ELECTROCHEMICAL APPROACHES TO ENVIRONMENTAL TREATMENT AND RECYCLING

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Keywords: batteries, decolorization, electrochemical de-halogenations, electrochemical methods, electrosynthesis, electro-osmosis, electro-remediation, electro-coagulation, electrodialysis, flow cells, fuel cells, metal recovery, oxidation of organics, recycling, redox flow cells, reduction of organics, soil remediation, supercapacitors.

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Summary

Important advances in electrochemical engineering technology over the last three decades have fostered the development of alternative methods to alleviate and prevent the generation of pollutants which damage the environment. The feasibility of zero emission of pollutants during production processes was envisaged over 30 years ago. In practice, this strategy is difficult to achieve and technologies to minimize and to convert pollutants into environmentally harmless sub-products are a more realistic and feasible option. In this article, the advantages and limitations of advanced electrochemical technologies are considered. Such technologies include waste-water treatment and metal ion recovery together with direct and indirect methods for oxidation of organic compounds. Electrochemical technologies have also contributed to methodologies for the elimination of noxious gases such as carbon dioxide, nitrous oxides and sulfur dioxide. Electrochemical methods are also useful in the treatment of metal- and organic contaminated soils. This article also summarizes the generation of clean energy from fuel cells which has achieved worldwide recognition as an alternative source of energy for transportation vehicles. Several fuels including hydrogen, methanol and hydrocarbons have been proposed in the open literature but hydrogen/oxygen fuel cells are amongst the most advanced systems at the present time. Electrochemical technologies are also proposed for electricity storage generated in power plants and renewable sources of energy during periods of low demand. This stored energy can then be used during peak periods of high demand. Such an approach avoids wastage of energy in power plants and reduction of greenhouse gas emissions.

1. Introduction

In 1990, the countries forming the Organization for Economic Co-operation and Development (OECD) produced 1430 million tonnes of industrial waste corresponding to 68 % of the world's industrial waste and approximately 90 % of the hazardous and special waste. This amount increased to 1930 tonnes in the year 2004. Most statistics predict an increase of 40-60 % in pollution generated from chemical processes over the next decade. The contribution of the chemical industry to the overall worldwide pollution is considerable but in general it is overestimated in comparison to the pollution caused by industries dominating other areas of everyday need, for instance, energy production by fossil fuels burning, transportation and agriculture. In the light of new evermore stringent and more rigidly enforced environmental regulations, the following guidelines should be implemented by the chemical industry in the 21st century and beyond: (1) avoid and minimize waste, as a priority, (2) eliminate, recover and recycle waste, (3) achieve ecological acceptable and benign waste disposal, (4) significantly lower pollutant generation and power in chemical process industry (CPI), e.g. by using fuel cells which are essentially pollution-free as no combustion of fossil fuels is involved and (5) clean energy generation and storage.

The United Nations Environment Programme (UNEP) defines cleaner production as involving "the continuous application of an integrated preventive environmental strategy to processes and products to reduce risks to humans and the environment". Many options exist in the waste-management hierarchy including; source reduction, recycle and reuse, end of-pipe treatment and suspension of production.

Throughout the chemical process industries, there has been an overwhelming tendency to focus on end-of-pipe treatments to meet environmental regulations. For example, in a high yield process for the production of organic dyes, one tonne of by-products and auxiliaries such as solvents and catalysts may arise per one tonne of finished dye. The waste is either dumped or treated at the end of the process together with waste from other processes. The traditional approach to waste-water treatment by centralizing the waste streams according to the slogan "dilution is the solution of pollution" is not longer acceptable (ocean dumping is becoming a serious concern). The practice of precipitating metals as hydroxides, carbonates or sulfides which are dumped in landfills, together with poorly soluble organics, such as printed circuit boards (PCBs) is unacceptable for environmental and economical reasons. These "postponing" methodologies offer little scope for recovering valuable process materials and are merely a transfer of waste from one environmental medium to another, often in a highly diluted form. A potential problem in wastewater is the number of pharmaceutical compounds and their degradation products, being detected in the environment. Their concentration levels in sewage treatment plants effluents, surface water, sea water and groundwater are still in the order of $\mu g\ L^{-1}$ but their effects on humans and animal life are largely unknown. It is suspected that continuous exposure to compounds known as endocrine disruptive chemicals (EDCs) such as pharmaceuticals but also surfactants, pesticides and brominated flame retardants can have effects on reproduction and cancers. More than 100 tons per year of antibiotics and anti-inflammatory drugs are used in the European Union. The approximate amounts of some pharmaceutical products used in Germany in 2001 for example were: 830 tonnes of acetylsalicylic acid, 620 tons of paracetamol, 340 tonnes of ibuprofen, 85 tonnes of diclofenac and 86 tonnes of carbamazepine. The quantities are high and further work is required to understand their disposal pathways but it is clear that advanced oxidation treatments are required for their complete degradation.

