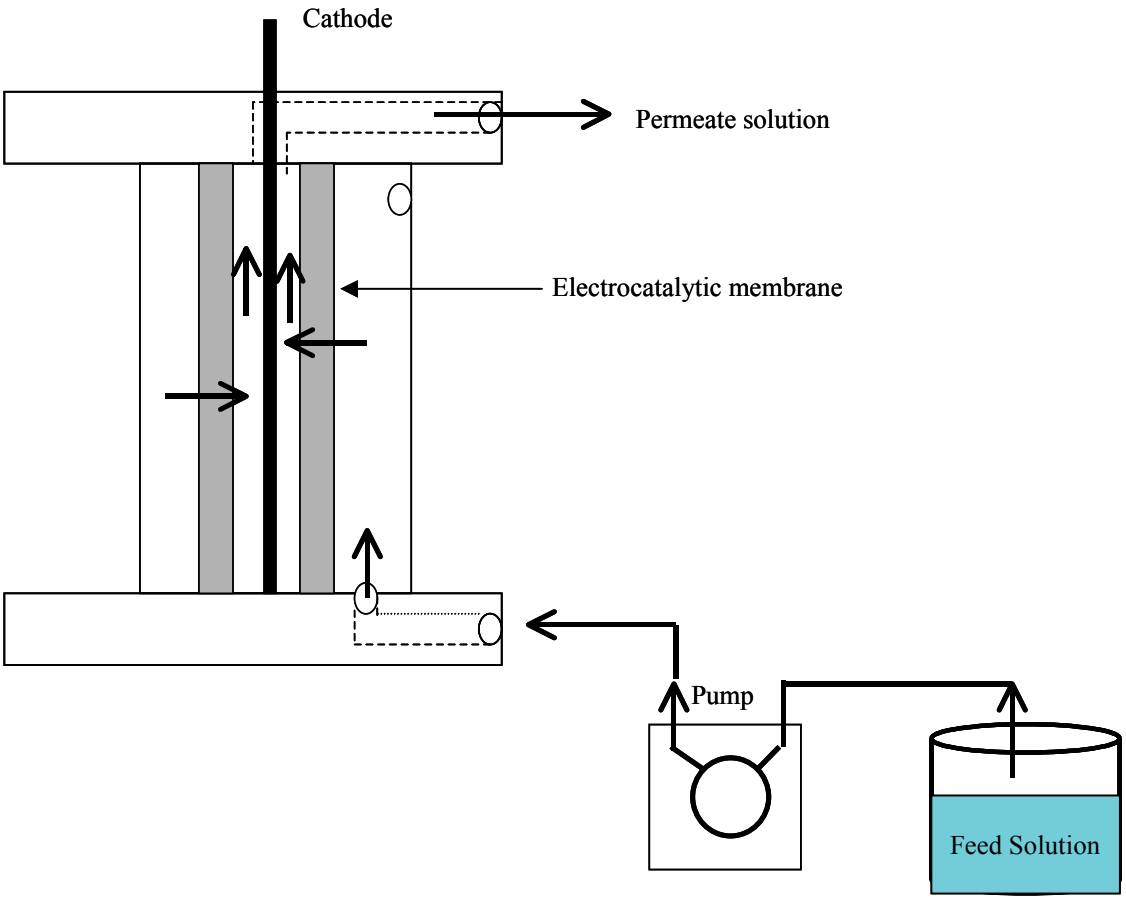

Figure E1: Experimental setup for the electrochemical oxidation of phenol in the tubular electromembrane reactor

The flow rate through the membrane was monitored throughout the experiments and the samples were collected at certain time intervals. In most cases, flux through the membrane remained fairly constant which also made it possible to collect equal volumes of the samples at similar time intervals.

The cathode had a lot of influence on the outcome of the electrooxidation results and it is, therefore, important to choose the suitable cathode material. p-Benzoquinone formed by during the electrochemical oxidation of phenol at the anode was partially reduced to hydroquinone at the cathode.

(B) Flat sheet type electromembrane reactor (laboratory scale)

The principle of permeation in the flat sheet type electromembrane reactors was such that cathode reactions were minimized. The electrocatalyst was coated on one side of the membranes' surface. The feed solution (5 liters) was pumped into the electromembrane reactor, coming into contact with backing layer, which also acted as a flow channel, and then coming into contact with the electrocatalytic layer before being collected as permeate solution (Figure E2).

The flow rate through the membrane was also monitored throughout the experiments. The entire volume (5 liters) was collected and labeled as run 1 and subsequently re-introduced into the electromembrane reactor for further phenol degradation. Each experiment was terminated after complete phenol degradation was achieved or when no further degradation could be achieved.

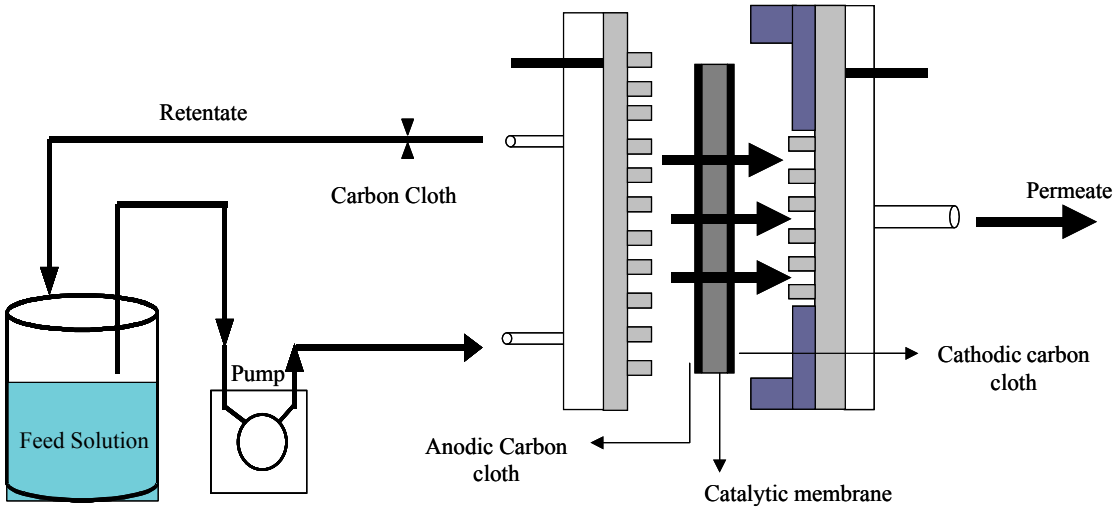

Figure E2: Experimental set-up for the anodic oxidation of phenol in the flat sheet type electromembrane reactor.

