Electrochemical oxidation of organic pollutants for the wastewater treatment: direct and indirect processes†‡

Carlos A. Martínez-Huitle* and **Sergio Ferro**

Received 21st April 2006
First published as an Advance Article on the web 10th July 2006
DOI: 10.1039/b517632h

In recent years, there has been increasing interest in finding innovative solutions for the efficient removal of contaminants from water, soil and air. The present *tutorial review* summarizes the results of an extensive selection of papers dealing with electrochemical oxidation, which is proposed as an alternative for treating polluted wastes. Both the direct and indirect approaches are considered, and the role of electrode materials is discussed together with that of other experimental parameters.

Apart from discussing the possibility of removing selected contaminants from water using different anodes, efficiency rates for pollutant removal have been collected, the dependence of these rates on operational conditions advantages and disadvantages determining the further full-scale commercial application.

Introduction

The intensification of industrial activities, since the latter half of the XIX century and throughout the XX century, has inevitably caused severe environmental pollution with dramatic consequences in atmosphere, waters, and soils. The consequent restrictions imposed by new legislation require effective initiatives for pollution reduction, not only in gaseous emissions and industrial aqueous effluents but also adequate decontamination in soils. Typically, in the case of the latter, different classes of pollutants may have accumulated during long periods of uncontrolled waste disposal and reclamation may represent a serious technological problem. Due to the extremely diverse features of pollution phenomena, universal strategies of reclamation have not been found.[1]

Generally, wastewater treatment is carried out using primary, secondary or tertiary methods, depending on the nature of the pollutants. As far as organic pollutants in wastewaters are concerned, biological abatement may sometimes be impossible, due to the bio-refractory character of the substrates. For this reason, physical-chemical methods are preferably applied, but an oxidation with ozone or chlorine dioxide is not always effective and also transportation and storage of reactants may be a significant inconvenience for safe processing.[2]

An alternative can be the application of electrochemical technologies for wastewater treatment, benefiting from advantages such as versatility, environmental compatibility and

Carlos A. Martinez-Huitle

Carlos A. Martinez-Huitle was born in Mexico City, in 1977. He graduated in chemistry at the Universidad de las Américas—Puebla (2000). After a work experience in Ciba—Specialty Chemicals, he moved to the University of Ferrara, Italy (2002), to work under the supervision of Prof. Achille De Battisti. Here, he earned a PhD in chemical sciences (2005). During the same period, he worked as visiting scientist in the group of Prof. Christos Comninellis at the EPFL Institute, Switzerland. He is a faculty member at the University of Milan. His research interests include electrochemical oxidation, electrocatalysis and electroanalysis.

Sergio Ferro

Sergio Ferro was born in 1972. He was awarded his ''Laurea'' in Chemistry in 1997, and earned a PhD in Chemical Sciences at the University of Ferrara in 2001, where he is now working as a research assistant. Author of about 30 papers in international journals, co-author of 2 book chapters and 3 patents, he has received awards from national and international scientific committees. His work deals mostly with electrocatalysis, regarded as an extension of heterogeneous catalysis (its principles and methods) to electrochemical reactions.

Department of Chemistry, University of Ferrara, via L. Borsari 46, I-44100 Ferrara, Italy. E-mail: Carlos.Martinez@unimi.it; Fax: +39 0532 240709

† Electronic supplementary information (ESI) available: Tables S1 and S2: direct and indirect anodic oxidation of organic compounds (anode materials listed in alphabetical order). See DOI: 10.1039/b517632h

‡ Graphical abstract photo by Davide Semeraro (Italy), reproduced with permission.

potential cost effectiveness among others described below.[2] Both direct and mediated electrochemical oxidations can be considered, and have proved to be interesting subjects for different research groups and industries seeking new technologies for wastewater treatment.[3]

In recent years, the applications of electrochemistry for environmental pollution abatement have been thoroughly investigated.[3,4] The feasibility of electrochemical conversion/destruction of organic substrates in wastewater, in particular, has attracted much attention since pioneering studies by Dabrowski in the 70's, Kirk, Stucki, Kotz, Chettiar and Watkinson in the 80's, and Comninellis in the early 90's to the present day. In these studies, the influence of the nature of the electrode material during the anodic mineralization of organics has been considered in detail, showing that optimal conditions for the process in question are obtained at high-oxygen-overpotential anodes.

Briefly, electrochemical oxidation is performed by the action of strong oxidants, similar to chemical destruction, but the *in-situ* electro-generation allows better efficiency of the abatement of the organic substrates. Direct electrochemical destruction has been investigated with particular focus since the end of the eighties, through the testing of different anodic materials for the oxidation of diverse organic pollutants dissolved in water. Many organic substrates show a complex reactivity toward the anodic mineralization; in these cases, the central role of adsorbed hydroxyl radicals and the mode of adsorption of the organic species should be taken into account.

Results obtained using simple molecules, *e.g.* oxalic acid, support the view that co-electrosorption of hydroxyl radicals and organic species affect the rate of the anodic mineralization, volcano-plot approaches of the type traditionally applied for ethylene electrochemical oxidation being possibly a good interpretative tool.[5] These considerations lend further evidence to the importance of the nature of the electrode material in electrochemical oxidation.[5] In this context, a general model mechanism proposed by Comninellis[6] considers the different stabilization exerted by the electrode material on electrosorbed hydroxyl radicals and satisfactorily accounts for the different results described in the literature. Accordingly, electrodes have been classified as active and non-active, on the basis of their electrocalytic properties.[7] On the other hand, indirect oxidation (also called mediated electrochemical oxidation) is based on the activity of strongly oxidant species,[4] *e.g.* $Cl^{\bullet}$, $S_2O_8^{2-}$ and Ce^{IV}, and may also represent an interesting alternative to the aforementioned wastewater treatments. The high acidic concentration needed to achieve significant concentrations of the above species makes this method more suitable for the treatment of low water-content sludges, the main process being essentially a two-phase one.[8–10] The oxidative attack of organics in aquatic media does not follow a conceptually different path. We can speak formally of direct and indirect (mediated) processes. Into the latter group we can include active-chlorine, ozone-mediated attacks and others, where the main reaction stages take place in the solution bulk. The former group would include those processes whose main stages occur at the electrode surface, through adsorption of reactants and intermediates, the strong oxidant being essentially the hydroxyl radical. Regarding the recent mechanism proposal by the Comninellis group,[11] which assumed the action of the latter extended to a reaction cage in the vicinity of the electrode surface, rather than limited at the surface itself, the distinction between direct and mediated oxidation becomes even less stringent.[12]

The role of mediators such as Cl^-—of particular interest for its common presence in many different types of wastewater—brings the role of the electrode material to a prominent position. The Cl^--mediated mineralization has been shown to give good results at low-oxygen-overvoltage electrodes, such as Pt.[13–15] The addition of chloride ions in the electrolyte allows an increase of the removal efficiency, and a degradation of pollutants can be obtained due to the participation of active chlorine. These results indicate indirect oxidation as second alternative in the elimination of the organic pollutants from water. Similar to chlorides, bromides can also be effectively used for the anodic oxidation of organic pollutants, but this anion has scarcely been investigated and only a limited number of examples are reported in the literature.[16–20]

In investigations of direct and indirect oxidations many organic substrates have been considered, as well as different experimental conditions and anode materials. Nevertheless, in many cases, the electrochemical process leads to the formation of stable carboxylic acids such as maleic, formic, acetic, malonic and oxalic acids. These molecules may represent the polluting content of industrial wastewaters, *e.g.*in oil manufacturing.[21]

While a thorough optimization of the process can suggest the use of a particular anode material, other motivations, such as the anode material availability and cost, can drive the choice. For these reasons, ''mediated electrochemical oxidation'' (MEO) was particularly studied by different research groups:[13–20,22–25] both the influence of the nature of the anion, and its concentration were analyzed in order to increase the effectiveness of the process. Particular interest has been addressed to chloride mediation due to the ubiquitous character of Cl^- species in wastewaters, and its relatively effective action. Different authors have already published the possible ''direct'' and ''indirect'' roles for the chloride anion in the electrochemical reaction.[13–15,22–25]

The aim of this work is to present a thorough analysis of the literature concerning wastewater treatments, emphasizing the use of direct and indirect electrochemical oxidation processes as an alternative to other wastewater treatments.

Wastewater treatment

The effective treatment of effluents represents a serious problem, especially for the chemical industry. Over the last twenty-five years, huge efforts have been made to limit at the source this type of pollution, by improving processes, recycling products and controlling the treatment of wastes at the production stage. However, considering the large amounts of industrial effluents to be treated, for example to retrieve certain solvents, there are inevitably residues requiring a final transformation, which is often delicate. Traditional destruction methods, for their part, pose problems of corrosion and, more seriously, of emissions, if the treatment conditions are not perfectly controlled.[1]

From the industry point of view, this problem must be examined as a whole since there are no universal or simple methods in this area. The wide variety of industrial discharges means that a diversification of techniques must be sought, adapting the treatment to each situation, as much as possible. In spite of the efforts made to develop clean processes, the increasingly severe environmental laws should encourage the research for better-performing treatments, making it possible to obtain environmentally compatible effluents.[26] Actually, the processes for the treatment of wastewater may be divided into three main categories: primary, secondary and tertiary. Tertiary treatment, also known as advanced wastewater treatment, includes acid/base neutralization, precipitation, reduction and oxidation processes.[1]

Advanced oxidation processes

Different advanced oxidation processes have been developed and investigated by several research groups for the elimination of organic pollutants from wastewater, such as Fenton processes, photo-assisted Fenton processes, UV/Fe^{3+}-oxalate/H_2O_2, photocatalysis, ozone water system, Mn^{2+}/oxalic acid/ozone, H_2O_2 photolysis, O_3/UV and others.[27] These technologies consist mainly of conventional phase separation techniques (adsorption processes, stripping techniques) and methods, which destroy the contaminants by chemical oxidation and/or reduction. Chemical oxidation aims at the mineralization of the contaminants to carbon dioxide, water and inorganics or, at least, their transformation into harmless products. Obviously, the methods based on chemical destruction, when properly developed, offer a complete solution to the problem of pollutant abatement, different from those in which only a phase separation is realized with the consequent problem of the final disposal. It has been frequently observed[28–31] that pollutants not amenable to biological treatments may also be characterized by high chemical stability and/or by a great reluctance to go to complete mineralization. Also, the adoption of these oxidation treatments requires that specific conditions must be considered during the process: the influence of pH, inhibition due to scavenger presence, light wasting, mass transfer limitations, direct ozone attack and appropriate equipment.[27] In these cases, it is necessary to adopt much more effective reactive systems than those adopted in conventional purification processes.

Electrochemistry and environment

Electrochemistry, as a branch of physical chemistry plays an important role in most areas of science and technology.[32] Electrochemistry offers promising approaches for the prevention of pollution problems in the process industry. The inherent advantage is its environmental compatibility, due to the fact that it uses a clean reagent, the electron. The strategies include both the treatment of effluents and waste and the development of new processes or products with less harmful effects, often denoted as process-integrated environmental protection.[33]

The application of electrochemistry for the protection of the environment has been the topic of several books and reviews.[2,3,33–39] Besides the process-oriented benefits, electrochemistry is also playing a key role in sensor technology. Electroanalytical techniques for monitoring and trace level detection of pollutants in air, water and soil as well as of microorganisms are needed for process automation. Sensors for environmental applications have been already reviewed,[34,35] while an interesting view on the role of electrocatalysis for electrochemistry and environment has recently been given by Trasatti.[40]

In a review by Rajeshwar *et al.*, the promising characteristics of approaches for the prevention and remediation of pollution problems have been explained in detail.[2,36] *Versatility*: several techniques can be applied such as direct and/or indirect oxidations and reductions, phase separations, biocide functions, concentrations or dilutions; electrochemical methods can deal with many pollutants and treat from microliters to millions of liters. *Energy efficiency*: these processes generally require lower temperature with respect to equivalent non-electrochemical counterparts (*e.g.*, thermal incineration); the potential can be easily controlled and operational parameters can be designed to minimize power losses. *Amenability to automation*: the electrical variables used in the electrochemical processes (j, E) are particularly suited for facilitating data acquisition, process automation and control. *Environmental compatibility*: the electron is a clean and very effective reagent, whose reactivity may be tuned by choosing a suitable electrocatalyst, in order to prevent the production of undesirable metabolites. *Cost effectiveness*: the required equipment and operations are generally simple and inexpensive, but diverse considerations must be studied for optimal efficiency.

For the above reasons, electrochemistry can be considered an alternative for the prevention of pollution problems. Therefore, intensive research proceeds with the goal of discovering more efficient techniques, processes, materials, technologies and applications of electrochemistry for the remediation and/or prevention of pollution problems.

