

Review of Electro-assisted methods for water purification

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Abstract

Many different methods for improving the hygienic quality of waste, industrial and drinking water are already established. These include pressure-driven membrane-based methods such as reverse osmosis, ultra-filtration and microfiltration, biological treatment, treatment of water by means of various chemicals such as ozone or chlorine, and treatment with UV radiation. This review deals with electro-assisted methods for water purification which stand apart from the well-established technologies. Although electro-dialysis is a competitive electro-assisted method for water treatment, electrochemical systems for water treatment have, in general, not yet attracted adequate attention. Electrochemistry, a link between physical chemistry and electronic science, has proved to be a clean, versatile and powerful tool for the development of new advanced methods for water purification. The freedom of choice in adjusting the electrode potential and electrode material, to meet almost any demand, makes electrochemistry extremely selective and flexible. This survey covers both established and recent developments in the field of electrochemical technologies for waste water and drinking water treatment.

Keywords: Contaminants, electrochemical assessment, anodic oxidation, nitrate removal, heavy metals, electro-sorption

1. Introduction

Water and electricity are both basic commodities which will be needed in ever-increasing quantities with continued industrialization and urbanization in the world. Water treatment in its broadest context, entails the subjection of the

water to an agent or process with the objective of improving its source quality, to meet application-specific criteria or standards. The challenge of the rising demand for quality water can only be met if we apply all available, suitable scientific and technical techniques to increase the productivity of process technology for converting low-grade water into pure water. Electrochemistry must therefore be taken into consideration. The adequate supply of quality water is of major concern

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for arid areas of the world as the main source of life and an important factor for industrialization. The treatment of waste water and delivery of high quality water is a wide field for research.

The supply of water to rural communities is of major concern, especially as groundwater, which plays a key role in supplying rural communities with water, can often not be consumed without pretreatment.

The post-19th century era of water treatment has seen a rigid application of the principles of chemistry and materials science, with improvements in processes such as ozone generation [1], microfiltration, ultrafiltration and reverse osmosis.

The purpose of this paper is firstly, to define the problems arising from certain contaminants in water and secondly, to review the electro-assisted methods which could be used to solve these particular problems. Emphasis will be placed on novel techniques rather than on well-established systems, which have already been described elsewhere [2].

2. Contaminants and their risks

In the industrialized countries improvements in water treatment have led to a near eradication of acute health hazards caused by water-borne diseases. At the same, however, time the situation in the less-developed countries has become more serious and advances in analytical chemistry and toxicological science have revealed a situation that gives cause for new concern regarding potential chronic health hazards from drinking water containing trace (less than 0.1 mg/l) levels of organic chemicals not of natural origin.

Drinking-water quality criteria and their impact on waterborne diseases have already been extensively studied [3].

A brief description of the major types of water pollutants is given below.

2.1. Biological contamination

Despite the fact that bacteriological contamination of water no longer plays a major role in the

industrialized countries, it remains of concern in rural and developing communities where the levels of sanitation, standards of living and education can be correlated with the occurrence of infections. Because of the long incubation periods of pathogens and problems of diagnosis, the paths of infection are often difficult to detect. In addition, the absence of an infrastructure for the detection and recording of such infections results in little available information on water-borne diseases in South Africa. The pathogens involved include a wide variety of viruses, bacteria and protozoan parasites, which usually belong to the group of organisms basically transmitted by the oral-faecal route.

Examples of common diseases related to pathogens in water are gastroenteritis and hepatitis. Methods for monitoring pathogens in water have been reported by Grabow [4]. As various water-borne pathogens are able to change their prevalence, electrochemical decomposition of all organics rather than chemical treatment and disinfection might be an effective method for their removal, as will be described in section 4.1.

