Comparative electrochemical removal of Tamoxifen from aqueous solutions

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Abstract. The increasing presence of pharmaceutical micropollutants in aquatic environments demands the advancement of effective treatment technologies. In this study, electro-oxidation (EO), electrocoagulation (EC), and electro-Fenton (EF) processes were comparatively evaluated for the removal and mineralization of tamoxifen citrate (TAM) from aqueous solutions. The effects of key operational parameters, including pH (3–11), conductivity (1.5–10 mS/cm), current density (50–500 A/m²), and initial concentration (2.5–10 ppm), were systematically investigated. Under optimized conditions, EO achieved the highest total organic carbon (TOC) removal efficiency (84.4%) at 300 A/m², pH 4.5, and conductivity 3.5 mS/cm. The EF process demonstrated comparable performance, achieving an 83.7% TOC removal rate with 0.1 mM Fe^{2+} at pH 5, confirming the effectiveness of hydroxyl radical-based oxidation. In contrast, EC resulted in a lower removal efficiency (60.3%), primarily due to its coagulation-dominant removal mechanism. Spectrophotometric analyses revealed significant mineralization in both EO and EF systems, demonstrating the formation and subsequent degradation of intermediate compounds. Overall, EO and EF showed superior performance compared to EC in TAM treatment, highlighting their potential for removing persistent pharmaceutical contaminants. These findings provide practical insights for selecting appropriate electrochemical treatment strategies in wastewater applications.

1 Introduction

The ecological impacts of pharmaceutical compounds in aquatic environments states significant concerns, as they are persistent, potentially bioaccumulating and other adverse effects. Conventional systems are often ineffective in removing such micropollutants, leading to their continuous discharge into receiving water bodies. Tamoxifen (TAM), an oral non-steroidal antiestrogen drug frequently used in breast cancer treatment, is one of the micropollutant. Previous studies have reported TAM concentrations of 369 ng/L in the discharge of a wastewater treatment plant and 212 ng/L in a river, demonstrating the very limited treatment capacity of conventional systems [1]. The presence of TAM in aquatic environments is concerning due to its known toxicity, adverse effects on the endocrine system, and bioaccumulation potential [2]and its effective treatment is an important issue that needs to be studied. The ability of generating highly reactive species like hydroxyl radicals (•OH) which can effectively degrade resistant organic pollutants, advanced oxidation processes

(AOPs) are attracting interest. Advanced oxidation systems are processes that can achieve effective results despite their small footprint. Due to their space requirements, they are attracting more attention considering the plant footprint of conventional treatment methods [3].

EF is one of the advanced oxidation processes which iron ions (Fe^{2+} and/or Fe^{3+}) act as catalysts and organic compounds are oxidised in the presence of a hydrogen peroxide (H_2O_2) solution. This process, based on the use of in-situ carbon cathodes, the electro-generation of H_2O_2 by $2e^-$ oxygen reduction and electro-regeneration of Fe^{2+} catalyst leads to the conversion of H_2O_2 to HO^- according to the Fenton reaction [4]. Over the past two decades, Fenton has been extensively studied as a potent technique for oxidizing various organic pollutants that are resistant to biodegradation. [5].

EO processes are a new generation of treatment technologies based on the removal or conversion of organic pollutants in wastewater through electrodes. The process structure is relying on the degradation of organic matter on a single anode material. With the EO, organic impurities can be degraded by direct or indirect oxidation process on the anode surface. These processes involve direct oxidation, where hydroxyl radicals are formed on the anode material, and indirect oxidation, where H_2O_2 is generated through the reduction of oxygen. Anodically produced agents such as chlorine, hydrogen peroxide, and ozone, which are potent in the oxidation of organic compounds, can be formed during indirect electrooxidation [6].

Electrocoagulation (EC) is a treatment process that forms metal hydroxide flocs by electrolysis, thereby removing pollutants from wastewater [7]. During the EC process, coagulants are produced in situ by electrically soluble iron or aluminum electrodes. When current is applied to an Al electrode, metal ions are released into the water environment. Unlike oxidative processes, EC primarily transfers pollutants from the aqueous phase to the solid phase, failing to achieve complete mineralization.