Electrochemical technologies for wastewater treatment

Electrochemical technologies have gained importance in the world during the past two decades. There are different companies supplying facilities for metal recoveries, the treatment of drinking water as well as process waters resulting from tannery, electroplating, dairy, textile processing, oil and oil-in-water emulsion, *etc.*[3] At present, electrochemical technologies have reached such a state that they are not only comparable with other technologies in terms of cost, but sometimes they are more efficient and compact. The development, design and application of electrochemical technologies in water and wastewater treatment has been focused on particularly in some technologies such as electrodeposition, electrocoagulation, electrofloculation and electrooxidation.[2]

Electrochemical oxidation: an alternative in wastewater treatment

Studies on electrochemical oxidation for wastewater treatment go back to the XIX century,[2] when the electrochemical decomposition of cyanide was investigated.[41] Extensive investigation of this technology commenced in the 70s, when Nilsson *et al.* in 1973 investigated the anodic oxidation of phenolic compounds.[42] Mieluch *et al.* studied for the first time the electrochemical oxidation of phenol compounds in aqueous solutions.[22] In 1975, Dabrowski *et al.* studied the electrochemical purification of phenol-containing wastes in a pilot plant,[43] while Papouchado *et al.* investigated the pathways of phenolic compounds anodic oxidation.[44] Later, in 1979, Koile and Jonhson examined the electrochemical removal of phenolic films from platinum anodes;[45] in the same period, Smith de Sucre obtained relevant results in phenol electro-oxidation during wastewater treatment,[46] and in the 80s these studies were continued in collaboration with Chettiar.[71,72]

During the last two decades, research work has focused on the efficiency in oxidizing various pollutants at different electrodes, on the improvement of the electrocatalytic activity and electrochemical stability of the electrode materials, the investigation of factors affecting the process performance and the exploration of mechanisms and kinetics of pollutant degradation.[3] Experimental investigations, focusing on the behaviour of different anodic materials, have been carried out by different research groups, the results of which warrant a detailed description. Attempts for an electrochemical oxidation/destruction treatment for waste or wastewater can be subdivided into two important categories: direct oxidation at the anode, and indirect oxidation using appropriate anodically-formed oxidants.[4]

Direct and indirect electrochemical oxidation

Electrochemical oxidation mechanism

Electrochemical oxidation of pollutants can occur directly at anodes through the generation of physically adsorbed "active oxygen" (adsorbed hydroxyl radicals, $^\bullet$OH) or chemisorbed "active oxygen" (oxygen in the oxide lattice, MO_{x+1}).[6] This process is usually called "anodic oxidation" or "direct oxidation" and the course for the anodic oxidation was described by Comninellis;[6] the complete destruction of the organic substrate or its selective conversion into oxidation products is schematically represented in Fig. 1.

When a toxic, non-biocompatible pollutant is treated, the electrochemical conversion transforms the organic substrate into a variety of metabolites; often, biocompatible organics are generated, and biological treatment is still required after the electrochemical oxidation. In contrast, electrochemical degradation yields water and CO_2, no further purification being necessary. Nevertheless, the feasibility of this process depends on three parameters: (1) the generation of chemically or physically adsorbed hydroxyl radicals, (2) the nature of the anodic material and (3) the process competition with the oxygen evolution reaction.

A mechanism for the electrochemical oxidation of organics, based on intermediates of oxygen evolution reaction in aqueous media, was formerly proposed by Johnson.[47–52] The process involves anodic oxygen transfer from H_2O to organics *via* hydroxyl radicals formed by water electrolysis.

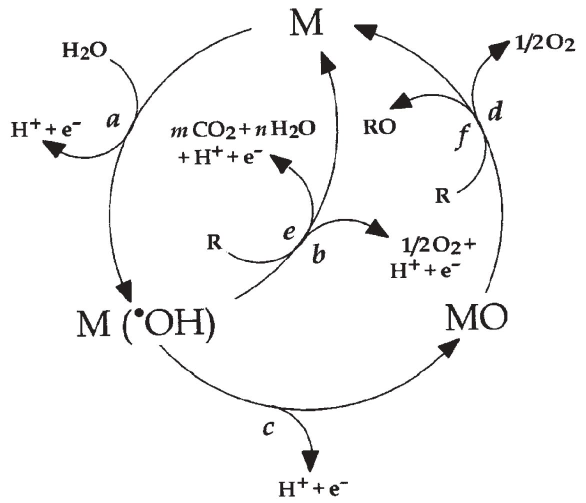

Fig. 1 Mechanistic scheme of anodic oxidation of organic compounds with simultaneous oxygen evolution on *non-active* anodes (reactions a, b and e) and on *active* anodes (reactions a, c, d and f). (a) Formation of hydroxyl radicals, OH*; (b) oxygen evolution by electrochemical oxidation of hydroxyl radicals; (c) formation of the higher metal oxide, MO; (d) oxygen evolution by chemical decomposition of the higher metal oxide; (e) electrochemical combustion of the organic compound *via* hydroxyl radicals; (f) electrochemical conversion of the organic compound, R, *via* the higher metal oxide. Reprinted with permission from *Electrochim. Acta*, 1994, **39**, 1857. Copyright 1994, Elsevier.[6]

The electrochemical oxidation of some organics in aqueous media may take place without any loss in electrode activity, except at high potentials, and with concomitant evolution of oxygen.[24,53–55] Furthermore, it has been described that the nature of the electrode material strongly influences both the selectivity and the efficiency of the process.[6,55–57] To interpret these observations, a comprehensive model for the anodic oxidation of organics in acidic medium, including the competition with the oxygen evolution reaction, has been proposed.[6,55–57] More recent results, obtained at conductive diamond electrodes[7] (which are characterized by a very high oxygen overpotential), fit the model predictions quite well. Based on these results, Comninellis explained the differences considering two limiting cases, *i.e.* the so-called "active" and "non-active" anodes.[7]

In both cases, the first reaction (eqn (a)) is the oxidation of water molecules leading to the formation of adsorbed hydroxyl radicals:

$$\mathrm{M} + \mathrm{H_2O} \rightarrow \mathrm{M(HO^\bullet)} + \mathrm{H^+} + e^- \tag{a}$$

Both the electrochemical and chemical reactivities of adsorbed hydroxyl radicals depend strongly on the nature of the used electrode material.

With *active electrodes* there is a strong interaction between the electrode (M) and the hydroxyl radical (OH$^\bullet$). Adsorbed hydroxyl radicals may interact with the anode, forming a so-called higher oxide MO (eqn (b)). This may be the case when higher oxidation states are available, for the electrode material, above the thermo-dynamic potential for the oxygen evolution (1.23 V *vs.* SHE).[6]

$$\mathrm{M(HO^\bullet)} \rightarrow \mathrm{MO} + \mathrm{H^+} + e^- \tag{b}$$

With active electrodes, the redox couple MO/M acts as a mediator in the oxidation of organics (eqn (c)). This reaction is in competition with the side reaction of oxygen evolution, which is due to the chemical decomposition of the higher oxide (eqn (d)):

$$\mathrm{MO} + \mathrm{R} \rightarrow \mathrm{M} + \mathrm{RO} \tag{c}$$

$$\mathrm{MO} \rightarrow \mathrm{M} + \frac{1}{2}\mathrm{O}_2 \tag{d}$$

The oxidative reaction *via* the surface redox couple MO/M (eqn (c)) may be much more selective than the reaction involving hydroxyl radicals (eqn (e)). A typical example of an active electrode is the case of IrO_2.[6]

With a *non-active electrode*, weak interactions exist between the hydroxyl radical and the electrode surface. In this case, the oxidation of organics is mediated by hydroxyl radicals (eqn (e)) and may result in fully oxidized reaction products such as CO_2.

$$\mathrm{M(HO^{\bullet})} + \mathrm{R} \rightarrow \mathrm{M} + m\mathrm{CO}_2 + n\mathrm{H}_2\mathrm{O} + \mathrm{H}^+ + e^- \tag{e}$$

In the above schematic equation, R is a fraction of an organic compound containing no heteroatoms, which needs one oxygen atom to be fully transformed into CO_2.[7] This reaction competes with the side reaction of hydroxyl radicals (direct or indirect consumption, through the formation of hydrogen peroxide as intermediate) to oxygen (eqn (f)) without any participation of the anode surface:

$$\mathrm{M(HO^{\bullet})} \rightarrow \mathrm{M} + \frac{1}{2}\mathrm{O}_2 + \mathrm{H}^+ + e^- \tag{f}$$

A non-active electrode does not participate in the anodic reaction and does not provide any catalytic active site for the adsorption of reactants and/or products from the aqueous medium. In this case, the anode serves only as an inert substrate, which can act as a sink for the removal of electrons. In principle, only outer-sphere reactions and water oxidation are possible with this kind of anode. Intermediates produced by the water oxidation are subsequently involved in the oxidation of organics in aqueous medium.[7]

The electrochemical activity (which may be related to the overpotential for oxygen evolution) and chemical reactivity (rate of the organics oxidation with electrogenerated hydroxyl radicals) of adsorbed $OH^{\bullet}$ are strongly linked to the strength of the $M–OH^{\bullet}$ interaction. As a general rule, the weaker the interaction, the higher the anode reactivity for organics oxidation (fast chemical reaction); boron-doped diamond electrodes (BDD) are typical non-active electrodes, characterized by high stability and acceptable conductivity. This model assumes that the electrochemical oxidation is mediated by hydroxyl radicals, either adsorbed at the surface (in the case of active electrodes) or free, in the case of the non-active ones.[7]

Direct anodic oxidation

The anodic oxidation does not require the addition of large amounts of chemicals to wastewater or the feeding of O_2 to cathodes, as in Fenton processes;[27] moreover, there is no tendency to produce secondary pollution and fewer accessories are required. These advantages make the anodic oxidation more attractive than other oxidation processes.[3] As previously commented, the most important parameter in this process is the anode material. Among the investigated anode materials, the following can be mentioned: stainless steel,[58] glassy carbon,[59] Ti/RuO_2, Ti/Pt–Ir,[60,61] carbon fibers,[62] MnO_2,[63,64] Pt–carbon black,[65,66] porous carbon felt[67] and reticulated vitreous carbon.[68,69] Unfortunately, none of them have either sufficient activity or satisfactory stability. Pt, PbO_2, IrO_2, SnO_2, and conductive diamond films are the most extensively studied anodes.

Based on the literature, a collection of data obtained at different anodes for the degradation of some important pollutants, under different conditions, can be found in Table S1 of the electronic supplementary information†. It is also worth mentioning that this table contains the most relevant research in the frame of the direct electrochemical oxidation from the beginning of its application to the present time. On the other hand, different parameters have been resumed: the current density, the current efficiency (CE)[53] and other efficiency parameters are of particular interest, as well as the possible intermediates and/or final metabolites. The current efficiency[53,56] is a measure of the process effectiveness; it can alternatively be expressed by means of the Electrochemical Oxidation Index (EOI), the Apparent Current Efficiency (ACE), and/or the Instantaneous Current Efficiency (ICE), as described in Appendix 1.

Phenol and derivates are among the most investigated examples in electrochemical studies. Initial research was carried out by Nilsson *et al.* in 1973;[42] Mieluch *et al.*,[22] and Dabrowski *et al.* also tried the use of electrochemical oxidation for the destruction of phenolic waste on a pilot-scale plant, in 1975,[43] while Smith de Sucre, Chettiar and Watkinson used synthetic wastewater solutions in early 80's.[70–72]

Smith de Sucre and Watkinson investigated the oxidation of phenol for wastewater treatment applications at packed lead dioxide anodes. They operated in both divided and undivided cells, obtaining analogous oxidation rates. The percentages of oxidized phenol ranged from 53% to 77%, depending on the type of cell and operational conditions (current intensity from 10 to 20 A, and variable pH values).[70]

Considering ref. 72, the process has not found a commercial use because of the low reaction rate and/or low efficiency. One reason for the low reaction rate, in the electrochemical oxidation of some organic compounds, is electrode fouling, *i.e.* the blocking of the electrode surface by reaction products. In the case of phenol, polymerization products are obtained. Under these conditions, a 96% destruction of phenol was obtained, with a 50% reduction in biological oxygen demand but a reduction in total organic carbon of only 22%.

From an examination of data in Table S1 of the ESI†, Pt and PbO_2 are the most widely investigated anode materials for electrooxidation. PbO_2 is one of the classic high-oxygen-overpotential materials and it is expected to perform quite well in electrochemical mineralization of organics (*e.g.*, for the oxidation of glucose at different anodic materials, Fig. 2). At this electrode material, Kirk realized the oxidation of aniline, obtaining good removal efficiencies: the current efficiency ranged from 15% to 40% for the complete oxidation of the organic substrate to CO_2.[73] The operating current density was also reasonably high: 80–160 A m^{-2}. The performance of this electrode material was further evaluated in terms of faradaic

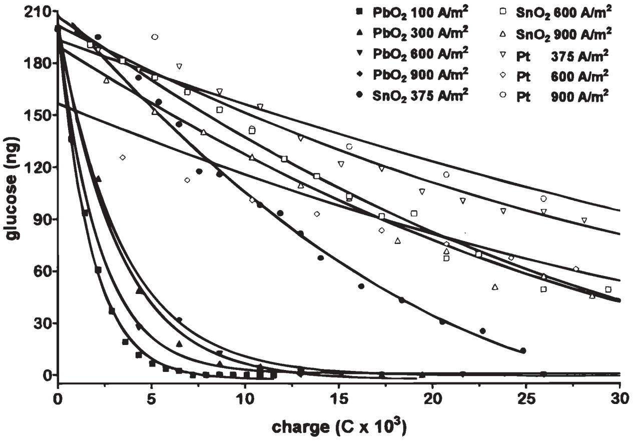

Fig. 2 Decrease of glucose content in solution, as a function of charge, at different electrode material and at different current densities. Solution: glucose 1 g dm^{-3} in 2 N H_2SO_4 at 25 °C. Reprinted with permission from *J. Electrochem. Soc.*, 1999, **146**, 2175.[76] Copyright 1999 The Electrochemical Society.

yield and fraction of removed toxic intermediates during the electrolysis of 2-chlorophenol.[74] Subsequently, this anode was used for the oxidation of several organic compounds, like *e.g.* indoles,[75] glucose,[76] oxalic acid,[77] choloranilic acid,[12] tryptophan[75] benzoquinone[78] and *p*-nitrophenol.[79] Moreover, Ti-supported PbO_2 electrodes (differing in terms of preparation, in the detail of their surface texture and, to a certain extent, also in their composition and microstructure, to the case of Pb/PbO_2) have been used for the oxidation of benzoquinone,[80] phenol,[81] chlorinated phenols,[82] landfill leachate[83] and others.[5,74,76] In all these works, good removal efficiencies were obtained; however, the CE values were different, depending principally on experimental conditions. An important application was realized by Kaba,[84] who treated urine waste biomass mixtures obtaining a 95% removal efficiency. On the other hand, the innovative use of lead pellets by Kirk gave low CE (16–21%), and removal efficiencies depended on the potential and various other parameters.[85] In this research, a pack bed reactor was used, and the anolyte was recirculated while following phenol loss and benzoquinone, maleic and carbon dioxide formation (Fig. 3 and 4).

