

OVERVIEW OF ELECTROCHEMICAL TREATMENT FOR WASTE WATER TREATMENT

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Abstract: With a rapidly growing world population and increasing levels of pollution, the protection of the environment and the preservation of resources have become a major issue for future technological progress. Strategies for ecological protection generally include the development of new or improved industrial processes that have no or minor effects on nature and of processes for the treatment of inevitable waste. With the development of industries, more and more pollutants are discharged into the environment, among them some of the (refractory organic compounds) wastes are typical contaminants considered to be hazardous and top priority toxic pollutants. They are toxic even at low concentration. The electrochemical treatment of wastewater is considered as one of the advanced oxidation process, potentially a powerful method of pollution control, offering high removal efficiency. Electrochemical processes generally have lower temperature and atmospheric pressure requirement than those of other equivalent non-electrochemical treatments and there is no need for additional chemicals. The required equipments and operations are generally simple. Their controls are easy and the electrochemical reactors are compact. Overall, this paper serves as a comprehensive guide for electrochemical treatment for waste water treatment and its scope in environmental problems.

Index Terms: Electrochemical treatment

I. INTRODUCTION

The treatment of water contaminated with the recalcitrant compounds is a common problem throughout the world. Dye and dye intermediates, textile processing units, petroleum products industries, tanneries, pulp and paper etc are some of the units which consume vast varieties of chemicals in their process. These industry effluents are considered to be difficult for treatment in view of their unique ever-changing properties and process variations in effluent characteristics. Moreover most of the chemicals are xenobiotic in nature and affects the biological process (Alinsafi et al, 2006; Bizani et al, 2006). This is due to the molecular structure of substances, which may prevent biological attack due to the size or the shape of the molecule. To meet the specific standards set, there is a need for new treatment method, which address questions at both local and global level in terms of related research and development of treatment technologies.

The treatment and safe disposal of hazardous organic waste material in an environmentally acceptable manner and at a reasonable cost is a topic of great universal importance.

The demand for water of very high purity has presented new challenges to scientists and engineers in the area of water purification. For years engineers have relied on a variety of traditional water treatment processes include phase transfer, biological treatment, thermal and catalytic oxidation and chemical treatment using Chlorine, Potassium Permanganate, Ozone, hydrogen peroxide and high energy ultraviolet light.

However, all the phase transfer technologies currently in use are non destructive in type. They rely on the physical separations of organics by merely transferring the pollutants from one phase to another thus retaining the requirement for the final and ultimate disposal of the transferred material. Proven methods include air or stream stripping (Nirmalakhandan et al 1997) and even adsorption by activated carbon (Stenzel 1993). The removal of volatile contaminants by air or steam stripping converts a liquid contamination problem into an air pollution problem and. Adsorption/Absorption on solid substrate creates solid waste generation and disposal problem.

II. IMPORTANCE OF WATER:

Water covers 70% of our earth's surface, water is most precious natural resource that exists on the planet is very much important for us in our daily use and also in lots of other processes to be carried out for our need. Our earth has water, which covers three-fourths of its surface and constitutes 60-70 wt % of living world. Actually only 1 % of the water present on earth is usable by us. Looking for the present global scenario in terms of water pollution, its extent is increasing due to industrialization and urbanization. The population also leads to water scarcity in some areas. So to decrease the water pollution and increase efficient water reuse, wastewater treatment must be done.

III. IMPORTANT CONSTITUENTS OF WASTEWATER AND THEIR CONSEQUENCE^{[10,13]:}

Wastewater is characterized in terms of physical, chemical and biological parameters. The important parameters are given below.

1. **Suspended solids:** Suspended solids can lead to the development of sludge deposits and anaerobic conditions when untreated wastewater is discharged into the aquatic environment.
2. **Biodegradable organics:** Biodegradable organics are measured in terms of BOD and COD. If discharged wastewater has high COD values then it can lead to the depletion of natural oxygen resources.
3. **Pathogens:** The pathogenic organisms that may be present in wastewater can transmit communicable diseases.
4. **Nutrients:** Both nitrogen and phosphorous along with carbon are essential for growth. These nutrients can lead to the growth of undesirable aquatic life.