Despite the limited number of studies on TAM removal available, in a study[8], different oxidation processes were tested and found a removal efficiency relationship of $O_3 > O_3/H_2O_2 > O_3/UV > UV/H_2O_2 > UV$. While ozonation yielded a tamoxifen removal percentage higher than 99% after 30 minutes in all setups, experiments using UV radiation required a reaction time of 240 minutes. The literature has focused particularly on photocatalytic systems, but not on electrochemical systems.

Although these processes have been studied individually for various pollutants, comparative studies are quite limited. In particular, TAM removal has been studied by very few researchers in the literature. While its toxic effects in aquatic ecosystems have been investigated, there are very few publications on water treatment. Therefore, this study aims to systematically compare the EO, EC, and EF processes in terms of removal efficiency, operational parameters, and treatment mechanisms, and to examine TAM removal.

2 Materials and methods

2.1 Chemicals

All studies were conducted using Tamoxifen Citrate (15.2 mg equivalent to 10 mg tamoxifen base and used without further purification). TAM obtained from a pharmaceutical company which is located in Tekirdağ/Türkiye. The chemical formula of TAM is $C_{32}H_{37}NO_8$. The synthetic TAM solution is prepared as 10 ppm stock solution. The original pH of the prepared solution varies between 4.5 ±0.2. For pH adjustments, 0.02 N H_2SO_4 or NaOH are used. $FeSO_4$-$7H_2O$ (Merck, USA) was additionally used for the hybrid electro-Fenton process. All chemicals were analytical grade.

2.2 Experimental setup and analysis procedures

A reactor volume of 250 mL was used in each experiment. In all experiments, a GW Instek power supply with a capacity of 30 V 30 A was used. For the EO and EF system, Nb/BDD electrodes (6 cm x 6 cm x 0.2 cm) were used. Two stainless steel plates (6 cm x 6 cm x 0.2 cm) were preferred for the cathode for EO system. For the EF system, carbon felt cathode was used. NaCl was added to the synthetic TAM stock solution as an electrolyte. In the EC process experiments, two 6 x 6 x 0.4 cm Al electrodes were used in the system. Optimization sets were studied with 10 ppm TAM. The distance between the electrodes was set to 2 cm, while the mixing speed was set to 300 rpm. The active electrode area is configured so that each system is set to the same value in current density adjustments.

To measure removal efficiency, samples were collected over time. TOC data were used for the analyses. TOC measurements were performed on a SHIMADZU TOC-L. Wavelength scanning (190-900 nm) was performed in a spectrophotometer Merck-Spectroquant® Prove 300. Time-dependent samples were analyzed by HPLC (Shimadzu) equipped with a C18 column to monitor the formation of transformation products. Mettler Toledo pH probes were used in pH monitoring studies.

3 Results and discussion

In this study, pH, conductivity, TAM concentration, and current density parameters were optimized for all three different processes. Iron concentration was also optimized for the hybrid EF process.

3.1. Electrooxidation process

During the electrooxidation process, a current density of 300 A/m² resulted in optimal removal efficiency. Increasing the current density beyond this value did not significantly enhance mineralization, suggesting that 300 A/m² provides an optimal balance between radical formation and current efficiency. At higher current densities, side reactions such as oxygen evolution likely reduce the effective utilization of the applied current.

Furthermore, operating at the original pH of the solution was considered optimal, as it eliminated the need for additional chemical reagents for pH adjustment, thus improving the economic feasibility of the process. It was observed that conductivity primarily affected the removal rate rather than the final removal efficiency. Although higher conductivity levels accelerated the degradation kinetics, the total TOC removal remained approximately constant after a reaction time of 90 minutes. Under optimized conditions, approximately 90% TOC removal was achieved. Spectrophotometric measurements at T15 and T30 revealed an increase in intermediate peaks, indicating the formation of oxidation intermediates in the degradation pathway (Figure 1 d,e,f). However, these intermediate peaks disappeared at the end of the process, confirming significant mineralization of the transformation products. Previous studies support these findings. Barisci& Suri (2021)[9] reported that high conductivity increases the formation of oxidative radicals during electrooxidation and improves degradation efficiency by increasing the number of active sites on the electrode surface. Similarly, another study indicated that the optimum pH in electrooxidation depends on the physicochemical properties of the target contaminant, acidic conditions generally support higher oxidation efficiency due to increased hydroxyl radical formation[10]. Repeated experiments have shown that the system achieves approximately 80% TOC removal efficiency. Furthermore, variations in parameters such as current density, TMX concentration, and conductivity also led to the observation of different peaks in the system. This phenomenon has been observed even in spectrophotometric analyses. The differences