PbO_2 electrodes are relatively inexpensive and quite effective in oxidizing pollutants; unfortunately, this electrode material is subjected to electrochemical corrosion (especially in media with no sulfate ions dissolved) and the release of Pb^{2+} ions can cause severe water contamination. As a viable solution, Ti can be used as a support for PbO_2 films obtained by thermal preparation.[86]

In the case of the Pt electrode, there have been various applications: urine wastes,[84] tannins,[87] herbicides,[88] as well as other model organic pollutants.[7,89–94] Ti-supported Pt was also used for the elimination of dyes,[95] tannery wastewater,[96] benzoic acid,[97] and bisphenol-A.[98] At this electrode material, a selective oxidation is generally attained and, in agreement with the model

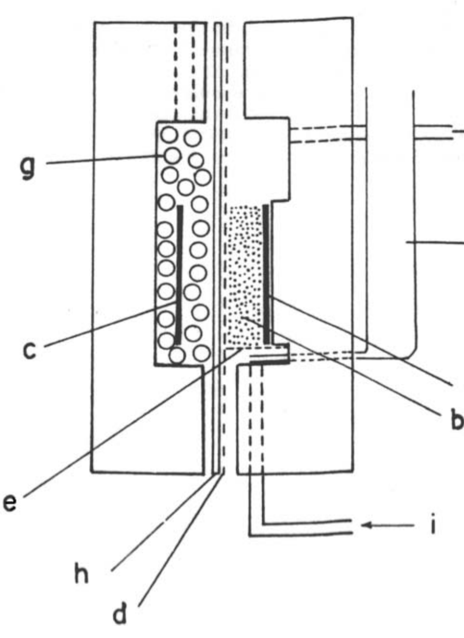

Fig. 3 Electrochemical cell: (a) Pb anode feeder; (b) bed of 1 mm lead pellets; (c) stainless steel cathode plate; (d) Nafion membrane; (e) stainless steel screen; (f) Luggin capillary; (g) glass beads; (h) gasket; (i) reactor inlet; (j) reactor outlet. Reprinted with permission from *J. Electrochem. Soc.*, 1986, **133**, 921.[85] Copyright 1986 The Electrochemical Society.

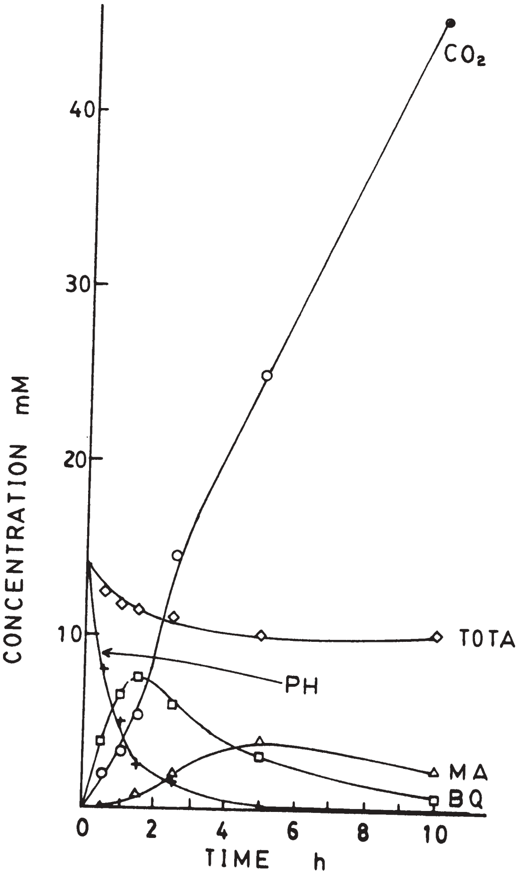

Fig. 4 Concentration of phenol (PH), benzoquinone (BQ), maleic acid (MA), and carbon dioxide (CO_2) as a function of electrolysis time for 1.4×10^{-2} M phenol in 1.0 M H_2SO_4. Temperature = 25 °C, flow rate = 1.0 mL s^{-1}. Reprinted with permission from *J. Electrochem. Soc.*, 1986, **133**, 921.[85] Copyright 1986 The Electrochemical Society.

proposed by Comninellis,[6] PtO_x can be formed during the oxidation process. For Pt and Ti/Pt, efficiency results are sometimes very different, probably as a consequence of material preparation.[77] Pt has been used for studying the passivation by phenol derivatives, due to polymeric film production;[93,99] in this context, pioneering works were made by Koile.[45] Modifications of the Pt electrode surface have also been described: Pt/WO_x[100,101] and Ti/Pt–Ir[95] have been applied for the oxidation of carboxylic acids and dyes, respectively. In both cases, high current efficiencies (80–100%) and conversions near 99% for the carboxylic acids[100,101] and 50% for the dyes[95] were obtained. Despite the satisfactory results obtained in the oxidation of simple inorganic pollutants, at very low current densities,[94] Pt electrodes showed poor efficiencies in anodic oxidation of organic compounds.[97,102]

For graphite electrodes, the maximum CE was approximately 70%, obtained at very low current densities (ranging from 0.03 to 0.32 A m^{-2}).[103] When current densities were increased to 10–100 A m^{-2}, the CE values decreased to only 6–17%.[104] However, the addition of carbon black was found to significantly enhance the performance of Ti/Pt anodic oxidation of aqueous phenol.[65]

Pure SnO_2 is a *n*-type semiconductor; this oxide material exhibits a very high resistivity at room temperature and cannot be used as an electrode. However, its conductivity can be improved significantly by doping with B, Bi, F, P and Sb.[105] For electrochemical applications, Sb is the most commonly used dopant for SnO_2. Kötz *et al.* reported the anodic oxidation of pollutants at Sb-doped SnO_2-coated titanium electrodes (Ti/SnO_2–Sb_2O_5).[106] They obtained CEs, at Ti/SnO_2–Sb_2O_5, approximately five times higher than that at Pt.[97] Comninellis[81] measured the CE obtained at SnO_2–Sb_2O_5 to be 0.58 for 71% degradation of phenol while values at PbO_2, IrO_2, RuO_2 and Pt were, respectively, 0.18, 0.17, 0.14 and 0.13 at $j = 500$ A m^{-2}, pH 12.5, initial concentration of 10 mM, reaction temperature of 70 °C. Zanta *et al.* studied the oxidation of *p*-chlorophenol, obtaining a 75% degradation of the organic substrate at this electrode material.[107] Chen *et al.* compared the degradation of different pollutants, achieving CE values of 11–50%, and 22–65% removal efficiency at different values of the charge consumed per square meter of electrode surface.[108]

The oxidation of phenol was investigated at SnO_2–Sb_2O_5 and PbO_2 using also the cyclic voltammetric approach, and the former electrode material was found to be more active than the latter.[109] It must also be noted, however, that Cossu *et al.* reported no substantial differences in activity between SnO_2–Sb_2O_5 and PbO_2 in treating landfill leachate.[83]

IrO_2 has been widely studied as an electrocatalyst for O_2 evolution. The low current efficiency for organics oxidation is thus expected.[81,82] The low activity of this anode in oxidizing 1,4-benzoquinone has been related to the low current density employed.[110] Nevertheless, IrO_2 has been used for the electrochemical elimination of aliphatic alcohols, allowing CE of 30–40%, and 90% conversion to CO_2.[111] In general, low current efficiencies and high removal efficiencies have been obtained at longer times, as a result of the competition between the oxidation of organics and the oxygen evolution reaction. The former process consists of a selective oxidation, which takes place through the formation of "higher oxides".[6]

TiO_2 is usually employed in wastewater treatment as a photocatalyst. By doping with Nb and/or Ta, the TiO_2 conductivity can be successfully improved,[112,113] allowing its use as an electrocatalyst for pollutant oxidation. This type of electrode is usually made by baking the Ti substrates coated with Nb and/or Ta-doped TiO_2 films. TiO_2 electrodes are stable at low current densities (below 30 A m^{-2}), their lifetimes being significantly shortened when operating at higher current densities.[113]

Another conductive titanium oxide is Ebonex®, a non-stoichiometric titanium oxide mixture consisting of Magneli phase titanium oxides Ti_4O_7 and Ti_5O_9, and made by heating TiO_2 to 1000 °C in the presence of H_2.[115] This kind of material was applied for the direct electrochemical oxidation of compounds such as phenol[110] and trichloroethylene;[115] the oxidation of the former has been investigated also by cyclic voltammetry at Ebonex/PbO_2.[109]

The boron-doped diamond (BDD) film electrode represents an attractive anode material for the degradation of refractory pollutants such as ammonia, cyanide, phenol, chlorophenols, aniline, various dyes, surfactants, alcohols and many other compounds.[5,7,11,12,15,77,116–152] Unlike PbO_2, SnO_2 and TiO_2, the BDD thin films deposited on Si, Ta, Nb and W by chemical vapor deposition have shown excellent electrochemical stability.[135] The application of BDD electrodes for wastewater treatment has been mostly studied at Si-supported devices, in spite of the difficulties related to their industrial transposition, due to the fragility and the relatively low conductivity of the Si substrate. BDD films synthesized on Nb, Ta and W are promising, but their large-scale utilization is impossible due to the unacceptably high costs of these metal substrates. On the contrary, titanium would possess all required features to be a good substrate material, if a proper synthetic route were available; preliminary samples of Ti/BDD have been used for the destruction of several pollutants, *e.g.* dyes,[153,108] carboxylic acids[108] and phenol.[108] Carey *et al.* patented the use of diamond films as anodes for organic pollutants oxidation.[131] The anodic oxidation of various pollutants, as well as the mechanism by which the organic substrates are oxidized at this electrode surface, have been investigated by Comninellis and coworkers: they suggested the formation of a film of relatively free hydroxyl radicals at the Si/BDD surface, representing a sort of "reaction cage" for the process.[118,122–127,130,133–135,140,151] Related results have been summarized in Table S1 of the ESI†. The obtained CEs are very high, ranging from 33.4 to more than 95%, depending on pollutant characteristics and oxidation conditions. The work by Beck[154] also reports results obtained by Comninellis,[135] comparing the Si/BDD with Ti/SnO_2, Ta/PbO_2 and Pt for the oxidation of phenol. At a charge loading of 20 Ah l^{-1}, the total organic carbon (TOC) content was reduced from an initial value of 1500 to about 50 mg l^{-1} at Si/BDD, and to about 300, 650 and 950 mg l^{-1} at the other electrode materials, in the above order. At BDD electrodes, another aspect to be taken into consideration is the production of powerful oxidants, like peroxodisulfate;[155,156] these species can participate in the oxidation of the organic substrates, permitting higher efficiencies. In particular cases, for high organic concentrations and low current densities, the COD decreased linearly and the Instantaneous Current Efficiency (ICE) remained at about 100%, indicating a kinetically controlled process, while for low organic concentrations or high current densities, the COD decreased exponentially and the ICE began to fall due to the mass-transport limitation and the side reactions of oxygen evolution. For example, Fig. 5 shows the trend of the COD and ICE during the electrochemical oxidation of 2-naphthol. In order to describe these results, the authors developed a comprehensive kinetic model that allowed them to predict the trend of the COD and current efficiency for the electrochemical degradation of the organic with BDD electrodes and estimate the energy consumption during the process.[139–141] This model is explained in Appendix 2.

As can be observed in Table S1 of the ESI†, other anode materials have been employed for the direct oxidation of pollutants: pure metals,[76,80,99] DSA®-type electrodes[76,77,79] and carbonaceous materials (*e.g.* glassy carbon, carbon felt, granular carbon, graphite).[59,67,80,157,158,99,159,103] The column of intermediates is also a key-point for the evaluation of data in the table†: in fact, several metabolites are generally produced during the oxidation of the original organic substrate. Starting from an aromatic compound, hydroxylated derivatives are found as initial intermediates but, in the final stages of the oxidation process, several carboxylic acids are produced, the last being usually oxalic acid. The formation of these acids increases the time process and highlights possible mass transport limitations; interestingly, some anode materials are more efficient than others for their elimination.