APPPENDIX F: pH MEASUREMENTS

Abstract

In this research, pH was one of the most important parameters in the electrochemical oxidation of phenol as the process also depends, highly on pH conditions. With every experiment, the pH of the feed was measured, adjusted to the required value and measured again after the electrooxidation process had been completed.

Introduction

A measure of the degree of the acidity or the alkalinity of a solution as measured on a scale ("pH scale") of 0 to 14. According to the Oxford Dictionary, the pH scale was originally introduced by the Danish biochemist S.P.L. Sorensen in 1909 using the symbol pH. Other symbols such as p_H have been used in the past. The letter p is derived from the German word potenz meaning power or exponent of, in this case, 10. Many chemists have used the pH scale and the p scales for many other quantities that they often take it for granted, without realizing the logic behind their usages. For example, we have used the pK_a, pK_b, pK_w, notations by analogy to the pH notations with out asking a question [1].

Sorensen has defined pH as:

$$pH = - \log [H^+]$$

Experimental

(A) Conditions for pH measurement

pH measurements should always be carried out at room temperature, ideally the buffers and samples should be 3 – 5 ºC apart in temperature difference with each measurement. If there are changes in temperature during the day, it is important to calibrate the electrode with every measurement. Temperature not only affects the voltage produced by the electrode but the electrolyte solution dissociates differently at different temperatures.

Another important procedure in the measurement of pH is the storage and maintenance of the pH electrodes. Different storage solutions are recommended by different manufactures but saturated KCl is the most popular storage solution. A weakly cleaning procedure, in Revono solution, for the electrode must also be adopted.

(B) Calibration

The calibration of most pH electrodes requires buffers of pH 4 and 7. The electrode measures the concentration of H^+ ions in mV. Ideally, a calibration of the two buffers should give signals of 155 mV for the pH 4 buffer and -20 mV for the pH 7 buffer (Figure F1).

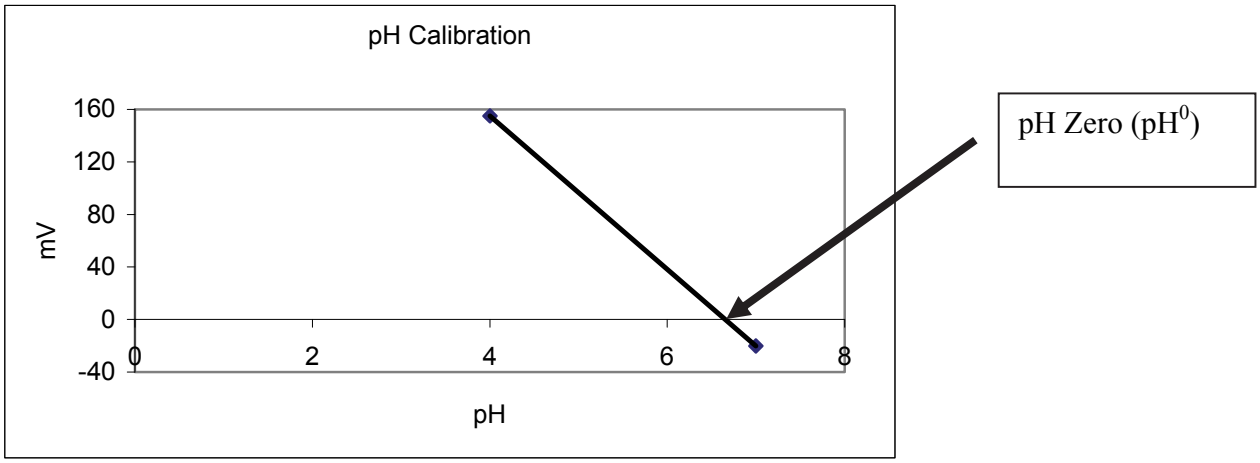

Figure F1: Calibration curve for pH measurements

A theoretical formula can be used to check the status of the pH electrode. The difference between any successive pH values (e.g. 1 and 2) should be 59 mV. Therefore, for pH 4 and 7, the (theoretical) value is 59 mV x 3 = 177 mV.

For an electrode in good condition,

Real difference/theoretical value x 100 %

should be between 97 – 103 %.

It is also important to record the pH^0 (figure F1) value, where the calibration line intercepts the pH scale (x-axis). A change of 0.11 on the pH scale means that the electrode should be cleaned.

APPENDIX G: ANALYSIS OF THE Sb DOPED SnO_2-BASED ELECTROCATALYST

Abstract

An electrocatalyst based on Sb doped SnO_2 was synthesized by impregnating carbon black with the Sb-doped SnO_2 catalyst prepared by sol-gel techniques. The carbon black-supported catalyst was then sprayed onto the membrane surface in a form of catalytic ink. The carbon black-supported catalyst was analyzed by means of XRD. TEM pictures of the electrocatalyst were also taken in order to study the distribution of the Sb-SnO_2 particles on the carbon black support as well as study the size of these particles.

Results and Discussions

(A) XRD measurements

Figure G1 depicts the results obtained from XRD studies of the blank (carbon black only) and the carbon black-supported Sb-SnO_2 electrocatalyst.

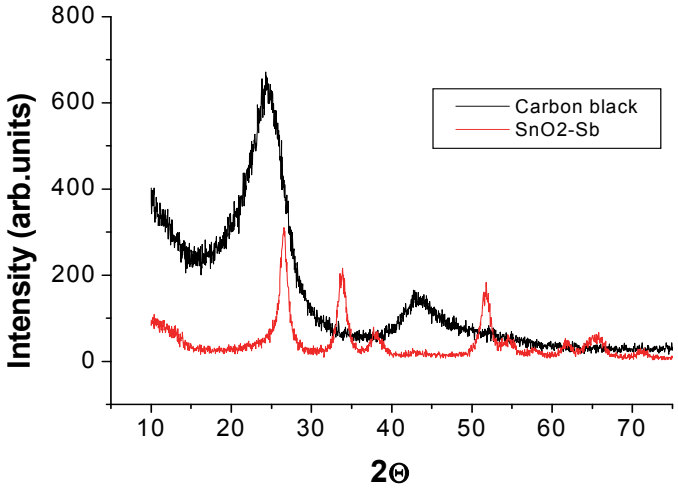

Figure G1: XRD analysis of the carbon black supported Sb-SnO_2 catalyst

The blank (carbon black) does not show any peaks, just the amorphous hump. A search performed on the peaks that appear on the carbon black-supported Sb-SnO_2 matches those of Sb and SnO_2.

