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A Review On Degradation Of Wastewater By Electrochemical Advanced Oxidation Process

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Abstract– As environmental preservation becomes a significant societal issue and more stringent laws on effluent discharge are enacted, more effective techniques to deal with non-biodegradable and harmful contaminants are necessary. Synthetic organic dyes in industrial effluents cannot be eliminated by standard wastewater treatment, making the development of new environmentally friendly methods capable of entirely mineralizing these non-biodegradable chemicals an essential task. In comparison to traditional wastewater treatment technologies, advanced oxidation processes (AOPs) have developed as effective, promising, and environmentally acceptable approaches for the treatment of wastewater with high levels of pollutants in recent years. AOPs have turned into a significant avenue of technology for treating resistant pollutants via several paths such as "Enhanced Electrolysis," "Ultraviolet radiation," and "Ozonation.", "Sonolysis," etc. Many AOPs rely on the production of powerful oxidants in situ, such as hydroxyl radicals, which can totally mineralize or destroy organic contaminants. This review study focuses on numerous research on the Electro-Fenton technique for treating industrial wastewater. The investigation of several parameters that influence the Electro-Fenton process, such as pH, current density, applied voltage, hydrogen peroxide concentration, and interfacial tension, The distance between the electrodes, the rate of oxygen sparging, and the temperature have all been investigated. This paper examines the Electro-Fenton process in depth, including its basic concept, mechanism, benefits, and drawbacks, in order to get a better scientific knowledge of how to treat industrial wastewater.

***Key Words*: Advanced oxidation processes, Electro-Fenton process, Wastewater treatment, Hydroxyl radicals.**

1. INTRODUCTION

Industrial wastewater treatment is a popular issue among scientists around the world, as it poses a significant threat to air, soil, and aquatic life, as well as human and animal health (Boczkaj et al. 2017). Industrial wastewater with high BOD, COD, color, recalcitrant/toxic compounds, heavy metals, and other pollutants is discharged from a variety of industries, including dyes, textiles, distilleries, paper and pulp, tanning, leather manufacturing, and breweries (Chandra and Kumar, 2015, 2018), where conventional treatment fails to remove all pollutants from the effluent due to inefficiency, high operation costs, and feasibility of treatment (Chandra and Kumar, 2015, 2018). (Scott and Ollis, 1995). The properties and content of industrial effluent differ depending on the industry, and no uniform method/technology exists.

Because it is mostly dependent on the concentration and kind of contaminants present in the effluent, it is viable to treat. Since the previous decade, the government has enacted legislation that restricts and regulates pollutant emissions, resulting in a significant growth in the number of research and businesses dealing with industrial wastewater treatment.

Furthermore, because the effluent comes from a variety of sectors such as textiles, pharmaceuticals, and chemicals, the quality and amount of the effluent is always changing, and the inflow properties of the wastewater vary according to the company and its procedures. As a result, the treatment of mixed wastewater has gotten a lot of attention. Furthermore, because the effluent contains some non-biodegradable recalcitrant chemicals, further treatment is not an option (Roshini et al., 2017). As a result, Advanced Oxidation Processes (AOPs) are gaining traction as a cost-effective way to remove hazardous, recalcitrant, and non-biodegradable substances from wastewater (Gogate and Pandit, 2004; Bagal and Gogate, 2014; Oturan and Aaron, 2014; Nidheesh, 2015, 2017). EAOPs have played an important role in wastewater treatment during the last decade since they have a tendency to remove a variety of organic contaminants from wastewater (Rodrigo et al., 2014; Vasudevan and Oturan, 2014; Nidheesh et al., 2018).

There are different EAOPs like anodic oxidation (Ammar et al., 2012; Murati et al., 2012; Trellu et al., 2017), electro-Fenton process (Özcan et al., 2009; Oturan et al., 2015), peroxi-coagulation process (Nidheesh and Gandhimathi, 2014; Nidheesh, 2018), bioelectro-Fenton (Olvera-Vargas et al., 2016b, 2016a), electroperoxone (Wang, 2017; Yang et al., 2018) etc. The main benefit of EAOPs is its affinity towards the environment which is due to the electron as the main reagent (Peralta-Hernández et al., 2009).