Indirect anodic oxidation

The electrooxidation of pollutants can be performed through different ways.[3] Electrochemical destruction of organics can be attempted by both direct and indirect oxidation. In addition, peroxide, Fenton's reagent, Cl_2, hypochlorite, peroxodisulfate and ozone are prominent oxidants that can also be electrochemically produced.[4] These oxidants react with the organic substrates, eventually leading to their complete conversion to CO_2, H_2O and other inorganic components. As far as the indirect oxidation is concerned (Table S2 of the ESI† summarizes different examples), the most used electrochemical oxidant is probably chlorine (hypochlorite, in neutral or alkaline media), as a result of the ubiquitous character of Cl^- species in wastewaters, and due to their quite effective action. Looking at the literature, the anodic oxidation of organics in the presence of NaCl was studied for the first time by Mieluch *et al.*, while investigating the direct electrochemical oxidation of phenol.[22] The phenol oxidation rate was influenced by the current density (1 to 24 A dm^{-2}), temperature (50 to 80 °C) and NaCl concentration (2 to 15%). According to the obtained results, phenol compounds in NaCl-containing wastewaters were eliminated by direct anodic reaction and/or through the mediation of $Cl^{\bullet}$ or ClO^- ions, which formed at the anode. Nevertheless, the possible role of the mediated process was not taken into account by the authors.

Anodically generated chlorine and/or hypochlorite can be used to destroy oxidizable pollutants. In most cases, both inorganic and organic pollutants can be eliminated in the presence of a suitable chloride concentration;[58,60,62,169–172] practical applications have been claimed in a number of patents.[173,174] The addition of chloride ions in the electrolyte caused an increase in removal efficiency, and the complete degradation of pollutants was attained due to the participation of active chlorine, in the form of chlorine (E° = 1.358 V), hypochlorous acid (E° = 1.63 V) and hypochlorite (E° = 0.90 V). A scheme for the MEO of organic pollutants in the presence of NaCl in alkaline media was proposed by Comninellis and Nerini,[24] who considered the anodic formation of hypochlorite and the successive indirect oxidation of the organic substrate in the bulk of the solution or in close proximity of the electrode surface. At the same time, a number of reactions may take place in parallel, decreasing the process efficiency: among the different possibilities, the formation of chlorate and the chlorine evolution must be mentioned. De Battisti and coworkers studied the oxidation of glucose in the

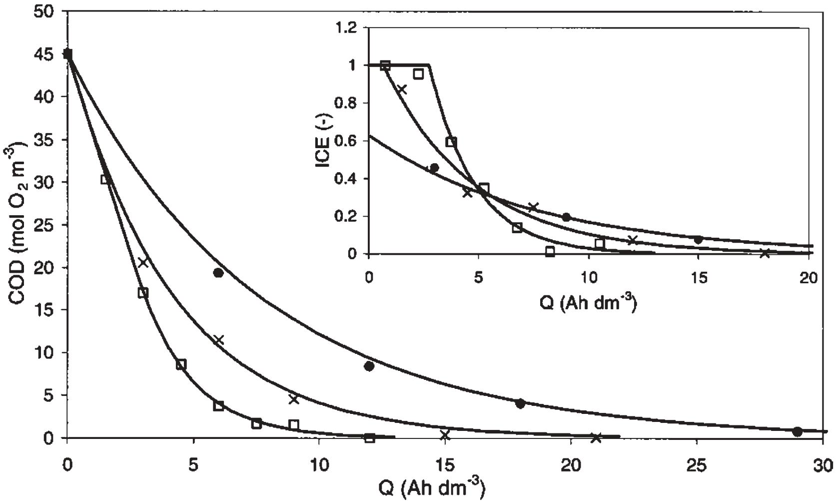

Fig. 5 Influence of applied current density on the trends of COD and ICE (inset) during electrolysis of 4-CP on BDD anode. (□) *i* = 15, (×) *i* = 30 and (●) *i* = 60 mA cm^{-2}. Electrolyte 1 M H_2SO_4; Initial 4-CP concentration 7.8 mM; *T* = 25 °C. (—) Representation model prediction (see Table 1). Reprinted with permission from *J. Electrochem. Soc.*, 2001, **148**, D60.[141] Copyright 2001, The Electrochemical Society.

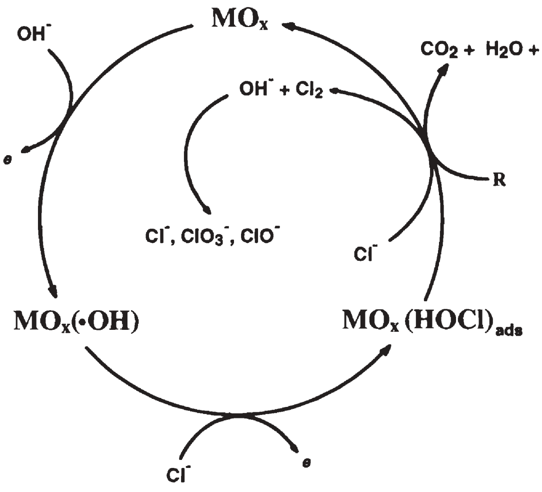

Fig. 6 Extension of the reaction pattern proposed by Comninellis,[6] for the electrochemical incineration of organics, to the case of active chlorine-mediated electrochemical incineration. Reprinted with permission from *J. Electrochem. Soc.*, 2000, **147**, 592.[13] Copyright 2000 The Electrochemical Society.

presence of chlorides,[13] and hypothesized HClO to be the oxidizing agent (formed at the anode, thanks to chloride oxidation and the concomitant oxygen evolution reaction). On the basis of the above studies, both chloro- and oxychloro-radicals, co-generated at the electrode surface, have to be considered in the mechanism of the electrochemical destruction, thus representing an extension of the model initially proposed by Comninellis[6] for the direct electrochemical oxidation. According to De Battisti and coworkers, in the case of active chlorine mediation, an oxygen transfer can be attained through adsorbed oxychloro-species[13,14] instead of from the more commonly cited hydroxyl radicals (Fig. 6, 7 and 8).

Zhang *et al.* made experiments on the elimination of dyestuffs from wastewaters (such media always contains a high concentration of sodium chloride).[175] The indirect electrochemical process removed the color completely and the COD content by 87%, in 50 minutes, while the direct electrochemical process removed 47% of the COD and the color by 50%, in 5 hours. Hypochlorite production at the anode was found to be diffusion-controlled and rate-limiting. A 99% current efficiency was estimated for the indirect process, while that of the direct oxidation was 16%; cost efficiency of the two processes was 8000 mg-COD kWh^{-1} and 1000 mg-COD kWh^{-1}, respectively.

Electrochemical oxidation of phenol using a Ti-supported TiO_2–RuO_2–IrO_2 ternary mixture was studied by Rajkumar, in a chloride-containing supporting electrolyte.[176] In these experiments, a complete degradation of phenol was achieved, with a pronounced formation of chlorinated organic compounds, at the beginning of electrolysis, which reduced to lower levels with extended electrolysis.

In the indirect oxidation, the possible formation of chlorinated organic intermediates or final products is a possible limitation for the real application of this technique.[60,177] Another drawback to be considered is that if the chloride content in the raw wastewater is low, a large amount of salt must be added to increase the process efficiency.[177]

As far as other chemical agents are concerned, several pollutants can be degraded by electrochemically generated hydrogen peroxide,[178–183] and electrically generated ozone is reported for wastewater treatment too.[184,185]

The anodic oxidation of organics in the presence of NaBr was studied in the case of isosorbide,[16] methyl-orange,[17] hydrazo-dicarbonamine[18] and lactic acid;[19] NaBr was also employed as a mediator for the indirect oxidation of alcohols, in a double mediator system.[20]

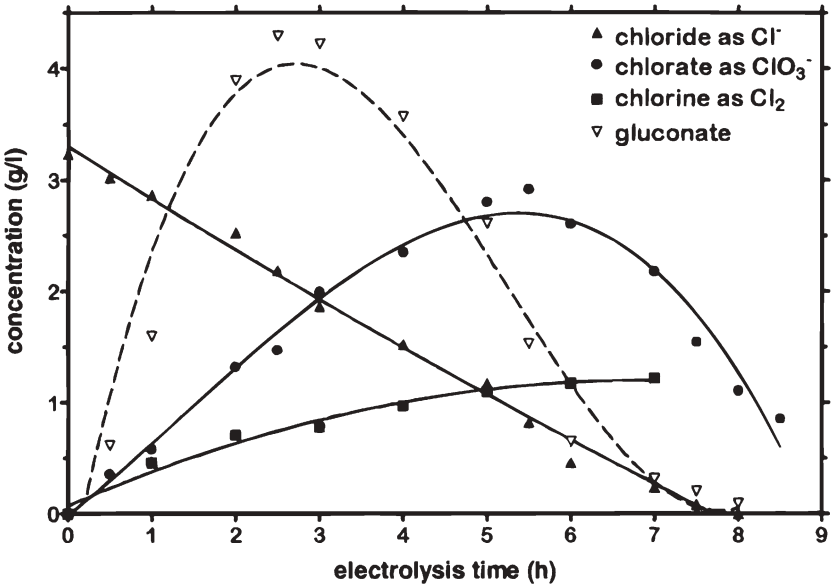

Fig. 7 Mass balance of inorganic chlorine species during mediated glucose mineralization. Glucose concentration: 10 g dm^{-3}; NaCl concentration: 5 g dm^{-3}; background electrolyte: 1 M Na_2SO_4 + 0.01 M NaOH. Electrode: Ti/Pt; j = 1200 A m^{-2}. Reprinted with permission from *J. Electrochem. Soc.*, 2000, **147**, 592.[13] Copyright 2000 The Electrochemical Society.

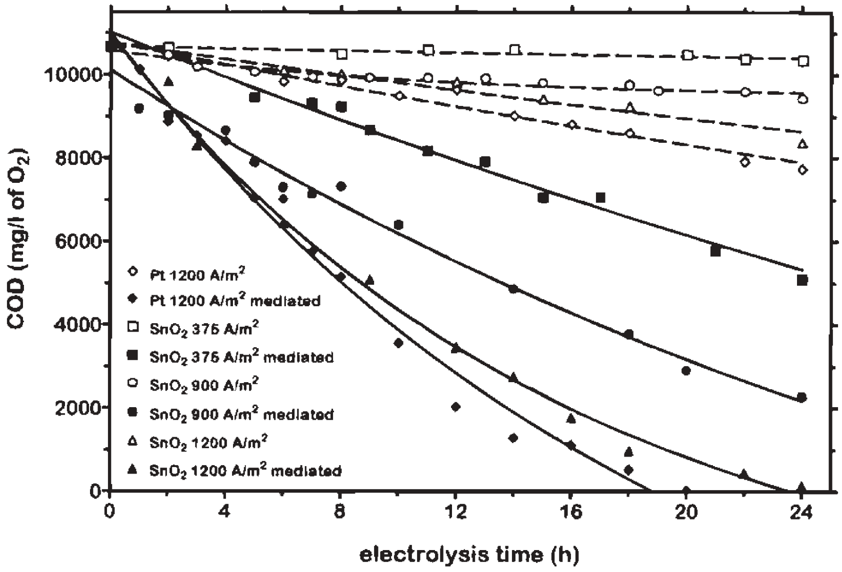

Fig. 8 Glucose electrochemical oxidation without and with chlorine mediation. Glucose concentration: 10 g dm^{-3}; NaCl concentration: 5 g dm^{-3}; background electrolyte: 1 M Na_2SO_4 + 0.01 M NaOH. Reprinted with permission from *J. Electrochem. Soc.*, 2000, **147**, 592.[13] Copyright 2000 The Electrochemical Society.

The "indirect electrochemical oxidation" has a wide range of applications, depending on mediator characteristics.[186] Redox couples with a high standard reduction potential (*e.g.*, Ag^{2+}, Co^{3+}) are mainly used for the total oxidation of organic pollutants from highly acidic wastewaters. In the presence of chloride ions or chlorinated compounds in the solution to be treated, the Co^{3+}/Co^{2+} redox couple should be preferred to Ag^{2+}/Ag^{+}, because the latter suffers from precipitation limitations. On the other hand, the presence of cobalt ions in solution, at the end of the process, may represent a serious problem, especially when the organic content has been totally eliminated and the water should be discarded. Mediators with lower standard reduction potentials are mainly used in selective organic syntheses[187] and redox couples having a negative standard reduction potential (*e.g.*, Ti^{3+}/Ti^{2+} and Cr^{3+}/Cr^{2+}) find applications in reductive organic syntheses.

Farmer *et al.* proposed a mediated electrooxidation for the treatment of mixed and hazardous wastes;[188] metal ions are oxidized at the anode from a stable, low-valence state to a reactive, high-valence state, which can directly attack organic pollutants. The reaction may also produce free hydroxyl radicals, which are useful for the destruction of the organic pollutants. Subsequently, the mediators are regenerated at the anode, thus forming a closed cycle. Typical mediators are Ag^{2+}, Co^{3+}, Fe^{3+}, Ce^{4+} and Ni^{2+}.[188–193] As previously mentioned, mediated electrooxidation usually requires to operate in highly acidic media—unfortunately the resultant pollution from the added heavy metals limits its application. Azzem *et al.* studied the indirect electrooxidation of 4-picoline with *in-situ* electrogenerated Co(III) acetate.[194] The pyridine-4-aldehyde diacetate product was obtained in good yield (45–68%), performing the electrolysis in acetic anhydride at 80 °C, in an undivided cell and under controlled current conditions.

