Treatment of Pharmaceutical Industry Wastewater by Photoelectro-Fenton Oxidation

A. Elif ATEŞ*, Sinan ATEŞ 1
1Department of Environmental Engineering, Istanbul University – Cerrahpasa, Turkey

* (ayseelif.ates@iuc.edu.tr) Email of the corresponding author

Abstract – The use of Photoelectro-Fenton oxidation to treat real pharmaceutical effluent is an attractive option for the elimination of complex and persistent organic contaminants. This advanced oxidation process combines the electrochemical generation of highly reactive hydroxyl radicals (OH•) with the photochemical degradation of by-products, resulting in the efficient removal of pharmaceutical compounds from wastewater. In the Photoelectro-Fenton process, an appropriate anode material, such as BDD or DSA, is used to generate OH• radicals through the electrochemical oxidation of Fe2+ ions. The addition of a small amount of Fe2+ and H2O2 facilitates the Fenton reaction, leading to the production of additional OH• radicals in the solution. The presence of these OH• radicals ensures the effective oxidation of pharmaceutical pollutants, which are often resistant to conventional wastewater treatment methods. The use of UV or sunlight irradiation further enhances the Photoelectro-Fenton process by promoting the photodecomposition of intermediate by-products formed during the oxidation process. This simultaneous electrochemical and photochemical degradation mechanism provides synergistic effects, resulting in enhanced degradation and mineralization of pharmaceutical compounds. Studies have demonstrated the successful application of Photoelectro-Fenton oxidation for the treatment of real pharmaceutical wastewater, showing significant removal efficiencies for a wide range of pharmaceutical compounds, including antibiotics, analgesics, and hormones. Additionally, the process has been shown to effectively degrade recalcitrant by-products and reduce the overall toxicity of the wastewater. However, it is important to consider factors such as optimal pH, Fe2+ and H2O2 dosages, irradiation intensity, and reaction time to achieve optimal treatment efficiency. Furthermore, the cost-effectiveness and scalability of the Photoelectro-Fenton process need to be evaluated for its potential implementation in large-scale wastewater treatment facilities.

Keywords – Oxidation, Photoelectro-Fenton, Electro-Fenton, Wastewater Treatment, Pharmaceutical Industry

I. INTRODUCTION

The pharmaceutical and biotechnology industry holds the top position worldwide in terms of research and development (R&D) investments. Nonetheless, the discharge of pharmaceutical substances into the natural environment poses a significant ecological and toxicological threat due to their nature as active compounds designed to elicit biological responses. Because conventional wastewater treatment plants cannot completely degrade pharmaceuticals and their byproducts, these compounds and their transforming products have been found in a variety of aquatic environments across the world [1,2]. While households and hospitals are the main sources of pharmaceuticals in the environment, pharmaceutical manufacturing companies also contribute significantly by releasing substantial quantities of poorly biodegradable organic compounds used in the production of active substances. The companies specialized in chemical production and fermentation techniques within the pharmaceutical industry are the leading contributors
to excessive water consumption and wastewater creation. [3].

Pharmaceutical manufacturing processes require a significant amount of clean water, resulting in the production of large volumes of wastewater. The estimated average daily wastewater output from a pharmaceutical manufacturing unit is 1.0068 billion liters, according to the United States Environmental Protection Agency (EPA) [4].

Pharmaceutical manufacturing activities have been classified as 'red category' due to factors such as high COD, BOD, TSS, additional chemicals, and the presence of pharmaceuticals or their byproducts, owing to the significant volume, complex composition, and hazardous characteristics of the wastewater produced. Consequently, if pharmaceutical wastewater is released into the environment without proper treatment, it can pose significant threats to the environment and ecosystems [5,6]. Even at a concentration as low as 0.001 parts per million (ppm), organic pollutants like pharmaceutical wastes can lead to water pollution and have negative effects [7]. Such chemicals not only pollute drinking water but also disrupt the endocrine function in marine life, including fish and other sea creatures, leading to adverse impacts on both humans and animals. Various conventional methods, including adsorption, chemical coagulation and flocculation, chemical precipitation, and solidification, have been used for the removal of organic pollutants. These approaches, however, have limitations such as high costs, poor effectiveness, and incomplete deterioration [8].

