



Performance Evaluation of Chemical Coagulation and Electro-Fenton Combined Processes Treating Real Pharmaceutical Wastewater



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ABSTRACT

Background: Pharmaceutical wastewater mainly contains high levels of organic matter. In order to produce a suitable wastewater for discharge into the municipal sewage, chemical and electrochemical methods have been studied. The aim of this study was to evaluate the efficiency of chemical coagulation/electro-Fenton combination process in chemical oxygen demand (COD) reduction of pharmaceutical wastewater.

Methods: The effect of Poly aluminum chloride (PAC) concentration 25-300 mg/L and pH of 3-7-10 were investigated. The effluent of chemical coagulation stage was transferred to the electro-Fenton stage. Further, the effect of H₂O₂ concentration 100 - 4000 mg/L, contact time of 15-120 min, voltage of 10-30 v and pH of 3-10 were investigated.

Results: The results showed that the highest removal rate of COD was 93.5% in the optimal conditions at coagulant dose 200 mg/L and pH of 7 for the coagulation process, and at concentration of 100 mg/L hydrogen peroxide, the voltage of 20, pH of 3 and contact time of 30 min for the electro-Fenton process (EFP). The results showed that chemical and electrochemical processes are effective methods for the pharmaceutical wastewater treatment.

Conclusion: It is generally concluded that combined processes are more effective than the coagulation process alone in removing organic compounds from pharmaceutical wastewater.

1. Introduction

Pharmaceutical wastewater is one of the highly polluted streams characterized by high concentrations of refractory organics and toxic pollutants [1]. The wastewater generated from pharmaceutical industries mainly contains agents, solvents of equipment washing and cleaning processes, reactants, and catalysts used in manufacturing processes [2]. In many cases, effluents of these industries contain low

biodegradability due to refractory organics in high concentrations. Therefore, the pollutant loads in terms of biological oxygen demand (BOD) may be negligible, and chemical oxygen demand (COD) would be significantly higher than BOD [3]. On the other hand, many pharmaceutical compounds are only partially removed during biological treatment processes in sewage treatment plants and consequently released into surface waters [4, 5].



Accordingly, there are restrictions in the United States and Europe that require prospective environmental risk assessments as part of the drug registration process [6] such as several different alternatives, including anaerobic-aerobic [7], membrane bioreactors [8,9], electrochemical oxidation [10], biochemical combined method [11], and advanced oxidation process (AOPS)[12-14].

Electrochemical methods have been used to treat highly toxic organic matter with low biodegradability in recent years. Electrochemical methods include electrical coagulation (EC), electrical oxidation and electrical photo-oxidation [15, 16].

EFP is a well-organized method that has some advantages, such as fewer chemicals requirement, cost-effectiveness, simple equipment, low retention time, intensity in varying reaction conditions, rapid sedimentation of the electro-generated oxidants, less sludge production, high performance for degrading refractory pollutants and color removal [17]. According to literature, electrochemical oxidation has been successfully used to treat textile dyeing wastewaters [18], tannery wastewater [19], landfill leachate treatment [17, 20], arsenic [21], olive oil mill wastewater [22], and petrochemical wastewater [23].

Various oxidation processes such as Fenton oxidation (FO), optical oxidation, and electrical oxidation are used to increase the efficiency of the electrochemical method. In the EFP method, FO and electrical coagulation are combined, which has high efficiency in treating highly polluted wastewater [2, 9, 24].

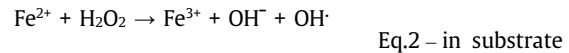
One of the most important advantages of the EFP method is low sludge production and high sedimentation potential compared to other standard conventional coagulation methods. There are generally two different types of EF functions: 1) EF system in which Fenton H_2O_2 and Fe^{2+} reagents are added to the reactor from the outside and stationary electrodes with high catalytic activity are used as anodes and 2) EF system in which H_2O_2 is added from outside and Fe^{2+} is supplied by iron anodes [25].

EFP is one of the advanced oxidation processes. The main purpose of this method is to generate hydroxyl radicals using a chemical reaction between H_2O_2 and Fe^{2+} (equation 2) [26, 27].

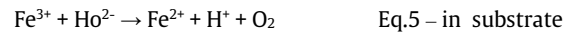
The hydroxyl radical is one of the most reactive free radicals and can easily decompose organic matter (equations 3 and 4) [28].

In the EFP, Fe^{2+} ions are electrochemically produced by the iron anode (Equation 5-7), and then hydrogen peroxide is added to the solution to provide the Fenton reaction conditions [29]. It also regenerates Fe^{2+} ions through equations 8 and 9 and increases efficiency of the process.

