

MODERN WATER TREATMENT BY ELECTROCHEMICAL OXIDATION - A REVIEW

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ABSTRACT

Electrochemical oxidation (EO) as electrochemical method is unique by three aspects. The first is that is the most versatility process in water treatment area and covers: various industrial effluent treatment including, amongst others, distillery, agrochemical, pulp and paper, textile dyes, oilfield and metal-plating wastes; hazardous effluent treatment including hospital wastes; removal of pathogens and persistent, pharmaceutical residues and biological from municipal wastewater treatment plant; removal of organic micro-pollutants such as pesticides and heavy metals such as arsenic and chromium from water. Another aspect is that EO is complementary with most other methods: chemical or electrochemical, and is often combined with one or more of them. And finally, this procedure is the most interdisciplinary of all. It includes: material science, (micro)biology, (electro)chemistry, environmental protection, water supply systems, etc.

Key words: electrochemical oxidation, electrooxidation, wastewaters, synergistic methods, interdisciplinary approach, ecology.

1. INTRODUCTION

Nowadays, various electrochemical treatments are methods used for removal of organic and inorganic impurities from fresh, drinking and waste waters. The most usual methods are: electrocoagulation, electroflotation, electrochemical oxidation, electrochemical reduction and electrodeposition.

The method consists of carrying out the oxidation reaction at the anode where pollutants are transferred into non-toxic substances, by decomposition into simpler compounds or transferring into oxidation form. It is used mostly for organic substances. Wastewater treatment by this procedure can be: direct or indirect electrochemical oxidation, as showed on Fig. 1.

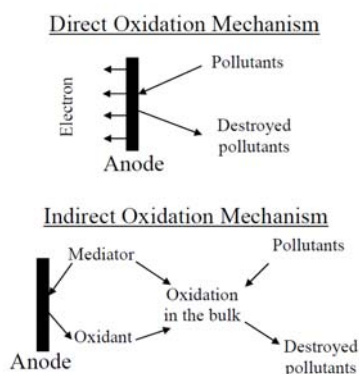


Figure 1. Pollutant removal pathway in electrochemical oxidation process [1]

Researches in this area are focused on increasing the process efficiency which depends from: electrocatalytic activity, electrochemical stability of the electrode materials and kinetics of degradation of pollutants. The first application of the electrooxidation (EO) was cyanide destruction. The EO is mainly used for degradation: aromatic compounds, pesticides, paints, industrial pollutants, pharmaceuticals waste and other organic. The advantage of this method is that finally products are mainly CO₂ and H₂O. This is the case for some organic as aliphatic, depending on stoichiometry. Even chlorine is not the problem since it is converted in the form of chloride ion.

1.1. Indirect electrochemical oxidation

Strong oxidants are produced on anode and then chemical oxidation take place. The most effective type of the indirect electrooxidation is creation of hydroxyl radicals via Fenton reagent. In Fenton reaction, highly reactive hydroxyl radicals ($\cdot\text{OH}$) are generated [2]:



To avoid the disadvantages of traditional Fenton oxidation such as potential risk in transportation of H₂O₂, a loss of reactive activity and sludge production, a modified process called Electro-Fenton method (EF) has been developed. The EF method has the advantage of allowing a better control of hydroxyl radical production; in the EF method, soluble Fe³⁺ can be cathodically reduced to Fe²⁺ which is known as electrochemical catalysis with E⁰ = 0.77 V/SHE [3].

The efficiency of this process can be increased if the anodic oxidation with BDD (boron deposited diamond) is paired with a classic electro-Fenton process with carbon fiber or oxygen diffusion cathode [4, 5]. Reaction rate of oxidation of organics with hydroxyl radical is extremely high, for example, the reaction rate constant of second order can be 10⁹–10¹⁰ mol⁻¹·s⁻¹ [6].

The indirect electro-oxidation rate is dependent on the diffusion rate of strong oxidants electroformed into solution which are able to completely convert all organic into water and carbon dioxide [1].

The electrochemical method of depollution presents many important advantages because it does not need auxiliary chemicals; it is applicable on a large range of pollutants and does not need high pressures and temperatures [7].

Further improvement could be achieved by using of UVA radiation. UV lights ($\lambda=365$ nm) was successfully used to accelerate the mineralization process [2]. This is the photoelectro-Fenton process.

1.2. Direct electrochemical oxidation

The Direct electrooxidation takes place directly at the anode through the generate of physically adsorbed "active oxygen" (adsorbed hydroxyl radical, $\cdot\text{OH}$). Direct EO process is also called electrochemical mineralization (EM) of organic contaminants. It is a relatively new technology for wastewater treatment with moderate concentrations of organic pollutants, the chemical oxygen demand (COD) up to 5 g/l.

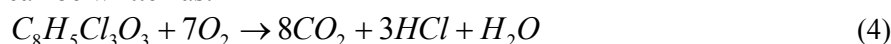
The main advantage of technology is that it does not consume chemicals, but just electrical energy. EO does not produce secondary pollution and requiring relatively little additional equipment and maintenance. These advantages make it attractive compared to most other waste water processes. A key element of this technology is anode material. Investigated the anode: glassy carbon, Ti/RuO₂, Ti / Pt-Ir, fiber carbon, MnO₂, Pt-black carbon, porous carbon felt and stainless steel. But none of the above has sufficient activity and stability.