Brillas et al., 2009; Zcan et al., 2009; Nidheesh and Gandhimathi, 2012) regard the electro-Fenton (EF) process to be one of the most significant EAOPs. The EF method was chosen for this investigation because of its quick reaction time, the creation of hydroxyl radicals by in-situ electro regeneration of H2O2 and Fe2+, the absence of H2O2 transit costs, the low cost of Fenton's reagent, and other factors (Nidheesh and Gandhimathi, 2012). When used to decompose organic contaminants from mixed industrial effluent, the EF process has proven to be an effective method.

The EF method is a new innovation in the realm of industrial wastewater treatment since it allows for full mineralization of pollutants without creating harmful byproducts in the system. In that respect, the current study focuses on the basic mechanics of the EF process as well as the parameters impacting the treated effluent produced by the EF process in order to tackle the refractory contaminants found in industrial wastewater.

2. Advanced Oxidation Processes (AOPs)

Initially, AOPs were proposed to deal with potable water treatment, but they have since evolved into effective treatment methods for eliminating refractory, low biodegradable, highly chemical stable, and inhibiting contaminants from wastewater (Kumar et at 2021). The AOPs study the process of in situ formation of oxidant species such as hydroxyl radicals (OH.), which are extremely reactive in the reaction. The OH. radical is a non-selective radical, ubiquitous in nature, powerful and has an oxidation potential of 2.8 V. The The presence of radicals in the system degrades organic contaminants in four ways: abstraction of hydrogen, electron transfer, radical addition, and radical combination. The produced OH. radical aids in the mineralization and degradation of organic contaminants, as well as their transformation into CO2, H2O, and a small quantity of inorganic ions (Eq.1) (Kumar et al 2021).

$$\text{Organic species} + OH^{\cdot} \longrightarrow CO_2 + H_2O + \text{inorganic ions} \quad (1)$$

The reactive agents can be produced with the help of different processes like Fenton based oxidation, photocatalysis, sonolysis, ozone-based oxidation and also by combining various processes like peroxone (O_3/H_2O_2), peroxone coupled with ultraviolet light ($O_3/H_2O_2/UV$), Fenton (H_2O_2/Fe^{2+}), $O_3/TiO_2/H_2O_2$, etc. (Fig.1).

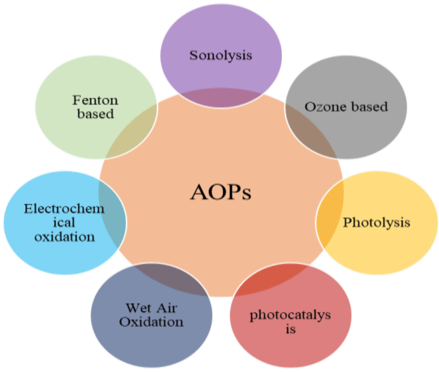

Fig -1: Classification of a major class of AOPs used to treat complex wastewater

3. Principle of Electro-Fenton Process

Apart from many other methods, the EF technique has been widely employed to reduce persistent organic compounds throughout the previous decade. EF is a popular treatment method due to its quick pollutant removal rate, greater degradation rate for persistent organic pollutant elimination, and environmental compatibility (Oturan et al., 2000; Brillas et al., 2009). The electro-generation of Fenton's reagent in the electrochemical cell produces hydroxyl radical in this procedure.

As shown in Figure 2, when reduction of O_2 electron occurs in the acidic medium, on the surface of cathode there is generation of hydrogen peroxide (Oturan et al., 2008a; Nidheesh and Gandhimathi, 2012). A continuous oxygen source is required nearby cathode to generate hydrogen peroxide in the electrochemical cell (Eq. 2). When ferrous ions in the form of catalyst is added in the solution it leads to the formation of OH. according to (Eq. 3).

$$O_2 + 2H^+ + 2e^- \longrightarrow H_2O_2 \quad (2)$$

$$Fe^{2+} + H_2O_2 \longrightarrow Fe^{3+} + OH^- + OH\cdot \quad (3)$$

Main Pros of the EF process are as follows (GemaPliegoa et al., 2015):