Mediated electrochemical oxidation of organics in wastewaters were discussed by Gray *et al.*,[195] including operating principles, modeling, and laboratory scale experiments. In one test, 0.5 l of ethylene glycol was destroyed in 22 h with a 99% removal efficiency. The destruction rate was limited by the rate at which Ag^{2+} was produced in the electrochemical cell.

The authors of ref. 196 studied the Co(III)-MEO of ethylene glycol, 1,3-dichloro-2-propanol, 2-monochloro-1-propanol and isopropanol in sulfuric acid. The electrochemical reactor had a rotating cylindrical anode, which operated well below the limiting current for Co(III) generation, allowing the obtainment of high current efficiencies for the process, together with a significant CO_2 evolution. Also, aniline was oxidized by either Ce^{4+} or Co^{3+}, and carbon dioxide was produced as the final oxidation product.[197] Other works based on Co(III) generation showed that the anodic oxidation of water and Co(III) formation are probably simultaneous reactions. The kinetics of the oxidation of water by the mediator depends on the temperature and represents the most important side reaction, which diminishes the electrochemical efficiency.[191] Other applications of metallic mediators were reported by several authors.[198–206]

Other studies were carried out using cylindrical fluorocarbon-impregnated carbon anodes, specifically designed for ozone generation, in a solid-polymer electrolyte cell.[207,208] As already mentioned, the use of metal ions with high oxidation potential like Ag(II) and Co(III) can lead to the complete oxidation of the organic compounds to CO_2. Therefore, this frequently called mediated oxidation method was developed for the treatment of hazardous organic wastes, and originally used in the nuclear industry to dissolve refractory plutonium dioxide in nitric acid.[209]

The successful experiments kicked-off the process development activities at the Lawrence Livermore Laboratory,[188] at AEA Dounreay[210] and at the Forschungszentrum in Karlsruhe,[211] where intermediates and reaction paths for the oxidation of phenol and chlorinated phenols were identified; the method was then applied to a plurality of hazardous wastes.[4] In the cathodic compartment of the cell, nitric acid is reduced according to the Vetter mechanism[212] to NO, which can be regenerated to nitric acid by the well-known oxidative absorption in columns.[213] Experiments with electrochemically generated Mn(III) in sulphuric acid,[214] whose synthesis was intensively investigated by Comninellis also for the production of aldehydes,[186] showed a fast and complete oxidation of NO to HNO_3. In this procedure, using two electrochemical cells, one for destruction of organics and the other for nitric acid recovery, hydrogen is the final cathodic reaction product.

The formation kinetics for the oxidizing state of mediators were investigated by rotating disc electrode experiments.[215] For the Ag(II) system, under favorable flow conditions, very high current densities of more than 5 kA m^{-2} could be obtained. The formation of Ag(II) is mainly transport controlled: an average value of 0.488 cm s^{-1} was determined for the pertaining mass transfer coefficient. During the oxidative degradation of chlorinated organic compounds, precipitation of silver chloride occurs, which is redissolved in the presence of an excess of Ag(II) by the oxidation of chlorides to perchlorates, which progressively enrich the anolyte and can be separated from time to time by cooling crystallisation, as potassium perchlorate.[216] Cathodically formed nitrogen oxides are oxidized back to nitric acid in a bubble column, which is continuously fed with a sulphuric acid Mn(III) solution generated at the anode of a second electrolytic cell, while hydrogen is generated as a useful by-product at the cathode of this cell.

Economic considerations and comparison with other processes

The above data mainly concern model organic substrates and/or synthetic wastes; as a matter of fact, the reality is often more complicated. Actual wastewaters are being polluted by a variety of organic substances, which are not always biodegradable and thus not suitable for being treated with the conventional technologies.

In some cases, prior technologies may still find useful applications.

Wet oxidation[225]. In the wet oxidation process (WOP), the oxidant is oxygen: the reaction occurs at high temperature (175–320 °C) and pressure (20–200 atm), in order to dramatically increase the solubility of oxygen in water. The process generally involves a number of oxidation and hydrolysis reactions in series that degrade the initial compound into a series of compounds of simpler structure. Complete WOP results in converting of hazardous organic compounds into carbon dioxide, water vapor and ammonia (for nitrogen-containing wastes), sulfate (for sulfur-containing wastes) and halogen acids (for halogenated wastes). Partial degradation products may remain in treated wastewaters from WAO and may be given subsequent treatment before being discharged. This technology is most applicable for waste streams containing dissolved or suspended organics in the 500 to 15,000 mg l^{-1} range; below 500 mg l^{-1}, the oxidation rates of most organic constituents are too slow to allow an efficient application. The WOP can be applied to wastes that have significant concentrations of metals (approximately 2%) whereas biological treatment, carbon adsorption, and chemical oxidation may have difficulty treating such wastes. The process is less energy intensive than incineration and is less likely to produce oxides of nitrogen as by-product air pollutants; on the other hand, only wastewaters containing oxidizable organic and inorganic compounds can be treated. For example, wet oxidation cannot destroy PCBs, some halogenated aromatics and some pesticides. Capital costs for wet oxidation systems depend on the capacity of the system, oxygen demand reduction of the wastewater, severity of the oxidation conditions required to meet the treatment objectives, and construction materials. The US Army Construction Engineering Research Laboratories estimated an expense of \$12 million for a 60 m^3 per day system able to treat TNT red waters; operation and maintenance would cost \$974,000 per year, while the disposal of hazardous waste costs \$300 per m^3. The economic analysis turned out a payback period, for investment in equipment/process, of 4.3 years.

Biological aqueous wastewater treatment (ref. 225). This approach is based on the use of naturally occurring microbes to process contaminated wastewater; however, where highly toxic or recalcitrant target compounds are present, innocuous, microbial amendments are introduced. The systems use aeration and biological processes to break down contaminants. This technology can be applied to a wide variety of wastewaters; contaminants amenable to treatment include pentachlorophenol, creosote components, gasoline and fuel oil components, chlorinated hydrocarbons, ketones, alcohols, phenolics, and solvents. Other potential targets of waste streams include coal tar residues and organic pesticides. The production of minimal sludge and air emissions, the elimination of biotoxicity in the waste-stream and minimal operator attention requirements are undeniable benefits, which unfortunately contrast with the non-applicability of the method in the presence of non-biodegradable contaminants, such as DDT, PCBs, dioxins, and heavy metals. The capital cost for this technology depends on the flow rate, being \$14,000 for a 5 to 10 m^3 per day unit and \$140,000 for a 500 m^3 per day unit. Operating costs are approximately \$0.20 per m^3 for a 25 m^3 per day unit and \$0.10 per m^3 for a 150 m^3 per day unit.

Looking at the disadvantages of the above technologies, an improved removal of refractory dissolved organic carbon can be achieved by means of so-called advanced oxidation processes (AOPs). Examples for well-established AOPs are the combined application of ozone and hydrogen peroxide ("Perozon"), the combination of dissolved ferrous iron and hydrogen peroxide ("Fenton process") and the "activation" of hydrogen peroxide by UV irradiation; several other advanced oxidation technologies involve various combinations of ozone, UV light, peroxide, photo-catalysts, homogeneous catalysts and mechanical processes. All these AOPs aim at the formation of highly reactive radicals (*e.g.*, hydroxyl radicals), which subsequently oxidize organic compounds. These radical reactions cause an improvement of biodegradability or even the complete elimination of the COD.

H_2O_2/UV radiation (ref. 225). Hydrogen peroxide is added to the contaminated water, and the mixture is fed into the treatment system, which contains one or more oxidation chambers. Each chamber contains one high-intensity UV lamp, mounted in a quartz tube. The contaminated water flows into the space between the chamber wall and the quartz tube in which each UV lamp is mounted. UV light catalyzes chemical oxidation of organic contaminants in water by its combined effect upon the organic substances and reaction with H_2O_2. First, many organic contaminants that absorb UV light may undergo a change in their chemical structure or may become more reactive with chemical oxidants. Secondly and more importantly, UV light catalyzes the breakdown of H_2O_2 to produce hydroxyl radicals, which subsequently react with organic contaminants destroying them and producing harmless carbon dioxide, halides, and water. This process produces no hazardous by-products or air emissions.

The reaction conditions affect both performance and cost: among the important variables, the type and concentration of organic contaminant, the light transmittance of the water (turbidity or colour), the nature and concentration of dissolved inorganic substances (*e.g.*, carbonates and iron) and the water pH are of utmost importance. In addition, UV and H_2O_2 dosage, pH and temperature conditions, and the use of supplementary catalysts treatment mode (batch, recycle, or continuous) have to be considered.

This AOP approach is comparatively expensive: the capital cost for the hydrogen peroxide oxidation system is between $100,000 and $200,000 for a 750 m^3 per day treatment facility; equipment capacities can range up to several thousands m^3 per day; operating costs range from $0.15 to $3 per m^3.

Ozonation (ref. 225). The oxidation potential of ozone is high enough ($E^\circ = 2.07$ V) for a direct oxidation of numerous organic materials; alternatively, with the aid of initiators (OH^-, H_2O_2), reactive OH radicals can be formed and, similarly to the previous AOP, the control of radical scavengers is thus quite important. Since ozone rapidly decomposes, it cannot be stored and must be generated on-site: most wastewater treatment plants generate ozone by imposing a high voltage alternating current (6 to 20 kV) across a dielectric discharge gap that contains an oxygen-bearing gas.

The ozone consumption can be estimated in terms of 2.3–3 g O_3 per removed gram of COD,[226] which means high costs for reagents and high energy consumption; moreover, the technology is relatively new and long-term performance data is not available. Among the disadvantages, no or low reduction of inorganic compounds, such as ammoniacal nitrogen, can be obtained; this AOP is more complex than chlorine- or UV-disinfection, requiring complicated equipment and efficient contacting systems; in addition, to obtain maximum benefit from the system, a full-time operator is required. Costs are largely influenced by site-specific factors: capital costs are $275,000 for the treatment of 3000 m^3 per day; maintenance expenditures are also not competitive with available alternatives.

Concerning other approaches, and the Fenton process in particular, specific pH conditions and temperature adjustment are often required; in addition, the process continuously demands chemicals, while leading to the formation of sludges requiring a subsequent separation and elimination; the process optimization is also water-specific.

Electrochemical methods. The latter remark may be applied to the electrochemical approach, since the effectiveness of the treatment depends on electrode materials and cell parameters (mass transport, current density, water composition… as discussed in the above paragraphs of this review). Unfortunately, the literature is lacking information concerning real application: cost efficiencies of 8000 mg-COD kWh^{-1} and 1000 mg-COD kWh^{-1} were estimated by Zhang *et al.* for the hypochlorite-mediated and direct anodic oxidation of dyestuffs from wastewaters, respectively.[175] Stucki and coworkers estimated an energy consumption in the order of 50 kWh kg^{-1} COD, asserting that the treatment is capable of operating with wastewaters having a COD from 500 to 15,000 mg l^{-1}, thus competing with the wet oxidation.[97] In the case of a plant for the recovery of heavy metals and the concomitant destruction of cyanides (wastewaters from plating baths), an electrolytic unit with a capital cost of about $13,000 has been suggested, to treat about 1000 m^3 of silver cyanide rinse waters a year. Comparing the capital and maintenance costs with those of waste treatment and disposal, only 19 months are necessary as a payback period for investment in equipment/process.[225]

While no indication about electrode materials is present in the above economic analysis, the lifetime of electrodes may represent the deciding parameter: a lot of work is still in progress, to enhance the performances of existing electrode devices (*i.e.*, noble-metal-based oxides), without disdaining possible new electrode materials (*e.g.*, boron-doped diamond thin films).

As previously discussed, mediated oxidation processes may overcome some of the limitations of the direct anodic oxidation approach; examples of commercialized devices includes the CerOx technology, which is based on the cerium(IV)-mediated oxidation of organic compounds.[10,227] The CerOx process utilizes an electrochemical reaction to produce (and regenerate) the active, waste-destroying reagent. Commercially available equipment is not necessarily expensive, having typically a relatively small size.

Another example of commercially available technology is the production of anolytes (which contain hydroperoxide and chlorine-oxygen compounds), obtained through the electrochemical treatment of more or less diluted brine solutions.[228,229] Different systems are already present on the market, having anolyte production capacities from 0.01 to 5 m^3 per hour (the maximum power consumption is about 4000 W). An oxidants mixture content from 50 to 500 mg l^{-1} has been judged suitable for disinfection, washing, sterilization of medical articles, potable water disinfection, treatment of purulent and septic diseases of humans and animals; even larger amounts of oxidants may be obtained (from 150 to 200 g l^{-1} of gaseous mixture of chlorine, chlorine dioxide and ozone), allowing application in waste and/or sewage treatment plants, swimming pools, poultry factories and livestock farms, all of which are epidemic danger areas.

The above technology is based on modular cells, which can be hydraulically connected in order to obtain monopolar or bipolar electrolyzer designs; each module may treat from 0.01

to 0.08 m^3 h^{-1} of water, corresponding to solution treatment times from 0.3 to 3 seconds (currents are in the range 0.5–8 A, while the cell potential is limited from 10 to 120 V, depending on requested current and brine concentration). Under the above conditions, the guaranteed period of the system operation without replacing its basic elements (electrochemical reactors, electrokinetic reactor loading) is 60,000 hours.