2.2. Contamination by heavy metals

Waste water containing toxic metal ions is produced in many industrial processes, such as electroplating, cellulose acetate production, photographic development and the production of printed circuits and batteries. Because of intensive gold-mining activities on the Witwatersrand in Gauteng, RSA, the water there is, in places, severely polluted. The removal of metal ions is of major concern, because the contaminants may accumulate in the human body and their presence manifests itself in long-term effects and diseases. As the problem has already been extensively described elsewhere [5], this article will only refer to the main contaminants which have major effects on human health.

Cadmium and associated contaminants

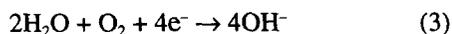
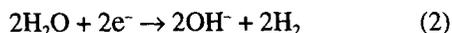
Cadmium is considered to be highly toxic [6, 7] and therefore its permitted concentration in water is limited to 5–10 ppb. In recent years cadmium has become of major environmental concern due to its introduction to natural water reservoirs. The main sources of cadmium contamination are: 1) Ni/Cd battery production which may deliver both cadmium and nickel to groundwater in untreated aqueous wastes, or because of uncontrolled disposal of used batteries; 2) cadmium plating, which also introduces cyanide which is used as a strong complexing agent; and 3) cadmium-rich phosphate fertilizers which introduce cadmium directly to the ground and into the water resources in cultivated areas. The latter has been reported to interfere with the metabolism by plants of some mineral substances, mainly calcium [8], magnesium [9] and phosphorus [10]. Symptoms such as osteoporosis, hypercalcuria and altered protein synthesis strongly suggest that cadmium disturbs calcium-dependent processes [11, 12].

The main electrochemical approach used for cadmium removal has been cathodic reduction [13].

The metal can be deposited on the electrode matrix according to the equation:



At sufficiently high cathodic potentials alkaline local pH values can be generated at the solution-electrode interface due to water and oxygen reduction:



Under such conditions $\text{Cd}(\text{OH})_2$ is formed and can be removed from the solution by adsorption to the electrode as a charged colloidal particle.

However, the most commonly used procedure is the precipitation of $\text{Cd}(\text{OH})_2$ by the addition of alkali. Both methods may also be used for the removal of nickel, if it is present in the solution. With cyanide as an associated contaminant electrochemical treatment by radicals can be used.

Mercury

Mercury levels in waters are generally very low and do not exceed more than 1(g/l [14]. Higher concentrations, however, occur in waste water discharged by certain industries. Strict attention must be paid to the control of Hg levels in water, because of the high toxicity of the metal. Mercury exhibits bioaccumulation phenomena and accumulates in fatty tissues, brain, renal systems, muscles, bones and nervous system, with a tendency to cause muscular paralysis, visual disruption and brain damage. The extent of Hg contamination and its becoming part of the trophic chain, is described in a study of Minimata, a town in Japan [15].

Lead

Lead is an important material with widespread industrial applications, as in accumulators and as an additive in fuels, paints, pesticides etc. As lead has been used in piping, high concentrations of the metal (up to 2 mg/l) may occur in the water in numerous households, where lead pipes have not yet been replaced. Its toxic characteristics and its tendency to accumulate in the body, makes analysis of the water and, if required, treatment of the water necessary. Electrochemistry may be used for the removal of lead by cathodic deposition.

2.3. Organic wastes

Apart from inorganic pollutants, industrial waste water also contains organic pollutants which have to be treated before the water can be discharged. Because of expansion of the chemical industry, it is not only the quantities of chemicals, but also the variety of organic pollutants released to waste water which is constantly increasing. The numerous new organic compounds entering the industrial sphere make their toxic classification increasingly difficult and, what is even more

serious, these substances may be stable and the traditional methods of biological treatment may not be effective. Chemical oxidation processes are effective but can generally not be carried out on halogenated organic compounds because of the stability of carbon-halogen bonds.

The electrochemical combustion of organics offers considerable advantages, as described in detail in section 4.1.1. Firstly, it can be carried out at moderate temperatures and under clean conditions. Secondly, electrochemistry provides a means for the total destruction of the pollutants, promoting their oxidation all the way down to CO_2 , and no by-products are left in the effluent. The electrochemical oxidation methods comprise direct and indirect oxidation, the latter oxidizing the organics by an intermediate formed at the anode.

