Chemical Oxygen Demand (COD) Reduction of Pharmaceutical Wastewater by Chemical Coagulation and Electro-Fenton Oxidation Process

**Shima Goodarzi*,
Shams Khorramabadi,
Mohammad Amin Karami**

Department of Environmental Health, Faculty of Health, Lorestan University of Medical Sciences, Khorramabad, Iran

Abstract

The pharmaceutical wastewater mostly 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 COD reduction of pharmaceutical wastewater. The effect of PAC (aluminum chloride) 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. Also the effect of H_2O_2 concentration 100 - 4000 mg/L, contact time of 15-120 min, voltage of 10-30 v and pH of 3-7-10 were investigated. The results showed that the highest removal rate 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 100 hydrogen peroxide, the voltage of 20, pH of 3 and contact time of 30 minutes for the Electro Fenton process. The results showed that chemical and electrochemical processes are effective methods for treatment of pharmaceutical wastewater. It is generally concluded that combined of processes are more effective than coagulation process alone in removal organic compounds from pharmaceutical wastewater.

Keywords: Chemical coagulation; Electro fenton; COD; Pharmaceutical industry wastewater

*Corresponding author:
Shams Khorramabadi

✉ shamskhorramabadi@gmail.com

Department Of Environmental Health, Faculty of Health, Lorestan University of Medical Sciences, Khorramabad, Iran.

Tel: +989188726836

Introduction

Pharmaceutical wastewater is one of the high polluted streams characterized by high concentrations of refractory organics and toxic p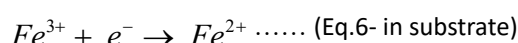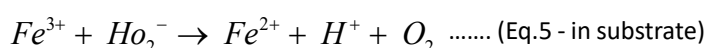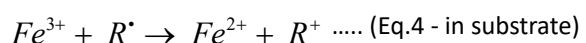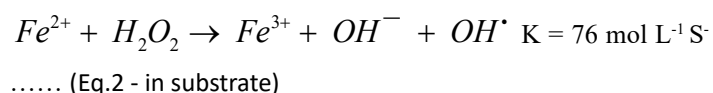ollutants [1]. The wastewater generated from pharmaceutical industries contains mainly agents, solvents of equipment washing and cleaning processes, and also reactants and catalysts used in manufacturing processes [2]. In many cases, effluents of these industries contain low biodegradability due to the presence of 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 very 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 release into surface waters [4,5]. So there are restrictions in the United States and Europe that require prospective Environmental risk assessments as part of the drug registration process [6]. 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]. In recent years, electrochemical methods have been used to treat highly toxic organic matter with low biodegradability. Electrochemical methods include electrical coagulation (EC), electrical oxidation and electrical photo-oxidation [15,16]. Electro-Fenton is a well-organized method which has some advantages, such as less chemicals requirement, cost-effectiveness, simple equipment, low retention time, intensity in varying reaction conditions, rapid sedimentation of the electro-generated oxidants, less sludge production and high performance for degradation of refractory pollutants and color removal [17]. According to literatures the electrochemical oxidation has been successfully used to the treatment of textile dyeing wastewaters [18], tannery wastewater

[19], and landfill leachate treatment [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 electro Fenton method, Fenton oxidation and electrical coagulation are combined which has a high efficiency in the treatment of highly polluted wastewater [24]. One of the most important advantages of electro-Fenton method is the low sludge production and with high sedimentation potential compared to other common conventional coagulation methods. There are generally two different types of EF functions: 1) Electro Fenton (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) Which H_2O_2 is added from outside and Fe^{2+} is supplied by iron anodes [25]. Electro-Fenton oxidation is one of the advanced oxidation processes. The main purpose of this method is the 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 (equation 3 and 4) [28]. In the EF method, Fe^{2+} ions are electrochemically produced by the iron anode (Equation 5-7), and then hydrogen peroxide added to the solution to provide the Fenton reaction conditions [29]. It also regenerates Fe^{2+} ions through equations 8 and 9 and increases process efficiency.

The electro-Fenton reactions are given below.

$$Fe \rightarrow Fe^{2+} + 2e \text{ ....}$$ (Eq.1- at anode surface)

