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Can Electrochemistry Make the Worlds Water Clean? – A Systematic and Comprehensive Overview

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Abstract

Water the generous gift of nature is sure to become scarce unless the ever growing population is enlightened enough in handling the increasing stress and to avoid the crisis due to the expanding demand on this precious commodity. Management of water and its resources by conservation and its judicious use help to preserve the available water. Even then, whether it is from surface or underground sources, it has become impossible to obtain good quality water for human consumption. Thus, the dwindling quantity and lessening quality of water require effective steps to be taken urgently for the sustenance of the living being of today and tomorrow.

What this glass of water contains? worries one before he starts quenching his thirst. The extent of water contamination is so much and so varied that organic, inorganic and biological impurities are present in the water due to natural as well as induced reasons. The responsibility fell on the scientists and engineers to provide appropriate technologies help not only to remove the contaminants but also to treat at the user end.

The conventional processes for pollution abatement are either physico-chemical or biological. The physicochemical methods aim at shifting the pollutants (land fill), concentrate the pollutant (adsorption), transfer the pollutant to another medium (air stripping) or cause secondary pollution (chemical precipitation leading to sludge). Biological techniques require narrow range of operating conditions. Electrochemistry provides technologies that have definite advantages than the above conventional methods.

Electrochemical methods are versatile and offer not only clean but also cleaning technologies. The utility of electrochemical environmental techniques are expanding with the understanding and development of electrochemical engineering that led to design and development of novel electrodes and cell structures. The invention and large scale availability of improved polymeric and perfluorinated ionomers membranes have totally changed the purification and separation processes. Electrochemical analytical and sensing techniques are playing an important role in pollution control.

Water quality up-gradation by electrochemical technique presents various alternatives, such as anodic, cathodic, direct and indirect methods to treat any type of contaminants in water and waste water. These methods, at the point of entry of pollutants into the environment, help not ony to remove the contaminant but also to recover and recycle useful chemicals. The electro-remediation of contaminated soil is, now, a proven and viable technology to prevent the pollution of water at the point of contamination itself.

In this paper, the environmental applications of electrochemistry and some of the important and recent developments in the electrochemical methods of water and effluent treatment are reviewed. Electrochemical processes for decontamination of water from ions developed by CSIR-CECRI are also briefly described.

Keywords: Landfill; Sludge; Electrodialysis

Introduction

Water crisis has become a part of our life. This is not altogether due to shortage of rain fall. Increasing population, growing industrialization, expanding urbanization, agriculture etc. demand more and more water. Coping up with these developments requires various tactics to overcome the water shortage and satisfy the need of all. The main activity in this direction is to decrease the pollution level of discharged effluents and treatment of contaminated water to acceptable quality. Conventionally, water purification methods involve physicochemical separation of contaminants or biological treatment. The physicochemical methods aim at shifting the pollutants (landfill), concentrate the pollutants (adsorption), transfer the pollutant to another medium (air stripping) or cause secondary pollution (chemical precipitation leading to sludge). Biological technologies require narrow range or operating conditions.

In this context, the role of electrochemistry to environmental applications is expanding due to the characteristics of electrochemical processes viz., versatility, energy efficiency, environmental compatibility, cost effectiveness [1-4]. The growth of electro catalysts and electrochemical engineering in the past two decades has made a total revolution in the electrode and cell design technologies that are

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particularly important for water and effluent treatment. In this review, brief accounts of a few successful electrochemical technologies are presented.

Electrochemical Water Treatment Processes

Electrochemical technologies for environmental applications can be broadly divided two categories viz., physical (eg. electro-dialysis, electrocoagulation and electro-flotation) and chemical involving direct reaction at the electrode or an indirect reaction with a reagent generated electrolytically [5-9].