The EFP reactions are given below.



$$K = 76 \text{ mol L}^{-1} \text{ S}^{-1}$$



Therefore the main aim of the present study is evaluating the efficiency of combined chemical coagulation by PAC and EFP in COD removal from pharmaceutical wastewater.

2. Materials and Methods

2.1. Wastewater Sources and Experiment Procedure

The real pharmaceutical wastewater was obtained from a pharmaceutical industry effluent. Samples were collected from the equalization tank of the treatment plant before any treatment processes and then were stored in a refrigerator at 4 °C before the experiments. Some main characteristics of the studied wastewater are given in Table 1.

All chemicals were prepared of analytical grade and supplied by Merck, and poly aluminum chloride (PAC) was used as a chemical coagulant. A Jar test set was used to determine the optimal coagulant dose. COD measurements were determined according to the Standard Methods for examining water, wastewater (APHA Method 5220), TS, and VS (APHA Method 2540) [30]. An HACH COD reactor was used for digestion of the sample in COD vials. COD was spectrophotometrically determined by using a Jenway 5350 spectrophotometer. In order to increase the accuracy of the experimental data, all the measurements of samples were done three times.

The removal efficiency of COD was calculated using the equation as follow (Eq.10);

$$R (\%) = C_0 - C_t / C_0 \times 100 \quad (\text{Eq.10})$$

Where C_0 is the raw leachate's initial COD, and C_t is the COD at the end of a predetermined settling time (t) after each running electro-Fenton.

Table 1: Characteristics of wastewater

Parameter	Value	Unit
BOD5	940±17	mg/L
COD	3765±83	mg/L
BOD5/COD	0.25±0.02	---
SO ₄ ²⁻	312±27	mg/L
TDS	1857±150	mg/L
TSS	343±21	mg/L
pH	7.6±0.0	---
EC	1740±56	µS/cm
Turbidity	36±7	NTU

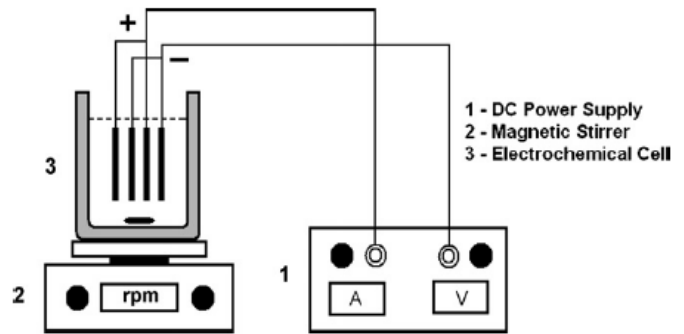
2.2. Experimental Set-up

A batch electrochemical cell with an operational capacity of 1000 mL was made of Plexiglas (Figure 1). Four electrodes with $2 \times 20 \times 200$ mm were used as cathode and anode. Two electrodes (cathode and anode) were installed in parallel form and the space between the electrodes was fixed 30 mm in all the experiments. A multi-output digital DC power supply (MICRO, PW-4053S) was used to establish optimum electrical condition. The current DC was kept constant at 10V, 20V, and 30V. To keep homogenous mixing of the reactor content, a stirring magnetic element by the speed of 200 rpm was used. In each experiment run, the current density and electrolysis time was changed. The electrocoagulation experiments were performed for 60 min and settling time of 60 min. After 60 min settling, the COD and NH₄-N of the effluent were measured.

3. Results and Discussion

3.1. PAC Effect Dosage on COD Removal

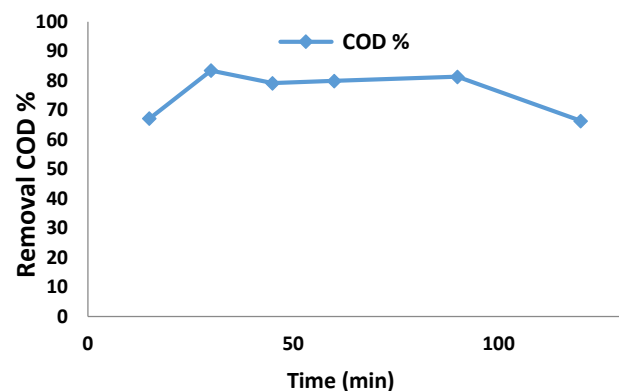
Chemical coagulation by Jar test device was operated at controlled conditions, e.g., room temperature, different concentrations of PAC, different pH values, rapid mixing (100 rpm for 1 minute), flocculation mixing conditions (40 rpm for 20 min), and 1 h settling time. All the experiments were carried out in pH=7 as optimal pH for chemical coagulation of PAC. Moreover, comparing the removal efficiencies at different concentrations (25-50-75-100-200-300mg/l) showed a difference in COD removal efficiency. As shown in Figure 2, the COD removal percentage increased as the coagulant concentration increased and the highest COD removal efficiency was achieved at 200 mg/L PAC. Furthermore, results indicated that by increasing PAC concentration from 25 to 200 mg/L, the COD removal efficiency increased to %49, but the removal efficiency decreased at PAC concentrations higher than 200 mg/L so the COD removal efficiency decreased to %21 at 300 mg/L initial PAC concentration. Therefore 200 mg/L PAC was selected as the optimal dose. According to the results, the COD removal efficiency increases as PAC concentration increases to 200 mg/L.