5. **Priority Pollutants:** Organic and inorganic compounds selected on the basis of their known or suspected carcinogenicity, mutagenicity, teratogenicity, or high acute toxicity.
6. **Refractory Organics:** These organics tend to resist conventional methods of wastewater treatment. Typical examples are surfactants, phenols, and agricultural pesticides.

Wastewater treatment methods:

Methods of treatment in which the application of the physical forces predominate are known as unit operations. Methods of treatment in which the removal of contaminants is brought about by chemical or biological reagents are known as unit processes. Wastewater treatments are carried out in the following steps:

Preliminary treatment: Removal of rags, sticks, grit and grease that may cause maintenance or operational problems with the treatment operations, processes and ancillary systems.

Primary treatment: Removal of a portion of suspended solids and organic matter from wastewater.

Secondary treatment: Removal of biodegradable organic matter and suspended solids. Activated sludge and trickling filter are main treatments.

Tertiary treatment: Removal of residual suspended solids usually by granular medium filtration or micro screens. Disinfection, Nitrogen removal, Phosphorous removal. Activated carbon Adsorption etc are considered as the tertiary treatments.

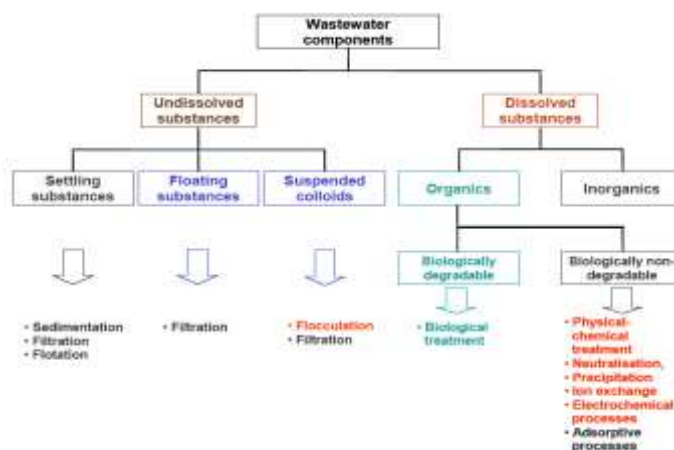


Figure 1 Main components of industrial wastewater

IV. ADVANCED OXIDATION PROCESSES:

AOPs are defined (Glaze and Chapin, 1987) as near ambient temperature and pressure water treatment processes which involve the generation of highly reactive radicals (specially Hydroxyl radicals) in sufficient quantity to effect water purification. These treatment processes are considered as very promising methods for the remediation of contaminated ground, surface and wastewater containing non-biodegradable organic pollutants. Hydroxyl radicals are extraordinarily reactive species that attack most of the organic molecules.

General oxidation methods carried out in the conventional way are given below [16,17]:

1 Chemical oxidation:

Chemical oxidation in wastewater treatment involves the use of oxidizing agents such as

- Ozone (O₃)
- Hydrogen Peroxide (H₂O₂)
- Permanganate (MnO₄)
- Chlorine dioxide
- Chlorine
- Hypochlorite (HOCl)
- Oxygen (O₂)

to bring about change in the chemical structure of the pollutants in wastewater to harmless and safe end products.

2 Biological oxidation:

Biological oxidation includes transformation of dissolved and particulate complex organic compounds into simpler acceptable end products with the help of microorganisms. Different types of biological oxidation methods are

- Aerobic oxidation
- Anaerobic oxidation
- Anoxic oxidation
- Facultative oxidation
- Combined aerobic/anaerobic/anoxic oxidation

3 Photochemical oxidation:

Oxidation of complex organic pollutants with the effect of UV light in presence of photo catalyst (def.). Conventional chemical oxidation treatment does not convert organics into CO₂ and H₂O. Completion of oxidation reactions as well as the oxidative destruction of compounds immune to unassisted ozone or hydrogen peroxide oxidation, can be achieved by supplementing the reaction with UV radiation.