Electro-dialysis

Electro-dialysis (ED) is a membrane based process involving the separation and concentration of electrolytes (dissolved salt concentration) by the electro-migration of the species through ion exchange membranes [10]. Anion and cation exchange membranes are arranged alternatively between two electrodes which enable ions to pass through one type of membrane while the other membrane blocks the passage thus creating a set of "concentrating" cells and "dilution/purification" cells. Cellulose acetate membranes are conventionally used in ED stacks and polysulfone, polyacrylonitrie and polyfluorosulphonic acid type membranes are some of the new membranes presently in use. The water to be purified is circulated through the dilution compartment and the dissolved salts get concentrated in the stream through the concentration compartment (Figure 1).

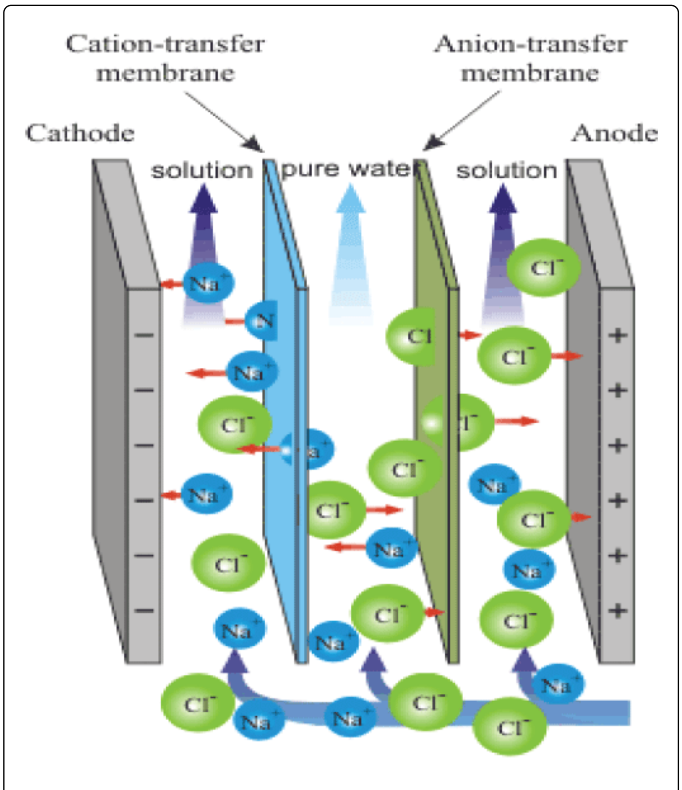

Figure 1: The working principle of electrodialysis system.

The electrodialysis process has important applications: (i) production and supply of potable water from brackish water (with typical salt concentration of 1000-3000 mg/L0, (ii) recovery and recycling of metal ions such as in plating industry effluents fo water recycling, (iii) salt removal from industrial effluents for water recycling, (iv) removing electrolytes from non-electrolytes and (v) salt splitting for eg., in the recovery of NaOH and H_2SO_4 (this require one pair of electrode for each pair of membrane). Brackish water ED systems can operate over wide pH range and upto 43°C (denpending on the membrane type) at a typical energy consumption of 1.6-2.6 kWh/m^3 of purified water.

Electroflotation and electrocoagulation

Electroflotation is a process in which the gases generated at an electrode (O_2 and H_2) forces the suspended impurities to the top of the solution where they are collected and removed [11-15]. This effect is partly by the neutralization of charge on the colloidal particles by virtue of their proximity of the electrodes and partly because of the tiny gas bubbles generated at the electrode. The ratio of the bubble to the suspended particles must close to unity for effective electro-flotation and pulsed electro-generation of bubbles and reported to yield bubbles of optimum size. Alum is conventionally used as a coagulant instead, if Al^{3+} or Fe^{2+} ion is produced at the anode, these can react with the hydroxides produced at the cathode generating aluminum or ferric hydroxide that will precipitate adsorbing the pollutant. This process is known as the electrocoagulation. The hydroxide precipitate thus produced has been found to be more effective than chemically produced hydroxides and also electrocoagulation produces more compact sludge. These two processes when combined are reported to result in 99% removal of suspended matter, 99% reduction of chemical oxygen demand, 91% reduction in biological oxygen demand, 100% removal of inorganic contaminates and 100% decoloration (Figure 2).