TEM pictures (figure G2) also show that the Sb-SnO_2 particles are distributed homogenously on the carbon black support. The size of the carbon black-supported catalyst was approximately 10 nm.

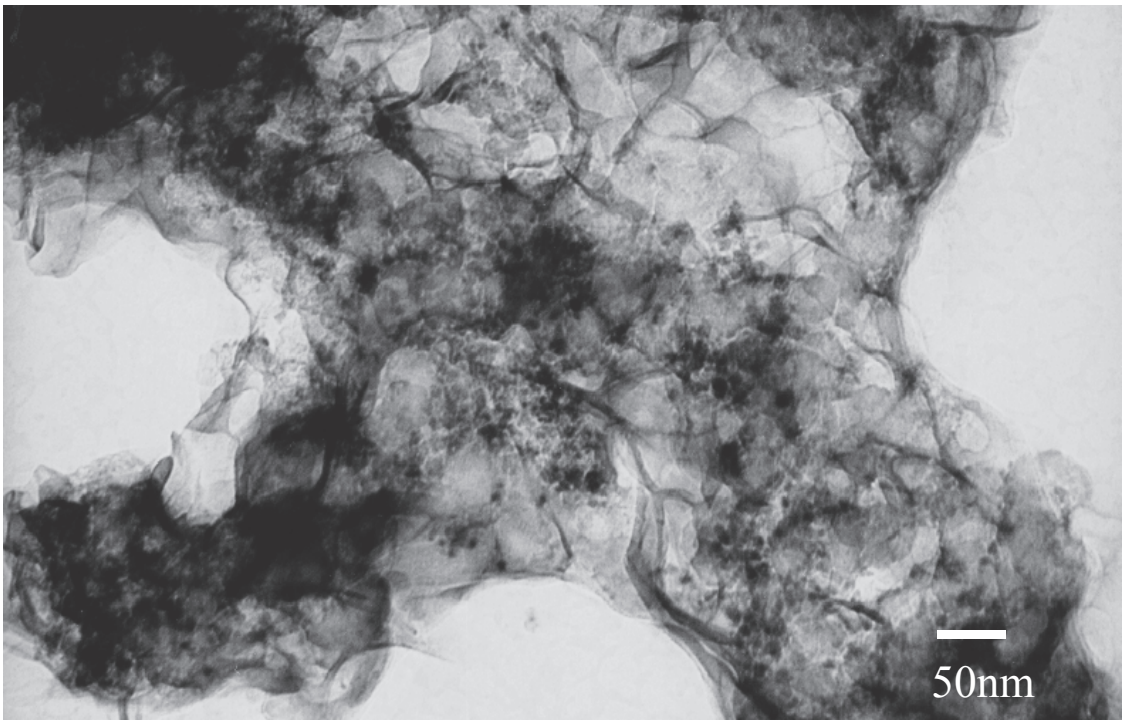

Figure G2: TEM picture of the carbon black-supported Sb-SnO_2 electrocatalyst.

APPENDIX H: EXPERIMENTAL ELECTROCHEMICAL OXIDATION OF PHENOL DATA

The data presented in this report has been accumulated from a lot of experiments that were conducted throughout the study. The charts that are presented in this section give an indication of the manner in which the data was collected during the experiments as well as the key parameters.

All the experiments were labeled in the following manner:

Date:
Membrane type and coating:
Backing material (if any):
Cathode:
Feed solution:
Catalyst loading ($mg.cm^{-2}$):
Feed volume:

The key experimental data that were collected during the experiments were:

Volume of collected samples
Time
Flow rate ($ml.min^{-1}$)
Flux (permeability x membrane area x driving force)
Current (mA)
Energy consumption ($kWh.g^{-1}$)

The concentration of phenol and its intermediates were monitored by HPLC.

Electrochemical Oxidation experiment: 04-Jun-02
Experiment: Alumina
Anode: Carbon coated membrane + Zirconia phosphate
Cathode: Stainless steel
Feed Solution: 100-ppm Phenol in 0.1M Na2SO4
Feed Volume (L) 1
Tubular membrane
Carbon coated membrane + Zirconia phosphate
100-ppm Phenol in 0.1M Na2SO4

Sample	Time (min)	Flow rate ml/min	Flow Rate (L/m2/h)	Current (mA)	Potential (V)	Phenol (mg/L)	% Removed (%)	g removed	kWh/g
P1	3.0	4.29	120.55	17.30	2.50	40.03	59.97	6.00E-02	0.003
P2	6.0	4.43	120.55	16.50	2.50	38.17	61.83	6.18E-02	0.003
P3	9.0	4.29	120.55	16.20	2.50	31.34	68.66	6.87E-02	0.002
P4	12.0	4.29	120.55	15.80	2.50	30.20	69.80	6.98E-02	0.002
P5	15.0	4.29	120.55	15.70	2.50	30.65	69.35	6.93E-02	0.003
P6	18.0	4.29	120.55	19.60	2.65	25.41	74.59	7.46E-02	0.003
P7	21.0	4.29	120.55	19.20	2.65	26.10	73.90	7.39E-02	0.003
P8	24.0	4.29	120.55	19.00	2.65	15.99	84.01	8.40E-02	0.002
P9	27.0	4.29	120.55	18.60	2.65	23.36	76.64	7.66E-02	0.003
P10	30.0	4.29	120.55	18.10	2.65	18.35	81.65	8.17E-02	0.002

Electrochemical Oxidation experiment: **05-Jun-02**
Experiment: **Alumina**
Anode: **Carbon coated membrane + Zirconia phosphate**
Cathode: **Stainless steel**
Feed Solution: **100-ppm Phenol in 0.1M Na2SO4**
Feed Volume (L) **1**
Tubular membrane
Carbon coated membrane + Zirconia phosphate
100-ppm Phenol in 0.1M Na2SO4