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + OH^\bullet \quad K = 76 \text{ mol L}^{-1}\text{S}^-$$ ...... (Eq.2 - in substrate)

$$OH^\bullet + RH \rightarrow R^\bullet + H_2O \text{ ....}$$ (Eq.3 - in substrate)

$$Fe^{3+} + R^\bullet \rightarrow Fe^{2+} + R^+ \text{ .....}$$ (Eq.4 - in substrate)

$$Fe^{3+} + Ho_2^- \rightarrow Fe^{2+} + H^+ + O_2 \text{ ....}$$ (Eq.5 - in substrate)

$$Fe^{3+} + e^- \rightarrow Fe^{2+} \text{ ......}$$ (Eq.6- in substrate)

$$Fe^{2+} + OH^\bullet \rightarrow Fe^{3+} + OH^- \text{ ......}$$ (Eq.7- in substrate)

$$H_2O_2 + OH^\bullet \rightarrow H_2O + Ho_2^\bullet \text{ ....}$$ (Eq.8- in substrate)

$$Fe^{2+} + Ho_2^\bullet \rightarrow Fe^{3+} + Ho_2^- \text{ ....}$$ (Eq.9 in substrate)
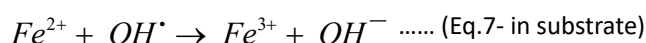
So the main aim of present study is the evaluation of efficiency of combined chemical coagulation by poly aluminium chloride (PAC) and electro-Fenton oxidation process in COD removal from pharmaceutical wastewater.

Materials and Methods

Wastewater sources and experiment procedure

The real pharmaceutical wastewater was obtained from a pharmaceutical industry effluent. Samples were collected from the equalization tank of treatment plant, prior to any treatment processes. Samples 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 aluminium chloride (PAC) was used as chemical coagulant. A Jar test set was used in order to determine the coagulant optimal dose. COD measurements were determined according to the Standard Methods for examination of water and wastewater (APHA Method 5220) and 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 Jenwey 5350 spectrophotometer. The removal efficiency of COD was calculated using the equation as follow (Eq.10);
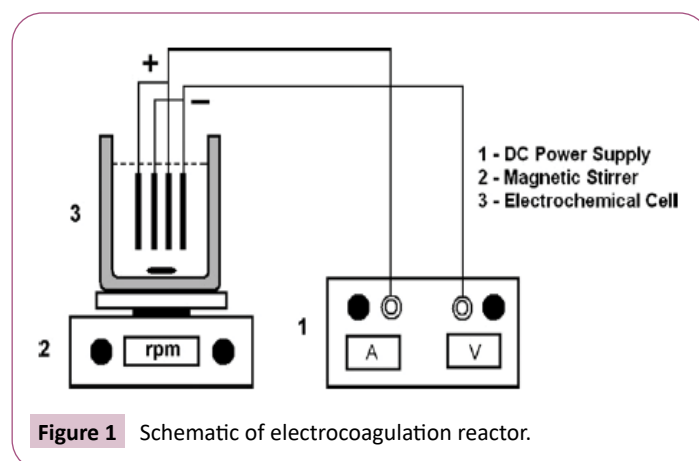
$$R\ (\%)\ =\ C_0 - C_t\ /\ C_0 \times 100$$ (Eq.10)

Where: C_0 is the initial COD of the raw leachate and C_t is the COD at the end of a predetermined settling time (t) after each running electrocoagulation.

Experimental set-up

A batch electrochemical cell with operational capacity of 1000 ml was made of Plexiglas **(Figure 1).** Four electrodes with the

Table 1 Characteristics of wastewater.

Parameters	Value	Unit
BOD_5	940 ± 17	mg/L
COD	3765 ± 83	mg/L
BOD_5/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

1 - DC Power Supply
2 - Magnetic Stirrer
3 - Electrochemical Cell

Figure 1 Schematic of electrocoagulation reactor.

dimensions of 2 × 20 × 200 mm were used as cathode and anode. Two electrodes (cathode and anode) 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, magnetic stirring element by the speed of 200 rpm was used. In each run of the experiment the current density and electrolysis time were changed. The electrocoagulation experiments were performed for 60 min and settling time of 60 min. After 60 min settling, the COD and NH_4-N of the effluent were measured.

Results and Discussion

Effect of PAC 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 minutes) and 1 hour settling time. All the experiments was carried out in pH=7 as optimal pH for chemical coagulation of PAC. Also comparing the removal efficiencies at different concentrations (25-50-75-100-200-300 mg/L) showed a difference in COD removal efficiency. As shown in **Figure 2** the COD removal percentage increased as the concentration of coagulant increases and the highest COD removal efficiency was achieved at 200 mg/L PAC. Also according to results 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 that 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 results the COD removal efficiency increases as the increasing in PAC concentration. So the COD removal efficiency increases with increasing the concentration of PAC to 200 mg/L. But the COD removal efficiency decreased at concentrations of higher than 200 mg/L that can be attributed to the re-stabilization of the clots formed in the sample and the accumulation of coagulant in substrate. As reported by previous studies when the amount of coagulant exceeds the optimum values, it increases the turbidity due to the presence of excess polymer in the effluent, which can reduce the removal efficiency of COD [31].

