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Electrochemical Oxidation for Industrial Wastewater Treatment

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A B S T R A C T

The field of industrial development has played an important role in economic growth but it has also resulted into massive volumes of waste liquids being released into nature. Effluents from industries dealing with textile, pharmaceuticals, tanneries, paper and pulp manufacturing, petrochemicals, food processing and electro-plating comprise complex mixtures of dyes, phenolic compounds, traces of drugs and pesticides, surfactants, heavy metals and a range of harmful organic contaminants. A number of them have high chemical stability, low biodegradability and toxicity, which activates problems of removal through standard wastewater treatment processes. Classical methods including coagulation-flocculation, adsorption, activated sludge treatment and membrane filtration do not provide a complete removal of persistent pollutants and may generate secondary waste requiring disposal. Electrochemical oxidation (EO) method is regarded as one of the most advanced methods of wastewater treatment because it involves generation of very powerful oxidizing agents in the process of electrolysis. During the process of electrolysis hydroxyl radicals (•OH), active chlorine species, hydrogen peroxide, ozone and sulfate radicals are generated which help in oxidization of difficult-to-treat organic material into CO_2, water and inorganic ions. In contrast to classical methods of wastewater treatment, EO requires only a small amount of chemicals, produces little sludge and can be run under standard ambient conditions and simple reactor design. Recent technological development in electrode materials in particular Boron Doped Diamonds (BDD), Mixed Metal Oxides (MMO), PbO_2, SnO_2, graphite and platinum have led to the increase of pollutants' degradation quality and decrease of operation constraints. Moreover, the combination of electrochemical processes and methods of photocatalysis, membrane separation, biological treatment and renewable energy sources in one system provides high efficiency of operation. This review gives an evaluation of the basic principles, chemical reactions, electrode materials, operational parameters, industrial applications, recent achievements of technologies, advantages and perspective development of the method in question.

Introduction

The use of water is indispensable in various sectors including households, agriculture, industry, environmental ecosystem, and the economy as a whole. However, the rapid industrial growth in recent years has led to an extraordinary increase in the activities consuming fresh water along with the production of a large volume of wastewater. The extent of water consumption and wastewater generation is reported to be very significant according to various international ecological assessments and the data indicate that a substantial part of the water that is consumed comes from industrial production. The wastewater produced in the industrial sector has quite different characteristics compared to the municipal one. Different types of waste exist depending on the fields involved in production of wastewater, such as waste from dyeing and bleaching factories, pharmaceutical plants, farms, oil extraction and refining, printing industry, etc. All these wastes increase Chemical Oxygen Demand, Biological Oxygen Demand, Total Organic Carbon, toxicity, and colour and decrease the concentration of dissolved oxygen as well. Traditional technologies used for purification of wastewater include various technologies such as sedimentation, coagulation, flocculation, activated sludge processes, adsorption, membrane filtration, ion exchange, etc.While these technologies work in an efficient manner with biodegradable substances and suspended solids, their results in the case of persistent organic wastes are not so promising. Besides that, some conventional methods only redistributing contaminants from one phase to another without mineralising them completely, thus producing secondary sludge and raising disposal fees. In order to overcome these disadvantages, scientists have focused on Advanced Oxidation Processes (AOPs) which are capable of creating reactive oxidizing agents for elimination of pollutants. Among many AOPs, electrochemical oxidation has become popular due to its simplicity, efficiency, and possibility to automate the process. More importantly, it does not need a lot of chemicals to operate properly and is eco-friendly.

Electrochemical oxidation combines electrical energy to create oxidizing agents both on the anode surface and in the electrolyte. Depending on the type of the electrode and the composition of the electrolyte one can obtain •OH radicals, active chlorine species, hydrogen peroxide, ozone, persulfate radicals, etc. These compounds involve organic substances in a series of oxidation reactions, so that the wastes are converted into CO2, H2O, and inorganic ions.

The efficiency of electrochemical oxidation is determined by the anode. The searches have been conducted into the use of advanced anode materials such as Boron-Doped Diamond (BDD), Mixed Metal Oxides (MMO), Lead Dioxide (PbO_2), Tin Oxide (SnO_2), graphite, and platinum, all of which have proved their effectiveness and the power to produce hydroxyl radicals. BDD electrodes are among the best in the field, due to their high oxygen evolution overpotential, corrosion resistance, and mineralization capacity. Apart from creating a previous electrode, scientists have been working on designing electrochemical reactors and energy efficiency improvement. Therefore, electrochemical oxidation can be used for wastewater from textile, pharmaceutical, petrochemical, electroplating, paper and pulp, food, and tanning industries.