Time	Phenol degradation	p-benzoquinone	Hydroquinone	catechol
3	60.00	0.00	0.00	0.97
6	61.83	0.00	0.00	0.00
9	68.66	0.00	0.00	0.00
12	69.80	0.00	0.00	0.00
15	69.35	0.00	0.00	0.00
18	74.59	0.00	0.00	0.00
21	73.90	0.00	0.00	0.00
24	84.00	0.00	0.00	0.00
27	76.64	7.97	0.00	0.00
30	81.65	10.12	5.91	0.00

Electrochemical Oxidation experiment: 10-Jun-02
Experiment: Alumina
Anode: Carbon coated membrane
Cathode: Stainless steel
Feed Solution: 100-ppm Phenol in 0.1M H2SO4
Feed Volume (L) 1

Sample	Time (min)	Flow rate ml/min	Flow Rate (L/m2/h)	Current (mA)	Potential (V)	Phenol (mg/L)	% Removed	g removed	kWh/g
P1	3	7.89	242.06	82.80	2.50	0.00	100.00	1.00E-01	0.0013
P2	6	8.11	238.06	82.70	2.50	0.00	100.00	1.00E-01	0.0013
P3	9	5.45	253.42	82.71	2.50	0.00	100.00	1.00E-01	0.0013
P4	12	6.32	247.00	79.90	2.50	0.00	100.00	1.00E-01	0.0013
P5	15	6.67	237.52	80.66	2.50	0.00	100.00	1.00E-01	0.0013
P6	18	4.62	239.82	79.64	2.50	0.00	100.00	1.00E-01	0.0013
P7	21	5.00	240.64	81.90	2.50	0.00	100.00	1.00E-01	0.0013
P8	24	5.22	246.75	79.95	2.50	0.00	100.00	1.00E-01	0.0013
P9	27	4.72	232.89	77.50	2.50	0.00	100.00	1.00E-01	0.0013
P10	30	4.67	231.33	76.57	2.50	0.00	100.00	1.00E-01	0.0013

Electrochemical Oxidation experiment: **10-Jun-02**
Experiment: **Alumina**
Anode: **Carbon coated membrane**
Cathode: **Stainless steel**
Feed Solution: **100-ppm Phenol in 0.1M H_2SO_4**
Feed Volume (L) **1**

HPLC analysis

Time	% Degraded	p-Benzoquinone	Hydroquinone
3	100.00	4.66	10.10
6	100.00	4.62	11.58
9	100.00	4.61	12.51
12	100.00	4.67	9.97
15	100.00	4.36	9.96
18	100.00	4.37	13.50
21	100.00	4.29	14.79
24	100.00	4.36	14.53
27	100.00	4.71	10.15
30	100.00	4.73	10.00

Electrochemical Oxidation experiment: **12-Jun-02**
Experiment: **Alumina**
Anode: **Carbon coated membrane**
Cathode: **Stainless steel**
Feed Solution: **100-ppm Phenol in 0.1M H2SO4**
Feed Volume (L) **1**

Sample	Time (min)	Flow rate ml/min	Flow Rate (L/m2/h)	Current (mA)	Potential (V)	Phenol (mg/L)	Removed (%)	g removed	kWh/g
P1	3	7.89	222.06	82.80	2.50	12.11	87.89	8.79E-02	0.0013
P2	6	4.17	117.20	82.70	2.50	13.44	86.56	8.66E-02	0.0013
P3	9	4.14	116.39	82.71	2.50	12.69	87.31	8.73E-02	0.0013
P4	12	4.29	120.55	79.90	2.50	14.2	85.8	8.58E-02	0.0013
P5	15	3.87	108.88	80.66	2.50	9.99	90.01	9.00E-02	0.0013
P6	18	4.00	112.51	79.64	2.50	10.08	89.92	8.99E-02	0.0013
P7	21	3.95	111.03	81.90	2.50	12.66	87.34	8.73E-02	0.0013
P8	24	3.99	112.14	79.95	2.50	15.2	84.8	8.48E-02	0.0013
P9	27	4.07	114.42	77.50	2.50	14.81	85.19	8.52E-02	0.0013
P10	30	4.00	112.51	76.57	2.50	16.42	83.58	8.36E-02	0.0013

Electrochemical Oxidation experiment: **12-Jun-02**
Experiment: **Alumina**
Anode: **Carbon coated membrane**
Cathode: **Stainless steel**
Feed Solution: **100-ppm Phenol in 0.1M H2SO4**
Feed Volume (L) **1**

HPLC analysis

Time	% Degraded	p-Benzoquinone	Hydroquinone
3	87.89	0.29	0
6	86.56	0.19	0.11
9	87.31	0.16	0.09
12	85.8	0.36	0.102
15	90.01	0.41	0.18
18	89.92	0.19	0.071
21	87.34	0.21	0.089
24	84.8	0.36	0.12
27	85.19	0.38	0.083
30	83.58	0.305	0.092

Electrochemical Oxidation experiment: **05-Aug-02**
Experiment: **Alumina**
Anode: **Gold Coated Membrane**
Cathode: **Stainless steel**
Feed Solution: **100-ppm Phenol in 0.1M Na2SO4**
Feed Volume (L) **1**
Tubular membrane

Sample #	Time (min)	Flow rate ml/min	Flow Rate (L/m2/h)	Current (mA)	Potential (V)	Phenol (mg/L)	% Removed (%)	g removed	kWh/g
P1	3	8.57	241.09	52.70	2.00	78.31	21.69	2.17E-02	1.47E-06
P2	6	8.57	241.09	52.50	2.00	77.61	22.39	2.24E-02	1.47E-06
P3	9	8.57	241.09	53.40	2.00	82.67	17.33	1.73E-02	1.41E-06
P4	12	8.57	241.09	53.50	2.00	80.28	19.72	1.97E-02	1.45E-06
P5	15	8.57	241.09	54.20	2.00	83.65	16.35	1.64E-02	1.39E-06
P6	18	8.57	241.09	53.50	2.00	79.02	20.98	2.10E-02	1.46E-06
P7	21	8.57	241.09	53.00	2.00	81.12	18.88	1.89E-02	1.41E-06
P8	24	8.57	241.09	52.50	2.00	80.98	19.02	1.90E-02	1.41E-06
P9	27	8.57	241.09	53.10	2.00	82.38	17.62	1.76E-02	1.4E-06
P10	30	8.57	241.09	51.80	2.00	79.58	20.42	2.04E-02	1.42E-06
P11	33	8.57	241.09	52.20	2.00	78.88	21.12	2.11E-02	1.44E-06
P12	36	8.57	241.09	51.40	2.00	87.16	12.84	1.28E-02	1.28E-06
P13	39	8.57	241.09	51.60	2.00	89.68	10.32	1.03E-02	1.25E-06
P14	42	8.57	241.09	50.40	2.00	82.1	17.90	1.79E-02	1.34E-06