- Complete mineralization and degradation of pollutants can be achieved.
- No transportation cost for H_2O_2OH. is produced in the electrochemical cell by in-situ electro regeneration of H_2O_2 and Fe^{2+}

The Cons of the EF process are as follows (GemaPliegoa et al., 2015):

- The process is operated in acidic conditions (pH-2 to 3)
- Higher operational and maintenance cost is required
- The EF process is linked with the concentration polarization in the electrodes

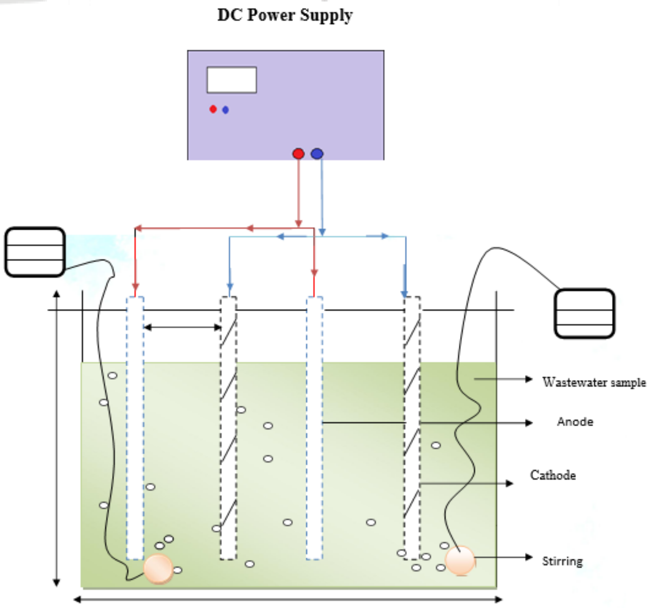

Fig-2: Electro-Fenton process

4. Parameters affecting Electro-Fenton Process

4.1 Effect of pH

One of the most essential elements in the E-Fenton process is the pH. In general, the Fenton reaction was carried out in an acidic environment. The ideal pH of the Fenton reaction, according to most research, is about 3. (Ghoneim et al. 2011; Zhou et al 2007; Wang et al. 2008; Mei et al. 2007). In the traditional Fenton process, iron species begin to precipitate as ferric hydroxides at higher pH values. On the other hand, iron species form stable complexes with H_2O_2 at lower pH values, leading to deactivation of catalysts. Consequently, the oxidation efficiency dramatically decreases (Wang et al. 2010). At higher pH, the efficiency of E-Fenton process decreases rapidly, especially pH> 5. This is due to the fact that H_2O_2 is unstable in basic solution. H_2O_2 rapidly decomposes to oxygen and water at neutral to high pH with rate constant of 2.3 × 10−2 and 7.4× 10−2 min−1 at pH 7.0 and 10.5, respectively (Shemer et al. 2006; Wang et al. 2001).

4.2 Effect of Oxygen sparging rate

Because raising the oxygen sparging rate can raise the dissolved oxygen concentration and mass transfer rate of dissolved oxygen, and therefore increase the formation of hydrogen peroxide, oxygen is one of the primary parameters that limits the performance of the Electro-Fenton system (Wang et al. 2010). Chen and Lin (2009) found that the electrochemical oxidation of TOC corresponds well with the hydrogen peroxide produced at the cathode, and that at a flow rate of 100 mL/min, the saturation solubility of oxygen in wastewater is almost obtained. However, even when the oxygen sparging rate was raised from 0.3 to 0.4 L/min, the colour removal efficiency remained nearly constant at a current density of 68 A/m2. 2008, Wang et al. The results show that when the oxygen sparging rate exceeded 0.3 L/min, color removal became governed by the kinetics of hydrogen peroxide formation (Wang et al. 2008). Wang et al. (2010) observed similar findings following the same procedure. The oxygen sparging rate was over 150 L/min for COD removal.

