

# **Electro-Coagulation integrated with Advance Oxidation Processes: Technical Review on Treatment of Industrial Wastewater**

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**ABSTRACT:** Worldwide scarcity of water is tending people to reuse the recycled wastewater. This can also be achieved at the industrial level. Treatment of industrial wastewater can be done by selection of the suitable and efficient method of treatment for the wastewater of particular industry. In this paper review has been done on the various studies on treatment of industrial wastewater by Electrocoagulation independently as well as when integrated with various advance oxidation processes. Literature shows that treatment efficiency of the system enhanced when Electrocoagulation combined with various advance oxidation processes for the industrial wastewater treatment.

**KEYWORDS:** Water problem, Industrial wastewater, wastewater treatment, Electrocoagulation, Advance Oxidation Process.

## **I. INTRODUCTION**

The water utilization and sanitary problems faced throughout the world are very serious. The requirement of water increases as population increases. Thus the correct management of the entire water cycle is important for sustainable water supply and also for our future generation. Extraction from the natural environment must be minimized [1]. Water extraction can be minimized by reducing the demand or by utilising the available water within the system. This is achieved by increased water reuse and recycling. Thus all forms of water, apart from of quality, should be identified as a valuable and useful resource. Reuse and recycling of can be achieved by water can be achieved by the efficient treatment of wastewater. Wastewater can be domestic or industrial wastewater. Main concern of this paper is to evaluate the suitable methods for treatment of any high strength industrial wastewater.

The treatment of industrial wastewater involves many challenges that are not only limited to the technical objectives of good water quality and solid/liquid separation. In developing a treatment method, its overall environmental impact, usefulness in various industrial applications, ease of installation and operation, energy efficiency, and cost-effectiveness must be considered. There are numerous wastewater treatment units employed around the world, each having its advantages and disadvantages [2].

The sensitivity of biological treatment processes and secondary pollution caused by conventional chemical techniques make electro chemical methods trendy. Electro-coagulation is one of the finest electro chemical treatment methods. Electrocoagulation is an impressive technology to upgrade water quality. It is easy is seen that electrocoagulation when integrated with advance oxidation process such as Fenton process, Ozonation and UV radiation improves the treatment efficiency.

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## II. ELECTROCOAGULATION

Electrocoagulation (EC) is a unique method for water and wastewater treatment that is based on the electrochemical dissolution of sacrificial metal electrodes into soluble or insoluble species that improves the coagulation, the adsorption or the precipitation of soluble or colloidal pollutants [3]. In an Electrocoagulation process the coagulating ions are generated continuously and it consists of three consecutive steps:

- (i) Formation of coagulant by electrolytic oxidation of the sacrificial electrode.
- (ii) Destabilization of the pollutants, particulate suspension, and emulsion breaking
- (iii) Aggregation of the destabilized stage to flocs formation.

The destabilization mechanisms of the contaminants, particulate suspension, and emulsion breaking have been summarized as follows:

1. The diffuse double layer compression around the charged species by the ions produced by oxidation of the sacrificial anode.
2. Neutralization of charge of the ionic group in wastewater by counter ions formed by the electrochemical dissolution of the sacrificial electrode. These counter ions decrease the electrostatic interparticle repulsion to such level that the Van der Waals attraction predominates, as a result cause coagulation in the solution. Result of the process is a zero net charge.
3. Formation of floc as a result of coagulation creates a blanket of sludge that entraps and bridges colloidal particles still remaining in the solution. The hydroxides, oxyhydroxides and solid oxides give active surfaces for the adsorption of the polluting species [4].

A direct current supply is applied to metal electrodes immersed in wastewater. The flow of electrical current helps in the dissolution of metal electrodes into the solution. The dissolved metal ion, forms wide ranges of coagulated species and metal hydroxides at appropriate pH. It helps in destabilize and aggregate the suspended particles or adsorb and precipitate dissolved contaminants [5], [6], [4], [7].

The diverse reactions occurring at anode, cathode and solution are prescribed below [8], [9], [10]:

- At the cathode:  
 $3\text{H}_2\text{O} + 3\text{e}^- \rightarrow 1.5 \text{H}_2(\text{g}) + 3\text{OH}^-$
- At the anode:  
 $4\text{Fe}(\text{s}) \rightarrow 4\text{Fe}^{2+}(\text{aq}) + 8\text{e}^-$
- With dissolved oxygen in solution:  
 $4\text{Fe}^{2+}(\text{aq}) + 10\text{H}_2\text{O}(\text{l}) + \text{O}_2(\text{g}) \rightarrow 4\text{Fe}(\text{OH})_3 + 8\text{H}^+(\text{aq})$
- Overall reaction:  
 $4\text{Fe}(\text{s}) + 10\text{H}_2\text{O}(\text{l}) + \text{O}_2(\text{g}) \rightarrow 4\text{Fe}(\text{OH})_3(\text{s}) + 4\text{H}_2(\text{g})$

During electro-coagulation due to the change in pH various kind of monomeric and polymeric iron species formed are mentioned as follows  $\text{Fe}(\text{H}_2\text{O})_6^{3+}$ ,  $\text{Fe}(\text{H}_2\text{O})_5\text{OH}^{2+}$ ,  $\text{Fe}(\text{H}_2\text{O})_4(\text{OH})_2^+$ ,  $\text{Fe}_2(\text{H}_2\text{O})_8(\text{OH})_2^{4+}$ ,  $\text{Fe}_2(\text{H}_2\text{O})_6(\text{OH})_4^{2+}$  and  $\text{Fe}(\text{OH})_4^{4-}$  [11].