Electrochemical Oxidation experiment:				**14-Jan-03**						
Experiment:				**Membrane: LFH (40%glass) blank**						
Anode:				**carbon cloth 6100-200**						
Cathode:				**carbon cloth 6100-200**						
Feed Solution:				**100 ppm Phenol in 0.01M H2SO4**						
Catalyst Loading:				**0**						
Feed Volume (L)				**5**						
Run	Volume (L)	Time (min)	Flow rate ml/min	Flow Rate (L/m2/h)	Current (mA)	Potential (V)	Phenol (mg/L)	Removed %	g removed	kWh/g
1	5.00	800	6.25	298.42	25.80	2.5	92.8	7.2	7.20E-03	0.60
2	4.50	720	6.25	298.42	18.50	2.5	84.2	15.8	1.58E-02	0.29
3	4.00	640	6.25	298.42	16.90	2.5	76.8	23.2	2.32E-02	0.23
4	3.50	560	6.25	298.42	18.00	2.5	54.2	45.8	4.58E-02	0.05
5	3.00	480	6.25	298.42	20.40	2.5	52.2	47.8	4.78E-02	0.34

Electrochemical Oxidation experiment:				**16-Jan-03**						
Experiment:				**Membrane: LFH (40%glass) with carbon black SnO2**						
Anode:				**carbon cloth 6100-200**						
Cathode:				**carbon cloth 6100-200**						
Feed Solution:				**100 ppm Phenol in 0.01M H2SO4**						
Catalyst Loading (mg/cm2):				**2.11**						
Feed Volume (L)				**5**						
Run	Volume	Time (min)	Flow rate ml/min	Flow Rate (L/m2/h)	Current (mA)	Potential (V)	Phenol (mg/L)	Removed (%)	g removed	kWh/g
1	5.00	800	6.25	298.42	49.9	2.5	49.2	50.8	5.08E-02	0.20
2	4.50	806	5.58	266.49	40	2.5	31	69	6.90E-02	0.33
3	4.00	666	6.00	286.48	38	2.5	13.4	86.6	8.66E-02	0.22
4	3.50	590	5.93	283.08	38	2.5	6.6	93.4	9.34E-02	0.39
5	3.00	594	5.05	241.14	45	2.5	3.4	96.6	9.66E-02	0.58

Electrochemical Oxidation experiment:	**14-Jan-03**
Experiment:	**Membrane: LFH (40%glass) with carbon black only**
Anode:	**carbon cloth 6100-200**
Cathode:	**carbon cloth 6100-200**
Feed Solution:	**100 ppm Phenol in 0.01M H2SO4**
Catalyst Loading (mg/cm2):	**2.11**
Feed Volume (L)	**5**

Run	Volume	Time (min)	Flow rate ml/min	Flow Rate (L/m2/h)	Current (mA)	Potential (V)	Phenol (mg/L)	Removed (%)	g removed	kWh/g
1	0.3	48.00	6.25	298.42	49.00	2.50	55.80	44.20	4.42E-02	0.22
2	0.2	32.00	6.25	298.42	45.20	2.50	35.00	65.00	6.50E-02	0.29
3	0.175	24.00	7.29	348.15	35.20	2.50	26.40	73.60	7.36E-02	0.41
4	0.1	16.00	6.25	298.42	41.00	2.50	15.00	85.00	8.50E-02	0.24
5	0.05	8.00	6.25	298.42	41.10	2.50	13.00	87.00	8.70E-02	0.69

Electrochemical Oxidation experiment:	**29-Jan-03**
Experiment:	**Membrane: LFH (40%glass) with CB-SnO2**
Anode:	**Anode: carbon cloth 6100-200**
Cathode:	**Cathode: carbon cloth 6100-200**
Feed Solution:	**100 ppm Phenol in 0.1M Na2SO4**
Catalyst Loading (mg/cm2):	**2.07**
Feed Volume (L)	**5**

Run	Volume	Time (min)	Flow rate ml/min	Flow Rate (L/m2/h)	Current (mA)	Potential (V)	Phenol (mg/L)	Removed (%)	g removed	kWh/g
1	5.00	800	6.25	298.42	27.40	2.5	82.6	17.4	1.74E-02	0.52
2	4.50	720	6.25	298.42	23.00	2.5	60.6	39.4	3.94E-02	0.31
3	4.00	640	6.25	298.42	23.10	2.5	57	43	4.30E-02	1.71
4	3.50	560	6.25	298.42	19.50	2.5	39	61	6.10E-02	0.25
5	3.00	480	6.25	298.42	17.10	2.5	29.6	70.4	7.04E-02	0.36
6	2.50	400	6.25	298.42	15.90	2.5	19.2	80.8	8.08E-02	0.32
7	2.00	320	6.25	298.42	15.10	2.5	12.6	87.4	8.74E-02	0.30
8	1.50	240	6.25	298.42	15.00	2.5	8.6	91.4	9.14E-02	0.29
9	1.00	160	6.25	298.42	14.70	2.5	6.2	93.8	9.38E-02	0.15
10	0.50	80	6.25	298.42	14.60	2.5	4.8	95.2	9.52E-02	0.14

Electrochemical Oxidation experiment: **29-Jan-03**

Experiment: **Membrane: LFH (40%glass) with CB-SnO2**

Anode: **Anode: carbon cloth 6100-200**

Cathode: **Cathode: carbon cloth 6100-200**

Feed Solution: **100 ppm Phenol in 0.1M Na2SO4**

Catalyst Loading (mg/cm2): **2.07**

Feed Volume (L) **5**

Slope 3.85E-04

Intercept -7.18E-03

COD ANALYSIS

Run	Absorbance	COD (mg/L)	COD Removed
1	0.0706	202.17	35.83
2	0.0641	185.28	52.72
3	0.0587	171.24	66.76
4	0.0553	162.41	75.59
5	0.053	156.43	81.57
6	0.0498	148.11	89.89
7	0.0486	144.99	93.01
8	0.0471	141.09	96.91
9	0.0439	132.78	105.22
10	0.0418	127.32	110.68