4.3 Effect of Temperature

Although temperature has a beneficial influence on Fenton and related processes, the increase in organic compound elimination owing to temperature is minimal in comparison to the other parameters. Temperatures that are either low or too high have a detrimental influence on the efficiency of the operation. Guedes et al. (2003) found that a temperature of 30 °C is best for the breakdown of cork cooking wastewater. Because of the considerably better treatment efficacy in this temperature range, temperatures between 20 and 30 °C can be regarded as an ideal range (Umar et al. 2010). The COD removal effectiveness of the Fenton process rose marginally as the temperature climbed from 15 to 36 °C, according to Zhang et al. 2005. According to Wang (2008), the rate of dye degradation was slower at low temperatures and the level of deterioration was greater before 100 minutes at 20–30 °C.

4.4 Effect of Applied current density

At the cathode, the supplied current drives the reduction of oxygen, resulting in the production of hydrogen peroxide. Higher applied current produces more hydrogen peroxide, which leads to a rise in the amount of hydroxyl radicals in the electrolyte medium, which are extremely reactive and responsible for deterioration (Sankara et al. 2003). An electrochemical system with a greater applied current density will have a higher applied voltage (Wang et al. 2010). At increasing current density efficiencies, E-efficiency Fenton's will be reduced. Because of this, the electrolytic cell's competitive electrode reactions According to some research, the current density in the E-Fenton process should not exceed 10 A/m2, while others say the top limit should be 6.4 A/m2 (Zhang et al. 2004).

4.5 Fe^{2+} Concentration

The quantity of Fenton reagent is a key factor in determining how many hydroxyl radicals are produced and how efficient Fenton processes are. The ratio of hydrogen peroxide to iron species concentration is a crucial parameter in every Fenton process, and there is an ideal ratio between these Fenton's reagents for maximal hydroxyl radical generation (Brillaset al. 2009; Nidheesh and Gandhimathi 2014b). The rate of hydrogen peroxide produced in the EF process is constant and is dependent on voltage, cathode material, and other parameters. ozcan and colleagues. the early phases of electrolysis, 2008a noticed a rapid electroproduction of H2O2, but after that, the H2O2 accumulation rate reduced and reached a steady-state value when the generation rate at the cathode and the decomposition rate at the anode were equal. In an electrolytic system, this phenomenon is extremely difficult to manage. As a result, the generation of hydroxyl radicals in the EF process is more dependent on the quantity of iron species.

4.6 Distance between the electrodes

Another key aspect that impacts the removal of pollutants in the E-Fenton process is the distance between electrodes. The ohmic drop process is reduced when the distance between the electrodes is reduced. through the electrolyte, resulting in a reduction in cell voltage and energy usage (Fockedey et al. 2002). According to Zhang et al. (2006), the COD removal efficiency from landfill leachate remained constant at electrode distances of 1.3 to 2.1 cm. For shorter or longer distances, the E-Fenton system's removal efficiency was lower. When the electrodes were put too close together, electro-regenerated Fe2+ might easily oxidize to ferric ion at the anode (Zhang et al. 2006). The limiting mass transfer of ferric ions to the cathode surface, which limits ferrous ion regeneration, is caused by a longer distance (Zhang et al. 2006). According to Atmaca (2009), alterations in the spacing between the electrodes have a negligible impact on treatment effectiveness.

5. CONCLUSION AND WAY FORWARD

Although extensive study has been done to protect the entire ecosystem from being harmed, one of the issues that today's world faces is the correct disposal and effective treatment of industrial wastewater. AOPs and their various combinations, on the other hand, have shown to be an effective treatment method for dealing with the resistant qualities of wastewater generated by diverse industries. They've been used in pilot and bench scale studies. However, commercial and long-term application is problematic since these technologies consume a lot of energy and are expensive to maintain and operate. As a result, attempts are being made to assess the benefits and drawbacks of implementing it on a large scale in various businesses. In the recent decade, the use of E-Fenton to remove organic pollutants from wastewater has gotten a lot of attention. Various types of electrolytic reactors were investigated. employed in the E-Fenton research The future scope of the EF process will be determined by the collaboration of engineers, electrochemists, and chemists in order to ensure that these technologies can be applied and used at a field size.

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