

DIRECT AND INDIRECT ELECTROCHEMICAL OXIDATION OF ORGANIC POLLUTANTS FROM INDUSTRIALLY POLLUTED WATER

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Key words : Electrochemical Oxidation, Organic pollutants, Electrochemical cells, Polluted water

(Received 23 September 2011; accepted 5 December 2011)

ABSTRACT

The main aim of this paper is to use "Electrochemical Technology for the removal of Organic Pollutants from Industrially Polluted Water". Today, hazardous pollution management has become one of the most challenging tasks to this technological world. Because, tons of organic pollutants, including various carcinogens, are being exposed without the sufficient treatment prescribed as per the prevailing laws. Also in the current scenario, Indian government has made it mandatory to treat polluted water before discharging it. Electrochemical De-pollution is a very efficient and economical method and it is suitable when the polluted water contains toxic and non-biodegradable organic pollutants. Thus, by means of Electrochemical Technology, which is cost effective and safe, we can help in reducing the concentrations of organic pollutants in water, to a minimum possible extent and maintain the present status of the chemical world.

INTRODUCTION

Water has a number of unique characteristics that are essential to life and that determines its environmental and chemical behaviour. Many of these characters are, due to the polar nature and the ability to form hydrogen bonds in water molecules. Water also has the highest dielectric constant of any common liquid, a more density as a liquid at 40°C and a higher heat capacity than any other liquid except ammonia. But most of the important chemical phenomena associated with water, do not occur in solution, rather through interaction of solutes in water with other phases. For example, the redox reactions catalyzed

by bacteria occur in bacterial cells. Many organic hazardous wastes are carried through water as emulsions of very small particles suspended in water. Some hazardous wastes are deposited as sediments in waterbodies from which they may later enter in water through chemical or physical processes and cause severe pollution, which need to be eliminated as much as possible.

The polluted waters are usually oxidised with ozone, which is a powerful oxidant but, the total organic carbon removal is not more than 30%. The results obtained is the same, when hydrogen peroxide is used in the presence of Fe²⁺ as a catalyst. In general, by a chemical oxidation, the organic pollutants

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are almost completely eliminated, but, the removal of total organic carbon still remains a problem. These are the reasons, why the Electro-oxidation of the hazardous pollutants has been the subject of extensive studies during recent years (Savall, *et al.* 1992).

The Electrochemical method of De-pollution presents many important advantages, because it does not need an auxiliary chemicals, it is applicable on a large range of pollutants and does not need high pressures and temperatures.

There has been new research on the Electrochemical oxidation of organic compounds from the polluted water, due to its greater efficiency and the excellent control, which it allows. The Electrochemical oxidation of pollutants from polluted water, has been studied using anodes, made from different materials. This is attributed to the oxidation of the absorbed organic compounds to carbon dioxide. It has also been proved that under the same conditions, the Electro-oxidation index obtained on the SnO₂ anode is higher than on the Pt anode, indicating a higher degree of phenol oxidation.

Polluted water Treatment - an Overview

As indicated above, industrial polluted water contains a vast array of pollutants viz., insoluble, colloidal and particular forms, both organic and inorganic pollutants. In addition, the required effluent standards are also diverse, varying with the industrial and pollutant classes. Consequently, there can be no standard design for industrial water pollution control. Rather, each site requires a customized design to achieve optimum performance. However, each of the many proven processes for industrial polluted water treatment, is able to remove more than one type of

pollutant and is generally applicable to more than one industry. Generally, a combination of several processes is utilized to achieve the higher degree of treatment required at the least cost. Much of the experience and data from polluted water treatment has been gained from municipal treatment plants. Industrial polluted liquid is similar to polluted water, but differs in significant ways. Thus, typical design parameters and standards developed for municipal polluted water operations must not be blindly utilized for industrial polluted water. It is best to run pilot tests with the specific industrial polluted water as a part of the design process. It is most important to understand the temporal variations in industrial polluted water strength flow, and polluted components and their effect on the performance of various treatment processes. Industry personnel, in an effort to reduce cost, often neglect laboratory and pilot studies. This strategy often results in failure, delay, and increased errors. Careful studies on the actual waste at a plant site cannot be overemphasized (Gherardini, *et al.* 1995).