There has been an increasing awareness of the potential risks associated with pharmaceutical wastewater, leading to numerous studies focused on its treatment. These studies have explored various methods, including activated carbon filtration and coagulation, membrane bioreactors, biological treatments, advanced oxidation processes [9].

Nowadays emerging technologies such as advanced oxidation processes (AOPs) and oxidation-reduction techniques using hydroxyl radicals have shown promising results in treating a variety of pollutants, including dyes, phenols, pesticides, pharmaceuticals, polymers, and chlorophenols. However, despite their success in laboratory settings, the commercial viability of AOPs for real wastewater applications remains challenging. Several obstacles hinder their implementation on a large scale, including longer treatment times, process optimization, higher energy costs, catalyst separation, and the availability of a suitable light source [10].

Among various advanced oxidation processes (AOPs), Fenton treatment has demonstrated its effectiveness in completely removing pharmaceuticals at trace levels from water. However, the requirement of a high dosage of H₂O₂ (hydrogen peroxide) and the generation of significant amounts of iron sludge have hindered its large-scale implementation. On the other hand, TiO₂ photocatalysis offers two approaches: slurry and fixed bed. The fixed-bed approach is generally preferred due to the additional costly step of catalyst separation in the slurry approach. Although there are several studies in the literature that use fixed photocatalysts, issues such as longer treatment time, a frequent combination of charges, mass transfer problems, and low catalyst recyclability efficiency have hindered its adoption on a broader scale [9,10]. Photoelectro-Fenton has emerged as effective methods for reducing organic pollutants [11].

II. FENTON OXIDATION

Dark-Fenton (DF) oxidation is a process that utilizes Fe²⁺ as a catalyst and H₂O₂ as an oxidant to produce highly reactive hydroxyl radicals (OH·) without the need for a light source. This method demonstrates enhanced efficiency under acidic conditions and is effective in generating OH· without the requirement of light [12].

The Fenton processes have certain limitations such as the cost associated with reagents, sludge production, and energy consumption. However, the involvement of Fe²⁺ and Fe³⁺ ions in these processes serves a dual function of both coagulation and oxidation. This capability enables the Fenton processes to potentially replace the coagulation process in primary treatment, leading to reduced sludge formation [11, 13].

A. Electro-Fenton

The electro-Fenton (EF) process, also known as Fered Fenton, combines electrochemistry and Fenton processes, offering several advantages. The EF process involves the electrochemical generation of Fe²⁺ ions, which then participate in a Fenton reaction. Additionally, during the procedure, H₂O₂ is directly injected into the reaction cell. This novel technique has been shown to be efficient in treating
concentrated wastewater containing high quantities of hazardous or resistant organic chemicals, promoting contaminant oxidation. [14].

The generation of hydroxyl radicals (OH\(^{-}\)) is a significant outcome of these techniques, achieved through the decomposition of H\(_2\)O\(_2\) with Fe\(^{2+}\) ions under acidic conditions. The electro-Fenton (EF) process, which uses electricity to create extra hydroxyl radicals, can considerably improve the effectiveness of this process. The EF process combines the benefits of both electrochemical and Fenton processes. It results in the production of more hydroxyl radicals, leading to the oxidation of organic compounds into CO\(_2\) during the treatment [15-17].

EAOPs have emerged as highly promising technologies for the treatment of stubborn organic pollutants, including pharmaceutical compounds, due to their exceptional mineralization efficiency and environmentally friendly nature. Among these processes, the Electro-Fenton (EF) process has garnered significant attention due to its simplicity and economic viability [18-20].

The electro-Fenton (EF) process generates H\(_2\)O\(_2\) cathodically by decreasing dissolved O\(_2\) (as indicated in Equation (1)) on an appropriate electrocatalyst. Carbon materials are widely available, affordable, non-toxic, and find diverse applications in various fields such as electrochemistry, electromagnetics, environment, and biomedicine. In EF, H\(_2\)O\(_2\) is then decomposed catalytically by Fe\(^{2+}\), leading to the production of hydroxyl radicals (OH\(^{-}\)) via the Fenton’s reaction (as shown in Equation (2)). These highly reactive OH\(^{-}\) radicals (with a standard electrode potential of 2.8 V/SHE) play a vital role in the oxidation and mineralization of organic pollutants. Remarkably only a little amount of Fe\(^{2+}\) is required since Fe\(^{2+}\) ions are continually replenished at the cathode according to Equation (3). Although Fe\(^{3+}\) ions may be regenerated in solution form by processes (4) and (5), their kinetics are slower [21-25].