**Figure 1:** Schematic of EF Reactor

However, the COD removal efficiency decreased at concentrations higher than 200 mg/L, which can be attributed to the re-stabilization of the clots formed in the sample and the accumulation of coagulant in the substrate. As reported by previous studies, when the amount of coagulant exceeds the optimum values, it increases the turbidity due to excess polymer in the effluent, which can reduce the removal efficiency of COD [31].

3.2. Effect of pH and Coagulant Dose on Turbidity Removal Efficiency

The turbidity removal efficiency at different concentrations of coagulant and at different pH values is shown in Figure 3. As can be seen, increasing in coagulant concentration leads to an increase in turbidity removal percentage. As a result, at 200 mg/L PAC, the removal efficiency was %93.86 which is the highest turbidity removal in the present study that showed the turbidity of the effluent was decreased less than 3 NTU. However, based on the results when the coagulant concentration increases from 200 to 300 mg/L, the efficiency dropped from %93.89 to 80%, which shows the maximum effect of the coagulant dose is at 200 mg/L. Further, high removal efficiency was achieved when pH value was adjusted at 7. Thus, 200 mg/L PAC and pH=7 determined as optimal coagulation condition.

**Figure 2:** Effect of different concentrations of PAC on COD removal efficiency at pH 7

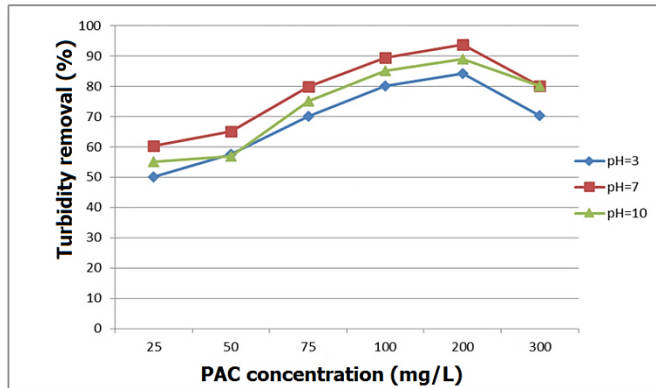


Figure 3: Removal of turbidity at 200 mg/L concentrations of coagulant at different pH values

3.3. The effect of Initial H_2O_2 Concentration on COD Removal Efficiency during the Electro-Fenton Process

As shown in Figure 4, the COD removal efficiency decreased by increasing in initial H_2O_2 concentration after 30 min oxidation time. According to the results increasing the initial H_2O_2 concentration from 100 mg/L to 4000 mg/L leads to a decrease in the efficiency of the electro-Fenton process in removing COD from %93.5 to %21, which indicates a decrease in process performance at 4000 mg/L H_2O_2 concentration.

The results show that by increasing the H_2O_2 concentration from 100 to 2000 mg/l, the decreasing trend is very slight and insignificant, but as the H_2O_2 concentration increased from 2000 to 4000 mg/L, the COD removal performance dropped sharply. Therefore, the optimal H_2O_2 concentration in the process was considered 100 mg/L. Moreover, excess H_2O_2 leads to the formation of hydroxyl radicals (HO_2^\bullet) with less reactivity than OH^\bullet (Equations 11 and 12). On the other hand, the OH^\bullet radical is neutralized or repelled by Fe^{2+} (Equation 13). It should be noted that the oxidation potential of hydroxyl radicals (1.25 eV) is less than H_2O_2 (1.3eV).



Therefore, reducing the access ability to active oxidizing species at high concentrations of H_2O_2 leads to a reduction in the removal of contaminants [30]. Excess H_2O_2 acts as an OH^\bullet receptor. Thus, an increase in H_2O_2 concentration leads to decrease in hydroxyl radicals [2].