Organic Hazards in Asia

Life-threatening poisons such as DDT, aldrin, chlordane, dieldrin and heptachlor-all of which are either severely restricted or banned in most countries- which continued to be manufactured, stored, used and traded freely in South Asia, according to an investigative report released by the International environmental group "Greenpeace". The report titled "Toxic Legacies", "Poisoned Futures", "Persistent Organic Pollutants in Asia" reveal a fact of potentially widespread contamination caused by irresponsible corporate behaviour, shortsighted lending agencies

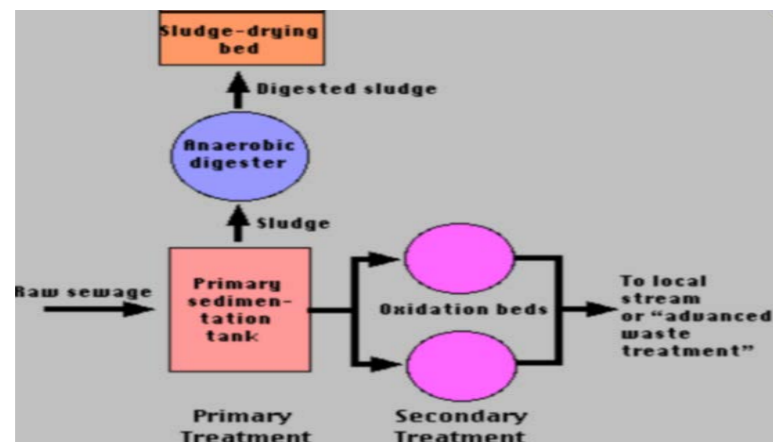


Fig. 1 Traditional overall treatment of polluted water

and misguided government policies.

Asia faces a frightening scenario of historic, current and potential poisoning by the most dangerous variety of persistent poisons. This situation is a result of existing stockpiles of obsolete PCBs, the continuing production of organophenols and other chemical pesticides and the unmitigated expansion of dirty chlorine-based industries in the region. Focusing on a class of poisonous chemicals called persistent organic pollutants or POPs which are now targeted for elimination by ongoing international negotiations under the United Nations Environment program (UNEP) Greenpeace, investigations conducted between April and August 2001 in seven Asian countries including Bangladesh, India, Nepal and Pakistan revealed that stocks of 5000 metric tons or more of absolute pesticides, including POP chemicals, are stored in extremely hazardous conditions in more than a thousand sites in Pakistan and Nepal. A sizeable portion of these pesticides are reported to have as a part of aid packages from western countries and almost all the pesticides were exported by developed nations and India to Pakistan and Nepal.

Chemical corporations whose products were identified in stockpiles in Pakistan and Nepal by Greenpeace investigators include: Bayer and Hoechst (Germany); DuPont, Dow Chemicals, Diamond Shamrock and Velsicol (USA); Shell (Netherlands); Sumitomo Chemical and Takeda Chemical (Japan); Rhone Poulenc (France); Sandoz (Switzerland); ICI (UK); Bharat Pulverising Mills (India).

India is among the three remaining known manufacturers of DDT (10,000 mt capacity) in the world, the other two being Mexico and China.

India exports nearly 800,000 kilograms of POP pesticides including aldrin, DDT, BHC, and chlordane to a long list of countries, including countries where their usage is banned. Exports of pesticides that could be branded POPs in the near future such as endosulfan, sodiumpentachlorophenate, 2,4-D, and lindane total more than two million tons. Some pesticides such as aldrin are illegal to manufacture in India.

In Pakistan, India, Nepal and Bangladesh, locally banned or severely restricted pesticides are freely available. Greenpeace found DDT, BHC, Dieldrin and Heptachlor openly sold in vegetable markets in Karachi. Hardware stores in New Delhi, stock the deadly pesticide aldrin, whose registration was withdrawn more than two years ago.