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. So that at 200 mg/L PAC, the removal efficiency was 93.86% which is the highest turbidity removal in present study. But according to the results when the coagulant concentration increases from 200 to 300 mg/L, the efficiency dropped from 93.89% to 80%, which shows that the maximum effect of the coagulant dose is at 200 mg/L. Also high removal efficiency was achieved when pH value was

adjusted at 7. As a result, 200 mg/L PAC and pH=7 determined as optimal coagulation condition.

## 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 decrease by increasing in initial H_2O_2 concentration after 30 minute oxidation time. According to 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 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. according to results presence of 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
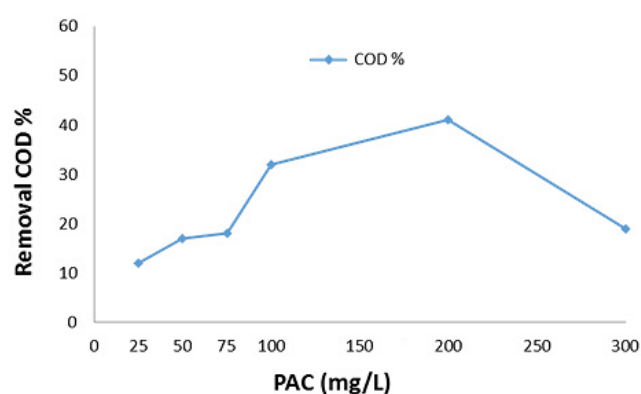
Figure 2   Effect of different concentrations of PAC on COD removal efficiency at pH 7.
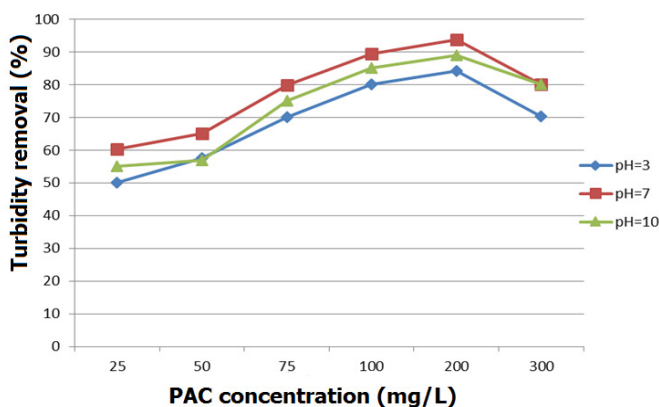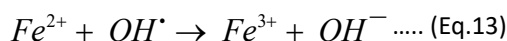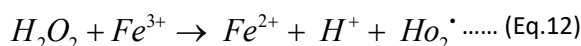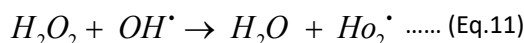

Figure 3   Removal of turbidity at 200 mg/L concentrations of coagulant at different pH values.
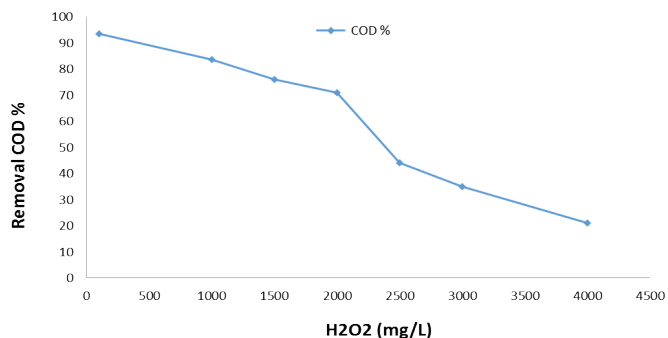
Figure 4 Effect of hydrogen peroxide on the removal efficiency in the electro-Fenton process (voltage: 20 V, Oxidation time: 30 min and pH=3).

(1.25 eV) is less than H_2O_2 (1.3eV).

$$H_2O_2 + OH^\bullet \rightarrow H_2O + Ho_2^\bullet \;\ldots\ldots \text{(Eq.11)}$$

$$H_2O_2 + Fe^{3+} \rightarrow Fe^{2+} + H^+ + Ho_2^\bullet \;\ldots\ldots \text{(Eq.12)}$$

$$Fe^{2+} + OH^\bullet \rightarrow Fe^{3+} + OH^- \;\ldots.. \text{(Eq.13)}$$

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● receptor. Therefore, an increase in H_2O_2 concentration leads to decrease in hydroxyl radicals [2].