The ideal pollution control strategy is to recover, recycle, and reuse substances before they become pollutants. For example, electrolytic regeneration of Na_2SO_4 by electrodialysis, instead of disposing of it as waste in landfills or discharged to deep-wells or water bodies - offers industry the capability to reduce or eliminate plant discharge while generating caustic soda and sulfuric acid which can be sold or returned to the process closing the loop.

The first priority for the chemical industry must be to avoid wastes, preferably by using clean production techniques (zero/low effluent technologies), minimal amounts of chemicals, water and energy.

Zero discharge has been a long-time goal for firms in the chemical process industries but few organizations have actually achieved it. In fact, many view it as unattainable.

Zero discharge is not a compelling goal for most CPI. Even if zero discharge could be achieved it would involve high costs and environmental problems for others. Discharging a weak solution of salt, free of toxic materials, may be more environmentally safer than zero discharge as many solid salts cannot be eliminated (e.g. landfill may be used) without some form of encapsulation. Waste-water discharge permits bear enormous paperwork requirements and harsh enforcement penalties. A zero discharge strategy can avoid these problems.

Recent environmental damage laws and case law practice, in some member states of the European Community, show a clear tendency towards making the polluter liable, regardless of whether or not the action was unlawful. The risk of damage is being allocated to the perpetrator, because the perpetrator is supposed to be in control of professional activities and be able to influence their effects. The overall concept of zero effluent is, however, only likely to be viable if the chemical industry has available a range of core technologies able to convert feed stocks into products without significant by-products. Elimination of pollutants at their source can be expensive or technically impossible. Often a preferred option is to add an "end-of-pipe" operation to change the pollutant that facilitates recycling or safe disposal. This is certainly less satisfactory in the long term because it tends to minimize rather than prevent pollution.

A significant reduction in hazardous waste remains elusive. Major chemical producers cite 49 % decrease in total release and transfers since 1989 to probe that pollution preservation has taken hold. However, recent evidence points to a disturbing trend. Despite measurable improvements in waste managements, total waste production may actually be increasing. Figure 1 shows the trend of municipal waste reported from 1995 and the forecast to 2020 in different regions of the world. The graph shows that waste generation increased steadily over the years and that in 2010 and 2020 the increase will be 32 % and 51 %, respectively, in comparison to the waste generated in 1995.

