

Electrochemical Oxidation of wastewater after Secondary Treatment for COD and Color Removal

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ABSTRACT: The newly growing world population with increasing level of pollution and continuous need for energy and food is forcing the exploration of the wastewater recycling and resource recovery. Due to the fact, water is a limited and vital resource, it should not be wasted after been used in industrial processes. Electrochemical oxidation (EO) as electrochemical method is deviated by three aspects. The first is the most versatile process in wastewater treatment area and captures different industrial effluent treatment including, 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 other heavy metals such as arsenic and chromium from water. Another aspect is that EO is complementary with most of the other methods, it can be chemical or electrochemical, and is often combined with one or more. And finally, this procedure is most interdisciplinary of all. It includes: material science, (micro)biology, (electro) chemistry, environmental protection, water supply systems, etc.

I. INTRODUCTION

Electrochemical processes have gained increasing interest in recent years for the treatment of polluted waters. They are considered to be versatile and capable of degrading a wide range of contaminants, including refractory carboxylic acids and even perfluorocarboxylic acids. Electrochemical systems offer several advantages over other approaches, such as operation at ambient temperature and pressure as well as robust performance and capability to adjust to variations in the influent composition and flow rate. They generally require no auxiliary chemicals and do not produce waste. Electrochemical processes can be adapted to various applications, and can be easily combined with other technologies. The modular design and small footprint of electrochemical systems also

Make them attractive for decentralized wastewater treatment. However, application of electrochemical treatment has been slowed down by the relatively high costs of electrodes and concerns about the presence of toxic by-products in the treated water. Numerous bench-scale studies have demonstrated the ability of electrochemical processes to remove organic contaminants from an electrolyte solution. While these studies provide an understanding of the effects of operational variables on process performance, the importance of these effects, as well as reaction kinetics, mechanisms, and expected by-products are likely to differ when electrochemistry is used to treat real waste streams. In particular, chlorine and bromine species formed at the anode can produce toxic organic chlorine and bromine-containing transformation products. Furthermore, the presence of chloride in wastewater may yield toxic chlorate and perchlorate. Most studies that have been conducted in authentic wastewater have focused on the removal of chemical oxygen demand (COD), ammonia, colour, and dissolved organic carbon (DOC). To gain insight into the use of electrochemical

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treatment under conditions likely to be encountered in industrial wastewater and water recycling systems, recent research on electrochemical treatment was reviewed. The main focus was placed on anodic oxidation because it is the most mature of the approaches employed for water treatment. Cathodic reduction, electro dialysis and related processes were also considered as alternatives for specific applications. Considering the importance of electrode materials to system performance and cost, a brief overview was made of the most commonly used anodes before assessing treatment applications.

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, electro-flotation, electrochemical oxidation, electrochemical reduction and electrode position. 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.

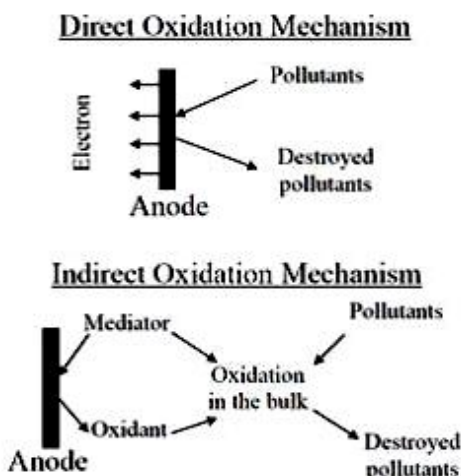
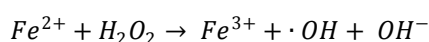


Figure 1. Pollutant removal pathway in electrochemical oxidation process [1]

Researches in this area are focused on increasing the process efficiency which depends from: electro-catalytic activity, electrochemical stability of the electrode materials and kinetics of degradation of pollutants. The first application of the electro-oxidation (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 electro-oxidation 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,

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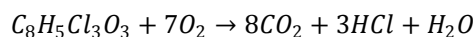
soluble Fe^{3+} can be cathodically reduced to Fe^{2+} which is known as electrochemical catalysis with $E^0 = 0.77 \text{ V/SHE}$ [3]. The efficiency of this process can be increased if the anodic oxidation with BDD (boron deposited diamond) is paired with a classic electro-Fenton process with carbon fibre 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 $109\text{--}1010 \text{ mol}^{-1}\cdot\text{s}^{-1}$ [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 ($\lambda=365 \text{ nm}$) was successfully used to accelerate the mineralization process [2]. This is the photoelectro-Fenton process.