The aim of the present paper is to provide an insight into the theory, mechanisms, materials of electrode, significant parameters, and industries where it is used of electrochemical oxidation more efficiently. Special attention is paid to the researches that try to increase the elimination of pollutants with minimum funds used.

Literature Review

Industrial wastewater has a broad spectrum of toxic organic and inorganic contaminants like synthetic dyes, pharmaceutical residues, pesticides, phenols, surfactants, oils, heavy metals. Some of such contaminants are resistant to standard biological and physicochemical treatment techniques due to their complex structure and high chemical stability. Therefore, researchers are focused on developing new technologies capable of completely destroying pollutants rather than only transferring them from one phase to another. Electrochemical oxidation (EO) provides one of the most advanced and promising techniques of Advanced Oxidation Processes (AOPs) aimed at wastewater treatment. The technique involves generation of highly reactive oxidizing agents, mainly hydroxyl radicals (•OH), in the process of which stubborn organic pollutants are converted into safe products, including carbon dioxide, water and inorganic ions. Due to its high efficiency of treatment, low sludge production, easy automation and no need for many chemicals, electrochemical oxidation has been widely adopted for treatment of industrial effluents from textile, pharmaceutical, leather, petrochemical, paper and food industries. Recent studies demonstrate improvements in electrode materials, reactor design and hybrid systems for pollutants removal. The technology of electrochemical oxidation has developed remarkably in the last three decades. The first electrochemical systems used graphite and platinum electrodes, which were effective in oxidation process but had low efficiency and high costs.The progress in electrochemical engineering has led to the emergence of novel electrode materials such as Boron-Doped Diamond (BDD), Mixed Metal Oxides (MMO), Lead Dioxide ($PbO2$), and $SnO2$ electrodes. BDD stands out among those materials since it is deemed one of the most effective anodes because of its high oxygen evolution overpotential, outstanding chemical stability, and remarkable production of hydroxyl radicals. Moreover, modern electrochemical reactors are designed in an improved hydraulic fashion and have optimum spacing between electrodes, as well as energy-saving power supplies to achieve the maximum extent of different types of pollutants degradation with minimum consumption of electrical energy. Over the past years, electrochemical oxidation has been supplemented by membrane filtration, biological treatment, photocatalysis, and use of renewable energy systems to achieve greater efficiency and sustainability of water treatment processes. All these advancements allowed moving electrochemical oxidation from laboratory research to pilot and industrial plants.

Direct and Indirect Electrochemical Oxidation- Electrochemical oxidation can be split into two main types, namely direct oxidation and indirect oxidation.

Direct Electrochemical Oxidation- Direct electrochemical oxidation implies the diffusion of contaminant molecules to the anode and oxidation via direct electron transfer. This method works well for pollutants that can easily go on the surface of the electrode. The efficiency of oxidation is determined by electrodes" electrocatalytic properties and applied current density. In this regard, BDD electrodes show excellent results in direct oxidation due to the their ability to deliver lots of hydroxyl radicals that are adsorbed physically and can mineralize complex organic substances.

Indirect Electrochemical Oxidation- The term indirect oxidation refers to the process of generating effective oxidizing agents in the electrolyte solution.Particularly hydroxyl radicals (•OH), active chlorine (Cl_2, HOCl, ClO^-), hydrogen peroxide (H_2O_2), ozone (O_3), and sulfate radicals ($SO_4^{\bullet-}$) account for the group of oxidizing agents. The active substances pass through the body of solution inducing oxidation process of pollutants even if contaminating substances do not come into contact with the surfaces of the electrodes. As a result of the process above, the direct electrochemical oxidation is more efficient in degrading complex industrial wastewater and achieving better results.

Electrode Materials- The efficiency of electric oxidation rely much on characteristics of electrode material. The ideal electrode has to show good conductivity, corrosion resistance, electrocatalytic activity, long service life, and energy saving.

Boron-Doped Diamond (BDD)- The BDD electrodes are believed to be the best anodes for electrochemical oxidation due to their ability to generate hydroxyl radicals and high overpotential for oxygen evolution. Therefore, the BDD electrodes are considered to be able to achieve very high COD removal and complete mineralization of hard-to-oxidize pollutants. The only disadvantage of BDD is high production costs.