2.4. Fluorides and nitrates

Fluorides are usually not regarded as having a great effect on the quality of groundwater, because their concentration is usually far below all international and national drinking-water standards. However, in the Western Bushveld area of South Africa, and in some of the western and northern areas in China, fluorine contamination of the groundwater results in endemic dental and, in fewer cases, skeletal fluorosis [16]. The enrichment of fluoride in the ground water takes place primarily as a result of dissolution of fluorite and the chemical weathering of F-containing minerals. Concentrations of fluorine in drinking water should not exceed 5 mg/l, although a recommended limit is 1 mg/l. In the area of Sun City, South Africa, Archean granite causes a concentration of fluorine exceeding 5 ppm in the groundwater. Electrochemical treatment of the fluorides is possible only by electrodialysis (section 4.3.1.), since oxidation in aqueous media is impossible because of the high electronegativity of fluorine.

Nitrate removal also plays an important role in improving the quality of drinking water. Intensive

farming and the application of agricultural fertilizers and inadequate control of human and animal excreta can result in high nitrate concentrations unfavorable to human health. It is recommended, that the concentration of nitrates in drinking water should be less than 10 mg/l. Electrochemical treatment methods range from electrodialysis to direct electrochemical reduction.

3. Why electrochemistry?

Electrochemistry, as a branch of physical chemistry, plays an important role in most areas of science and technology. Furthermore, it is increasingly acknowledged as a significant means for handling environmental and energy problems facing us today and in the near future.

Briefly, electrochemistry deals with the charge transfer at the interface between an electrically conductive (or semi-conductive) material and an ionic conductor (e.g. liquids, melts or solid electrolytes) as well as with the reactions within the electrolytes and the resulting equilibrium.

Electrochemical waste destruction shows several benefits in terms of costs and safety. The process runs at very high electrochemical efficiency and operates essentially under the same conditions for a wide variety of wastes. Operation at room temperature and atmospheric pressure reduces the possibility of volatilization and the discharge of unreacted waste. The waste treatment can be terminated within seconds by simply cutting off power to the electrodes.

The removal of undesired components from aqueous phases is based on the choice of the appropriate electrode material and potential, or by assisting membrane systems to drive the electrode processes selectively. In addition to the low cost of electricity in South Africa, it has the advantage of being applicable to a wide range of wastewater purification process. Furthermore, electrochemical combustion offers a means of oxidising the pollutants to water and CO_2 so that a simple

shift of the problem, by moving the contaminants from one phase to the other, is avoided. Electrochemical combustion is therefore presented as a clean and versatile method.

The following electrochemical approaches may be distinguished:

- indirect electrochemical oxidation of inorganic or organic contaminants;
- direct electrochemical oxidation of the contaminants;
- cathodic removal of metal-cations (mostly heavy metals);
- separation through membranes using an electric field.

The choice of electrode material must focus on high activation energies for undesired side-reactions. If side-reactions are to be reduced cathode materials should have high over-voltages for hydrogen-evolution, such as Pb or Cd. The anodes should preferably show high over-voltages [17] for the evolution of oxygen.

For a better understanding of the principles of electrochemical design, a description of the main purposes of reactor design is given in section 4.

4. Electrochemical reactor design

Thinking of three-dimensional electrode-structures one would first consider porous electrodes where reactions would then occur inside the pores of a porous bulk. Unfortunately such configurations are of little use for water treatment because the mass transport of the contaminants to the inside of the pores is slow. This can be improved by arranging thin, porous layers of electrodes, as in fuel cells.

Another possibility is the use of particle-electrodes. These electrodes have already been extensively studied for their use in the deposition of heavy metals from waste waters [2].

The two different types of construction are

- an electrochemical packed-bed reactor,
- and
- an electrochemical fluidised-bed reactor.