1.2 DIRECT ELECTROCHEMICAL OXIDATION

The Direct electro oxidation takes place directly at the anode through the generate of physically adsorbed "active oxygen" (adsorbed hydroxyl radical, $\bullet\text{OH}$). 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 22 kWh/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 Silver (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 over potential for oxygen, the greater the oxidizing power of the anode material.

2.1 How Electrochemical Oxidation Works

In Electro Chemical Oxidation, There are two electrodes and an electrolyte. The two electrodes are connected with the rectifier for the current supply. Two electrodes are dipped into the electrolyte. When the current is supplied then the electrons will flow from one of the electrode, through the electrolyte and finally will come out of the other electrode. Here one of the electrode will be called Anode and other will be called Cathode. Before knowing that which is Cathode and which is anode, let's try to know exact meaning of two terms anode and cathode.

2.2 Anode vs. Cathode

The anode, is electrode where electricity flows into. And cathode is the electrode where the electricity flows out of. If a battery is connected to a load, like a bulb, then electricity flows from the positive terminal to the negative terminal. In this case, the positive terminal is the cathode, and the negative terminal is the anode. But when the battery is charging, the electricity flows into the positive terminal instead of out of it. In this case, the roles are reversed.

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Hence from this we have concluded that in our case the Anode will be on which will be connected to the Positive terminal and the Cathode will be connected to the Negative terminal.

2.3 Electrolyte

An electrolyte is that which produces an electrically conducting solution when dissolved in a polar solvent, like water. Dissolved electrolyte is separated into cations and anions, which in result disperse uniformly through the solvent. Electrically, such solutions are neutral. Most soluble salts are included in this.

In our case, the effluent will be our Electrolyte, as it will conduct electricity. Both the electrodes are dissolved in the effluent.

2.4 Rectifier

A rectifier converts alternating current (AC) into direct current (DC). The process is also known as rectification, as it "straightens" current direction. Rectifier will also be useful to alter Current and Voltage as needed.

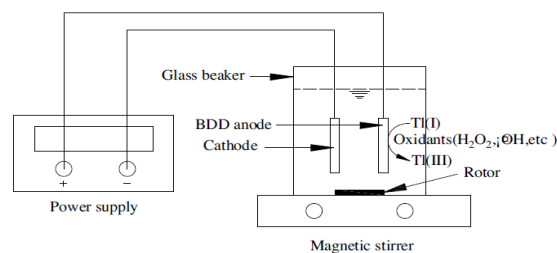


Fig: 1 Schematic diagram of Experimental setup

2.5 Experimental Procedure

- Take reactor and clean it properly with tap water.
- Fill water in the reactor and check for any of the leakages.
- Now, take two electrode plates and connect one side of both the electrodes with wires.
- Now keep electrodes in the groves.
- Give connection of electrodes to the power supply, one to positive and one to negative.
- Positive electrode is Anodes and negative one is Cathode.
- Fill 500 ml of sample liquid in the reactor.
- Start power supply and adjust the required Volt.
- Ampere reading will be set automatically on the basis of conductivity of the liquid.
- Run the batch for required time.
- Keep watch on Ampere reading as it will reduce as time passes.
- After desire time period, switch off power supply and take out the electrodes from the reactor.
- Take out treated sample in the sample bottle and then measure the COD. Compare initial and final COD.

2.6 Reactor and Electrodes

- An acrylic batch reactor having dimensions:
L= 9.4 cm, B= 6.3 cm, H= 12 cm.
- It has grooves at every 04 mm, to fit in electrodes within it.
- It has two nozzles, input at lower end and output at upper end.
- It can also be used in a continuous pattern.
- Capacity: 500 ml of liquid.
- Electrodes dimensions:

L= 125 mm, B = 50 mm, Thickness = 2 mm

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III. RESULT AND CONCLUSION

3.1 observation table

Effluent	Electrode	Time (hr.)	Voltage (V)	Electrode gap (cm)	Initial COD (ppm)	Final COD (ppm)	Initial ampere (A)	Final ampere (A)
CETP	Titanium	1	4	3	1000	700	0.88	0.71
CETP	Titanium	1.5	4	3	1500	650	0.87	0.71
CETP	Titanium	2	4	3	1000	500	0.88	0.72
CETP	Titanium	1	3	3	1000	700	0.88	0.75
CETP	Titanium	1.5	3	3	1300	900	0.86	0.77
CETP	Titanium	2	3	3	1000	650	0.88	0.78
CETP	Titanium	1	4	2	1400	1000	0.55	0.36
CETP	Titanium	1.5	4	2	1000	950	0.52	0.37
CETP	Titanium	2	4	2	1500	700	0.5	0.37
CETP	Titanium	1	3	2	1000	900	0.51	0.44
CETP	Titanium	1.5	3	2	1000	700	0.5	0.36
CETP	Titanium	2	3	2	1000	500	0.52	0.36
CETP	Aluminium	1	4	3	1200	1000	0.77	0.63
CETP	Aluminium	1.5	4	3	1200	750	0.76	0.63
CETP	Aluminium	2	4	3	1000	500	0.75	0.64
CETP	Aluminium	1	3	3	1100	950	0.78	0.71
CETP	Aluminium	1.5	3	3	1500	1200	0.76	0.64
CETP	Aluminium	2	3	3	1500	650	0.77	0.7
CETP	Aluminium	1	4	2	1200	900	0.77	0.7
CETP	Aluminium	1.5	4	2	1200	850	0.76	0.69
CETP	Aluminium	2	4	2	1350	900	0.77	0.71
CETP	Aluminium	1	3	2	1200	1000	0.69	0.64
CETP	Aluminium	1.5	3	2	1000	850	0.77	0.72
CETP	Aluminium	2	3	2	1500	700	0.73	0.66

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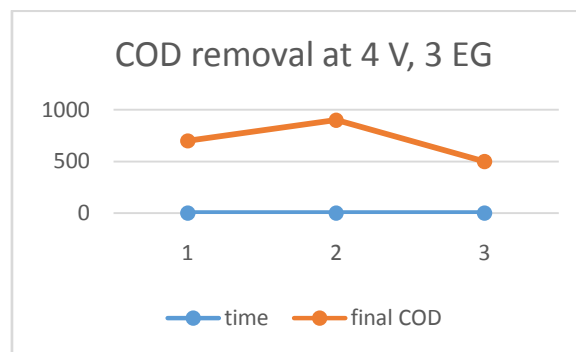
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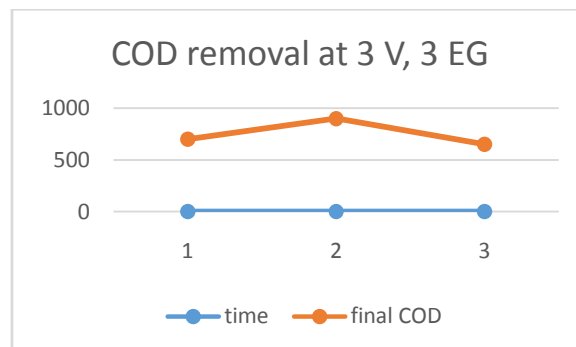
IV. GRAPHICAL REPRESENTATION OF THE OBSERVATIONS

4.1 For titanium

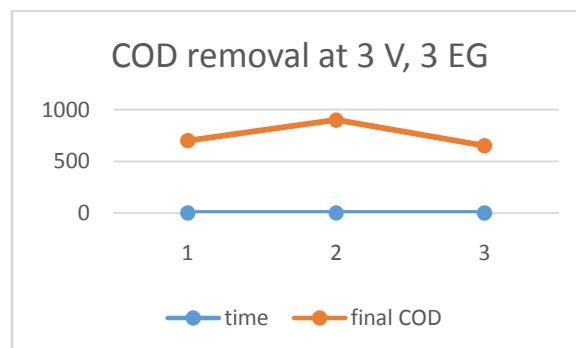
At 4 V and 3 EG



At 3 V and 3 EG



At 3 V and 3 EG



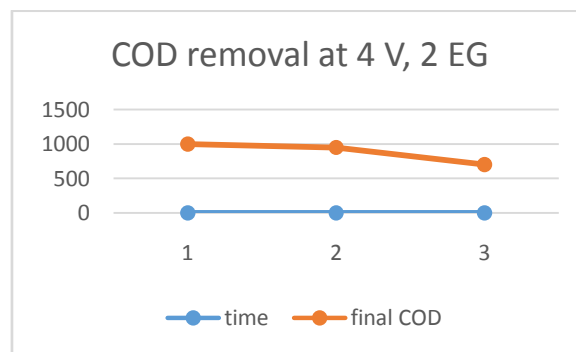
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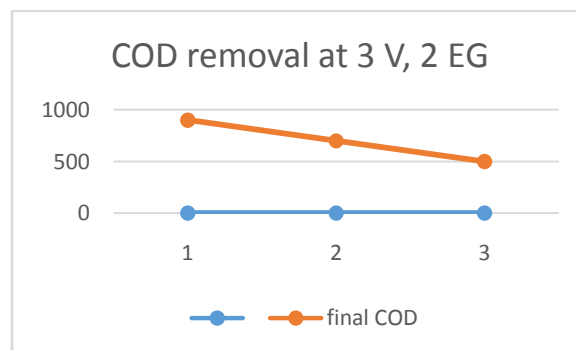
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At 4 V and 2 EG

