

EXECUTIVE SUMMARY

Preparation and characterisation of electrodes for the electrochemical conversion of organic pollutants in water

Introduction

Many different methods for improving the quality of wastewater, such as pressure-driven membrane-based methods, biological treatment, chemical treatment and treatment with chlorine or ozone are already established.

Electrochemical oxidation has recently been proposed as an alternate method for the removal of organic pollutants from water, especially for dilute solutions of biorefractory organics. The use of high oxygen-overvoltage anodes for the direct oxidation of refractory organic chemicals is of great potential value in wastewater treatment.

The economic feasibility of this type of process is associated with its ability to limit side reactions and its good current efficiency. Anodic oxidation does not release undesirable chemicals into the water (as chlorination does).

For the efficient use of the above process, two areas required close attention:

- the choice of electrode material and
- the design of the electrode system for the maximum contact of impurities onto the electrode.

To increase energy efficiency per unit volume of water treated, anodic electrocatalysts are required to hinder the oxygen evolution reaction and yet be electrocatalytically active towards the oxidation of dissolved organics.

Research in the field of material science, for better and more cost-effective electrodes that could improve existing water purification processes was undertaken. Attention was to be paid to the improvement of existing electrocatalytic systems by creating novel and potentially useful metal oxide electrocatalysts (subsequently based on SnO_2). A further way in which the efficiency of electrochemical methods for wastewater treatment could be increased was by supporting the system on solid polymer electrolytes (SPE). An SPE system thus makes possible electro-organic reactions at an electrode on the surface of an ion-exchange membrane, without the need for addition of a supporting electrolyte.

Broadly speaking, the project was to address the design, preparation, characterisation and evaluation of new and improved electrodes for the electrochemical conversion (oxidation) of hazardous organic pollutants in water. The oxidation (conversion and combustion) of phenol, considered a standard/model contaminant for hazardous organic compounds in water, and widely used as a model compound to assess methods of treating aqueous solutions containing organic waste, was to be investigated.

Objectives

The main objectives of this project were:

- 1 To create a document describing the state-of-the-art in electrolytic processes, other than electrodialysis, in water treatment.
- 2 To design and prepare novel electrode materials for the electrocatalytic oxidation of phenol in water, by optimising the $\bullet\text{OH}$ radical production electrochemically. This included the preparation of new doped SnO_2 sol-gel layers.
- 3 To characterise the above electrodes, by various methods, including: surface analysis by microprobe and by XPS.
- 4 To determine the electrochemical oxidation of phenol by cyclic voltammetry and conductivity measurements of the electrode materials.
- 5 To use a novel electrode material in a SPE reactor for the electrocatalytic oxidation of phenol, without the addition of salt to the electrolyte solution.

Overview of the project

With the assistance of technology available at Max Planck, Germany, we learnt how to make sol-gel electrode materials of tin oxide and with the assistance of Essen University (Germany), the electro-deposition of lead oxide electrodes. This progress then brought us in-line with the existing American technology. However, although tin oxide is conductive, it does not have the conductivity of a good electrode material. Both our group and overseas experts in the field then deemed it necessary to increase the overpotential further. Hence, we were to aim at making electrodes from materials that do not desire to have extra oxygen in the ceramic lattice.

Towards this aim, antimony oxide, Sb_2O_3 , was copolymerised with tin oxide, by sol-gel synthesis, from its metal salts. This put excess oxygen into the lattice and did indeed increase the overpotential for oxygen generation, while the increased conductivity of the electrode allowed more efficient hydroxyl radical generation on the electrode surface.

This report describes progress made with the design and preparation of new SnO_2 -based electrodes for the electro-catalytic oxidation of hazardous organic contaminants in water, the characterisation of the electrode materials and determination of the electrochemical oxidation of phenol by cyclic voltammetry. The following electrodes were evaluated for oxidation of phenol: Ebonex, Ebonex/ PbO_2 and Ti/SnO_2 and Sn-doped Ti/SnO_2 .

Phenol is considered to be a major water pollutant and phenol oxidation can be used as a model reaction to assess methods for treating aqueous organic waste. The oxidation (conversion and combustion) of phenol, considered a

standard/model contaminant for hazardous organic compounds in water, was chosen as the model pollutant with which to evaluate the new electrode materials in this study.

Good results were obtained with the new electrodes, especially the Sb-doped ones. The cyclic voltammograms revealed a high overpotential for oxygen evolution, resulting in well-separated peaks for the oxidation of phenol. (Good separation of the peaks for oxygen evolution from water and from organics, respectively, is required). Improvements in the conductivities of above films and higher current densities for the oxidation reaction were obtained by doping the film sol-gel solution with 10% Sb. Doping with fluoride increased the conductivity, but decreased the oxidation peaks.

These electrodes were fully characterised by advanced techniques, both in South Africa and Germany. What was desired was indeed synthesised. In an electrolytic cell, using sulphuric acid as electrolyte, the combustion of phenol was proved beyond doubt. The organics were combusted very rapidly, even from solutions with concentrations as high as 1g per litre. Hence the concept of anodic oxidation and the use of the new membrane materials was proved.