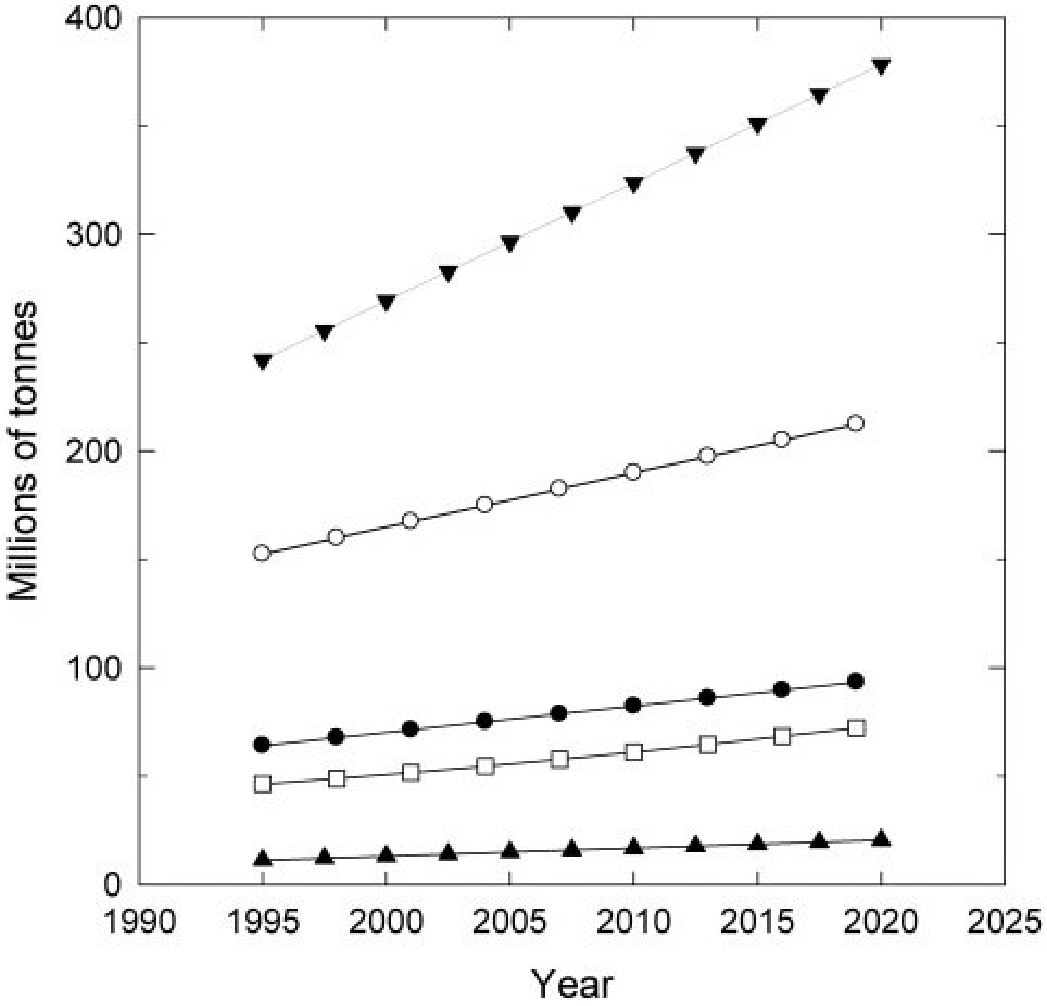

Figure 1 Comparison of municipal waste in different regions of the world over 25 years. ▼) Canada, USA and México, ○) Western Europe, ●) Japan and Korea, □) Central and Eastern Europe, ▲) Australia and New Zealand. Source: OECD.

Recycling has been increasing in some industries, e.g. in the battery industry. More than 350 million per year rechargeable batteries are purchased in the USA but the non-profit rechargeable battery recycling corporation RBRC, only collected over 4 million batteries between USA and Canada in 2003 which represented an increase of 22 % compared to 2002. Cadmium has been recovered from used NiCd batteries, alloys and dust from electric arc furnaces (EAF) typically containing 0.003 % to 0.07 % cadmium. Cadmium is one of the 11 bioacumulative toxic pollutants and the European Union proposed to eliminate all NiCd batteries containing more than 0.002 % cadmium by January 2008. Lithium recycling is still very insignificant but a USA recycling company has produced a small quantity of lithium carbonate from solutions recovered from recycling lithium batteries.

2. Electrochemical Processes for Water Treatment and a Cleaner Environment

Electrochemical technologies often escape discussion in monographs on environmental protection or in overview articles. Such methods for environmental applications are not completely new, for example anodic oxidation for wastewater treatment was first mentioned as early as 1890. The potential for electrochemical techniques in environmental control, pollution avoidance and clean energy conversion has attracted more attention in the last four decades, due to the availability of a large range of commercial, off-the-shelf electrochemical cells, better understanding of the ongoing electrode processes and the stronger development of education and training in electrochemical science and technology.

The Journal of the Electrochemical Society has suggested the following "environmental issues" for a cleaner and non-waste production processes: wastewater treatment, metal recovery, destruction of organic pollutants and on-site production of chemicals to reduce incidents during transport.