Between 1994 and 2001, the Brillas and Oturan groups conducted ground-breaking research on EF for wastewater treatment. Their studies demonstrated the rapid degradation of organic pollutants, but highlighted the challenge of weak mineralization due to the limited effectiveness of hydroxyl radicals in attacking persistent Fe(III) carboxylate species. To address this issue, the Brillas group introduced UVA light illumination to the EF-treated solution, leading to the development of the photoelectron-Fenton (PEF) process in 1995. In 2007, they further advanced the technology by harnessing sunlight as an economical and renewable light source, resulting in the solar PEF (SPEF) process. Since then, PEF and SPEF have gained considerable attention and have been extensively investigated by numerous research groups due to their outstanding efficacy in removing organic pollutants from wastewater [26-28].

In the homogeneous EF process, by adding a moderate amount of catalytic Fe\(^{2+}\), the oxidation power of the produced H\(_2\)O\(_2\) is greatly increased, typically around 0.5 mM. This addition leads to the production of Fe\(^{3+}\) ions and homogeneous OH\(^{-}\) radicals through the well-known Fenton’s reaction (5). The EF process achieves optimal performance at a pH value close to 3 [28-29].

Organic pollutants are largely oxidized by both homogeneous OH\(^{-}\) radicals and heterogeneous M(OH) species in the homogeneous electro-Fenton (EF) treatment, outperforming the oxidation capabilities of AO and AO- H\(_2\)O\(_2\), where only the latter oxidant is active. However, the homogeneous EF process has significant drawbacks: (i) it is only viable in acidic conditions, with optimal performance at pH 3, as its effectiveness rapidly declines at pH values above 4 due to the precipitate of iron hydroxides; and (ii) the formation of resistant Fe(III) compounds with certain intermediaries, such as final carbohydrates, significantly inhibits organic mineralization [27, 30].

B. Photoelectro-Fenton Oxidation

The cathodic reduction of O\(_2\), injected directly into the mixture or at the cathode interface, is a well-known two-electron process that generates H\(_2\)O\(_2\) according to reaction (1) under acidic conditions (E = 0 V/SHE). Carbonaceous cathodes exhibit excellent electrocatalytic activity for reaction (1), resulting in efficient H\(_2\)O\(_2\) production under homogeneous conditions. However, the cathode material and operating circumstances have the most impact on the amount of stored H\(_2\)O\(_2\) in the electrolytic solution. In an undivided cell, At the anode M surface, H\(_2\)O\(_2\) is oxidized to O\(_2\) by the hydroperoxyl radical (HO\(_2^•\)) produced by the process from reaction (2) [11, 26, 30-33].

\[
O_2 + 2H^+2e^- \rightarrow H_2O_2 \quad (1)
\]
\[ H_2O_2 \rightarrow HO_2^- + H^+ + e^- \] (2)
\[ M + H_2O \rightarrow M(\cdot OH) + H^+ + e^- \] (3)
\[ 3H_2O \rightarrow O_3 + 6H^+ + 6e^- \] (4)

Reaction (3) generates the primary oxidant M(OH) responsible for the oxidation of organic pollutants in advanced oxidation (AO) processes. Another variation of this process, called AO-H_2O_2, involves the cathodic generation of H_2O_2. AO-H_2O_2 exhibits slightly higher oxidation power compared to AO, as H_2O_2 itself has a limited oxidation capability [11, 27-29].

\[ Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + HO^- \] (5)

In the homogeneous PEF process, an acidic wastewater is subjected to EF treatment while simultaneously exposed to UV light. Artificial lamps emitting 315-400 nm (UV-A), 280-315 nm (UV-B), or 100-280 nm (UV-C) wavelengths are used. The enhanced mineralization observed in Photoelectro-Fenton with ultraviolet-A or ultraviolet-B irradiation is attributed to the improved Fenton's reaction (5) through additional Fe^{2+} regeneration [11, 26, 34].