HPLC ANALYSIS

Sample	pBenzouinone	Catechol	Hydroquinone	Oxalic acid
Run1	5.4	0.0	5.8	0.0
Run2	8.4	0.0	10.2	0.0
Run3	14.0	0.0	22.4	0.0
Run4	13.4	0.0	22.8	0.0
Run5	14.2	0.0	33.6	0.0
Run6	13.8	0.0	28.4	0.0
Run7	12.2	0.0	36.2	0.0
Run8	13.8	0.0	31.2	0.0
Run9	12.8	0.0	32.4	0.0
Run10	13.8	0.0	39.4	0.0

Electrochemical Oxidation experiment:	**04-Feb-03**
Experiment:	**Membrane: LFH (40%glass) with CB-SnO2**
Anode:	**Anode: carbon cloth 6100-200**
Cathode:	**Cathode: carbon cloth 6100-200**
Feed Solution:	**100 ppm Phenol in 0.1M NaOH**
Catalyst Loading (mg/cm2):	**2.01**
Feed Volume (L)	**5**

Run	Volume	Time (min)	Flow rate ml/min	Flow Rate (L/m2/h)	Current (mA)	Potential (V)	Phenol (mg/L)	Removed (%)	g removed	kWh/g
1	5.00	800	6.25	298.42	79.1	2.5	89.01	11	1.10E-02	2.40
2	4.50	720	6.25	298.42	65.5	2.5	81.98	18	1.80E-02	2.81
3	4.00	640	6.25	298.42	121.3	2.5	75.12	25	2.50E-02	4.62
4	3.50	560	6.25	298.42	125.4	2.5	60.23	39.8	3.98E-02	1.98
5	3.00	480	6.25	298.42	131.9	2.5	56.43	43.6	4.36E-02	6.94
6	2.50	400	6.25	298.42	138.3	2.5	35.00	65	6.50E-02	1.87
7	2.00	320	6.25	298.42	140	2.5	23.95	76	7.60E-02	1.82
8	1.50	240	6.25	298.42	139.1	2.5	20.10	80	8.00E-02	1.72
9	1.00	160	6.25	298.42	138.3	2.5	4.30	95.7	9.57E-02	1.43
10	0.50	80	6.25	298.42	140.1	2.5	0.00	100	1.00E-01	1.38

Experiment:				**Bench-scale membrane: LFH (40%glass) with CB-SnO2**						
Anode:				**Anode: carbon cloth 6100-200**						
Cathode:				**Cathode: carbon cloth 6100-200**						
Feed Solution:				**100 ppm Phenol in 0.01M (1.0g/l) H2SO4 pH 0.04**						
Catalyst Loading (mg/cm2):				**0.97**						
Feed Volume (L)				**5**						
Run	Volume	Time (min)	Flow rate ml/min	Flow Rate (L/m2/h)	Current (mA)	Potential (V)	Phenol (mg/L)	Removed (%)	g removed	kWh/g
1	5.00	59.90	83.47	165.63	187.60	2.50	50.00	50.00	5.00E-02	0.18
2	4.75	53.85	88.21	166.36	144.00	2.50	38.40	61.60	6.16E-02	0.56
3	4.50	51.35	87.63	165.28	132.00	2.50	25.00	75.00	7.50E-02	0.42
4	4.25	49.00	86.73	163.53	132.00	2.50	16.60	83.40	8.34E-02	0.64
5	4.00	45.50	87.91	165.75	125.70	2.50	11.60	88.40	8.84E-02	0.95
6	3.75	42.60	88.03	166.03	125.00	2.50	7.00	93.00	9.30E-02	0.96
7	3.50	40.15	87.17	164.29	119.50	2.50	3.20	96.80	9.68E-02	1.05
8	3.25	37.15	87.48	164.86	115.00	2.50	2.00	98.00	9.80E-02	2.97
9	3.00	33.60	89.29	168.42	113.00	2.50	0.00	100.00	1.00E-01	1.58
10	2.75	30.50	90.16	169.99	108.40	2.50	0.00	100.00	1.00E-01	N/A
11	2.50	26.75	93.46	177.31	104.90	2.50	0.00	100.00	1.00E-01	N/A
12	2.25	24.35	92.40	174.33	103.10	2.50	0.00	100.00	1.00E-01	N/A
13	2.00	21.25	94.12	177.45	100.00	2.50	0.00	100.00	1.00E-01	N/A
14	1.75	19.00	92.11	173.65	99.20	2.50	0.00	100.00	1.00E-01	N/A

Experiment:	**Bench-scale membrane: LFH (40%glass) with CB-SnO2**
Anode:	**Anode: carbon cloth 6100-200**
Cathode:	**Cathode: carbon cloth 6100-200**
Feed Solution:	**100 ppm Phenol in 0.01M (1.0g/l) H2SO4 pH 0.04**
Catalyst Loading (mg/cm2):	**0.97**
Feed Volume (L)	**5**
Slope 0.00039435	
Intercept 0.0508103	

Run	Absorbance	COD (mg/L)	COD Removed
		(mg/L)	(%)
1	0.1169	167.59	29.58
2	0.1011	127.53	46.42
3	0.0911	102.17	57.07
4	0.0869	91.52	61.55
5	0.0849	86.45	63.68
6	0.0841	84.42	64.53
7	0.0839	83.91	64.74
8	0.0858	88.73	62.72
9	0.0844	85.18	64.21
10	0.0858	88.73	62.72
11	0.0862	89.74	62.29
12	0.087	91.77	61.44
13	0.0876	93.29	60.80
14	0.0887	96.08	59.63

HPLC ANALYSIS

Sample	pBenzouinone	Catechol	Hydroquinone	Oxalic acid
Run1	5.00	0.00	0.00	0.00
Run2	7.40	0.00	0.00	0.00
Run3	11.60	0.00	0.00	0.00
Run4	16.20	0.00	0.00	0.00
Run5	22.20	0.00	0.00	0.00
Run6	25.80	0.00	0.00	0.00
Run7	19.00	0.00	0.00	0.00
Run8	23.60	0.00	0.00	0.00
Run9	22.20	0.00	0.00	0.00
Run10	18.00	0.00	0.00	0.00
Run 11	21.20	0.00	0.00	0.00
Run 12	20.80	0.00	0.00	0.00
Run 13	20.00	0.00	0.00	0.00
Run 14	20.00	0.00	0.00	0.00