The electron as a reagent avoids the use of additional chemicals and simplifies subsequent recovery, recycling or disposal of treated solutions. The wide applicability of the electrochemical processes in its preventive mode (electrosynthesis) and in the curative mode (elimination, recovery, recycling) in the process industry derives from the fact that electrons can, unlike standard chemicals, readily be removed (oxidation) or added (reduction). This can be achieved by using electrode materials that are not easily oxidized or reduced and inert electrolytes that can withstand electrode potentials up to ± 3V *vs.* SCE. Reduction can be performed with a power equal to or better than that associated with sodium or lithium metals in amine solvents and oxidations at the chemical fluorine level. The electron is cheap, very pure and versatile reagent. Prices of various redox reagents and comparison of the costs of various chemical reactants used in the oxidative destruction of organic compounds are shown in Table 1.

Reagent	**£ per tonne equivalent**
Electron	8
Iron powder	27
Zinc dust	29
Sodium borohydride	59
Potassium permanganate	95
Sodium dichromate	164
Lithium aluminium hydride	417

Table 1 Approximate comparison of the price for various redox reagents.

The advantages of using electrons as reagent to produce chemical changes are: i) the cost competitive situation with respect to alternative processes, ii) selective chemistry, iii) broad applicability, iv) less pollution than most competing processes, v) lower temperature requirements than those of equivalent counterparts, especially high temperature techniques, vi) the required equipments and operations are generally simple and, if properly designed, inexpensive as compared with conventional technologies and vii) the main electrochemical parameters, current (I) and potential (E), are particularly suited for data acquisition, process automation and control.

Electrochemistry is moving fast from traditional roles in the chlor-alkali and aluminium plants to specialist chemical production in the preventive mode, recycling and cleaning-up in the curative mode. Thus electrochemistry can be a real alternative to many hazardous, difficult and expensive processes in a broad range of industries. It is likely that electrochemistry will play a more important role in the development of cleaner and more efficient processes in all industries which manufacture or use chemicals as it can contribute to the solution of environmental challenges.

Properly designed electrochemical processes should not introduce hazards of their own, although, accidental formation of H_2/O_2 or H_2/Cl_2 mixtures or of noxious gases such as H_2S, AsH_3, CCl_4, SbH_3 or NO_x can be a significant risk. Electrochemistry can deal with many pollutants: gases, liquids and solids, and can treat from milliliters to million of liters. The scope for electrochemistry in pollution avoidance, control and recycling is summarized in Table 2.

Process, methodology	**Example of application**
Metal ions	(Used as catalysts, complexants, mediators, wear-off, etc): removal, recovery, recycling
In-situ (*in-cell*, *ex-cell*) generation and regeneration of inorganic: Organics	Ce(IV)/Ce(III), Sn(II)/Sn(IV), Mn(II)/Mn(III)/Mn(IV), Pb(II)/Pb(IV) e.g. violanthrones
Redox reagents Direct, indirect degradation and destruction of harmful organics:	Phenols, polychlorinated aromatics
Decolourization of wastewaters,	Effluents from dyestuff production plants, dye houses, sugar mills
Deodorisation of effluents, wastewaters,	Nitrotoluene, to remove a nuisance
Desinfection of waters	Cl_2, OCl^-, O_3, O^-, H_2O_2
Removal of noxious gases	H_2S, SO_2, NO_X
Concentrating and separating process streams using membrane processes	Via electrodialysis and electrochemical ion exchange without the use of additional chemicals

Table 2 The scope for electrochemistry in pollution control and recycling.

Electrochemistry also offers approaches for the controlled *in-situ* manufacture of inorganic and organic chemicals, for instance, the electrochemical generation on-site of chemicals such as hypochlorite Ce(IV), N_2O_5, H_2O_2 and O_3 on a safe electrochemical cell rigs such as the ElectroCell Systems AB or the FM01-LC electrochemical cells.