3.4. The Effect of pH Changes on the Efficiency of the Electro-Fenton Process

The effluent from the chemical coagulation and settling stage entered the electro-Fenton reactor. In order to evaluate

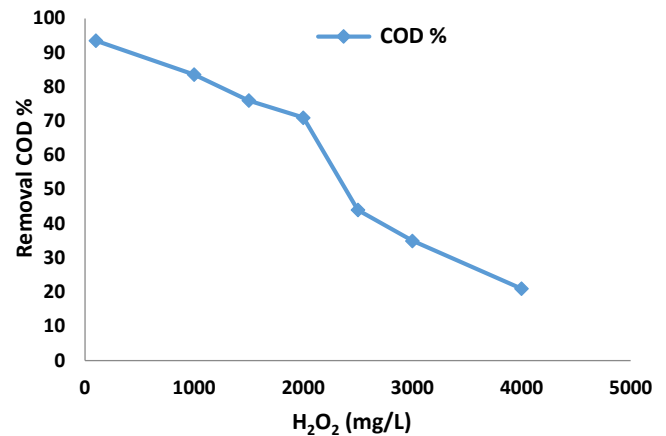


Figure 4: Effect of different hydrogen peroxide concentrations on the COD removal efficiency in the EFP (voltage: 20 V, Oxidation time: 30 min and pH=3)

the effect of pH changes, the initial pH of the oxidation medium was fixed in three ranges of 3, 7, and 10. Figure 5 shows the effect of pH changes on the efficiency of the electro-Fenton process. As can be seen, the removal efficiency decreases with increasing pH. The highest amount of COD removal at pH = 3 and the lowest COD removal efficiency at pH = 10 were 93.58% and 76%, respectively, which shows the inverse effect of increasing pH on process efficiency. According to literature all Fenton oxidation processes are generally more efficient in relatively acidic environments [27]. Increasing the initial pH of the oxidation medium from 3 to 10 reduces the COD removal efficiency due to the decrease in OH^\bullet oxidation potential. At pH values higher than 3, especially above 5, H_2O_2 converted to water and oxygen with a constant coefficient due to its instability. The conversion factor is $2.3 \times 10^{-2} \text{ min}^{-1}$ and $7.4 \times 10^{-2} \text{ min}^{-1}$ at pH = 7 and pH = 10.5 respectively.

At pH values above 7, the hydroxyl radical rapidly converted to O^\bullet , which has a much slower oxidation rate than OH^\bullet . At high pH values, ferrous ions precipitate as $Fe(OH)_3$ and inhibit the reaction between Fe^{2+} and H_2O_2 . Therefore, the reproducibility of Fe^{2+} , which is necessary for the continuous hydroxyl radical production process, is reduced. The absence of H^+ when the pH is highly alkaline prevents the H_2O_2 decomposition. As a result, the hydroxyl radicals production and pollutants' decomposition efficiency reduced significantly. In addition, $Fe(OH)_3$ generated in high pH values accelerates the decomposition of H_2O_2 to O_2 and H_2O , which reduces the production of OH^\bullet radicals and ultimately reduces the efficiency of the electro-Fenton process [16].

3.5. The Effect of Voltage Changes on the Efficiency of the Electro-Fenton Process

Figure 6 shows the effect of voltage changes on the COD removal efficiency in the electro-Fenton process.

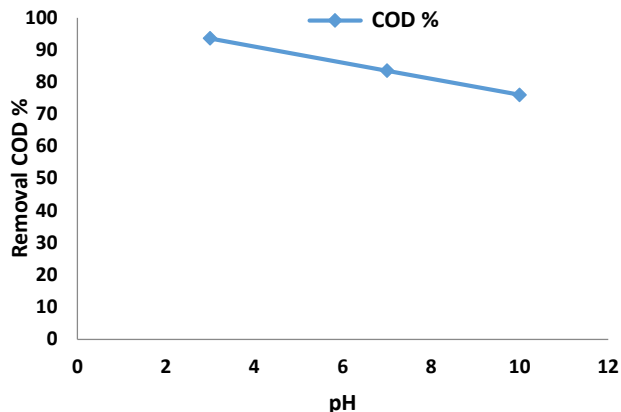


Figure 5: Effect of different initial pH values on the COD removal efficiency in the EFP