also observed in HPLC peaks, samples will be measured and interpreted using LC/MS-MS device in future studies.

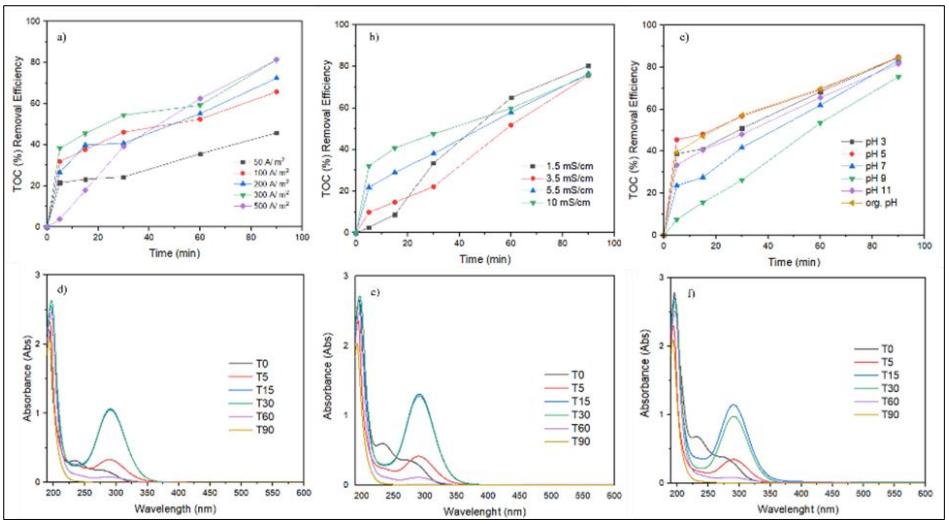

Fig. 1. Electrooxidation process results a) Current density effect on TOC(10 ppm TAM, 3.5 mS/cm, original pH), b) Conductivity effect on TOC(10 ppm TAM, 300 A/m^2, original pH),c) pH effect on TOC(10 ppm TAM, 3.5 mS/cm, 300 A/m^2), d) Spectrophotometric results of current density effect (5 ppm TAM, 3.5 mS/cm, 300 A/m^2, original pH), e)Spectrophotometric results of conductivity effect (10 ppm TAM, 5.5 mS/cm, 300 A/m^2, original pH), f)Spectrophotometric results of pH effect (Constant parameters: 10 ppm TAM, 3.5 mS/cm, 300 A/m^2, original pH).

3.2. Electrocoagulation process

Since electrocoagulation is by nature a fast treatment process, current density experiments were performed for a maximum reaction time of 60 minutes. Under most study conditions, about 60% TOC removal efficiency was achieved. However, at 500 A/m², removal efficiency declined over time, likely due to excessive flocculation, higher turbidity, sludge buildup, and challenges in analysis and measurement. These findings align with existing literature. Kobya et al., (2016) [11] stated that higher current densities significantly increased both the amount and rate of flocculation, leading to increased sludge production. While improved coagulant production may initially improve the removal of pollutants, excessive metal hydroxide flocs can lead to operational disadvantages, including poor flotation properties and sludge processing difficulties. In this study, conductivity was found to have no statistically significant effect on TOC removal efficiency. Original and neutral pH conditions yielded more favorable results compared to highly acidic or alkaline environments. Bener et al. (2019)[12] examined how pH levels (5, 8, and 10) affect electrocoagulation treatment of real textile wastewater. The highest TOC removal, at 65%, occurred at pH 5, with efficiency decreasing at higher pH levels. The authors explained this pattern by the formation of hydrogen gas at the cathode in alkaline conditions, which can hinder floc formation and lower coagulation effectiveness. Furthermore, spectrophotometric analyses performed in this study confirmed that the system showed a strong cleaning coagulation effect even at 100 A/m² and produced sufficient metal hydroxide flocs to effectively capture organic matter. No peak was observed in HPLC or spectrophotometric measurements except for the T0 sample. EC was included in the study as a baseline to investigate its effect on TAM removal when applied as the simplest system. Considering energy consumption, electrode usage cost, sludge problem and the problem of TAM trapped in the sludge, it is not considered a fully effective process.