POPs are a class of synthetic toxic chemicals they

cause severe and long-term effects on wildlife, ecosystems and human health. POPs have been implicated in the rising incidence of certain cancers (e.g. breast, prostate, endometriosis, etc.), reproductive deficits such as infertility and sex-linked disorders, declining sperm counts, fetal malformations, neurobehavioral impairment, and immune system dysfunction. Because of major threats to human health, the UNEP process has shortlisted an initial twelve substances for elimination which include organochlorine pesticides (DDT, chlordane, mirex, hexachlorobenzene, endrin, aldrin, toxaphene, heptachlor), industrial chemicals like cancer-causing PCBs (polychlorinated biphenyls), and the super-toxic dioxins and furans.

In line with the emerging requirements of the UNEP POPs process, Greenpeace also urges governments in the region to take action now by abolishing inventory of all sources of POPs in their countries and preventing the expansion of POP-producing technologies such as incinerators, PVC manufacturing, pesticide production facilities, and pulp and paper mills using chlorine bleaching processes.

It is unfortunate that while government in the region is still grappling for the ways to dispose of their stockpiles of obsolete imported pesticides, the continuing production and trade of these chemicals goes on unabated. This could only lead to an endless cycle of poisoning whose unwitting and eventual victims are communities and future generations. Government should aim for an eventual phase-out of such polluting practices and push for international Co-operation in developing viable and sustainable non-chemical alternatives.

While governments in the region are responsible for taking action against POPs pollution, the liabilities associated with such action must always fall on the polluter -the corporations and international lending agencies- and not on the citizens who have long-endured the polluter- the corporation- and international consequences of toxic pollution, added

- Jayaraman, Former Minister for Environment and Forestry, Govt. of India.

Advancement in polluted water treatment

Several effective, affordable and environmentally sound waste disposal options are available; others are within scientific research. Separating waste categories can go a long way in addressing waste problems. By some estimates, intensive reuse and recycling systems could take care of nearly 80 percent of municipal wastes. Current data suggest much

Table 1. List of advanced technologies (non-combustion) available for polluted water treatment

Technology	Non combustion destruction technology	Intrinsic PCDD/F formation	Capable of containing all process streams	Capable of reprocessing all process streams	Demonstrated high DE
Incineration (Janetm, <i>et al.</i> 2001)	No	Yes	No	No	No
GPCR - Ecologic	Yes	No	Yes	Yes	yes
Base Catalysed Dechlorination	Yes	No	Yes	Yes	yes
Sodium reduction process(es)	Yes	No	?	?	no
Solvated electron process	Yes	No	Yes	Yes	yes
Super Critical Water Oxidation	Yes	?	Yes	yes?	yes
Electrochemical oxidation	Yes	No	Yes	Yes	Yes
Vitrification	No	Yes	No	No	No
Ball milling	Yes	No	Yes	yes?	No
Molten salt	?	?	?	?	?
Molten metal (Janetm, <i>et al.</i> 2001)	?	?	?	?	?
Catalytic hydrogenation	Yes	No	?	?	Yes
Solvent washing	No	No	N/A	N/A	No
Landfill/burial	No	No	No	N/A	No
Solidification/Stabilization	No	No	No	N/A	No
Land spreading	No	No	No	N/A	No
Deep-well injection	No	No	No	N/A	No

Table 2. List of technologies that meet initial screening

Technology	Commercial scale	Countries where licensed and/or used for commercial treatment
Gas Phase Chemical Reduction	Full	Australia, Canada, USA, Japan (Argentina?)
Sodium reduction process(es)	Full	France, Germany, UK, Netherlands, South Africa, Australia, USA, Saudi Arabia, Japan, New Zealand
Base Catalysed Dechlorination	Full	Australia, USA, Mexico, Spain, New Zealand
Solvated electron process	Full	USA
Electrochemical oxidation	limited	USA
Catalytic hydrogenation	Limited	Australia
Super-critical water oxidation	Limited	USA
Ball milling	limited/demo	Germany
Molten salt	Demo	N/A

lower rates of recycling in most locations: 8 percent in the UK, 28 percent in the US, and so on. Conversion to clean production technologies can both help save business dollars and protect the environment. For toxic industrial and medical wastes, non-incineration technologies such as the gas phase thermo-chemical reduction process achieve virtually 100 percent efficiency in POPs destruction and capture all residues and releases. Other emerging technologies include electrochemical oxidation, molten metal technology, solvated electron process, and supercritical water oxidation. Advanced technologies (non-combustion) available for polluted water treatment are listed in

Table 1.