## III. ADVANCED OXIDATION PROCESSES

Advanced oxidation is chemical oxidation with hydroxyl radicals, which are highly reactive, oxidants having short life. The radicals must be generated in a reactor on site, where the organics in the wastewater can get in contact with radicals and oxidized.

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Advanced oxidation Processes may be used in wastewater treatment for:

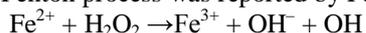
1. Overall organic matter reduction (COD)
2. Specific pollutant destruction
3. Sludge treatment
4. Increasing bioavailability of recalcitrant organics
5. Color and odor reduction

Generation of Hydroxyl radicals may be done in system using Fenton's reagent (ferrous iron and hydrogen peroxide), ultraviolet radiation/hydrogen peroxide, ultraviolet radiation/ozone, ozone/hydrogen peroxide, and other means [12].

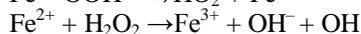
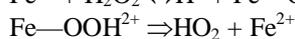
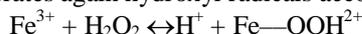
Different advanced oxidation processes for production of OH radicals are summarized here under [13]:

### a. Fenton Oxidation Process ( $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ )

The Fenton process was reported by Fenton already over a century for maleic acid oxidation:



In the presence of excess amounts of hydrogen peroxide the rate constant for the reaction of Fe ion with  $\text{H}_2\text{O}_2$  is more and Fe (II) oxidizes to Fe (III) in a few seconds to minutes. Fe (III) catalytically decomposes hydrogen peroxide and generates again hydroxyl radicals according to the reactions:



For this reason, it is assumed that the majority of waste destruction catalyzed by Fenton's reagent is simply a Fe (III)- $\text{H}_2\text{O}_2$  system catalyzed destruction method, and Fenton's reagent with an overdose of  $\text{H}_2\text{O}_2$  is Fe(III)- $\text{H}_2\text{O}_2$  process also known as Fenton-like reagent. Therefore, the ferric ion can replace the ferrous ion in Fenton's reagent. For hydrogen peroxide decomposition iron salts act as a catalyst, in further reactions Fe (II) regenerated. In the previous studies it has been observed that Fenton's reagent can be utilized as a promising oxidant for soil contaminants. Fenton's reagent is capable to destroy different phenols, herbicides, and nitrobenzene in water also reduces COD in municipal wastewater. The use of Fe (II)/ $\text{H}_2\text{O}_2$  as an oxidant for treatment of wastewater is attractive due to the facts that:

1. Iron is a very abundant and non-toxic element.
2. Hydrogen peroxide is eco friendly and simple method.

Thus, the Fenton process is very effective for generation of Fe(III)- $\text{H}_2\text{O}_2$  OH radicals; On the other hand, it involves consumption of single molecule of  $\text{Fe}^{2+}$  for every OH radical generated, require a high amount of Fe(II) [13].

### b. Ozonation at elevated pH

The decomposition rate of ozone in water increases at the higher pH for example, the half-life of ozone in water can be less than 1 min at pH 10. Oxidation of organic pollutant may take place due to a combination of reactions with OH radicals and reactions with molecular ozone. The reaction between ozone and hydroxide ions leads to the formation of super-oxide hydroperoxyl radical  $\text{HO}_2$  and anion radical  $\text{O}_2^-$ . The ozonide anion radical  $\text{O}_3^-$  is formed by the reaction between ozone and the super-oxide anion radical, which decomposes instantly giving OH radical. Here it is given in the reaction; three ozone molecules produce two OH radicals:



Naturally bicarbonate and carbonate play a significant role as scavengers of OH radicals. Passive carbonate or bicarbonate radicals are the products of a reaction between OH radical and carbonate or bicarbonate ions, which do not interact further with ozone or organic compounds. *tert*-Butyl alcohol also suppresses the chain reaction, if present. The rate of the attack by OH radicals is usually around 110 times quicker than the corresponding reaction rate for molecular ozone. The cost of electricity for ozone generation is the major operating cost for the ozone oxidation process [13].

### c. Ozone - hydrogen peroxide ( $\text{O}_3/\text{H}_2\text{O}_2$ ) - (Peroxone)

Addition of hydrogen peroxide to ozone can initiate the decomposition cycle of ozone, resulting in the formation of OH radicals:

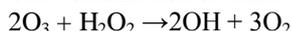
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The reaction continues along the indirect pathway described above and OH radicals are produced

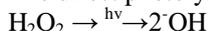
The combination of different reaction steps shows that two ozone molecules produce two OH radicals:



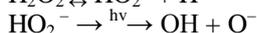
Research shows better degradation of the pesticide in water treated with ozone–hydrogen peroxide combination as compared to ozone alone. The performance of the process depends on the ozone dose, contact time, and alkalinity of water [13].