Different photochemical oxidation methods are as below:

- Ozone UV radiation
- Hydrogen peroxide UV radiation
- Ozone –hydrogen peroxide- UV radiation
- Photo catalytic oxidation with TiO₂

Using electricity to treat water was first proposed in UK in 1889. Elmore patented the application of electrolysis in mineral beneficiation in 1904. Electrocoagulation with Aluminum and Iron electrodes was patented in the US in 1909. The

electrocoagulation of drinking water was first applied on a large scale in the US in 1946. Because of the relatively large capital investment and the expensive electric supply, electrochemical water or wastewater technologies did not find wide application worldwide then. Extensive research, however in the US and the former USSR during the following half-century has accumulated abundant knowledge on the subject. With the ever increasing standard of drinking water supply and the stringent environmental regulations regarding the wastewater discharge, electrochemical technologies have regained their importance worldwide during the last two decades. There are companies supplying facilities for metal recoveries, for treating drinking or process water, treating various wastewaters resulting from tannery, electroplating, dairy, textile processing, oil and oil-water emulsions etc. Nowadays, electrochemical technologies have reached such a state that they are not only comparable with other technologies in terms of cost but also are more efficient and more compact. For some situations, electrochemical technologies may be the indispensable step in treating wastewaters containing refractory pollutants.

The problem of petrochemical wastewater purification is a challenging issue (see Wise and Fahrenthold 1981, Wong 2000, Sponza 2003). The traditional treatment of effluents of refineries is based on the mechanical and physiochemical methods such as oil-water separation and coagulation, followed by biological treatment within the integrated activated sludge treatment plant. The petrochemical wastewater (PCWW) is also treated with coagulants like alum, ferric chloride, ferrous sulfate and lime. Table: 4.1.shows some of the products wastewater stream COD and BOD values and other important characteristics of the wastewater. Table 4.2 gives the required liquid effluent characteristics from the petrochemicals wastewaters stream. There is always a change in the liquid effluent characteristics in the petrochemical wastewater streams. CPCB limits for the petrochemicals wastewater liquid effluent is given in the Table 4.2.

Table: 4.1 Characteristics of wastewater from Petrochemical plant

Product	Flow of wastewater, m ³ /tonnes	BOD, mg/l	COD, mg/l	Other important characteristics
Ethylene	0.18-5.4	100-1000	500-3000	Heavy metals, color solids, pH
Acrylates	3.6-10.8	500-5000	2000-15000	Solids, cyanide, color
Acrylonitrile	3.6-28.8	300-5000	500-15000	CN, color, pH
Phenol	1.8-9	1200-10000	2000-15000	Phenols, solids

Table 4.2: CPCB standards for liquid effluent from petrochemical complex

Parameter	Concentration not to exceed limits in mg/l (except pH)
pH	6.5 - 8.5
BOD (3 days at 27°C)	50
Phenol	5
Sulphide as S	2
COD	250
Cyanide as CN0.	2
Fluoride as F	15
Total suspended solids	100

A new treatability test based on a direct far UV photo oxidation of the sample has been applied to different samples from chemical and petrochemical industries. The UV treatability test is currently being used for checking up on petrochemical wastewater and chemical sewage.

The potential advantage of the UV/H₂O₂ process becomes evident when the process is used as the direct pretreatment of the petrochemical wastewater (Juang et al 1997). The results of the direct pretreatment with UV/H₂O₂ process revealed that the recalcitrant compounds found in raw wastewater could be destroyed to small molecules and might reduce some degree of activity inhibition to bioculture.