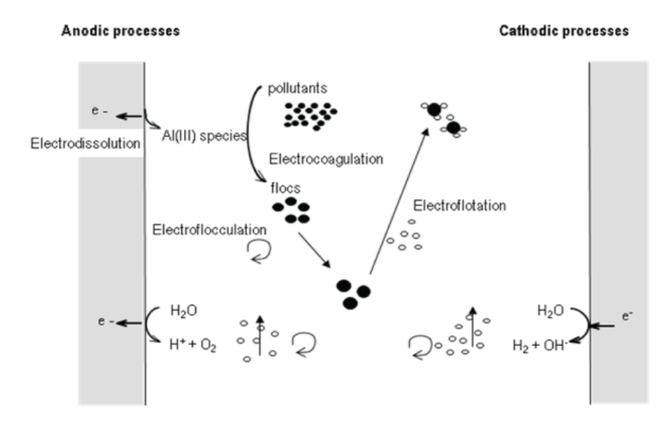

Figure 2: The working principle of electrocoagulation process.

Direct electrochemical processes

In an electrochemical cell the anodic reaction is oxidation (dissolution in the case of soluble anodes) and cathodic reaction is reduction. Under appropriate conditions, these two reactions can be effectively exploited to removal of pollutants from water or effluents [16].

Anodic processes

Cyanide destruction is an important example of direct electrochemical oxidation used for effluents from electroplating industry. The process is more suitable for effluents with high cyanide concentration. In this process, the cyanide is oxidized to cyanate which is much less harmful. The cyanate then rapidly reacts with the alkali generated at the cathode to produce NH_4HCO_3, Na_4CO_3 and NH_4OH. The oxidation of Cr^{3+} to Cr^{6+} is commercially adopted for the recycling of the pharmaceutical, electronic and aerospace industries. The oxidation is carried out at a lead-dioxide anode and continuous flow cells with Nafion membranes to separate the anolyte and catholyte are in use.

Cathodic processes

The permissible metal ion concentration in water and effluents are in the range of 0.02 to 5 mg/L, whereas water from various sources contain unacceptable levels of metallic impurities. The reduction of these metal ions to their elemental state by electrochemical deposition is a convenient and cheap method for purification. The metals are deposited in the strippable form so that they can be recovered as a saleable product. For solutions of fairly low concentrations, electrolysers with two dimensional and three dimensional electrode structures and a variety of mass transfer enhancement methods have been developed and successfully operated. Thus processes for removal and recovery of copper, lead, mercury, zinc, silver, chromium etc., are in practice. The toxicity of polychlorinated biphenyl wastes by cathodic reduction is a new process to remove the chlorine and generate the parent compounds which is less energy intensive than complete oxidation.

Indirect electrochemical processes

Direct electrochemical oxidation or reduction may not be possible in certain cases due to limitations of the required potential for driving the desired reaction. Under these circumstances it is advisable to identify a suitable reversible or irreversible redox system that can be efficiently generated and allowed to react with the pollutant. Examples of such redox pairs are: Fe^{2+}/Fe^{3+}, Mn^{2+}/Mn^{3+}, Ag^{2+}, Cl^-/ClO^- etc., These reactions can be made to occur *in-situ* in the electrolytic cell itself by maintaining a low concentration of the reactant redox intermediate or externally, by generating high concentration of the reactant in an electrochemical cell and reacting in an external reactor with the effluent to be treated (Figure 3).

The generation of short lived intermediates such as hydroxyl radical, peroxide ion, hydro-peroxide radical, is another area of electrochemical treatment for the destruction of toxic chemicals. The oxidation of phenols and discoloration of dye effluents at tin-oxide electrode involves the generation of OH^-. This is produced by reduction of hydrogen peroxide with Fe^{2+}. With this system, oxidation of substituted benzene derivatives, formaldehyde and cyanide has been effectively carried out.