\[ Fe(OH)^{2+} + hv \rightarrow Fe^{2+} \cdot OH \] (6)
\[ Fe(OOCR)^{2+} + hv \rightarrow Fe^{2+} + CO_2 + R^+ \] (7)
\[ H_2O_2 + hv \rightarrow 2 \cdot OH \] (8)

The efficiency of Photoelectro-Fenton oxidation processes is influenced by various experimental variables, including the configuration of the cell, the type and intensity of the incident radiation, the choice of electrode materials, the applied current, the pH and composition of the solution, the stirring rate, and the concentrations of catalyst and pollutants [11].

c. Purification Studies of Different Drug Active Substances by Photoelectro-Fenton Oxidation

A 100 mL sample containing Flumequine with a drug concentration of 62 mg/L was subjected to degradation. The solution included 0.050 M Na_2SO_4 and 0.50 mM Fe^{2+} as a catalyst. A BBD electrode was used as the anode, and an ADE electrode served as the cathode. The experiment was conducted at pH 3 and 35°C, with a constant current of 100 mA applied for 360 minutes. A 6 W UVA lamp was utilized. Under these conditions, complete drug degradation (100%) and 96% removal of total organic carbon (TOC) were achieved [11, 35].

In the acetaminophen degradation study, four-liter samples with a drug concentration of 5 mM were utilized. The solution contained 25 mM H_2O_2 and 0.50 mM Fe^{2+} as a catalyst. DSA and SS were employed as the anode and cathode materials, respectively. The experiment was carried out at pH 3 with a current density of 11.3 mA/cm² applied for 120 minutes. A 24 W UVA lamp was utilized during the process. Under these specified conditions, a drug degradation efficiency of 99% and a total organic carbon (TOC) removal rate of 37% were achieved [11, 36].

In the study, a 100 mL sample containing dopamine at a concentration of 1.04 mM was subjected to degradation. To facilitate the process, 0.050 M Na_2SO_4 and 0.50 mM Fe^{2+} were added as catalysts to the solution. The anode and cathode materials used were BDD and ADE, respectively. The experiment was carried out at pH 3, a temperature of 35°C, and a constant current of 300 mA for a duration of 240 minutes. Additionally, a 6 W UVA lamp was employed throughout the experiment. Notably, these specific conditions resulted in an impressive 97% removal of total organic carbon (TOC) from the sample [11, 37].

III. RESULTS

Homogeneous PEF (photoelectron-Fenton) and SPEF (solar photoelectron-Fenton) processes are effective methods for treating persistent and toxic organic pollutants in wastewater. These processes also utilize UV or sunlight irradiation to degrade the by-products formed during treatment. While homogeneous OH radicals primarily target aromatic and cyclic pollutants, heterogeneous M(OH•) species can react with a wide range of organic compounds, similar to AO and AO- H_2O_2 treatments. Studies have demonstrated that homogeneous Photoelectro and Solar Photoelectro Fenton processes can rapidly remove contaminants from synthetic solutions containing industrial chemicals at pH 3. Under dark conditions, the removal rate is comparable to that of homogeneous EF treatment. The presence of light, on the other hand, considerably improves the mineralization process by boosting the photo-decomposition of by-products, notably Fe(III) complex of short-linear carbohydrates. This improved performance
distinguishes homogeneous Photoelectro and Solar Photoelectro Fenton from homogeneous EF treatments. The type and power of UV radiation have a significant impact on the success of the homogenous PEF process. In particular, sunlight with its higher irradiance and broader wavelength range greatly improves the efficiency of homogeneous SPEF, enabling almost complete mineralization of synthetic solutions.

Various studies have proposed mineralization pathways for target molecules by analyzing by-products using techniques like GC-MS and chromatography. The presence of chloride ions in the medium can lead to the formation of persistent chlorinated derivatives, which hinder the mineralization process. However, photo-assisted treatments remain highly effective for treating real wastewater samples when non-active anodes like BDD (boron-doped diamond) are used. BDD generates BDD(OH•) that is the powerful oxidizing agent which can decompose these recalcitrant by-products [11].

IV. DISCUSSION

Despite promising results, there has been little emphasis on conducting economic research and performance assessments for homogenous Photoelectro-Fenton and Solar Photoelectro-Fenton processes. It is crucial to assess the industrial feasibility of these photo-assisted technologies and compare them with other alternatives.

REFERENCES