A methanogenic consortium (anaerobic process) was used to degrade phenol and ortho cresol from a specific effluent of a petrochemical plant in a continuous fixed film anaerobic reactor (Charest et al 1999). The application of laccase and manganese dependent peroxidase from *Trametes versicolor* to facilitate removal of aromatic hydrocarbons from a petrochemical industrial effluent was investigated by Edwards et al 2002.

V. VARIOUS ELECTROCHEMICAL TREATMENT METHODS [7,12,20]:

The challenge of the increasing demand for quality water can be met only by applying all suitable scientific and technical methods to increase the productivity of process technology for the conversion of low-grade water into pure water. Sterilization and elimination of organic micro impurities from drinkable water and wastewater for many processes. Many different methods for improving water quality are already established: these include membrane based methods, ultra and micro filtration, biological, chemical and physicochemical processes.

A solution to these problems can be sought in electrochemical technologies based on electric field and faradaic effects, specially designed electrochemical cells. Two main types of treatment can be considered are:

(1) Drinkable water suffering degradation of properties (due to lengthy routes, pipe damages, and uphill treatment problems) may be subjected to a "Direct" electrochemical treatment, i.e. the water is passed through anodic and cathodic compartments of one or more electrochemical cells with specific features. The process depends on applied electric field, pH and faradaic processes (anodic oxidation and cathodic reduction) and results in the elimination of biological and chemical impurities.

(2) Good quality water for food industry, specific processes etc may be obtained through an "Indirect" treatment, adding suitable amounts of so called "neutral analytes", which are produced by electrolyzing diluted brines; under optimal conditions, a complete elimination of the biological and chemical impurities can be obtained.

Good technologies for treatment of bio refractory pollutants are of critical environment importance since they cannot be treated by conventional biological methods. Treatment of wastewater by conventional biological methods is often inadequate to remove pollutants completely. In contrast, electrochemical technologies are becoming more reliable and are gaining popularity for the treatment of industrial wastewater.

AOPs producing high oxidation potential hydroxyl radicals are often investigated on their role in pretreatment or mineralization process of wastewater treatment. Apart from the well-known AOPs such as Fenton reaction, Ozonation, Photo catalysis, electro catalysis seems to be an increasingly popular way for wastewater treatment.

Intensive research to improve electrochemical treatment efficiency focused on two areas. One area is development of better performance stable anodes with high catalytic activity and high oxygen over voltage anodes such as PbO_2 and boron doped diamond electrodes which had been found to be very effective. The other area is exploration of novel processes such as partial degradation process, Electro Fenton process and Photo-electro-Fenton process.

Electrochemical processes used for the recovery or treatment of wastewater from industrial plants play an important role. Oxidative processes have a continuously increasing importance in the reduction of toxic pollutants or at least in their conversion to biocompatible species. Economical and efficient oxidation rates for industrial water recycling, however, require appropriate anode materials.

Several parameters can be tuned to optimize the process as salt concentration of solution, number of electrodes and distance between them, stirring, current intensity

Electrochemical techniques are becoming more reliable and are gaining popularity for the treatment of industrial wastewater. They have proved efficient in destroying a variety of pollutants. Electrochemical methods have been successfully applied to treat various wastewaters, i.e. wastewater containing poly aromatic organic pollutants, petrochemical wastewater, textile dye wastewater, refractory organic pollutants including lignin, landfill leachate, EDTA etc.

Many kinds of electrochemical applications are now commercial realities for process stream recycle, product isolation, and water and effluent treatment, including:

- Removal of heavy, transition, and precious metals from effluent to levels $\ll 1$ ppm.
- The removal of many organics, commonly to a COD < 10 ppm.
- The decolorization or detoxification of effluent streams by selective oxidation/reduction.
- Removal of salinity from water to < 200 ppm (by electrodialysis, ED).
- The selective removal of ions –e.g., NO_3^- from aqueous solutions using special membranes (ED).
- The concentration of transition metal ions from plating wash waters (ED).
- The conversion of waste salt streams to acid and base (either by electrolysis or bipolar membranes).
- Recovery of pure NaCl from seawater (ED).
- Isolation of pure organic acids from chemical streams (ED).
- On-site electrogeneration of ClO^- , H_2O_2 , and ozone for effluent treatment.