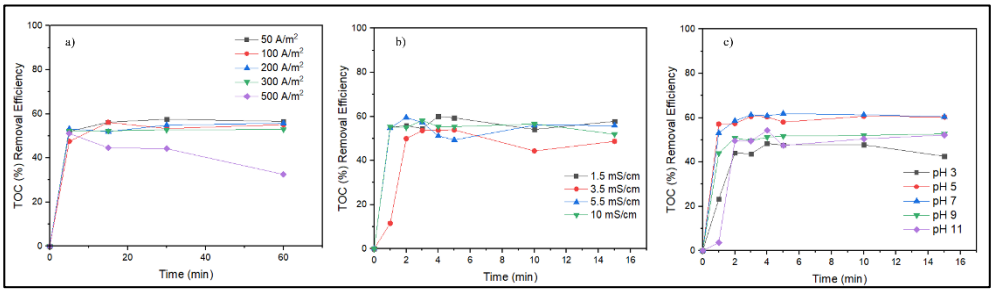

Fig. 2. Electrocoagulation process results a) Current density effect(10 ppm TAM, 3.5 mS/cm, original pH), b) Conductivity effect (10 ppm TAM, 300 A/m^2, original pH), c) pH effect, (10 ppm TAM, 3.5 mS/cm, 300 A/m^2).

3.3 Hybrid electro-Fenton process

The hybrid EF process was used in the studies, and Fe^{+2} dosage was the first parameter optimized in this system. According to the results obtained, 0.1 mM yielded more successful results, and a concentration similar to that in the literature was achieved[13]. The high removal efficiency observed in the EF process is attributed to the continuous in situ generation of •OH radicals. Increasing current density increased H_2O_2 production and Fe^{2+} regeneration; however, beyond a certain threshold, efficiency plateaued due to side reactions such as oxygen formation (Figure 3.b). Excessive conductivity reduced treatment efficiency due to the presence of competing ions, whereas increasing current density enhanced removal efficiency up to 86%, beyond which no further improvement was observed. Although BDD electrodes were used, the presence of chlorinated active species in the system due to the use of NaCl as an electrolyte may have contributed to the radical scvenging effect. As seen in Figure 3.c, the removal efficiency decreased as conductivity increased. This can be explained by the presence of chlorinated active species. Furthermore, at lower current densities, the system performs better than the EO system. This situation makes the system more energy efficient.

3.4 TAM concentration effect

In the studies on TAM concentration, the same concentrations were applied to all three systems, and removal efficiencies were monitored in time-dependent samples using TOC and HPLC measurements. Similar removal efficiencies were obtained for the EO and hEF systems, while relatively lower results were obtained for the EC system in a shorter time, although the amount of TAM removed from the system remained unchanged after 2 minutes (Figure 4). This finding is supported by HPLC analysis; however, HPLC analyses were insufficient for transformation products identification, although significantly more transformation products were formed in the hEF system compared to the EO system. This is also relatively supported by spectrophotometric results (Figure 1d,e,f and Figure 3d). Since TAM removal has not been previously investigated with electrochemical treatment, removal efficiencies and transformation products are not clearly defined in the literature for electrochemical treatment. It has been observed that it decomposes more rapidly than photocatalytic oxidation processes, which have been studied more frequently in the literature[14]. While removal efficiencies approaching 99% can be achieved in studies when TAM removal is considered, the mineralization of transformation products emerges as an area that needs improvement.