Conclusions

The analysis of available literature points out the validity of the electrochemical approach for the elimination of different organic pollutants; in consideration of the specific reactivity of each organic substrate, dedicated tests should be carried out in order to identify the most suitable electrode materials and experimental conditions. Generally speaking, the mediated electrochemical approach can be considered more effective than the direct one, because of the minor problems of electrode fouling and/or corrosion. In contrast with other technologies, the form of the waste (liquid, sludge) and its homogeneity are relatively unimportant: the CerOx approach is surely more appropriate in the case of a sludge, while Bakhir's modular plants are dedicated to clear water solutions (*i.e.*, without suspended solids) when a direct oxidation is chosen, but the limitation disappears in case of a mediated (anolyte-based) approach.

Abbreviations

ACE	Apparent current efficiency
BDD	Boron doped diamond
CE	Current efficiency
COD	Chemical oxygen demand (g dm^{-3} or mol m^{-3})
CV	Cyclic voltammetry
CVD	Chemical vapor deposition
D	Diffusion coefficient (m^2 s^{-1})
DSA	Dimensionally stable anodes
F	Faraday constant (96 487 C mol^{-1})
GCE	General current efficiency
i_{appl}	Applied current
i_{lim}	Limiting current
IEO	Indirect electrochemical oxidation
I_L	Electrolysis limiting current (A)
j	Current density
k_m	Mass transport coefficient (m s^{-1})
M	Metal
Re	Reynolds number
SHE	Standard hydrogen electrode
S_v	Sample volume
TCE	Total current efficiency
TOC	Total organic carbon

Appendix 1

The efficiency values, summarized in Tables S1 and S2 of the ESI†, are estimated on the basis of experimental parameters, thanks to some specific equations.

The instantaneous current efficiency for the anodic oxidation is calculated using the following relation:[53,56]

$$\text{ICE} = FV\left(\frac{[(COD)_t - (COD)_{t+\Delta t}]}{8I\Delta t}\right) \tag{g}$$

where $(COD)_t$ and $(COD)_{t+\Delta t}$ are the chemical oxygen demands (g dm^{-3}) at times t and $t + \Delta t$, respectively; I is the current (A), F the Faraday constant (96487 C mol^{-1}), V the electrolyte volume (dm^3) and 8 is the oxygen equivalent mass (g eq^{-1}).

The general current efficiency for the anodic oxidation is calculated from values of COD, using the following relation:[12]

$$GCE = FV\left(\frac{[(COD)_0 - (COD)_t]}{8It}\right) \tag{h}$$

where $(COD)_0$ and $(COD)_t$ are the chemical oxygen demands (g dm^{-3}) at pertaining times, and the other variables have the same meaning as described above. This equation is similar to that proposed in ref. 24, for the determination of instantaneous current efficiency (ICE), but the expression used for GCE represents an average value between the initial time t = 0 and t.

$$TCE = FV\left(\frac{[(COD)_i - (COD)_f]}{8I\Delta t}\right) \tag{i}$$

In the case of the TCE, the COD values are considered at the initial and final times. Subsequently, from the ICE *vs.* time curves, the EOI value can be calculated. The EOI for a given organic compound supplies information about the reactivity of the considered species; its evaluation, during a period of sufficiently short time, and in particular at the beginning of the electrolysis, can be considered specific for the substrate.

The energy consumption for the removal of one kg of COD is calculated and expressed in kWh. The average cell voltage,

Table 1 Equations that describe COD and ICE evolution during organics oxidation at BDD electrode.[a] Reproduced with permission from ref. 141, *J. Electrochem. Soc.*, 2001, **148**, D60. Copyright 2001 The Electrochemical Society

	Instantaneous current efficiency ICE (-)	Chemical oxygen demand COD (mol O_2 m^{-3})
$i_{\text{appl}} < i_{\text{lim}}$ Under current-limited control	$ICE = 1$	$COD(t) = COD^0\left(1 - \frac{\alpha A k_m}{V_R}t\right)$
$i_{\text{appl}} > i_{\text{lim}}$ Under mass-transport control	$ICE = \exp\left(-\frac{Ak_m}{V_R} + \frac{1-\alpha}{\alpha}\right)$	$COD(t) = \alpha COD^0 \exp\left(-\frac{Ak_m}{V_R}t + \frac{1-\alpha}{\alpha}\right)$

[a] V_R is the reservoir volume, k_m the mass transfer coefficient in the electrochemical reactor (m s^{-1}), A the electrode area (m^2), COD^0 the initial chemical oxygen demand (mol O_2 m^{-3}), $\alpha = i/i^0_{\text{lim}}$ and i^0_{lim} is the initial limiting current density (A m^{-2})

during the electrolysis, is taken for calculating the energy consumption, as follows:[176]

$$\text{Energy consumption} = \left(\frac{\left[\left[tVA/S_{\text{v}}\right]/1\times10^{3}\right]}{\Delta COD/1\times10^{6}}\right) \quad \text{(j)}$$

where t is the time of electrolysis (h); V and A are the average cell voltage and the electrolysis current ; S_v is the sample volume (l), and ΔCOD is the difference in COD (mg l^{-1}).

Appendix 2

A theoretical model that permits the prediction of the evolution of COD and ICE with time, during the electrochemical oxidation of organic pollutants at BDD thin-film electrodes, has been developed for an electrochemical reactor operating in a batch recirculating mode under galvanostatic conditions.[139–141] The anodic oxidation of organics was assumed to be a fast reaction and the oxidation of organics in the bulk of the electrolyte, by means of electrogenerated oxidants (O_3, H_2O_2, and $H_2S_2O_8$), was not considered. The formulation of the model starts from the estimation of the limiting current density, from COD values:

$$i_{(\text{lim})}(t) = 4Fk_{\text{m}}COD(t) \quad \text{(k)}$$

where $i_{\text{lim}}(t)$ is the limiting current density (A m^{-2}) at a given time t; 4 is the number of exchanged electrons; F is Faraday constant (C mol^{-1}); k_m the mass-transport coefficient in the electrochemical reactor (m s^{-1}); and $COD(t)$ is the chemical oxygen demand (mol O_2 m^{-3}) at the given time t. Depending on the applied current density, two different operating regimes can be identified: (1) $i_{\text{appl}} < i_{\text{lim}}$: the electrolysis is under current control, the current efficiency is 100%, and the COD decreases linearly with time; and (2) $i_{\text{appl}} > i_{\text{lim}}$: the electrolysis is under mass-transport control, secondary reactions (such as oxygen evolution) are involved, resulting in a decrease of ICE. Under these conditions, the COD removal, due to mass-transport limitation, follows an exponential trend. From the mass-balances on COD over the electrochemical reactor and the reservoir, the equations that describe the temporal evolution of COD and ICE can be obtained, as summarized in Table 1.

Acknowledgements

The helpful comments provided by Professor Achille De Battisti (University of Ferrara, Italy) are greatly appreciated; CAMH is also indebted to Professor Christos Comninellis (EPFL Lausanne, Switzerland) for encouraging this research and for his very fruitful discussion.

References

1 S. E. Manahan, *Environmental Chemistry*, Lewis Publishers, Boca Raton, USA, 1994, pp. 223–240.
2 K. Rajeshwar, J. G. Ibáñez and G. M. Swain, *J. Appl. Electrochem.*, 1994, **24**, 1077–1091.
3 G. Chen, *Sep. Purif. Technol.*, 2004, **38**, 11–41.
4 K. Juttner, U. Galla and H. Schmieder, *Electrochim. Acta*, 2000, **45**, 2575–2594.
5 C. A. Martínez-Huitle, S. Ferro and A. De Battisti., *Electrochim. Acta*, 2004, **49**, 4027–4034.
6 Ch. Comninellis, *Electrochem. Acta*, 1994, **39**, 1857–1862.
7 B. Marselli, J. Garcia-Gomez, P. A. Michaud, M. A. Rodrigo and Ch. Comninellis, *J. Electrochem. Soc.*, 2003, **150**, D79–D83.
8 U. Galla, P. Kritzer, J. Bringmann and H. Schmieder, *Chem. Eng. Technol.*, 2000, **23**, 230–233.
9 G. A. Steward, *US Pat.*, 5 756 874, 1998.
10 N. Nelson, *Platinum Met. Rev.*, 2002, **46**, 18–23.
11 P. A. Michaud, *Thesis No. 2595, EPFL, Switzerland*, 2002.
12 C. A. Martínez-Huitle, M. A. Quiroz, Ch. Comninellis, S. Ferro and A. De Battisti, *Electrochim. Acta*, 2004, **50**, 949–956.
13 F. Bonfatti, S. Ferro, F. Lavezzo, M. Malacarne, G. Lodi and A. De Battisti, *J. Electrochem. Soc.*, 2000, **147**, 592–596.
14 F. Bonfatti, A. De Battisti, S. Ferro, G. Lodi and S. Osti, *Electrochim. Acta*, 2000, **46**, 305–314.
15 C. A. Martínez-Huitle, S. Ferro and A. De Battisti, *Electrochem. Solid-State Lett.*, 2005, **8**, D35–D39.
16 F. Jacquet, A. Gaset, J. Simonet and G. Lacoste, *Electrochim. Acta*, 1985, **30**, 477–484.
17 M.-L. Tsai, W.-L. Lee and T.-C. Chou, *J. Chin. Inst. Chem. Eng.*, 2001, **32**, 517–524.
18 V. R. Islamgulova, E. N. Shitova, A. P. Tomilov and V. S. Pilyugin, *Russ. J. Electrochem.*, 1999, **35**, 899–901.
19 H. Li and L.-C. Jiang, *Jingxi Huagong*, 1999, **16**, 27–29.
20 T. Inokuchi, S. Matsumoto and S. Torii, *J. Org. Chem.*, 1991, **56**, 2416–2421.
21 D. Mantzavinos, R. Hellenbrand, A. G. Livingston and I. S. Metcalfe, *Appl. Catal., B*, 1996, **7**, 379–396.
22 J. Mieluch, A. Sadkowski, J. Wild and P. Zoltowski, *Przem. Chem.*, 1975, **54**(9), 513–516.
23 A. Boscolo Boscoletto, F. Gottardi, L. Milan, P. Pannocchia, V. Tartari, M. Tavan, R. Amadelli, A. De Battisti, A. Barbieri, D. Patracchini and G. Battaglin, *J. Appl. Electrochem.*, 1994, **24**, 1852–1858.
24 Ch. Comninellis and A. Nerini, *J. Appl. Electrochem.*, 1995, **25**, 23–28.
25 M. Panizza and G. Cerisola, *Electrochim. Acta*, 2003, **48**, 1515–1519.
26 A. Savall, *Chimia*, 1995, **49**, 23–27.
27 R. Andreozzi, V. Caprio, A. Insola and R. Marotta, *Catal. Today*, 1999, **53**, 51–59.
28 O. Legrini, E. Oliveros and A. M. Braun, *Chem. Rev.*, 1993, **93**, 671–698.
29 P. M. Fedorak and S. E. Hrudey, *Water Res.*, 1984, **18**, 361–367.
30 R. Barreiro and J. R. Pratt, *Water Environ. Res.*, 1992, **64**, 632–641.
31 T. Reemtsma and M. Jekel, *Water Res.*, 1997, **31**, 1035–1046.
32 J. Grimm, D. Bessarabov and R. D. Sanderson, *Desalination*, 1998, **115**, 285–294.
33 *Electrochemistry of cleaner environments*, ed. J. O'M. Bockris, Plenum, New York, 1972.
34 *Industrial Electrochemistry*, ed. D. Pletcher and F. Walsh, Chapman and Hall, London, 1990.
35 D. Pletcher and N. L. Weinberg, *Chem. Eng.*, 1992, **98–103**(Aug.), 132–141.
36 K. Rajeshwar and J. G. Ibáñez, *Fundamentals and Application in Pollution Abatement*, Academic Press, San Diego, CA, 1997.
37 *Environmentally oriented electrochemistry*, ed. C. A. C. Sequeira, Elsevier, Amsterdam, 1994.
38 P. Tatapudi and J. M. Fenton, in *Advances in electrochemical sciences and engineering*, ed. H. Gerischer and C. W. Tobias, Vol. 4, VCH-Veragsgesellschaft, Weinheim, 1995, p. 363.
39 D. Simonson, *Chem. Soc. Rev.*, 1997, **26**, 181–189.
40 S. Trasatti, *Int. J. Hydrogen Energy*, 1995, **20**, 835–844.
41 A. Kuhn, *J. Appl. Chem. Biotechnol.*, 1971, **21**, 29–64.
42 A. Nilsson, A. Ronlan and V. D. Parker, *J. Chem. Soc., Perkin Trans.*, 1973, **1**, 2337–2345.
43 A. Dabrowski, J. Mieluch, A. Sadkaoski, J. Wild and P. Zoltowski, *Prezm. Chem.*, 1975, **54**, 653–655.
44 L. Papouchado, R. W. Sandford, G. Petrie and R. N. Adams, *J. Electroanal. Chem.*, 1975, **65**, 275–284.
45 R. C. Koile and D. C. Johnson, *Anal. Chem.*, 1979, **51**, 741–744.
46 V. Smith de Sucre, *M.A. Sc. Thesis*, University of British Columbia, (1979).