Research done on variety of pollutants treatment by electrochemical methods include: Ammonia, Nitrites, Benzoquinone, Benzene, thiourea dioxide, Phenol, Chlorophenol, Dyes, Formaldehyde, Cyanides, Toluene, Alcohols, and Hydrocarbons.

The scope for electrochemical technology in environmental problems [24]:

- Avoidance of pollution - clean electro synthesis
- Recycling of valuable materials - precious metal deposition
- Remediation of polluted sites - soil remediation by electro dialysis
- Monitoring and sensors - in the gas and liquid phase
- Efficient energy conversion - fuel cells and redox flow cells
- Avoidance of corrosion - *choice of materials/protective coatings*
- Removal of contaminants - metal ion, organics, and inorganic removal from water and process liquors
- Disinfection of water - chlorination, peroxy species, or ozone

The Advantages and Limitations of Electrochemical technology:

Advantages

- Electrons are clean reagents (at least at their source of supply).
- Effective control of the electron transfer rate (current density).
- Measurement of reaction conditions (current density and electrode potential).
- The process can be turned on and off via the current.
- Can often use benign (e.g., ambient) conditions of temperature and pressure.

Possible Limitations

- Many research workers have little industrial/large-scale experience of electrochemical technology, hindering technology transfer.
- Some industrial sectors have limited knowledge or experience of electrochemical technology.
- There are relatively few "showcases" for the technology.
- There is a shortage of experienced electrochemical engineers.
- Chemical reactions, corrosion, adsorption, etc., at electrode surfaces can cause complications.
- Damage to electrodes and membranes via, e.g., corrosion and fouling, can restrict performance and longevity.

SUMMARY

Electrochemical treatment for wastewater is an innovative and efficient method that utilizes electrochemical processes to remove pollutants and contaminants from water. This approach offers several advantages, including cost-effectiveness, environmental sustainability, and the ability to treat a wide range of pollutants. The process involves the application of an electric current to induce various electrochemical reactions that facilitate the transformation or removal of contaminants.

Key components of electrochemical wastewater treatment include electrodes, which serve as catalysts for electrochemical reactions, and an electrolyte solution that conducts the electric current. The electrodes can be configured as anodes and cathodes, each contributing to specific reactions. Common electrochemical processes include electrocoagulation, electrooxidation, and electrochemical reduction.

1. **Electrocoagulation:** This process involves the generation of metal hydroxide coagulants through the dissolution of sacrificial anodes. These coagulants aid in the destabilization and precipitation of pollutants, leading to their removal from the water.
2. **Electrooxidation:** In electrooxidation, contaminants are directly oxidized at the anode, resulting in their decomposition into less harmful byproducts or mineralization. This process is effective for the removal of organic pollutants.
3. **Electrochemical Reduction:** This involves the reduction of metal ions or the transformation of specific pollutants at the cathode. It is particularly useful for the removal of heavy metals and certain toxic substances.

The advantages of electrochemical wastewater treatment include its versatility in addressing various pollutants, low chemical consumption, and the ability to operate continuously. Additionally, it minimizes the generation of sludge, reducing the need for additional disposal methods.

However, challenges such as high energy consumption and electrode fouling need to be addressed to enhance the overall efficiency of electrochemical treatment. Ongoing research aims to optimize system design, electrode materials, and operating conditions to make electrochemical wastewater treatment more economically viable and sustainable.

In summary, electrochemical treatment offers a promising approach to wastewater treatment by harnessing the power of electrochemical reactions to remove contaminants. While there are challenges to overcome, ongoing advancements in technology and research continue to improve the efficiency and applicability of this method for addressing environmental concerns associated with water pollution.

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