Experiment:					**Bench-scale membrane: LFH (40%glass) with CB-SnO2**					
Anode:					**Anode: carbon cloth 6100-200**					
Cathode:					**Cathode: carbon cloth 6100-200**					
Feed Solution:					**100 ppm Phenol in 0.1M NaCl**					
Catalyst Loading (mg/cm2):					**1.098**					
Feed Volume (L)					**5**					
Run	Volume	Time (min)	Flow rate ml/min	Flow Rate (L/m2/h)	Current (mA)	Potential (V)	Phenol (mg/L)	Removed (%)	g removed	kWh/g
1	5.00	59.17	84.51	159.33	112.14	2.5	79.99	20	2.00E-02	0.28
2	4.90	62.50	80.00	150.83	93.53	2.5	64.61	35.4	3.54E-02	0.32
3	4.50	56.05	80.28	151.36	69.5	2.5	62.44	37.6	3.76E-02	1.56
4	4.00	50.22	79.65	150.16	58.1	2.5	42.22	57.8	5.78E-02	0.14
5	3.75	36.44	83.20	156.87	57.62	2.5	29.80	70.2	7.02E-02	0.20
6	3.00	9.72	82.33	155.23	62.51	2.5	21.38	78.6	7.86E-02	0.25
7	2.50	30.44	82.12	154.82	54.59	2.5	20.20	79.8	7.98E-02	0.25
8	2.00	24.67	81.08	152.87	50.87	2.5	16.81	83.2	8.32E-02	0.24
9	1.65	20.05	82.28	155.13	50.68	2.5	13.24	86.8	8.68E-02	0.11
10	0.60	21.11	75.79	142.89	49.9	2.5	12.60	87.4	8.74E-02	0.10

Experiment:	**Bench-scale membrane: LFH (40%glass) with CB-SnO2**
Anode:	**Anode: carbon cloth 6100-200**
Cathode:	**Cathode: carbon cloth 6100-200**
Feed Solution:	**100 ppm Phenol in 0.1M NaCl**
Catalyst Loading (mg/cm2):	**1.098**
Feed Volume (L)	**5**

Slope	0.000415373
Intercept	0.076734795

Sample	Absorbance	COD (mg/L)	COD Removed (%)
Run1	0.1507	178.07	25.18
Run2	0.1317	132.33	44.40
Run3	0.1192	102.23	57.04
Run4	0.111	82.49	65.34
Run5	0.1052	68.53	71.21
Run6	0.1008	57.94	75.66
Run7	0.1028	62.75	73.63
Run8	0.0959	46.14	80.61
Run9	0.093	39.16	83.55
Run10	0.0912	34.82	85.37

HPLC ANALYSIS

Run	pBenzoquinone (mg/L)	Catechol (mg/L)	Hydroquinone (mg/L)	Oxalic acid (mg/L)
1	0	0	0	0
2	0	0	0	0
3	0	0	0	0
4	0	0	0	0
5	0	0	0	0
6	0	0	0	0
7	0	0	0	0
8	3	0	0	0
9	0	0	0	0
10	0.6	0	0	0

Electrochemical Oxidation experiment:	**27-Mar-03**
Experiment:	**Bench-scale membrane: LFH (40%glass) with CB-SnO2**
Anode:	**Anode: carbon cloth 6100-200**
Cathode:	**Cathode: carbon cloth 6100-200**
Feed Solution:	**100 ppm SAPREF effluent in Acid mine drainage**
Catalyst Loading (mg/cm2):	**0.95**
Feed Volume (L)	**5**

Run	Volume	Time (min)	Flow rate ml/min	Flow Rate (L/m2/h)	Current (mA)	Potential (V)	Phenol (mg/L)	Removed (%)	g removed	kWh/g
1	5	63.33	78.95	0.01	125.20	2.50	78.40	21.60	2.16E-02	0.18
2	4.6	59.96	76.72	0.01	124.70	2.50	70.40	29.60	2.96E-02	0.47
3	4.2	56.70	74.07	0.01	112.30	2.50	44.39	55.61	5.56E-02	0.21
4	3.75	50.58	74.14	0.01	98.90	2.50	39.99	60.01	6.00E-02	0.17
5	3.33	43.04	77.37	0.01	93.90	2.50	34.20	65.80	6.58E-02	0.30
6	2.92	37.54	77.78	0.01	88.80	2.50	24.58	75.42	7.54E-02	0.17
7	2.5	32.92	75.94	0.01	74.70	2.50	15.61	84.39	8.44E-02	0.14
8	2.1	27.21	77.18	0.01	73.80	2.50	8.40	91.60	9.16E-02	0.14
9	1.7	21.25	80.00	0.01	83.30	2.50	0.00	100.00	1.00E-01	0.10
10	1.25	16.42	76.13	0.01	83.70	2.50	0.00	100.00	1.00E-01	N/A

Electrochemical Oxidation experiment:	**27-Mar-03**
Experiment:	**Bench-scale membrane: LFH (40%glass) with CB-SnO2**
Anode:	**Anode: carbon cloth 6100-200**
Cathode:	**Cathode: carbon cloth 6100-200**
Feed Solution:	**100 ppm SAPREF effluent in Acid mine drainage**
Catalyst Loading (mg/cm2):	**0.95**
Feed Volume (L)	**5**
Slope 0.000670275	
Intercept -0.01443497	

COD ANALYSIS

Run	Absorbance	COD (mg/L)	COD Removed (%)
1	0.1	170.73	28.26
2	0.0707	127.02	46.63
3	0.0508	97.33	59.11
4	0.0398	80.91	66.00
5	0.0324	69.87	70.64
6	0.0317	68.83	71.08
7	0.0246	58.24	75.53
8	0.022	54.36	77.16
9	0.0205	52.12	78.10
10	0.0184	48.99	79.42

HPLC ANALYSIS

Run	pBenzouinone	Catechol	Hydroquinone	Oxalic acid
1	0.0	0.0	0.0	0.0
2	0.0	0.0	0.0	0.0
3	0.0	0.0	0.0	0.0
4	3.2	0.0	0.0	0.0
5	4.6	0.0	0.0	0.0
6	7.2	0.0	0.0	0.0
7	8.6	0.0	0.0	0.0
8	9.0	0.0	0.0	0.0
9	10.2	0.0	0.0	0.0
10	12.8	0.0	0.0	0.0