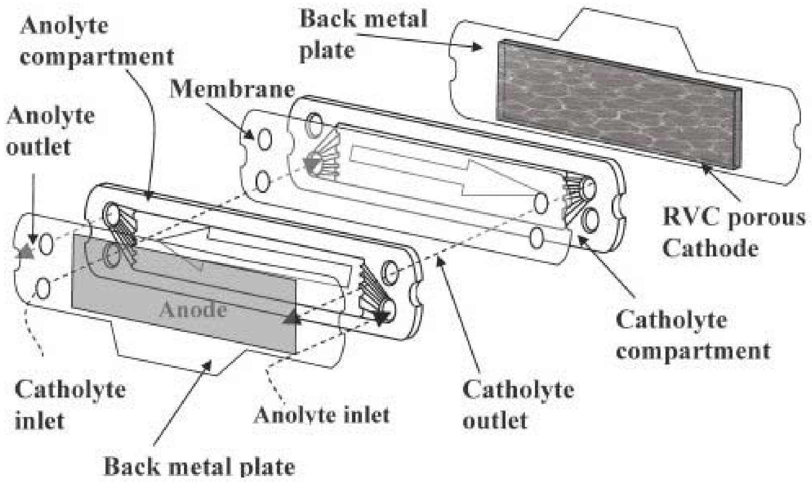

Figure 2 FM01-LC electrochemical cell with a three-dimensional reticulated vitreous (RVC) cathode separated from the anode by a cationic membrane.

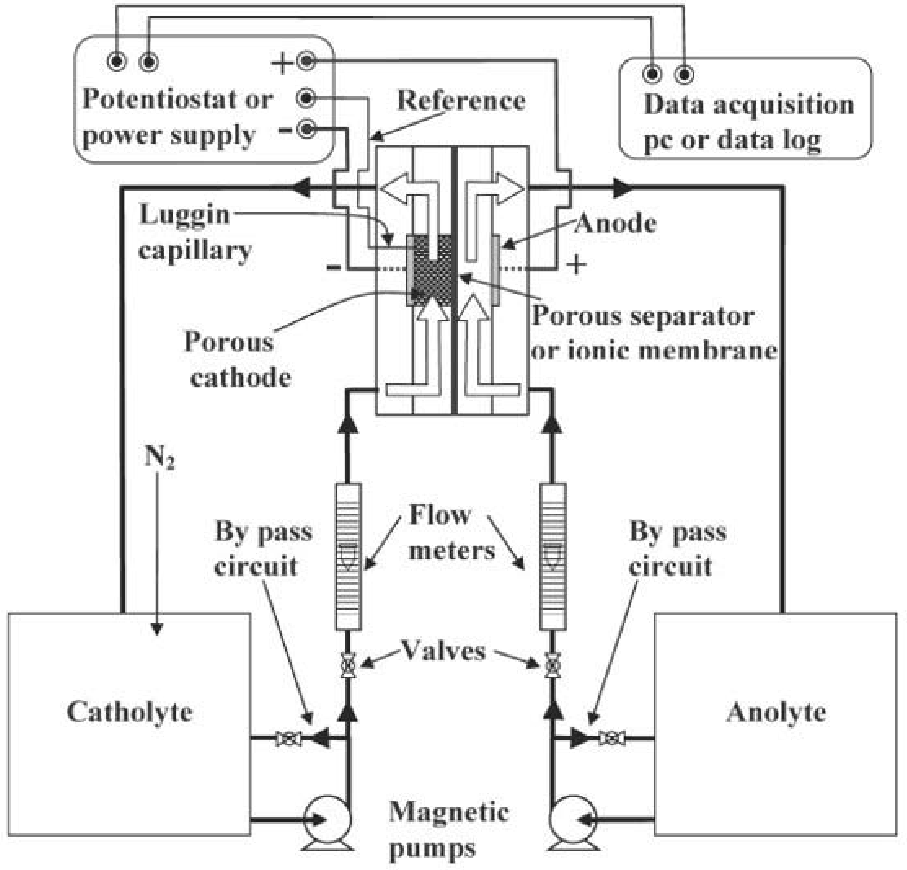

Figure 3 Typical flow system used for metal ions removal and oxidation of dissolved organic compounds.