Significance of Electrochemical Oxidation

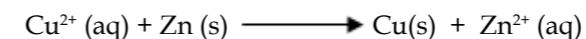
In electrochemical oxidation (EO), an electrochemical cell, operating at 50 to 60°C (120° to 140°F) and atmospheric pressure, is used to generate an oxidizing species (a mediated metal ion) at the anode (the negative electrode) in an acidic solution. As indicated in the flowsheet, this is accomplished by supplying a voltage across two electrodes immersed in an acidic solution containing the oxidizing species in its reduced, more natural state.

Table 3. Comparison of various electrodes (Canizares, *et al.* 2005 and Edison, *et al.* 1991).

Compound	Anode	Cathode	Conducting oxide	Non conducting oxide
4-chloro phenol	Titanium	Lead dioxide		
4-catecheol	TiO ₂	---	Indium oxide	
Phenolics	Titanium	Strontium oxide	RuO ₂	TiO ₂
Phenolics	Titanium	Strontium oxide	IrO ₂	ZrO ₂
Phenolics	Titanium	Strontium oxide	Platinum oxide	Ta ₂ O ₅
Phenolics	SnO ₂	----		
Phenolics	Stainless steel	Diamond thin film	--	--
Phenolics	Titanium	Lead dioxide	--	--
Phenolics	Titanium	Oxide		
Phenol	Titanium	Strontium oxide		
Phenol	Titanium	Ruo		
Phenol	Titanium	Iridium oxide		

What are electrochemical cells?

Many oxidation-reduction reactions occur spontaneously, giving off energy. An example involves the spontaneous reaction that occurs when zinc metal is placed in a solution of copper ions as described by the net ionic equation shown below.

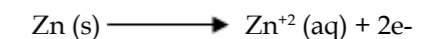


The zinc metal slowly "dissolves" as its oxidation produces zinc ions, which enter into solution. At the same time, the copper ions gain electrons and are converted into copper atoms, which coats with the zinc metal, or sediments to the bottom of the container.

The energy produced in this reaction is quickly dissipated as heat, but it can be made to do useful

work by a device called, an Electrochemical cell. This is done by the following way. An Electrochemical cell is composed of two compartments or half-cells, each in turn composed of an electrode dipped in a solution of electrolyte. These half-cells are designed to contain the oxidation half-reaction and reduction half-reaction separately as shown below.

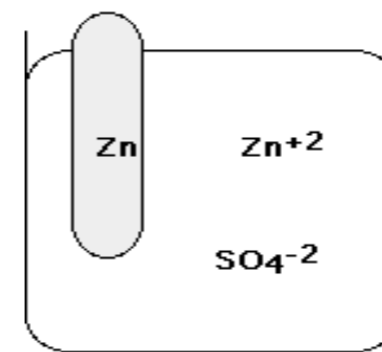
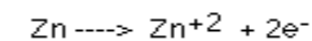
The half-cell, called the anode, is the site at which the oxidation of zinc occurs as shown below (Fig. 2).



During the oxidation of zinc, the zinc electrode will slowly dissolve to produce zinc ions (Zn²⁺), which enter into the solution containing Zn²⁺ (aq) and SO₄⁻² (aq) ions.

The half-cell, called the cathode, is the site at which

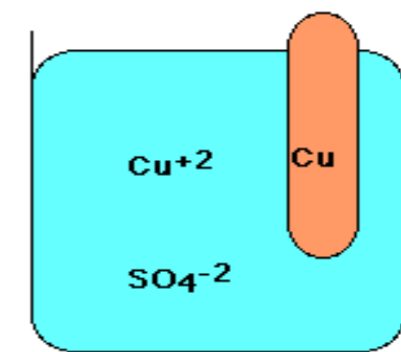
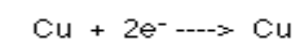
Oxidation half-cell



Zinc electrode in zinc sulfate solution

Fig. 2

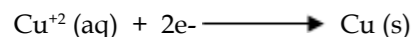
Reduction half-cell



Copper electrode in copper sulfate solution

Fig. 3

reduction of copper occurs as shown below (Fig. 3).