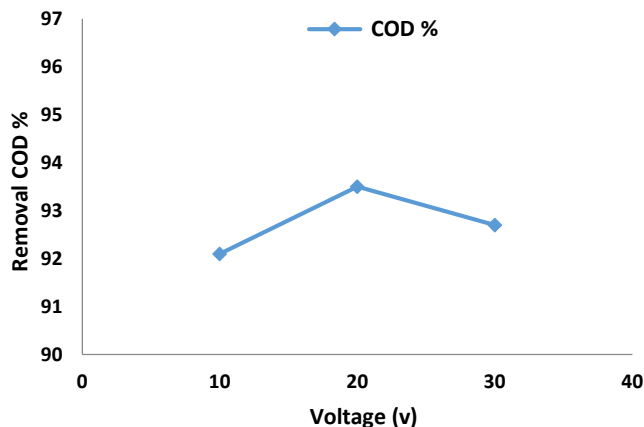


Figure 6: Effect of voltage on COD removal efficiency in EFP (H₂O₂= 100 mg/L, Time= 30 min and pH =3)

Based on Figure 6, the COD removal efficiency increased from 92 to 93.5 when the voltage increased from 10 to 20 V. However, the COD removal efficiency decreased by increasing the voltage to 30 V. According to the results, the efficiency of the electro-Fenton process decreases by increasing the voltage by more than 20 V. So 20 V value was determined as optimum voltage for electro-Fenton process. An important issue in the efficiency of the electro-Fenton process is that by increasing the voltage above the optimum value, energy consumption increases, which is not economically viable [32, 33].

In general, voltage is a driving force for oxygen depletion that results in hydrogen peroxide production at the cathode. High voltage values increase the amount of hydrogen peroxide produced. Hence, the number of highly active hydroxyl radicals increases.

Also, with increasing voltage, the electrical production of Fe²⁺ ferrous ion increases and increases the efficiency of Fenton cycle reactions (Equation 14).

According to the results of the study, the efficiency of the electro-Fenton process was reduced at high voltages that is because of the competitive reactions of the electrode in the electrolyte cell. At high voltages, oxygen depletion occurs at the anode surface (Equation 15) and hydrogen reduction occurs at the cathode (Equation 16). These reactions prevent the main oxidation reaction (Equation 17), which ultimately leads to a decrease in the oxidation efficiency of the electro-Fenton.



3.6. The Overall Turbidity and COD Removal Efficiency in Combined Chemical Coagulation and Electro-Fenton Oxidation

The overall efficiency of the combined process of chemical coagulation and oxidation of electro-Fenton is given in Table 2. As can be seen, for PAC coagulation under optimal conditions, the PAC concentration (200 mg/ l), pH=7 rapid agitation (100rpm in 1 min), flocculation (40rpm in 20 min), and 1 h settling time, %93.85 and 49% removal was observed for turbidity and COD respectively. Also, the overall efficiency of the combined process Electrochemical coagulation and in pH=3, voltage (20 V) reaction time (30 min) and H₂O₂ concentration (100 mg / L) %93.85 and 93.5% removal was observed for turbidity and COD respectively.

Table 2: Overall efficiency of the combined process of chemical coagulation and electro-Fenton

Process	PAC coagulation		Electro-Fenton oxidation	
Parameter	Turbidity	COD	Turbidity	COD
Removal (%)	93.85	49	93.85	93.5

4. Conclusion

Since no harmful reagents are used in the electro-Fenton process, it is considered an environmentally friendly method for water and wastewater treatment. The present study showed that, with increasing oxidation time of more than 30 min, the removal efficiency did not significantly change due to resistant organic compounds in the sample. Also, the removal efficiency decreased because of the increase in PAC concentration in amounts more than 200 mg/L (due to the destabilization of the clots). In addition, H₂O₂ concentration increase in amounts more than 2000 mg/L (due to the radical abduction of •OH by the Excess H₂O₂) was observed. It was also observed that increasing the pH of the oxidation

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medium and increasing the voltage to higher than 20 volts reduce the removal efficiency of COD and turbidity. In this study, turbidity and COD values in the effluent from the oxidation reactor were 2 and 243 mg/L, respectively, which are still far from environmental standards, but the ease and efficiency of the process are acceptable. Overall, according to the results of the present study the electro-Fenton process is an efficient and promising technology for water and wastewater treatment purposes.

Authors' Contributions

Shima Goodarzi: Conceptualization; Carried Out the Experiment; Funding Acquisition Methodology; Soft Ware; Writing Original Draft; Writing Review and Editing; Visualization. **Ghodratollah Shams Khorramabadi:** Conceptualization; Formal Analysis; Supervision; Administration. **Mohammad Amin Karami:** Conceptualization; Formal Analysis; Supervision; Administration.

Conflicts of Interest

The Authors declare that there is no conflict of interest.

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