Apart from these, electrochemical pH adjustment is an efficient and cheap method of neutralization of acid and alskline waters and effluents which simultaneously help in precipitating certain metal ions such as iron, calcium, chromium, magnesium etc., without the need of any external chemicals addition (Figure 3).

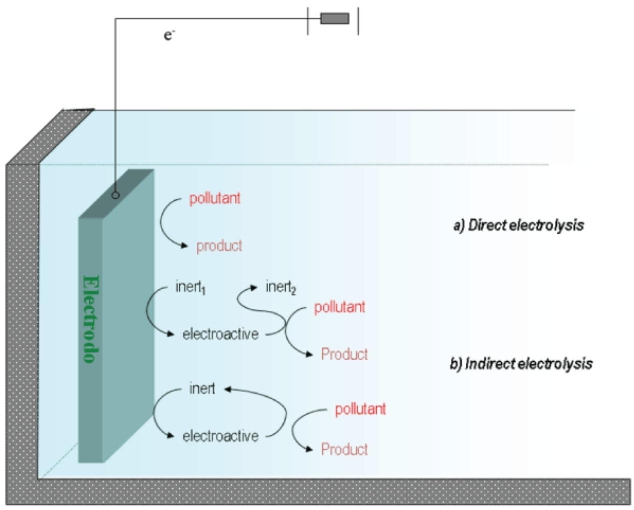

Figure 3: The working principle of direct and indirect oxidation process.

Electrochemical disinfection of water

Usually disinfection is carried out with chlorine, bleaching powder or hypochlorite. The basic chemical, chlorine itself is an electrochemical product from which the others are produced. Even if chlorination is done, hypochlorite is the effective reactant in most instances. Electrolytic chlorination or hypochlorination is a simple, cost effective and onsite process which eliminates the transport and storage of gaseous chlorine. User-friendly portable chlorine and hypochlorite generators are available for water and effluents treatment [17].

Recent findings indicate that generation of toxic dioxin and Absorbable Organic Halide (AOX) due to the usage of chlorine or hypochlorite and alternatively chlorine dioxide, ozone and hydrogen peroxide are recommended. Chlorine dioxide generators employing a membrane cell approach has been developed in which a sodium chlorate solution as anolyte is electrolyzed in a cell with nafion membrane. The anolyte becomes acidic and the chlorate is decomposed to give chlorine dioxide. Electrochemical ozone generator employing a Proton Exchange Membrane (PEM) electolyzer generates ozone at an efficiency of over 15% and at a concentration in the range of 60-75 mg/L which is much higher than the ozone generator based on the air oxidation of electric discharge. This high concentration of ozone is cabable of destructing any pollutants and bacteria and combined with ultraviolet radiation even destroy viruses and pathogens.

Hydrogen peroxide of 2 to 3% concentration can be conveniently produced onsite using a trickle-bed. Oxygen is reduced under alkaline conditions at a highly catalytic carbon bed electrode over which the electrolyte trickles down generating hydrogen peroxide.

Photo-electrochemical methods

In recent years, photo-electrochemistry has led to a new and interesting possibility for treatment of pollutants from wastewater. In this case, suspensions of semiconductor particles (mostly TiO_2) can be used to harness the light with production of electrons and holes in the solid, which can destroy pollutants by means of reduction and oxidation, respectively. In this way, water containing organic, inorganic or microbiological pollutants can be effectively treated [18].

Electrochemical Advanced Oxidation Processes (EAOPs)

In the case of industrial and/or agricultural wastewater treatment, chemical oxidation is often necessary to remove organic matter (biodegradable or not) that consumes oxygen dissolved in water. The oxidations by ozone or hydrogen peroxide (H_2O_2) are methods used as complement or in competition with the activated carbon filtration or nanofiltration. But in some cases, the conventional oxidation is still inadequate and remains inefficient. Moreover, the conventional oxidation treatments as well as biological treatments prove ineffective against certain types of organic micro pollutants. To eliminate these kind pollutants from water, more powerful processes, namely advanced oxidation processes (AOPs) have been developed. The AOPs are based on the *in-situ* generation of strong oxidizing agent hydroxyl radicals (OH) and their high oxidation power. The use of OH in the treatment/remediation of contaminated water is justified by a number of advantages: i) they are not toxic (very short lifetime); ii) they are simple to produce and use; iii) they are very efficient to remove organic pollutants: the main feature of these powerful species is their ability to transform refractory inorganic compounds to biodegradable products; iv) they are not corrosive to the equipment; v) they do not induce secondary pollution: the final products of oxidation are CO_2 and H_2O, and inorganic ions (mineralization).