When the reduction of copper ions (Cu^{2+}) occurs, copper atoms accumulate on the surface of the solid copper electrode.

The reaction in each half-cell does not occur unless the two half cells are connected to each other. Recall that in order to the oxidation to occur, there must be a corresponding reduction reaction that is linked or "coupled" with it. Moreover, in an isolated oxidation or reduction half-cell, an imbalance of electrical charge would occur, the anode would become more positive as zinc cations are produced, and the cathode would become more negative as copper cations are removed from solution. Using a "salt bridge" connecting the two cells as shown in the diagram below can solve this problem. A "salt bridge" is a porous barrier, which prevents the spontaneous mixing of the aqueous solutions in each compartment, but allows the migration of ions in both directions to maintain electrical neutrality. As the oxidation-reduction reaction occurs, cations (Zn^{+2}) from the anode migrate via the salt bridge to the cathode, while the anion, (SO_4^{-2}), migrates in the opposite direction to maintain electrical neutrality.

The two half-cells are also connected externally

(Figure 4) In this arrangement, electrons provided by the oxidation reaction are forced to travel via an external circuit to the site of the reduction reaction. The fact that the reaction occurs spontaneously once these half-cells are connected indicates that there is a difference in potential energy. This difference in potential energy is called an electromotive force (emf) and is measured in terms of volts. The zinc/copper cell has an emf of about 1.1 volts under standard conditions.

Any electrical device can be "spliced" into the external circuit to utilize this potential energy produced by the cell for useful work. Although the energy available from a single cell is relatively small, electrochemical cells can be linked in series to boost their energy output. A common and useful application of this characteristic is the "battery". An example is the lead-acid battery used in automobiles. In the lead-acid battery, each cell has a lead metal anode and lead (IV) oxide (lead dioxide) cathode both of which are immersed in a solution of sulfuric acid. This single Electrochemical cell produces about 2 volts. Linking 6 of these cells in series produces the 12-volt battery found in most cars today. One disadvantage of these "Wet cells" such as the lead-acid battery is that, it is very heavy and bulky. However, like many other "Wet cells", the oxidation-reduction reaction, which occurs, can be readily reversed via an external current

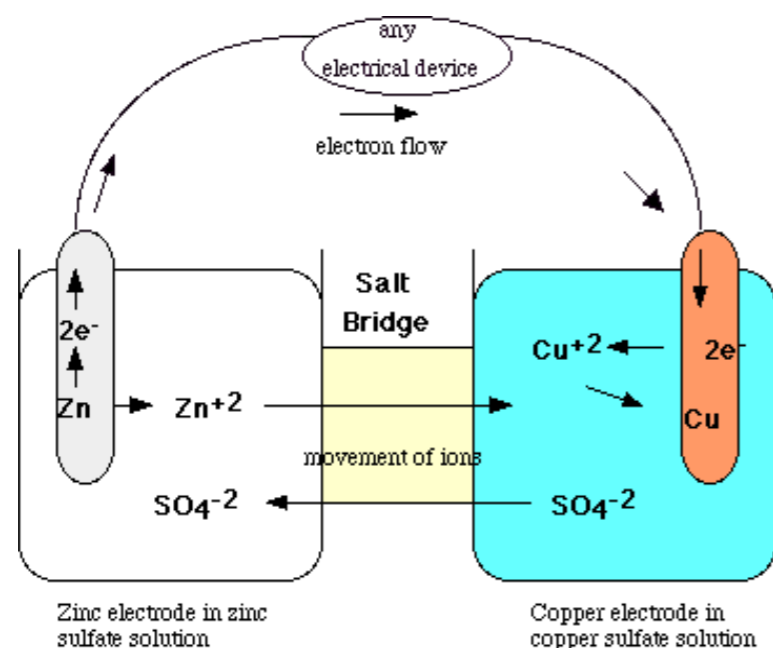


Fig. 4

such as that provided by an automobile's alternator. This prolongs the lifetime and usage of such devices as an energy source (Gherardini, *et al.*1995).