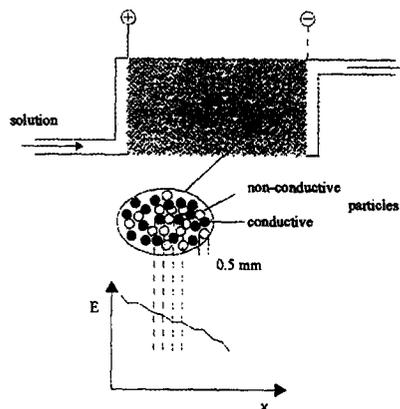


Fig. 1. Scheme of a packed bed reactor and the potential decay along the cross-section

For the evaluation of the economic efficiency of an electrochemical cell, the Space-Time-Gain is a useful tool. The Space-Time-Gain (∂) is described as the product gain per cell-volume and operating hour. The unit is $\text{kg l}^{-1} \text{h}^{-1}$ and is calculated by:

$$\partial = \frac{M}{nF} \cdot a \cdot j \cdot A_v \quad (4)$$

where a is the gain-factor and AV the proportion of electrode-surface to the volume of the cell (cm^{-1}). (See table of symbols at the end). Desirable high Space-Time-Gains are thus related to high current-densities and/or high A_v values. Three-dimensional electrodes guarantee a high value for A_v .

The electrochemical packed-bed reactor is shown schematically in Fig. 1. A bed of conductive and non-conductive spherical particles, such as graphite and synthetics, is situated between two electrodes and the contaminated water flows through it. If the conductivity of the solution is not too high and the voltage across it is sufficiently high, the conductive particles will act as a multitude of bipolar electrodes. In three-dimensional electrodes the penetration depth of the current in a direction parallel to the current flow is

limited. Ohmic losses in the electrolyte are the main cause of the decrease in local current density. For a diffusion-controlled reaction, the penetration depth of the limiting current density can be calculated with the formula:

$$h_p = \left[\frac{2 v \chi S \Delta \eta}{a e k z F c} \right]^{0.5} \quad (5)$$

According to this equation, the penetration depth of the limiting current density increases with decreasing concentration of the metal ions. The application of this principle led to the design of the Enviro-Cell which is shown schematically in Fig. 2. The penetration depth of the bed increases as the metal ion concentration decreases. The metal concentration can be reduced by as little as 1/1000 of the initial concentration.

The principle design of the fluidised-bed reactor is illustrated in Fig. 3. In this reactor a loose bed of particles of size diameter 0.1–1 mm is flooded upwards, from the bottom. The fluidised particles are charged cathodically by a feeder electrode. Metal ions are adsorbed at the surface of the particles and, once the particles contact the working-electrode, its potential drives the charge-transfer reaction and the discharged metal is deposited. When the metals lose contact with the electrode, they either desorb and collect at the bottom of the reactor or the particles grow and the larger ones sink to the bottom and are replaced by fresh particles.

The principle has been widely studied and purification by this means has been carried out on an industrial scale [18]. For hydraulic reasons the height of such a cell is usually restricted to 2m. Consequently, only a limited concentration drop per pass can be achieved. Continuous operation and serial arrangement of the cells can reduce these problems.

The A_v value of a fluidised-bed reactor is about 50 cm^{-1} . According to Eq. (2) the Space-Time-Gain for the removal of Cd-ions equals, for $j = 0.2 \text{ A cm}^{-2}$, approximately $20 \text{ g l}^{-1} \text{ h}^{-1}$. Apart