Hazards associated with storage and transportation is thus avoided while producing highly active species *in-situ* at a controlled rate. Figure 2 shows a typical laboratory flow electrolyser, the FM01-LC electrochemical flow cell which has been used for organic or inorganic electrosynthesis and in waste-water treatment such as metal recovery and organic oxidation. The cell consists of catholyte and anolyte compartments containing cathode and anode electrodes, respectively, divided by a micro porous separator or by an ion-exchange membrane. To maximize the average space yield of the cell, three dimensional electrodes, such as reticulated vitreous carbon (RVC), carbon felt, reticulated nickel or reticulated copper foams can be used. Figure 3 shows a typical arrangement of electrolyte and electronic circuits used for the recovery of metal ions and oxidation of organic compounds. The example shows the cell fitted with a porous electrode and the electrolyte flowing perpendicular to the current flow that is in a flow-by configuration. This type of set up is popular in electrochemical engineering because it facilitates adjustment of the electrolyte while the process is running, sample collection and scale-up of the system.

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Biographical Sketches

Pierre M. Bersier holds a Ph.D. (inorganic chemistry) from the University of Bern (1958-1962). He has a long experience of electrochemical methods following a research career which has involved many developments in chemical analysis, particularly for environmental applications. His early career (1962-1967) included research on potentiometry and polarographic assays at the Siemens Schuckert Research Laboratory in Erlangen. A substantive part of Pierre Bersier's career was spent in the Central Research Laboratories of Ciba-Geigy, Basle, where his responsibilities involved electrochemical and thermochemical analysis and the development of methods for research, development and production covering inorganic, metal organic and organic compounds. From the mid 1960s, Pierre Bersier specialised in effluent treatment (metal elimination and recovery, decolorisation of dye-stuffs and bench-scale synthesis (1967–1991). Since the early 1990s, he has acted as a consultant to organisations such as Electrocell AB, Täby, Sweden in the subject areas of electroanalysis and electrolytic processes. Pierre Bersier has over 35 scientific papers and has presented numerous lectures in Europe, USA, Canada, Japan, Argentina and Chile.

Carlos Ponce de León holds B.Sc. and M.Sc. degrees in chemistry from the Autonomous Metropolitan University; México together with a Ph.D. in electrochemistry and electrochemical engineering from the University of Southampton (1994). He has industrial experience in quality control (Schering/Proquina), data acquisition and fuel cells (Mexican Petroleum Institute) together with analytical chemistry (Ciba-Geigy). His research interests have developed through postdoctoral research periods spent in México and at the University of Bath, UK. His research interests include electrochemical techniques, metal ion removal, the characterization of novel electrode materials, electrochemical strategies for pollution control and redox flow cells for energy conversion, resulting in more than 30 scientific papers. Carlos Ponce de León is currently a Lecturer (Energy Technology) in the School of Engineering Sciences at the University of Southampton, UK.

Frank Walsh holds the degrees of B.Sc. (Applied Chemistry), M.Sc. (Materials Protection and Ph.D. (Electrochemical Engineering) following periods of study at from the Universities of Portsmouth, UMIST and Loughborough. He has held the academic positions of Research Fellow (Southampton), Lecturer in Chemical Technology (Strathclyde) Senior Lecturer/Reader/Professor and Head of the Department of Pharmacy & Biomedical Sciences (Portsmouth). His previous position was Head of the Chemical Engineering Department at the University of Bath. Frank has over 20 years industrial experience of electrochemical reactor design gained via consultancy assignments and direct industrial projects. He has published and presented over 250 papers and three text books in aspects of electrochemical engineering and surface finishing of metals. Frank Walsh and colleagues have been awarded the Westinghouse Prize (Institute of Metal Finishing, 1998) for studies on electrochemical deposition and characterization of metallic coatings, the Breyer Medal (Royal Australian Chemical Institute, 2000) for international contributions to electrochemical science and engineering and the Johnson Matthey Silver Medal (Institute of Metal Finishing, 2007) for precious metal deposition. Frank is currently a Professor in Electrochemical Engineering at the University of Southampton, UK where he directs the Electrochemical Engineering Laboratory.