Importance of removing organic pollutants and carcinogens

Phenol is human poison by inhalation, ingestion, and skin absorption. It is a severe irritant to the eyes, skin and respiratory system. Human mutation data have been reported for phenol. Also it is a questionable carcinogen in animals and a suspected carcinogen in humans, although the data are inconclusive. Phenol is a general protoplasmic poison that is corrosive to any living tissue it contacts. Phenol is highly soluble in water. Concentrations of 1000 milligrams and more will mix with a cubic decimeter of water. About 26.3% of phenol will eventually end up in air, approximately 73.3% in water, and about 0.2% in terrestrial soil and aquatic sediments. It is used to manufacture various phenolic and epoxy resins, for refining lubricating oils, a fuel-oil sludge inhibitor, and as a reagent in chemical analysis. It is also used in the production of a large variety of aromatic compounds including fertilizers, illuminating gases, coke, explosives, lampblack, paints, paint removers, asbestos goods, wood preservatives, textiles, perfumes, bakelite, rubber, and other plastics. Many industrial processes generate polluted water flows with a high concentration of phenols and other related compounds. These compounds are known to be toxic, even at low concentrations, and their treatment is very important.

The removal of phenols from wastewaters is, therefore, an important problem and electrochemical oxidation technologies offer the prospect of relatively simple equipment, environmental friendliness and the possibility of high-energy efficiency by using Electrochemical oxidation techniques (Subramanian, *et al.* 2003).

Benefits of electrochemical over other technologies

1. The advantages of Biological treatments are very well known, but also their limitations either for a high COD (Chemical Oxygen Demand) value or the presence of very toxic compounds. The possible presence of inorganic compounds, such as heavy metals, may cause a drop of the bacterial count. On the other hand, the incineration of organic compounds can originate the formation of toxic products that are dragged at the same time by the combustion gases; also, the presence

of corrosive agents can cause problems in the stability of the materials of the incinerator.

2. Electrochemical degradation (direct and indirect Electrochemical oxidation) and electrocatalysis of hazardous polluted water have several advantages compared with incineration and biological treatment.
3. Electrochemical treatment is able to treat very toxic pollutants.
4. This process can operate at room temperature and atmospheric pressure
5. The energy consumption depends on COD
6. The Electrochemical treatment can be stopped simply by switching off the power.
7. Cost and safety effective switching off the power.

Other Applications of Electrochemical Technology

- The PCBs degradation
- In-situ chlorine production
- Ozone generation (Jiangning Wu, 1995)
- Destruction of cyanides and nitrites
- Purification of polluted water using oxidising agents and in general as a method for the reduction of COD from any effluent.
- Elimination of phenol (William, *et al.* 1994).
- Elimination of tensioactives compounds and dyes
- Electrochemical technology is able to treat toxic polluted water with high concentrations of organic compounds.
- Suitable when traditional treatment methods are not effective due to: non-biodegradable materials, heavy metals, hazardous compounds are not completely degraded
- It avoid the problem of dropping of the bacterial count on the biological treatments
- Innovative aspects of electrochemical technology

Major Drawbacks

The major drawbacks of this technology mainly include:

1. Passivation: The Passivation of electrodes is due to building of successive layers of blocking films of high molecular weight unreactive materials thus leading to the decrease in rate of reaction and after sometime complete end of reaction.

2. De-stabilisation of electrode material: The de-stabilisation of electrode material widely confines to the corrosion problem. Due to improper selection of electrode pair sometimes the organic pollutant in

long reaction time corrodes the electrode material leading to destabilisation.

Present State of Electrochemical Technology

At present Electrochemical technology is applicable for following treatment units:

- Elimination of lead and lead oxides from polluted waters.
- Recovery of NaCl by electro dialysis.
- Textile polluted water treatment using Electrochemical technology.

CONCLUSION

From the overall study of "Electrochemical oxidation of organic pollutants" and Electrochemical technology it has been concluded that this electrochemical degradation has proved to be faster than the usual treatments such as biodegradation, photooxidation. It is a clean technique, it does not need any chemical reagent which may be harmful or expensive, it can be easily operated (needs no complex controls) and also optimum safety condition prevails since the oxidizing agents generated in-situ.

The only drawback of this technology is the high operating cost of the reactor. It has been suggested that, in future, this kind of treatment should be preferentially employed for the preliminary treatment of organic polluted water constituents.

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