### d. Hydrogen peroxide–UV radiation ( $\text{H}_2\text{O}_2/\text{UV}$ )

The direct photolysis of hydrogen peroxide leads to the formation of OH radicals:



And  $\text{HO}_2^-$  which is in acid–base equilibrium with  $\text{H}_2\text{O}_2$  soaks up the UV rays of the wavelength 254 nm, the reaction is as follows:



Previous studies show that  $\text{H}_2\text{O}_2/\text{UV}$  process has been successfully used for the destruction of chlorophenols and other chlorinated compound. In addition the molecules of desethylatrazine, simazine and atrazine can be mineralized ultimately to carbon dioxide within practical irradiation period of time in the presence of  $\text{H}_2\text{O}_2$  [13].

### e. Ozone–hydrogen peroxide–UV radiation ( $\text{O}_3/\text{H}_2\text{O}_2/\text{UV}$ )

The adding up of  $\text{H}_2\text{O}_2$  to the  $\text{O}_3/\text{UV}$  process speeds up the decomposition of ozone, which causes an increase in the rate of OH generation. It is very cost effective to add hydrogen peroxide from outside at a reduced UV flux in processes involving pollutants that are weak absorbers of UV radiation.  $\text{O}_3/\text{H}_2\text{O}_2$  must be considered as a substitute to photo oxidation processes if direct photolysis of pollutants is not a major issue. The types of wastewater, wastewater flow rate, and the extent of removal required are the key factors which influence the capital and operating costs for the  $\text{UV}/\text{O}_3$  and/or  $\text{H}_2\text{O}_2$  systems [13].

## IV. INDUSTRIAL APPLICATIONS

From the literature study of earlier work done in the field of Electrocoagulation and Advance treatment processes like Fenton oxidation and Ozonation it has been observed that these methods are useful in the treatment of wastewater from various industries.

Electrocoagulation (EC) treatment is applied widely in the numerous industries such as textile, potato chips manufacturing [14] [15], paint manufacturing [16], distillery [17], chemical mechanical polishing (CMP) [18], tannery [19], vegetable oil refinery wastewater (VORW) [20], paper and pulp [21] pharmaceutical [22] other industries successfully. Results show that EC is very effective in the removal of COD and solids from most variety of wastewater.

Fenton and Electro Fenton has proved to be a simple and efficient methods for the treatment of wastewater in aspect of COD and color removal from Basic Dyes [23], [24] pharmaceuticals industry wastewater [25] Agate Industry [26] etc. Results shows that Fenton oxidation method efficiently removes color and COD which indicates that Fenton Oxidation method elements the organic and refractory inorganic matters.

Ozonation alone and combined with other treatment process shows a very good results in the treatment of water and wastewater of various industries such as bamboo industry wastewater [27], Leather dye effluent [28], Distillery and Tomato wastewater [29]. [30], investigated the efficiency of different ozone-based advanced oxidation processes like  $\text{O}_3$ ,  $\text{O}_3/\text{UV}$  and  $\text{O}_3/\text{UV}/\text{H}_2\text{O}_2$  on the treatment of wastewater from winery industry. Ozonation showed a great efficiency in the COD removal from above mentioned industries and other wastewaters. Ozonation has been successfully employed in decolorization and degradation of Dye stuffs like anthraquinone dye C.I. Reactive Blue 19 [31] and Bomaplex Red CR-L dye [32].

Some literature shows the use of Electrocoagulation with hydrogen peroxide and ozone in combination for the treatment of wastewater. [33], has used the electrochemical treatment of alcohol distillery wastewater by electrocoagulation with and without the presence of  $\text{H}_2\text{O}_2$ . According to the results obtained, only electrocoagulation was not very effective and Electro Fenton (EF) i.e. electrocoagulation with  $\text{H}_2\text{O}_2$  was found to be more efficient than EC alone for the treatment of

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wastewater from alcohol distillery which has high concentration of refractory organic matters. [34] in their work makes a comparison between Electrocoagulation, photoelectrocoagulation, and peroxi-photoelectrocoagulation processes in the COD removal peroxi-electrocoagulation from pharmaceutical industry wastewater. Results show that under the optimal conditions the superior COD removal efficiency was achieved in the peroxi-electrocoagulation i.e. Fenton oxidation combined with Electrocoagulation. Also [35] investigated the hybrid technique of electrocoagulation assisted with ozone for color and COD removal in distillery effluent. The result shows that the hybrid technique was more efficient as compare to electrocoagulation and ozonation individually.

## V. CONCLUSION

An observation from the earlier studies on the hybrid system for treatment says that application of Electrocoagulation with hydrogen peroxide and ozone individually or both combined together could result in a more powerful method of generating hydroxyl radicals and thus improve the rate of organic/inorganic content degradation in wastewater. The integration of the Electrocoagulation with Fenton and Ozonation method can be the good option for the treatment of wastewater from various industries.

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