Therefore, Pt, PbO₂, IrO₂ and SnO₂ were extensively studied anodes [8]. They were the most used ones before new development of the conductive diamond films. Currently an ideal material for the anode is boron doped diamond (BDD). Its characteristics are: high reactivity for organic oxidation, high stability and efficient use of electrical energy. Specific energy consumption for this treatment with 100% current efficiency is approximately 22kWh/kgHPK [9].

Example of complete (electro) mineralization is a direct electrochemical oxidation of the herbicide 2,4,5-Trichlorophenoxyacetic acid, also known as 2,4,5-T and Silvex (trade name) [10]. The whole process can be represented by the following reaction:



or by COD during electrochemical decomposition, the theoretical reaction of mineralization 2,4,5-T can be written as:



Oxidation potential of the anode is directly dependent on the over potential for oxygen separation and adsorption enthalpy of hydroxyl radicals on the anode surface. It follows that for an anode material: the higher the overpotential for oxygen, the greater the oxidizing power of the anode material.

2. TECHNOLOGICAL PARAMETERS OF ELECTROCHEMICAL OXIDATION

The two most important parameters are current density and current efficiency. The process may have good efficacy removing contaminants above 80% and up to 95%, but at the same current efficiency below 50% down to 15% depending on the reaction and anode material.

The literature data [12] given in table 1 shows the efficiency of the different indirect electrooxidation processes for treatment. The degradability of 2,4-dichlorophenoxyacetic acid (2,4-D) was performed for initial concentration of 2,4-D of 230ppm in 0.05M Na₂SO₄ with H₂SO₄ at pH=3.0 and temperature of 25°C [12]. Pollutant (2,4-D) is common systemic pesticide/herbicide used in the control of broadleaf weeds and is chemically similar to 2,4,5-T mentioned earlier.

Table 1. Percentage of TOC removal and apparent current efficiency (ACE) obtained for the mineralization of 100ml of 230ppm 2,4-D solution [12]

Method	Applied current, mA	% of TOC removal	ACE, %
Anodic oxidation in the presence of electrogeneration of H ₂ O ₂	100	11	4.7
	300	23	3.1
	450	26	2.5
Electro-Fenton process	100	52	7.4
	300	63	9.4
	450	73	7.7
Photoelectro-Fenton process	100	83	37.3
	300	88	12.8
	450	82	8.9

It is obvious that photoelectro-Phenton process is the most effective one. It should be noted that even that process has not great current efficiency even for the optimal conditions. Nevertheless, removal efficiency is the more important parameter, especially for the organic with less than 500ppm concentration which is mainly the case for electrooxidation. Nevertheless, removal efficiency is the more important parameter, especially for the organic with less than 500ppm concentration which is mainly the case for electrooxidation.

For the direct EO the best technological parameters are obtained using a borated diamond electrode (anode), BDD. This material features high hardness, strength, stability and resistance to thermal shocks and IR radiation with high thermal conductivity, high electric field degradation and outstanding chemical stability [13, 14]. Laboratory studies on the Si/BDD electrode give very good results and are shown in Table 2 [15]. However, in industrial conditions is not recommended for use BDD on Si substrates due to poor electrical and thermal conductivity of Si and brittleness of the electrodes. Top features of the electrode with the film have BDD on Ti substrates, (Diachem[®] as famous commercial and is trademark of Condias GmbH), but their prices are very high.

Table 2. Oxidation of organic pollutants on Si/BDD electrode [15]

Pollutant	Oxidation conditions	Current efficiency, %
Phenol	Initial concentration 0.002mol/dm ³ , current density 300A/dm ² , pH=2, charge 4,5Ah/dm ³ , final conc. of phenol <3mg/dm ³	33.4
Cyanide, CN ⁻	Initial concentration 1mol/dm ³ , current density 360A/dm ² , elimination more then 95% CN ⁻ ion, 1mol/dm ³ KOH	41
Isopropanol, IPA	Initial concentration 0.17mol/dm ³ , current density 300A/dm ² , efficiency about 90%.	>95
Acetic Acid	Initial concentration 0.17mol/dm ³ , current density 300A/dm ² , efficiency about 90%, 1mol/dm ³ H ₂ SO ₄	85

The current efficiency (CE) obtained on Ti/BDD was 46.9-78.5% in oxidizing acetic acid, maleic acid, phenol, and dyes, which is 1.6-4.3 fold higher than that obtained on the typical Si/BDD electrode [13].

3. CONCLUSION

The electrooxidation process forms an attractive alternative and is successfully applied for industrial wastewater treatment. It does not produce any undesired reaction co-product nor use toxic or hazardous materials [12]. It, therefore, eliminates the use of oxidation reagents to carry out the process which is very useful and suitable for on-site treatment, especially in small-scale facilities. Electrooxidation processes could be a pre-treatment step to biodegradation process. It enhances the biodegradability of wastewater containing inhibitory compounds by their decomposition resulting easily degradation of the rest in subsequent biological treatment. It could be an ideal finishing step in various combinations, virtually with all existing technologies and wastewater treatment systems.

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