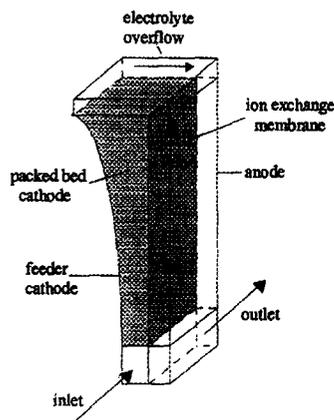


Fig. 2. Schematic representation of the Enviro cell

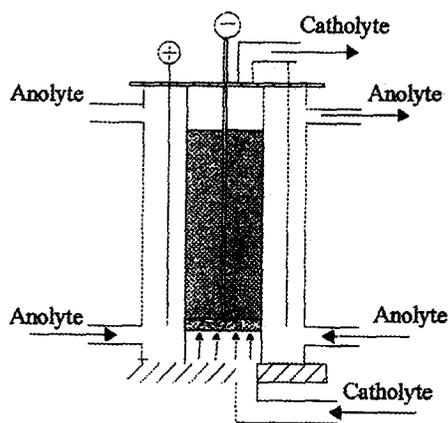


Fig. 3. The principle design of a fluidised bed reactor

from the high values of A_v , another advantage of the fluidised-bed reactor is the rapid mass-transport and the low real-current density which means that even very low concentrations of metals can be removed from the waste-water.

5. Electrochemical methods

5.1. Anodic oxidation

Anodic oxidation is a powerful tool for the treatment of organics in water, especially as far as the removal of organic wastes in industrial effluents is concerned. The main objective of the process is to oxidize any organics to H_2O and CO_2 .

Two different approaches may be distinguished:

- direct anodic oxidation, where the organics are destroyed at the electrode's surface, or
- indirect oxidation, where a mediator, for example Ag^{2+} , is electrochemically generated to carry out the oxidation.

5.1.1. Direct oxidation

Two different pathways are described in the literature for the anodic oxidation of undesired organics [19]:

- electrochemical conversion and electrochemical combustion (Fig. 4).

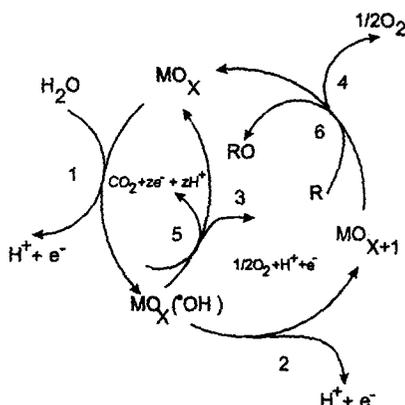


Fig. 4. Pathway of electrochemical combustion/conversion (scheme adopted from Comninellis, 1993)

Electrochemical conversion transforms only the toxic non-biocompatible pollutants into biocompatible organics, so that biological treatment is still required after the electrochemical oxidation.

In contrast, electrochemical combustion yields water and CO_2 and no further purification is necessary. This means that research should rather focus on studies of the mechanisms of the anodic combustion. Fig. 4 is a schematic representation of the electrochemical conversion/combustion, adopted from C. Comninellis [20].

Experimental results indicate that the accumu-

lation of $\bullet\text{OH}$ radicals favours the combustion reaction, while introduction of oxygen into the electrode's lattice results in combustion. This opens a challenging field for materials science, as electrodes need to be optimized. Chemically stable and electrically conductive material must be selected as a carrier for the electrocatalytic material. Usually Ti is used as the base material. There are a variety of methods for coating the catalyst support to obtain dimensionally stable anodes.

Methods of film preparation include:

- chemical vapour deposition
- reactive sputtering
- sol-gel dip coating
- spray-pyrolysis.

H. Sharifan and D.W. Kirk [21] reported on results obtained after using PbO_2 as electrode material, while Comninellis et al. [22] focused their research on SnO_2 coatings obtained by spray pyrolysis. Surface properties of the electrodes such as pore-size, roughness and catalytic activity can be examined by electrochemical methods such as impedance spectroscopy or cyclic voltammetry. Favoured goals of electrode design are high surface roughness with many catalytic sites (that might be smoothed during application), high exchange current densities and steep Tafel Slopes [17] for a high electron transfer rate. High porosity provides a large surface area and the pore sizes must not be too small, to allow for a rapid mass transport. Catalytic activity should be at a maximum, if the undesired molecules fit closely into the pores.