Mixed Metal Oxide (MMO) - The MMO electrodes are electrodes where titanium substrate is covered by oxides, such as ruthenium oxide and iridium oxide. These materials are distinguished by their high efficiency of oxidation and long service life as well as low price in comparison to the BDD electrodes.Lead Dioxide (PbO_2)

Lead dioxide has the advantage of good oxidation capacity and is widely applied in the degradation of dyes and treatment of phenolic wastewaters, though its possible lead leaching during the long-term operation leads to some environmental concerns.

Graphite and Platinum- Graphite electrodes can be produced at a low cost, whereby they are often used for laboratory research. On the other hand, platinum electrodes exhibit excellent chemical robustness as well as catalytic activity, although they are too expensive for industrial-scale usage.

Factors Influencing Electrochemical Oxidation- There are a number of operational factors that affect electrochemical oxidation efficiency. One of the most crucial factors is current density, as it determines the amount of hydroxyl radicals being generated. Generally, higher value of current density means better concentration degradation, however, the use of excessive values of current might only lead to increasing the operational energy costs and lowering current efficiency. The solution pH is also important for oxidation processes. In principle, acidic or neutral systems are more efficient in generating oxidizing radicals, thus improving the pollutant degradation rate. The time of electrolysis is another factor that determines the length of time pollution is exposed to oxidizing agents. The longer pollutants are treated, the better their degradation will be, but this will also increase the costs of treatment. An electrolyte, such as NaCl or Na_2SO_4, affects the effectiveness of processes by enhancing wastewater conductivity. Other factors such as temperature, initial concentration of pollutants, electrode gap, etc. should also be monitored to achieve high treatment efficiency while minimizing energy consumption.

Industrial Applications- Electrochemical oxidation method has proven itself to be successful in treating wastewater from numerous industries, such as textile, pharmaceutical, leather, etc. In textile industry it can effectively remove synthetic dyes, color and high COD, while in pharmaceutical industry it can easily degrade drugs and hormones, as well as other contaminants that are hardly removed by conventional biological treatment. Another important application of electrochemical oxidation technology is wastewater treatment from the leather industry where water contains sulfides, chromic compounds and big organic matter amount. The technology successfully solves tasks for other industries as well such as paper and pulp, petrochemical, food processing and galvanizing industries.

Due to its efficiency and disinfection capacity, electrochemical oxidation becomes one of the most important technologies in contemporary industry.

Experimental Methodology

The study being presented is an extensive review of the existing data on electrochemical oxidation treatment which is used to treat wastewaters from industries. As it is a review study, it does not involve any experimental work in the laboratory. All information has been collected from various sources such as journals, review papers, books, conferences, and publications from reputable organizations. The literature that has been collected has then been analyzed in an effective manner to get information about the principles, use, benefits, drawbacks, and other recent developments related to the technology of electrochemical oxidation.

Data Collection- The relevant data for this study has been obtained from reliable resources including peer-reviewed journals. Only papers that were published in the journals between 2015 to 2025 have been considered in order to present the latest developments in the area of electrochemical wastewater treatment.

Methodology

The methodology of the work consisted of four stages. First of all, thorough literature review has been conducted in which scientific articles, books, and reports relevant to the subject have been collected. For the purpose of collecting authentic information, various databases have been used including Science Direct, Wiley Online Library, Springer Link, and Google Scholar. The collected literature was then screened and relevant information has been extracted based on the relevance of papers to electrochemical oxidation, electrochemical methods, design of the reactor, operating parameters, etc. Finally collected information was analyzed by comparing the performance of different electrode materials and operating conditions, as well as studying relevant compensating parameters like COD, TOC, color removal, current density, power consumed, etc.

Parameters Considered- The following parameters have been taken into consideration while conducting the literature review to analyze the performance of electrochemical oxidation:

•Chemical Oxygen Demand (COD) removal rate
•Total Organic Carbon (TOC) removal rate
•Color removal rate
•Current density
•Solution pH
•Electrolysis process duration
•Electrolyte used
•Material for electrode
•Power consumption
•Mechanism of mineralization.