47 J. Feng and D. C. Johnson, *J. Electrochem. Soc.*, 1990, **137**, 507–510.
48 H. Chang and D. C. Johnson, *J. Electrochem. Soc.*, 1990, **137**, 2452–2457.
49 H. Chang and D. C. Johnson, *J. Electrochem. Soc.*, 1990, **137**, 3108–3113.
50 J. E. Vitt and D. C. Johnson, *J. Electrochem. Soc.*, 1992, **139**, 774–778.
51 J. Feng, D. C. Johnson, S. N. Lowery and J. Carey, *J. Electrochem. Soc.*, 1994, **141**, 2708–2711.
52 S. E. Treimer, J. Feng, M. D. Scholten, D. C. Johnson and A. J. Davenport, *J. Electrochem. Soc.*, 2001, **148**, E459–E463.
53 Ch. Comninellis and E. Plattner, *Chimia*, 1988, **42**, 250–252.
54 N. B. Tahar and A. Savall, *J. Electrochem. Soc.*, 1998, **145**, 3427–3434.
55 Ch. Comninellis and A. De Battisti, *J. Chim. Phys.*, 1996, **93**, 673–679.
56 G. Foti, D. Gandini and Ch. Comninellis, *Curr. Top. Electrochem.*, 1997, **5**, 71–91.
57 O. Simond, V. Schaller and Ch. Comninellis, *Electrochim. Acta*, 1997, **42**, 2009–2012.
58 G. V. Sleptsov, A. I. Gladikii, E. Y. Sokol and S. P. Novikova, *Elektron. Obrab. Mater.*, 1987, **6**, 69–72.
59 M. Grattell and D. W. Kirk, *Can. J. Eng.*, 1990, **68**, 997–1003.
60 J. Naumczyk, L. Szpyrkowicz and F. Z. Grandi, *Water Sci. Technol.*, 1996, **34**, 17–24.
61 O. J. Murphy, G. D. Hitchens, L. Kaba and C. E. Verostko, *Water Res.*, 1992, **26**, 443–451.
62 L. Szpyrkowicz, J. Naumczyk and F. Z. Grandi, *Toxicol. Environ. Chem.*, 1994, **44**, 189–202.
63 G. Rajalo and T. Petrovskaya, *Environ. Technol.*, 1996, **17**, 605–612.
64 N. N. Rao, K. M. Somasekhar, S. N. Kaul and L. Szpyrkowicz, *J. Chem. Technol. Biotechnol.*, 2001, **76**, 1124–1131.
65 J. L. Boudenne, O. Cerclier, J. Galea and E. V. Vlist, *Appl. Catal., A*, 1996, **143**, 185–202.
66 J. L. Boudenne and O. Cerclier, *Water Res.*, 1999, **33**, 494–504.
67 A. M. Polcaro and S. Palmas, *Ind. Eng. Chem. Res.*, 1997, **36**, 1791–1798.
68 J. Manriquez, J. L. Bravo, S. Gutierrez-Granados, S. S. Succar, C. Bied-Charreton, A. A. Ordaz and F. Bedioui, *Anal. Chim. Acta*, 1999, **378**, 159–168.
69 C. S. Hofseth and T. W. Chapman, *J. Electrochem. Soc.*, 1999, **146**, 199–207.
70 V. Smith de Sucre and A. P. Watkinson, *Can. J. Chem. Eng.*, 1981, **59**, 52–59.
71 M. Chettiar, *M.A. Sc. Thesis*, University of British Columbia, (1981).
72 M. Chettiar and A. P. Watkinson, *Can. J. Chem. Eng.*, 1983, **61**, 568–574.
73 D. W. Kirk, H. Sharifian and F. R. Foulkes, *J. Appl. Electrochem.*, 1985, **15**, 285–292.
74 A. M. Polcaro, S. Palmas, F. Renoldi and M. Mascia, *J. Appl. Electrochem.*, 1999, **29**, 147–151.
75 P. G. Keech and N. J. Bunce, *J. Appl. Electrochem.*, 2003, **33**, 79–83.
76 F. Bonfatti, S. Ferro, F. Lavezzo, M. Malacarne, G. Lodi and A. De Battisti, *J. Electrochem. Soc.*, 1999, **146**, 2175–2179.
77 C. A. Martínez-Huitle, S. Ferro and A. De Battisti, *J. Appl. Electrochem.*, 2005, **35**, 1087–1093.
78 C. Bock and B. MacDougall, *J. Electrochem. Soc.*, 1999, **146**, 2925–2932.
79 M. A. Quiroz, S. Reyna, C. A. Martínez-Huitle, S. Ferro and A. De Battisti, *Appl. Catal., B*, 2005, **59**, 259–266.
80 L. L. Houk, S. K. Johnson, J. Feng, R. S. Houk and D. C. Johnson, *J. Appl. Electrochem.*, 1998, **28**, 1167–1177.
81 Ch. Comninellis, *Trans. IChemE, B*, 1992, **70**, 219–224.
82 J. D. Rodgers, W. Jedral and N. J. Bunce, *Environ. Sci. Technol.*, 1999, **33**, 1453–1457.
83 R. Cossu, A. M. Polcaro, M. C. Lavagnolo, M. Mascia, S. Palmas and F. Renoldi, *Environ. Sci. Technol.*, 1998, **32**, 3570–3573.
84 L. Kaba, G. D. Hitchens and J. O'M Bockris, *J. Electrochem. Soc.*, 1990, **137**, 1341–1345.
85 H. Sharifian and D. W. Kirk, *J. Electrochem. Soc.*, 1986, **133**, 921–924.
86 T. Shimamune and Y. Nakajima, *U.S. Pat.*, 5 545 306, 1996.
87 A. Buso, L. Balbo, M. Giomo, G. Farnia and S. Sandonà, *Ind. Eng. Chem. Res.*, 2000, **39**, 494–499.
88 E. Brillas, M. A. Baños and J. A. Garrido, *Electrochim. Acta*, 2003, **48**, 1697–1705.
89 Ch. Comninellis and C. Pulgarin, *J. Appl. Electrochem.*, 1991, **21**, 703.
90 B. Idbelkas and D. Takky, *Ann. Chim. (Paris, Fr.)*, 2001, **26**(2), 33–44.
91 S. K. Johnson, L. L. Houk, J. Feng, R. S. Houk and D. C. Johnson, *Environ. Sci. Technol.*, 1999, **33**, 2638–2644.
92 C. Seignez, C. Pulgarin, P. Péringer and Ch. Comninellis, *Swiss Chem.*, 1992, **14**, 25–30.
93 M. Grattell and D. W. Kirk, *J. Electrochem. Soc.*, 1992, **139**, 2736–2744.
94 L. Marincic and F. B. Leitz, *J. Appl. Electrochem.*, 1978, **8**, 333–345.
95 L. Szpyrkowicz, C. Juzzolino, S. N. Kaul, S. Daniele and M. D. De Faveri, *Ind. Eng. Chem. Res.*, 2000, **39**, 3241.
96 L. Szpyrkowicz, J. Naumczyk and F. Zillio-Grandi, *Water Res.*, 1995, **29**, 517.
97 S. Stucki, R. Kötz, B. Carcer and W. Suter, *J. Appl. Electrochem.*, 1991, **21**, 99–104.
98 S. Tanaka, Y. Nakata, T. Kimura, Yustiawati, M. Kawasaki and H. Kuramitz, *J. Appl. Electrochem.*, 2002, **32**(2), 197–201.
99 M. Grattrell and B. MacDougall, *J. Electrochem. Soc.*, 1999, **146**, 3335.
100 C. Bock and B. MacDougall, *Electrochim. Acta*, 2002, **47**, 3361.
101 C. Bock, A. Smith and B. MacDougall, *Electrochim. Acta*, 2002, **48**, 57.
102 C. C. Ho and C. Y. Chan, *Water Res.*, 1986, **20**, 1523–1527.
103 Y. M. Awad and N. S. Abuzaid, *J. Environ. Sci. Health, Part A*, 1997, **32**, 1393–1414.
104 N. Kannan, S. N. Sivadurai, J. L. Berchmans and R. Vijayavalli, *J. Environ. Sci. Health, Part A*, 1995, **A30**, 2185–2203.
105 C. A. Vincent and D. G. C. Weston, *J. Electrochem. Soc.*, 1972, **119**, 518–521.
106 R. Kötz, S. Stucki and B. Carcer, *J. Appl. Electrochem.*, 1991, **21**, 14–20.
107 C. L. P. S. Zanta, P. A. Michaud, Ch. Comninellis, A. R. De Andrade and J. F. C. Boodts, *J. Appl. Electrochem.*, 2003, **33**, 1211–1215.
108 X. Chen, G. Chen, F. Gao and P. L. Yue, *Environ. Sci. Technol.*, 2003, **37**, 5021–5026.
109 J. Grimm, D. Bessarabov, W. Maier, S. Storck and R. D. Sanderson, *Desalination*, 1998, **115**, 295–302.
110 C. Pulgarin, N. Alder, P. Péringer and Ch. Comninellis, *Water Res.*, 1994, **28**, 887–893.
111 O. Simond and Ch. Comninellis, *Electrochim. Acta*, 1997, **42**, 2013–2018.
112 O. Weres and M. R. Hoffmann, *US Pat.*, 5 419 824, 1995.
113 J. M. Kesselman, O. Weres, N. S. Lewis and M. R. Hoffmann, *J. Phys. Chem. B*, 1997, **101**, 2637–2643.
114 J. R. Smith and F. C. Walsh, *J. Appl. Electrochem.*, 1998, **28**, 1021–1033.
115 G. Chen, E. A. Betterton and R. G. Arnold, *J. Appl. Electrochem.*, 1999, **29**, 961–970.
116 A. Kraft, M. Stadelmann and M. Blaschke, *J. Hazard. Mater.*, 2003, **103**, 247–261.
117 A. Morao, A. Lopes, M. T. Pessoa de Amorim and I. C. Goncalves, *Electrochim. Acta*, 2004, **49**, 1587–1595.
118 A. Perret, W. Haenni, N. Skinner, X. M. Tang, D. Gandini, Ch. Comninellis, B. Correa and G. Foti, *Diamond Relat. Mater.*, 1999, **8**, 820–823.
119 A. M. Polcaro, A. Vacca, M. Mascia and S. Palmas, *Electrochim. Acta*, 2005, **50**, 1841–1847.
120 A. M. Polcaro, A. Vacca, S. Palmas and M. Mascia, *J. Appl. Electrochem.*, 2003, **33**, 885–892.
121 A. M. Polcaro, M. Mascia, S. Palmas and A. Vacca, *Electrochim. Acta*, 2004, **49**, 649–656.
122 B. Boye, P. A. Michaud, B. Marselli, M. M. Dieng, E. Brillas and Ch. Comninellis, *New Diamond Front. Carbon Technol.*, 2002, **12**, 63–72.
123 D. Gandini, Ch. Comninellis, A. Perret and W. Haenni, *IChemE Symp. Ser.*, 1999, **145**, 181–190.