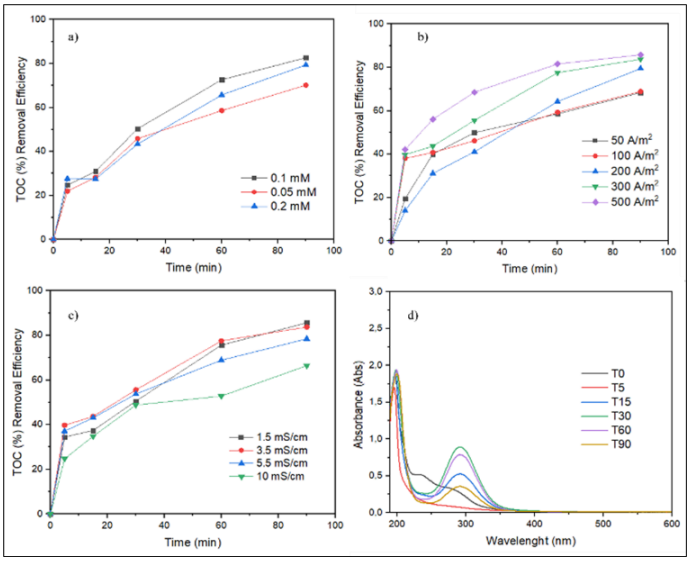

Fig. 3. Hybrid electro-Fenton process results a) Effect of iron concentration (10 ppm TAM, 3.5 mS/cm, 300 A/m^2, original pH), b) Current density effect (10 ppm TAM, 3.5 mS/cm, original pH), c) Conductivity effect (10 ppm TAM, 300 A/m^2, original pH), d) Spectrophotometric results (10 ppm TAM, 3.5 mS/cm, 300 A/m^2, original pH).

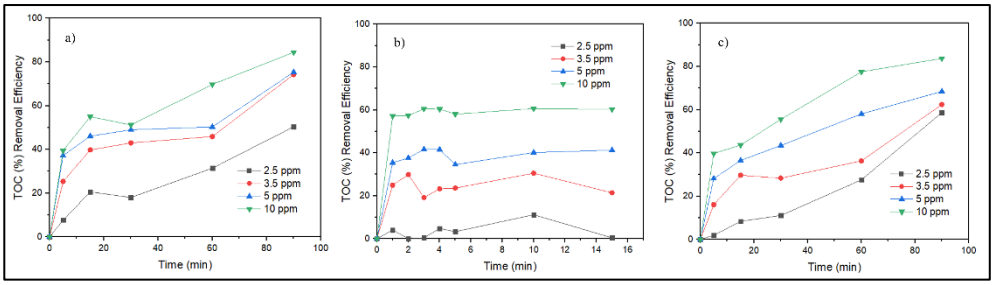

Fig. 4. TAM concentration effect for a) electrooxidation, b) electrocoagulation, c) hybrid electro-Fenton (Constant parameters: 3.5 mS/cm conductivity, 300 A/m^2 current density, original pH and 0.1 mM Fe^{+2} only for hybrid-EF).

4 Conclusion

This study presents a comprehensive comparative evaluation of EO, EC, and EF processes for the removal and mineralization of TAM from aqueous solutions. The results demonstrate that operational parameters, including current density, conductivity, pH, and initial contaminant concentration, play critical roles in the performance of each electrochemical method. Among the methods investigated, EO achieved the highest mineralization efficiency (84.4%) under optimum conditions, as evidenced by a significant reduction in UV-Vis absorbance and loss of aromatic intermediates. The EF process exhibited comparable performance (83.7%) at 0.1 mM Fe^{2+} and pH 5. In contrast, EC provided a moderate removal efficiency (60.3%), driven primarily by coagulation and flotation mechanisms rather than complete mineralization. Furthermore, sludge formation and associated process challenges limit its practical applicability compared to oxidative processes. Additionally, the successful operation of the EF system even at low voltages makes it more energy-efficient. Further

detailed research on conversion products and toxicity in later stages of the study may provide a better understanding of the research.

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