Electrochemistry constitutes one of the clean and effective ways to produce in- situ hydroxyl radical (OH), a highly strong oxidizing agent of organic matter in waters. Due to its very high standard oxidation power ($E^o(\bullet OH/H_2O)$ = 2.80 V/SHE), this radical species is able to react non-selectively with organic or organometallic pollutants yielding dehydrogenated or hydroxylated derivatives, which can be in turn completely mineralized, i.e., converted into CO_2, water and inorganic ions.

Recently, the electrochemical advanced oxidation processes (EAOPs) have received great attention by their environmental safety and compatibility (operating at mild conditions), versatility, high efficiency and amenability of automation [19].

Environmental Technologies at CSIR-Central Electrochemical Research Institute, Karaikudi

The CSIR-Central Electrochemical Research Institute with its vast experience in the field of electrochemical technologies has developed a number of processes mentioned above. The electrochemical hypochlorite generator of 100 and 500 gm/hr is already on the market. The process for the production of sodium chlorate, the precursor for the production of chlorine dioxide has been commercialized long back.

The electrochemical removal of fluoride from drinking water based process is already commercialized. The process involves the generation of aluminum hydroxide by the anodic dissolution of aluminum, which adsorbes the fluoride and settles. The process is very much energy efficient utilizing just 3 to 5 watts of electric energy per liter of water and cost of defluoridation is Rs. 35 /m^3 (Figure 4).

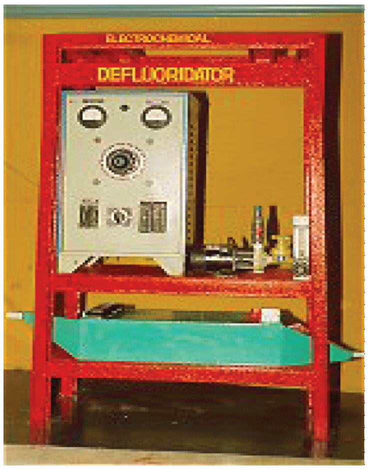

Figure 4: Electrochemical defluoridator.

The removal of chromium from solid effluents based on electro oxidation is developed. The process involves the indirect oxidation of Cr^{3+} in the residue from chromate producing plants to Cr^{6+} with the electrochemically generated hypochlorite. The recycling of spent chromium solution, recovery of silver from photographic solution, recovery of lead from battery waste, recovery of copper from spent etch solutions are some of the other important technologies at CSIR-CECRI.

The electrochemical removal of arsenic from drinking water based process is ready for commercialization. Electrochemical removal of other inorganic ions like chromium, mercury, copper, boron etc., is under development (Figures 5 and 6).

Figure 5: Electrochemical dearsenator.

Figure 6: PEM ozone generator.

Electrochemical ozone generator based on PEM technology has been tested in the laboratory scale and a portable ozone generator is also available for demonstration.

The electrochemical removal of nitrate from drinking water based on the oxidation-reduction process is successfully developed. The technology is ready for commercialization (Figure 7).

Figure 7: Electrochemical nitrate removal unit.

Conclusions

Electrochemical technologies offer simple, efficient and cost effective solutions to environmental problems and in certain applications superiority over conventional clean up processes have been demonstrated. The superiority is due to the fact that by itself electrochemical methods do not require any external reagents for pollution treatment. Simple user friendly processes can be designed with help of latest advantage in electroe and cell design technologies.

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