124 D. Gandini, E. Mahe, P. A. Michaud, W. Haenni, A. Perret and Ch. Comninellis, *J. Appl. Electrochem.*, 2000, **30**, 1345–1350.
125 D. Gandini, P. A. Michaud, I. Duo, E. Mahe, W. Haenni, A. Perret and Ch. Comninellis, *New Diamond Front. Carbon Technol.*, 1999, **9**, 303–316.
126 E. Brillas, B. Boye, I. Sires, J. A. Garrido, R. M. Rodriguez, C. Arias, P. L. Cabot and Ch. Comninellis, *Electrochim. Acta*, 2004, **49**, 4487–4496.
127 F. Montilla, P. A. Michaud, E. Morallon, J. L. Vazquez and Ch. Comninellis, *Electrochim. Acta*, 2002, **47**, 3509–3513.
128 G. Lissens, J. Pieters, M. Verhaege, L. Pinoy and W. Verstraete, *Electrochim. Acta*, 2003, **48**, 1655–1663.
129 I. Troster, M. Fryda, D. Herrmann, L. Schafer, W. Haenni, A. Perret, M. Blaschke, A. Kraft and M. Stadelmann, *Diamond Relat. Mater.*, 2002, **11**, 640–645.
130 J. Iniesta, P. A. Michaud, M. Panizza, G. Cerisola, A. Aldaz and Ch. Comninellis, *Electrochim. Acta*, 2001, **46**, 3573–3578.
131 J. J. Carey, J. C. S. Christ and S. N. Lowery, *US Pat.*, 5 399 247, 1995.
132 L. Codognoto, S. A. S. Machado and L. A. Avaca, *J. Appl. Electrochem.*, 2003, **33**, 951–957.
133 L. Gherardini, P. A. Michaud, M. Panizza, Ch. Comninellis and N. Vatistas, *J. Electrochem. Soc.*, 2001, **148**, D78–D82.
134 L. Ouattara, I. Duo, T. Diaco, A. Ivandini, K. Honda, T. N. Rao, A. Fujishima and Ch. Comninellis, *New Diamond Front. Carbon Technol.*, 2003, **13**, 97–108.
135 M. Fryda, D. Hermann, L. Schafer, C. P. Klages, A. Perret, W. Haenni, Ch. Comninellis and D. Gandini, *New Diamond Front. Carbon Technol.*, 1999, **9**, 229–240.
136 M. Panizza and G. Cerisola, *Electrochim. Acta*, 2003, **48**, 3491–3497.
137 M. Panizza and G. Cerisola, *Electrochim. Acta*, 2004, **49**, 3221–3226.
138 M. Panizza, M. Delucchi and G. Cerisola, *J. Appl. Electrochem.*, 2005, **35**, 357–361.
139 M. Panizza, P. A. Michaud, G. Cerisola and Ch. Comninellis, *Electrochem. Commun.*, 2001, **3**, 336–339.
140 M. Panizza, P. A. Michaud, G. Cerisola and Ch. Comninellis, *J. Electroanal. Chem.*, 2001, **507**, 206–214.
141 M. A. Rodrigo, P. A. Michaud, I. Duo, M. Panizza, G. Cerisola and Ch. Comninellis, *J. Electrochem. Soc.*, 2001, **148**, D60–D64.
142 P. Canizares, C. Saez, J. Lobato and M. A. Rodrigo, *Electrochim. Acta*, 2004, **49**, 4641–4650.
143 P. Canizares, C. Saez, J. Lobato and M. A. Rodrigo, *Ind. Eng. Chem. Res.*, 2004, **43**, 1944–1951.
144 P. Canizares, C. Saez, J. Lobato and M. A. Rodrigo, *Ind. Eng. Chem. Res.*, 2004, **43**, 6629–6637.
145 P. Canizares, F. Martinez, M. Diaz, J. Garcia-Gomez and M. A. Rodrigo, *J. Electrochem. Soc.*, 2002, **149**, D118–D124.
146 P. Canizares, J. Garcia-Gomez, C. Saez and M. A. Rodrigo, *J. Appl. Electrochem.*, 2003, **33**, 917–927.
147 P. Canizares, J. Garcia-Gomez, C. Saez and M. A. Rodrigo, *J. Appl. Electrochem.*, 2004, **34**, 87–94.
148 P. Canizares, J. Garcia-Gomez, J. Lobato and M. A. Rodrigo, *Ind. Eng. Chem. Res.*, 2003, **42**, 956–962.
149 P. Canizares, J. Garcia-Gomez, J. Lobato and M. A. Rodrigo, *Ind. Eng. Chem. Res.*, 2004, **43**, 1915–1922.
150 P. Canizares, M. Diaz, J. A. Dominguez, J. Garcia-Gomez and M. A. Rodrigo, *Ind. Eng. Chem. Res.*, 2002, **41**, 4187–4194.
151 R. Bellagamba, P. A. Michaud, Ch. Comninellis and N. Vatistas, *Electrochem. Commun.*, 2002, **4**, 171–176.
152 S. Hattori, M. Doi, E. Takahashi, T. Kurosu, M. Nara, S. Nakamatsu, Y. Nishiki, T. Furuta and M. Iida, *J. Appl. Electrochem.*, 2003, **33**, 85–91.
153 X. Chen, G. Chen and P. L. Yue, *Chem. Eng. Sci.*, 2003, **58**, 995–1001.
154 F. Beck, W. Kaiser and H. Krohn, *Electrochim. Acta*, 2000, **45**, 4691–4695.
155 P. A. Michaud, E. Mahe, W. Haenni, A. Perret and Ch. Comninellis, *Electrochem. Solid-State Lett.*, 2000, **3**, 77–79.
156 Ch. Comninellis, P. A. Michaud, W. Haenni, A. Perret and M. Fryda, *PCT Pat.*, WO 01/25508, 2001.
157 K.-W. Kim, M. Kuppuswamy and R. F. Savinell, *J. Appl. Electrochem.*, 2000, **30**, 543–549.
158 N. E. Jiménez Jado, C. Fernández Sánchez and J. R. Ochoa Gómez, *J. Appl. Electrochem.*, 2004, **34**, 551–556.
159 S. Hofseth and T. W. Chapman, *J. Electrochem. Soc.*, 1999, **146**, 199–207.
160 D. Rajkumar and K. Palanivelu, *Ind. Eng. Chem. Res.*, 2003, **42**, 1833.
161 A. Wang, J. Qu, H. Liu and J. Ge, *Chemosphere*, 2004, **55**, 1189–1196.
162 R. H. de Lima Leite, P. Cognet, A.-M. Wilhelm and H. Delmas, *J. Appl. Electrochem.*, 2003, **33**, 693–701.
163 Y. Xiong, P. J. Strunk, H. Xia, X. Zhu and H. T. Karlsson, *Water Res.*, 2001, **35**, 4226–4230.
164 M. R. V. Lanza and R. Bertazzoli, *Ind. Eng. Chem. Res.*, 2002, **41**, 22–26.
165 M. Grattell and D. W. Kirk, *J. Electrochem. Soc.*, 1993, **140**, 903–911.
166 M. Grattell and D. W. Kirk, *J. Electrochem. Soc.*, 1993, **140**, 1535–1540.
167 Y. M. Awad and N. S. Abuzaid, *Sep. Purif. Technol.*, 2000, **18**, 227–236.
168 Ch. Comninellis and C. Pulgarin, *J. Appl. Electrochem.*, 1993, **23**, 108–112.
169 T. D. Kubritskaya, I. V. Drako, V. N. Sorokina and R. V. Drondina, *Surf. Eng. Appl. Electrochem.*, 2000, **6**, 62–75.
170 M. N. Rabilizirov and A. M. Gol'man, *Khim. Tekhnol. Vody*, 1986, **8**, 87–88.
171 V. Il'in, V. A. Kolesnikov and Yu. I. Parshina, *Glass Ceram.*, 2002, **59**, 242–244.
172 I. A. Zolotukhin, V. A. Vasev and A. L. lukin, *Khim. Tekhnol. Vody*, 1983, **5**, 252–255.
173 R. Nikolaevsky, M. Monosov, E. Monosov, E. Sharony and D. Gurevich, *US pat., 5,792,336*, 1998.
174 N. Djeiranishvili, S. Boutine and G. E. Meerkop, *PCT Int. Appl., WO 9,827,013*, 1998.
175 X. M. Zhan, J. L. Wang, X. H. Wen and Y. Qian, *Environ. Technol.*, 2001, **22**, 1105–1111.
176 D. Rajkumar, J. G. Kim and K. Palanivelu, *Chem. Eng. Technol.*, 2005, **28**, 98–105.
177 S. H. Lin and C. L. Wu, *J. Environ. Sci. Health, Part A*, 1997, **32**, 2125–2138.
178 T. Matsue, M. Fujihira and T. Osal, *J. Electrochem. Soc.*, 1981, **128**, 2565–2569.
179 E. Brillias, R. M. Bastida and E. Llosa, *J. Electrochem. Soc.*, 1995, **142**, 1733–1741.
180 E. Brillias, E. Mur and J. Casado, *J. Electrochem. Soc.*, 1996, **143**, L49–L53.
181 E. Brillias, R. Sauleda and J. Casado, *J. Electrochem. Soc.*, 1997, **144**, 2374–2379.
182 E. Brillias, R. Sauleda and J. Casado, *J. Electrochem. Soc.*, 1998, **145**, 759–765.
183 E. Brillias, E. Mur, R. Sauleda, L. Sanchez, F. Peral, X. Domenech and J. Casado, *Appl. Catal., B*, 1998, **16**, 31–42.
184 S. Stucki, H. Baumann, H. J. Christen and R. Kotz, *J. Appl. Electrochem.*, 1987, **17**, 773–778.
185 W. El-Shal, H. Khordagui, O. El-Sebaie, F. El-Sharkawi and G. H. Sedahmed, *Desalination*, 1991, **99**, 149–157.
186 D. Dobos, *Electrochemical Data*, Elsevier Scientific Publishing Company, Amsterdam-Oxford-New York, 1975.
187 P. Vaudano, E. Plattner and Ch. Comninellis, *Chimia*, 1995, **49**, 12–16.
188 J. C. Farmer, F. T. Wang, R. A. Hawley-Fedder, P. R. Lewis, L. J. Summers and L. Foiles, *J. Electrochem. Soc.*, 1992, **139**, 654–662.
189 J. C. Farmer and F. T. Wang, *IChemE Symp. Ser.*, 1992, **127**, 203–214.
190 R. G. Hickman, J. C. Farmer and F. T. Wang, *ACS Symp. Ser.*, 1993, **518**, 430–438.
191 F. Bringmann, K. Ebert, U. Galla and H. Schmieder, *J. Appl. Electrochem.*, 1995, **25**, 846–851.
192 V. Cocheci, C. Radovan, G. A. Ciorba and I. Vlaiciu, *Rev. Roum. Chim.*, 1995, **40**, 615–619.
193 A. Paire, D. Espinoux, M. Masson and M. Lecomte, *Radiochim. Acta*, 1997, **78**, 137–143.
194 M. Abdel Azzem and E. Steckhan, *Heterocycles*, 1990, **31**, 1959–1965.

195 L. W. Gray, R. G. Hickman and J. C. Farmer, *Solvent Substitution, Annu. Int. Workshop Solvent Substitution, 1st*, 1990, 281–284.
196 J. C. Farmer, F. T. Wang, P. R. Lewis and L. J. Summers, *J. Electrochem. Soc.*, 1992, **139**, 3025–3029.
197 Y. H. Chung and S. M. Park, *J. Appl. Electrochem.*, 2000, **30**, 685–691.
198 W. K. Choi, K. W. Lee, Y. M. Kim, B. G. Ahn and W. Z. Oh, *J. Nucl. Sci. Technol.*, 2000, **37**, 173–179.
199 C. M. Goncea, *Rev. Chim. (Bucharest)*, 2000, **51**, 896–897.
200 I. S. Vasil'eva, V. L. Kornienko and G. A. Kolyagin, *Khim. Interesakh Ustoich. Razvit.*, 2001, **9**, 529–532.
201 C. M. Goncea, *Rev. Chim. (Bucharest)*, 2002, **53**, 251–252.
202 I.-S. Kim, S.-W. Choi, C.-D. Heo and S.-C. Park, *Kongop Hwahak*, 2002, **13**, 33–36.
203 Z. Sun, X. Hu and D. Zhou, *TheScientificWorldJOURNAL [electronic resource]*, 2002, **2**, 48–52.
204 C. M. Goncea, *Rev. Chim. (Bucharest)*, 2003, **54**, 963–964.
205 C. M. Goncea, *Rev. Chim. (Bucharest)*, 2003, **54**, 643–644.
206 S.-C. Park and I.-S. Kim, *Kongop Hwahak*, 2005, **16**, 206–211.
207 K. Scott, *IChemE Res. Event, Two-Day Symp.*, 1994, **1**, 344–346.
208 K. Scott, *Proc. Electrochem. Soc.*, 1994, **94**, 51–64.
209 S. D. Fleischmann and R. A. Pierce, US-Report WRSC-MS- 91-192, 180th Meeting of The Electrochemical Society, Phoenix Arizona, 1991.
210 F. Steele, *Platinum Met. Rev.*, 1990, **34**, 10–14.
211 U. Leffrang, K. Ebert, K. Flory, U. Galla and H. Schmieder, *Sep. Sci. Technol.*, 1995, **30**, 1883–1899.
212 *CRC Handbook of Chemistry and Physics*, ed. R. D. Lide, CRC Press, 73rd edn, 1992–1993, p. 17–27.
213 W. J. Plieth, in *Encyclopedia of Electrochemistry of the Elements*, ed. A. J. Bard, Marcel Decker Inc., New York, 1978, Vol. 8, p. 440.
214 J. Bringmann, K. Ebert, U. Galla and H. Schmieder, *J. Appl. Electrochem.*, 1997, **27**, 870–872.
215 J. Bringmann, K. Ebert, U. Galla and H. Schmieder, *J. Appl. Electrochem.*, 1995, **25**, 846–851.
216 J. Bringmann, K. Ebert, U. Galla, U. Leffrang and H. Schmieder, *ASME Heat Transfer Division*, 1995, **HTD-Vol. 317–2**, IMECE 289–297.
217 L.-C. Chiang, J.-E. Chang and T.-C. Wen, *Water Res.*, 1995, **29**, 671–678.
218 C.-C. Sun and T.-C. Chou, *Ind. Eng. Chem. Res.*, 1999, **38**, 4545–4551.
219 A. S. Vaze, S. B. Sawant and V. G. Pangarkar, *J. Appl. Electrochem.*, 1999, **29**, 7–10.
220 G. A. Bogdanovskii, T. V. Savel'eva and T. S. Saburova, *Russ. J. Electrochem.*, 2001, **37**, 865–869.
221 N. S Abuzaid, Z. Al-Hamouz, A. A. Bukhari and M. H. Essa, *Water, Air, Soil Pollut.*, 1999, **109**, 429–442.
222 J. Iniesta, J. Gonzalez-Garcia, E. Exposito, V. Montiel and A. Aldaz, *Water Res.*, 2001, **35**, 3291–3300.
223 A. G. Vlyssides, P. K. Karlis and G. Mahnken, *J. Appl. Electrochem.*, 2003, **33**, 155.
224 M. Panizza and G. Cerisola, *Environ. Sci. Technol.*, 2004, **38**, 5470–5474.
225 Joint Service Pollution Prevention Opportunity Handbook, the Naval Facilities Engineering Service Center (http://www.p2library.nfesc.navy.mil/P2_Opportunity_Handbook).
226 M. Steensen, Removal of non biodegradable organics from leachate by chemical oxidation, *Proceedings Sardinia 93, Fourth International Landfill Symposium*, CISA publisher, Cagliari, vol. I, 945–958, (1993).
227 http://www.cerox.com.
228 V. M. Bakhir, S. A. Panicheva and Y. G. Zadorozhni, *US Pat.*, 6 843 895, 2005.
229 http://www.vbinstitute.ru/.