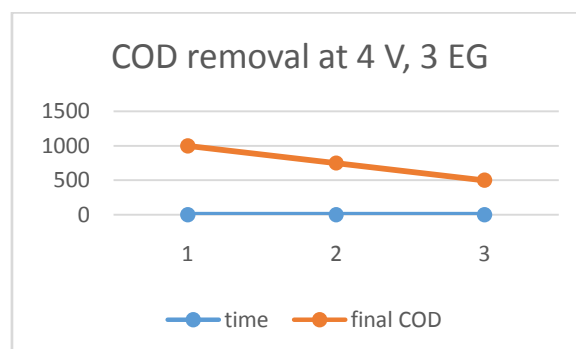


At 3 V and 2 EG



4.2 Foraluminium

At 4 V and 3 EG



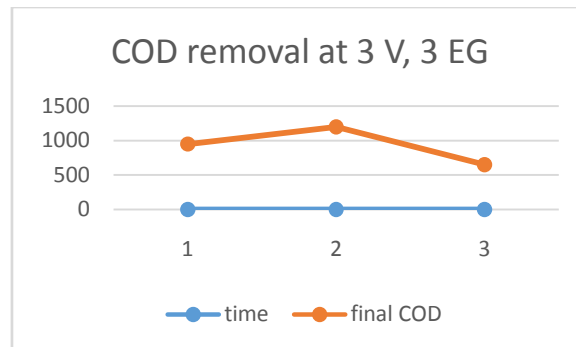
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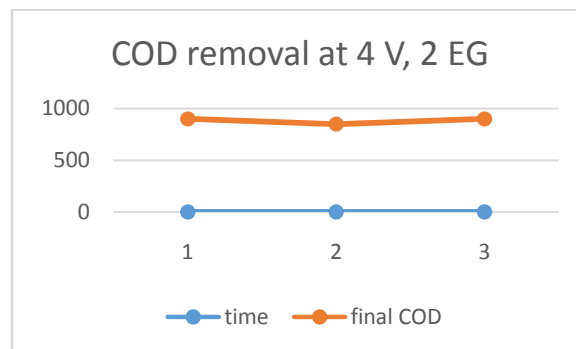
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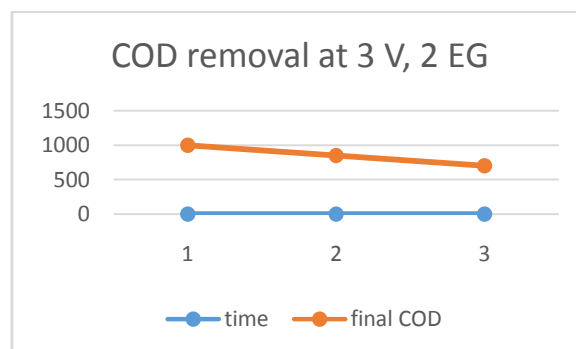
At 3 V and 3 EG



At 4 V and 2 EG



At 3 V and 2 EG



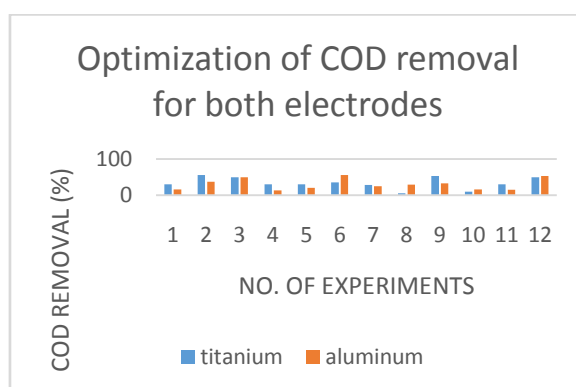
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4.1.1 Graphical Conclusion



4.3 Conclusions:

- On reducing electrode gap, at constant parameters, COD reduction increases.
- Reducing Voltage will reduce the COD reduction, eventually it will increase the time for the treatment.
- Reduction of COD will increase with increase in time.
- Decolourisation of sample will take place.
- Ampere will be reduced at constant Voltage, as conductivity of the sample will reduce.
- Titanium Electrode performs better than aluminium Electrode.
- Colour reduction by Titanium Electrode is higher compared to aluminium Electrode, at constant parameters.
- Stirring has less/no effect on the COD reduction at constant parameters (for small volume)

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