5.1.2. Indirect oxidation

During indirect electrochemical oxidation the organic pollutants are destroyed by an electron-transfer agent, such as ClO^-/Cl^- [23] or $\text{Ag}^{2+}/\text{Ag}^+$ [24]. The extremely high standard potential of the reaction (1.96V/NHE, in nitric acid medium): $\text{Ag}^+ \rightarrow \text{Ag}^{2+}$, establishes silver ions as the ideal mediator which attack organic species such as tri-

butylphosphate (TBP), tetraphenylborate (TPB) and benzene [25]. The process has the potential for use in waste treatment as well as even for the disposal of radioactive organic waste. When used as an electron-transfer agent, silver acts as a reusable catalyst, and no silver waste is generated. Because the anodic reaction is balanced by the cathodic reduction of nitric acid,



nitric acid must be regenerated by the chemical reaction of nitrous acid with oxygen. Furthermore, separators must be inserted into the cell to prevent the HNO_2 from migrating to the anolyte compartment and reducing the Ag^{2+} .

The mechanism has been studied by means of spectroscopic and potentiometric methods [24].

5.2. Membrane-assisted methods

Membranes serve as separators and solid electrolytes in many fields of applied electrochemistry. For the treatment of polluted water two main principles are:

- Electrodialysis
- Solid-Polymer-Electrolyte (SPE) applications.

Electrodialysis has been already reported on widely and will such be omitted in this publication. The literature describes both oxidative and reductive treatment for water purification by SPE. An adverse effect of using an electrochemical oxidation approach for water purification is the low ionic conductivity of many types of waste water. For the electro-oxidation process to be effective for organic contaminants, acid, base or salt must be added to form an electrolyte. This is impractical for many purposes. Ion-exchange membranes work as solid polymer electrolytes (SPE), even in non-conductive fluids. Of special importance in the SPE-process is the electro-osmotic transport through the membrane, which should be used to enhance the mass transfer at the electrodes and thus improve selectivity and yield.

The direction of the mass transport is determined by the choice of a cation or an anion exchange membrane. Fig. 5 illustrates the principle of an SPE configuration. The ionic flux is maintained by the protons and the electro-dialytic removal of heavy metals can be carried out simultaneously. When an anion-exchange membrane is used for separation, the organics are ionized at the cathode and driven through the membrane to the anode where electrochemical oxidation takes place, as illustrated in Fig. 6.

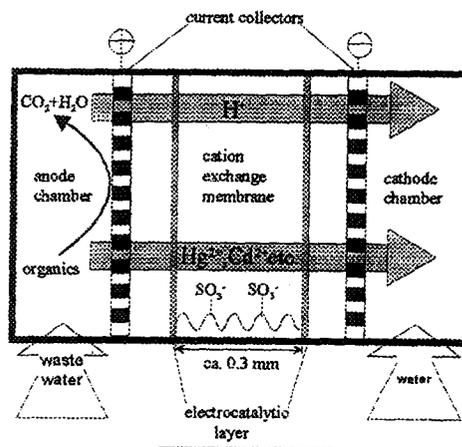


Fig. 5. SPE configuration for combined combustion and anion removal supporting an anion-exchange membrane

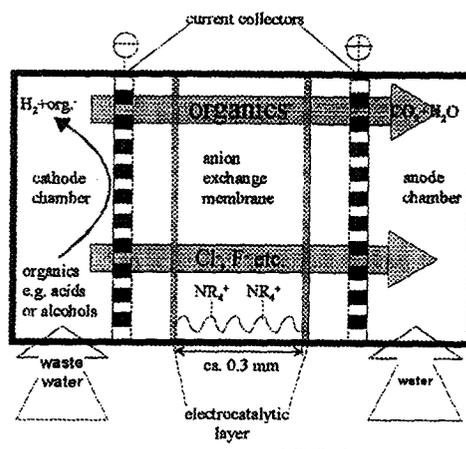
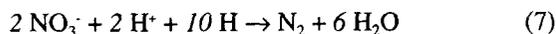