For the kinetic measurements of the reactions by which $\bullet\text{OH}$ radicals were formed at the anodes, the PbO_2 -based electrode material on the Ebonex and the $\text{Ti/SnO}_2/\text{Sb}_2\text{O}_5$ anode material were compared. RNO was used as a spin trap for the $\bullet\text{OH}$ radicals.

One way in which the efficiency of electrochemical methods for wastewater treatment can be further increased is by supporting the system on a solid polymer electrolyte (SPE). As organic pollutants do not form sufficiently conductive electrolytes for electrochemical treatment without the addition of supporting salts, an SPE reactor was designed. This meant that we were able to move away from using an aqueous electrolyte to using a solid polymer electrolyte (SPE), namely Nafion, which requires no salt in the water to be treated.

Since perfluorinated ion-exchange membranes such as Nafion as an SPE are used to separate the anode and the cathode in the electrochemical oxidation process, no conductive liquid is required in the cell. This is feasible since the fixed sulphonic acid groups in the polymer, similar to the immobilised sulphuric acid, provide the conductivity through proton mobility inside the membrane. Hydrogen ions are formed at the anode during oxidation and migrate through the cation-exchange membrane.

Sb-doped SnO_2 anodes were coupled with a perfluorinated cation-exchange membrane to build a system for the anodic oxidation, and evaluated.

Porous titanium electrodes of up to 50 cm^3 in size were coated with doped SnO_2 for a SPE galvanostatic solid polymer electrolyte (SPE) application. Results indicated very low voltage across the stack, even without adding supporting electrolytes to the water. Once again, phenol breakdown was achieved.

There were however problems with the cell design. The first cell design was rather simple and the water to be combusted, or rid of organics, needed to be in total contact with the electrode. Unfortunately, mass transport problems and

current deficiency limited the total efficiency of contact as the liquid flowed past the flat electrode in a cell designed for gaseous reactions ie. a fuel cell. A standard laboratory test system, a reversed fuel cell, had been used [Grimm, 2000].

Although good progress was made on the materials side of the project, in terms of the preparation of new and efficient electrode materials and assessment of their efficiency in the electrocatalytic conversion of phenol in wastewater, further work is strongly recommended. It should focus on even newer and improved electrode materials and, most importantly, on the improvement of the cell design. A better understanding of the mass-transport limitations of the reactor is also required.

Conclusions

The main conclusions of this project were:

- A written review of electro-assisted methods for water purification was compiled, and subsequently published. (Desalination **115**, 1998, 285-294)
- Various electrode materials (anodes) were prepared, characterised and evaluated for their catalytic potential as oxidation catalysts for the electrochemical oxidation of phenol, a model of organic pollutants in water. These electrodes were to have well separated peaks for the overpotential and the oxidation peak, in the cyclic voltammograms, for the oxidation of phenol.
- Determination of the electrochemical oxidation of phenol was successfully carried by means of cyclic voltammetry.
- Most favourable results were obtained with the new Sb-doped films on Ti foil, $\text{Ti/SnO}_2/\text{Sb}_2\text{O}_5$, prepared by a special sol-gel dip-coating technique. This new electrode material had a high overpotential for oxygen evolution, resulting in a well-separated peak in the cyclic voltammogram.
- Kinetic measurements, confirmed by UV/Vis spectroscopy, revealed that $\bullet\text{OH}$ radicals were formed as intermediates during the combustion of phenol in a second order rate-determining step. Using an on-line technique, the combustion of phenol in an electrolytic cell, using sulphuric acid as electrolyte, was established. This proved the concept of anodic oxidation and the suitability of the new membrane material.
- *The Ebonex® electrode did not absorb the phenol on the electrode, hence the electrochemical reaction took place at a very much lower potential, much lower than the overpotential for oxygen evolution.*
- With the Ebonex/ PbO_2 electrode the oxygen overpotential interfered with the oxygen evolution peak.

- Overall, a new electrode material that separates the overpotential from the oxidation peak, while maintaining excellent kinetics at the electrode surface, has been prepared. With increasing current densities, increasing degrees of oxidation were obtained.
- Further, instead of using an aqueous electrolyte, a solid polymer electrolyte (SPE) reactor was designed. It required no salt in the water to be treated. Nafion was used to separate the anode and cathode in the electrochemical oxidation process. The new electrodes in the SPE for the combustion of phenol were efficient.

Unfortunately, with the simple cell design used there were mass-transfer problems. Current deficiency limited the total efficiency of contact as the solution flowed past the flat electrode in a cell designed for gaseous reactions ie. a fuel cell. The present cell design used had poor current efficiency and conversion.

In order to improve the current efficiency it is necessary to improve on reactor design. It is envisaged that with the design of a suitable commercial reactor, this technology could be effectively used. Such a design was, however, considered to be beyond the scope of this present research project (which focuses on the materials science aspects of a novel electrode materials). It should be undertaken by chemical engineers.

Lastly, the development and use of improved analytical techniques for the more accurate determination of the products of phenol oxidation should be considered.