Electrochemical Oxidation experiment:	**17-Mar-03**
Experiment:	**Bench-scale membrane: LFH (40%glass) with CB-SnO2**
Anode:	**Anode: carbon cloth 6100-200**
Cathode:	**Cathode: carbon cloth 6100-200**
Feed Solution:	**100 ppm Phenol in Seawater**
Catalyst Loading (mg/cm2):	**1.11**
Feed Volume (L)	**5**

Run	Volume	Time (min)	Flow rate ml/min	Flow Rate (L/m2/h)	Current (mA)	Potential (V)	Phenol (mg/L)	Removed (%)	g removed	kWh/g
1	5	48.51	103.07	194.48	180.90	2.50	65.80	34.20	3.42E-02	0.13
2	4.6	55.58	82.77	155.54	131.40	2.50	26.40	73.60	7.36E-02	0.09
3	4.6	59.75	76.99	144.69	100.80	2.50	13.60	86.40	8.64E-02	0.24
4	4.2	52.49	80.01	149.63	93.00	2.50	6.60	93.40	9.34E-02	0.35
5	3.75	48.33	77.59	146.28	84.80	2.50	0.00	100.00	1.00E-01	0.31
6	3.33	41.79	79.68	150.33	81.90	2.50	0.00	100.00	1.00E-01	0.11
7	2.92	31.86	91.64	151.12	81.70	2.50	0.00	100.00	1.00E-01	0.11
8	2.5	23.31	107.24	151.50	81.40	2.50	0.00	100.00	1.00E-01	0.11
9	0.25	25.67	9.74	152.87	81.90	2.50	0.00	100.00	1.00E-01	0.10
10	0.2	20.83	9.60	150.83	80.80	2.50	0.00	100.00	1.00E-01	0.07

Electrochemical Oxidation experiment:	**17-Mar-03**
Experiment:	**Bench-scale membrane: LFH (40%glass) with CB-SnO2**
Anode:	**Anode: carbon cloth 6100-200**
Cathode:	**Cathode: carbon cloth 6100-200**
Feed Solution:	**100 ppm Phenol in Seawater**
Catalyst Loading (mg/cm2):	**1.11**
Feed Volume (L)	**5**

Slope	0.000415373
Intercept	0.076734795

Sample	Absorbance	COD (mg/L)	COD Removed (%)
Run1	0.1507	178.07	25.18
Run2	0.1317	132.33	44.40
Run3	0.1192	102.23	57.04
Run4	0.111	82.49	65.34
Run5	0.1052	68.53	71.21
Run6	0.1008	57.94	75.66
Run7	0.1028	62.75	73.63
Run8	0.0959	46.14	80.61
Run9	0.093	39.16	83.55
Run10	0.0912	34.82	85.37

HPLC ANALYSIS

Run	pBenzoquinone (mg/L)	Catechol (mg/L)	Hydroquinone (mg/L)	Oxalic acid (mg/L)
1	0.6	0	0	0
2	1.4	0	0	0
3	1.8	0	0	0
4	2.4	0	0	0
5	2.4	0	0	0
6	2.2	0	0	
7	2.3	0	0	0
8	2.3	0	0	0
9	2.6	0	0	0
10	2.8	0	0	0

Electrochemical Oxidation experiment:	**20-Mar-03**
Experiment:	**Bench-scale membrane: LFH (40%glass) with CB-SnO2**
Anode:	**Anode: carbon cloth 6100-200**
Cathode:	**Cathode: carbon cloth 6100-200**
Feed Solution:	**100 ppm SAPREF effluent in Seawater**
Catalyst Loading (mg/cm2):	**1.21**
Feed Volume (L)	**5**

Run	Volume	Time (min)	Flow rate ml/min	Flow Rate (L/m2/h)	Current (mA)	Potential (V)	% Phenol (mg/L)	Removed (%)	g removed	kWh/g
1	5.0	66.28	75.44	142.22	183.30	2.5	68.39	31.6	3.16E-02	0.21
2	4.6	63.58	72.58	136.84	133.40	2.5	40.17	59.8	5.98E-02	0.16
3	4.2	57.17	73.99	139.50	104.70	2.5	29.00	71	7.10E-02	0.29
4	3.9	52.10	73.89	139.31	104.60	2.5	28.05	72	7.20E-02	2.95
5	3.5	46.39	74.59	140.62	96.60	2.5	26.84	73.2	7.32E-02	2.02
6	3.1	42.36	73.17	137.95	93.90	2.5	25.21	75	7.50E-02	0.56
7	2.7	35.61	75.81	142.93	99.30	2.5	17.00	83	8.30E-02	0.60
8	2.3	30.93	74.69	140.82	95.90	2.5	15.81	84.2	8.42E-02	0.64
9	2.3	26.31	73.17	137.95	99.80	2.5	15.20	84.8	8.48E-02	0.68
10	1.5	24.09	63.83	120.34	105.30	2.5	14.00	86	8.60E-02	0.45

Electrochemical Oxidation experiment:	**20-Mar-03**
Experiment:	**Bench-scale membrane: LFH (40%glass) with CB-SnO2**
Anode:	**Anode: carbon cloth 6100-200**
Cathode:	**Cathode: carbon cloth 6100-200**
Feed Solution:	**100 ppm SAPREF effluent in Seawater**
Catalyst Loading (mg/cm2):	**1.21**
Feed Volume (L)	**5**

Slope 0.000670275
Intercept -0.014434975

HPLC ANALYSIS

Run	Absorbance	COD (mg/L)	COD Removed (%)
1	0.1	170.73	28.27
2	0.0707	127.02	46.63
3	0.0508	97.33	59.11
4	0.0398	80.91	66.00
5	0.0324	69.87	70.64
6	0.0317	68.83	71.08
7	0.0246	58.24	75.53
8	0.022	54.36	77.16
9	0.0205	52.12	78.10
10	0.0184	48.99	79.42

Sample	pBenzouinone (mg/L)	Catechol (mg/L)	Hydroquinone (mg/L)	Oxalic acid (mg/L)
Run1	0.0	0.0	0.0	0.0
Run2	0.0	0.0	0.0	0.0
Run3	0.0	0.0	0.0	0.0
Run4	3.2	0.0	0.0	0.0
Run5	4.6	0.0	0.0	0.0
Run6	5.2	0.0	0.0	0.0
Run7	8.6	0.0	0.0	0.0
Run8	8.2	0.0	0.0	0.0
Run9	8.6	0.0	0.0	0.0
Run10	6.2	0.0	0.0	0.0