Fig. 6. SPE configuration for combined combustion and anion removal supporting an anion-exchange membrane

Another membrane assisted approach has been made for the so-called electro-catalytic nitrate-elimination (NKE-process) [26]. Doing this, NO_3^- is electrochemically reduced at a catalytic active surface (Pd) according to the following equation:



Hydrogen ions form at the anode, pass the cation exchange membrane to reach the cathode. At the cathode the hydrogen necessary for the nitrate reduction is produced electrochemically in the very reactive state of status nascenti. The major advantage of the reductive treatment of nitrates is that the only endproducts are nitrogen-gas and water. Fig. 7. describes the set-up of for the nitrate-removal installation.

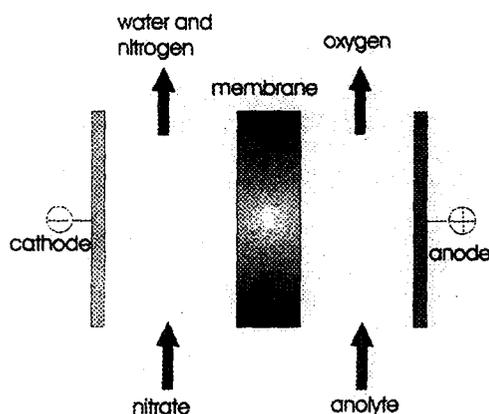


Fig. 7. Principle of the EKN-process

5.3. Electrochemically generated species for disinfection

Once water has been purified, measures must be taken to guarantee the safety of the water during storage. Electrochemically generated species for disinfection can serve that purpose. The production of chloride and hypochlorite at graphite or dimensionally stable titanium-anodes can be used for the destruction of micro-organisms and macro-organisms, especially for the disinfection of the water in pools, according to Eq. (8).



Hydrogen peroxide, a powerful oxidizing agent, is another substance that can prevent bacterial growth in the water. It can be accumulated at the cathode as an intermediate of the oxygen-reduction reaction:



The heterogeneous reaction is favoured at high temperatures and low pH-values, and preferably runs at electrodes such as Pt, Ag and activated carbon.

5.4. Adsorption methods

Electrosorption, for the removal for all kinds of contaminants, is best carried out with activated carbon, because of its extremely high surface area. A new device, called the flow-through capacitor, which might be important for future applications of water purification, has recently been patented [27]. As the effluents pass the carbon electrodes a small voltage is applied to cause electrosorption. The electrosorbed species are released in small amounts of concentrated water by short-circuiting the electrodes.

6. Conclusion

Water is the source of life, a fundamental requirement for health and the main need for industrialization; it is mankind's most precious commodity. The availability of water is decreasing and the treatment of existing water resources is therefore obvious.

The many ways in which electrochemistry can be applied to purify polluted water, as described above, demonstrate that research in this field is important.

Water purification systems based on anodic oxidation and disinfection units are already on the market (AEG, Electrosynthesis), but at a very

high cost. Research in the field of materials science, for better and more cost-effective electrodes, could improve the existing water purification systems. The Institute for Polymer Science at the University of Stellenbosch, in cooperation with the South African Water Research Commission, have therefore initiated new projects for elucidating the mechanism of anodic oxidation. The scaling-up of electrode systems for industrial or rural applications is the major goal.

Acknowledgments

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Symbols

a	– gain factor
a_e	– specific electrode area
AEM	– anion-exchange membrane
A_v	– specific electrode surface [cm^{-1}]
c	– concentration [kmol/m^3]
CEM	– cation-exchange membrane
F	– Faraday constant [As/mol]
h	– penetration depth [m]
j	– current density [A/m^2]
k	– mass transfer coefficient
M	– molar mass [kg/mol]
n	– number of electrons
z	– electron number
η	– overpotential
ρ	– space time gain [$\text{kg}/\text{m}^3\text{s}$]
v	– degree of vacancy
X_s	– electrolyte conductivity [S/m]

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