Results and Discussion

The current research relies on an extensive literature review on electrochemical oxidation used for the treatment of industrial wastewater. The information obtained from the studies reveals that electrochemical oxidation is one of the most effective advanced oxidation methods for eliminating persistent organic pollutants from industrial wastewater. The effectiveness of this method is influenced by various factors such as electrode material, current density, electrolysis time, pH of solution, presence of supporting electrolyte, and wastewater composition. This chapter contains the comparison and analysis of findings of the studies done by different scientists.

Influence of Material of Electrodes- The literature review shows that electrode material plays an important role in electrochemical oxidation performance. Talking about the most common types of electrodes, Boron-Doped Diamond (BDD) is different from the others because of its exceptional ability to produce free hydroxyl radicals and high oxygen evolution overpotential. The results of several studies conducted prove that BDD electrodes can remove more than 95% of COD and almost completely remove color from dye wastewater. Mixed Metal Oxide (MMO) electrodes also showed good results while being more affordable in terms of operational costs. Though graphite and platinum electrodes are effective in oxidation processes in laboratory conditions, they are not flexible to be used for industrial needs due to either lack of efficiency or high price.

Table 1 Comparison of Different Electrode Materials

Electrode Material	Advantages	Limitations
Boron-Doped Diamond (BDD)	Very high oxidation efficiency and excellent stability	High cost
Mixed Metal Oxide (MMO)	Good efficiency and economical	Moderate oxidation efficiency
Lead Dioxide (PbO_2)	High oxidation capability	Risk of lead leaching
Platinum	Excellent chemical stability	Expensive
Graphite	Low cost and easy availability	Lower treatment efficiency

Effect of Operating Parameters- Electrochemical oxidation is influenced by different operational variables such as current density, pH, electrolysis time, and concentration of the electrolyte. Studies have shown that increasing the current density increases the degradation rate of pollutants due to more generation of hydroxyl radicals. However, the major disadvantage of using high current density is the increase in energy consumption, alongside the decrease in current efficiency. In addition to current density, the pH of the medium has an important role in oxidation processes. It is known that slightly acidic to neutral pH condition gives better results than the highly alkaline pH level. Moreover, more extended electrolysis time results in better degradation rate of pollutants; however, it means more expenses. Hence, adequate conditions are to be maintained to achieve maximum efficiency and lower energy consumption.

Table 2 Industrial Applications of Electrochemical Oxidation

Industry	Major Pollutants	Treatment Performance
Textile	Synthetic dyes	High colour and COD removal
Pharmaceutical	Antibiotics and hormones	Effective degradation of pharmaceutical residues
Tannery	Sulphides and chromium compounds	Significant COD reduction
Paper & Pulp	Lignin compounds	Colour and TOC reduction
Petrochemical	Phenols and hydrocarbons	Efficient organic pollutant removal
Food Processing	Organic matter	Improved effluent quality

Conclusion

Wastewater released from various industries such as textiles, pharmaceuticals, food processing, leather, paper and pulp, and petrochemicals include many hazardous and non-biodegradable waste materials that impose a threat to the ecosystem and public health in general. Conventional wastewater treatment methods are not capable of treating such difficult-to-treat contaminants, which creates a need for implementing advanced treatment methods to treat waste. This paper provides a systematic review of electrochemical oxidation (EO), which is one of the best Advanced Oxidation Processes (AOP) of wastewater treatment. The method is based on the use of electrical energy to produce effective oxidizing agents (mainly hydroxyl radicals) that can decompose organic pollutants into harmless products for the environment such as carbon dioxide and inorganic salts. Relevant literature has been analyzing the effect of various operational parameters on the electrochemical oxidation efficiency. In particular, such factors as the type of electrodes, current, time of treatment, properties of an electrolyte and its concentration should be taken into consideration. According to the analyses made, the best performance can be achieved when using Boron-Doped Diamonds electrodes, while metals with mixed oxides can combine efficiency and cost-effectiveness. Electrochemical oxidation has proven to be effective in that it can be applied for treating waste coming from the industries where textiles, pharmaceuticals, leather, paper and pulp, petrochemicals, and other commodities are produced. Electrochemical oxidation process has a number of advantages. It is considered to be highly effective at degrading contaminants, it produces almost no sludge during treatment, and it does not consume many chemicals. The configuration of the EO process can easily be automated. In conclusion, it can be said that electrochemical oxidation is considered to be one of the most ecologically friendly and reliable methods of wastewater treatment.

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