The effect of pH changes on the efficiency of the electro Fenton process

The effluent from the chemical coagulation and settling stage entered the electrofenton reactor. In order to evaluate 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 electrofenton 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● 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. That the conversion factor is 2.3 × 10^{-2} min^{-1} and 7.4 × 10^{-2} min^{-1} at pH = 7 and pH = 10.5 respectively. At pH values above 7, the hydroxyl radical rapidly converted to O●-, which has much slower oxidation rate than OH●. At high pH values, ferrous ions precipitate as Fe(OH)$_3$ and inhibit the reaction between Fe^{2+} and H_2O_2. So the reproducibility of Fe^{2+}, which is necessary for the continuation of the hydroxyl radical production process, get reduced. The absence of H+ when the

pH is highly alkaline prevents the decomposition of H_2O_2. As a result, the production of hydroxyl radicals and consequently the decomposition efficiency of pollutants reduced significantly. Also, 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 radicals and ultimately reduces the efficiency of the electrofenton process [16].

The effect of voltage changes on the efficiency of the electro Fenton process

The effect of voltage changes on the COD removal efficiency in the electrofenton process is shown in **Figure 6.** As can be seen 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 electrofenton process decreases by increasing the voltage by more than 20 V. So 20 V value was determined as optimum voltage for electrofenton process. An important issue in the efficiency of the electrofenton 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 the production of hydrogen peroxide at the cathode.
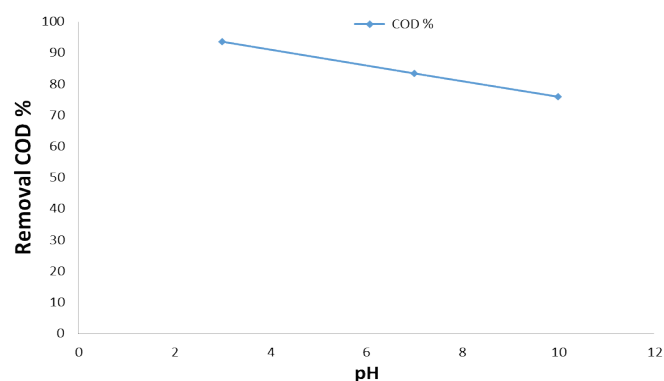
Figure 5 Effect of pH on the removal efficiency in the electro-Fenton process (voltage: 20 V, Oxidation time: 30 min).
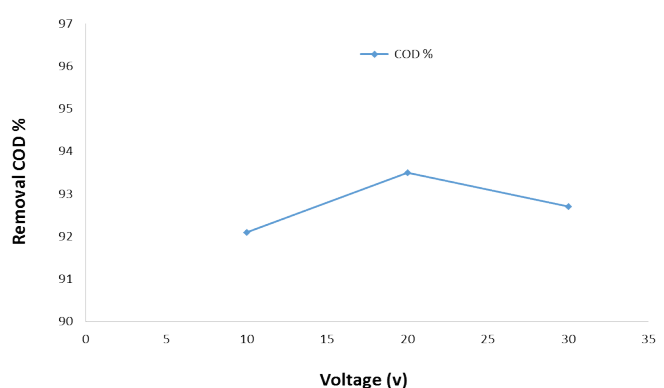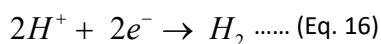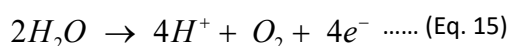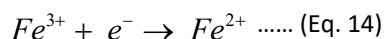

Figure 6 Effect of voltage on removal efficiency in electro Fenton process (H_2O_2= 100 mg/L, Time= 30 min and pH =3).

Table 2 Overall efficiency of the combined process of chemical coagulation and electrofenton.

Process	PAC coagulation		Electro-Fenton Oxidation	
parameter	Turbidity	COD	Turbidity	COD
Removal (%)	93.85	49	93.85	93.5

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 Fe^{2+} 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. This 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.

$$Fe^{3+} + e^- \rightarrow Fe^{2+} \text{ ...... (Eq. 14)}$$

$$2H_2O \rightarrow 4H^+ + O_2 + 4e^- \text{ ...... (Eq. 15)}$$

$$2H^+ + 2e^- \rightarrow H_2 \text{ ...... (Eq. 16)}$$

$$H_2O \rightarrow OH^* + H^+ + e^- \text{ ...... (Eq. 17)}$$

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 (100 rpm in 1 min), flocculation (40rmp in 20 min) and 1 hour settling time, 93.85% and 49% removal was observed for turbidity and COD respectively. Also the overall efficiency of the combined process Electro-chemical coagulation and in pH=3, voltage (20 V) reaction time (30 min) and H_2O_2 concentration (100 mg /L) 93.85% and 93.5% removal was observed for turbidity and COD respectively.

Conclusion

Since no harmful reagents are used in the electro Fenton process, it is considered as an environmentally friendly method for water and wastewater treatment. Present study showed that, with increasing oxidation time of more than 30 minutes, the removal efficiency did not significantly change due to the presence of resistant organic compounds in the sample. Also, the removal efficiency decreased due to the increase in the concentration of PAC in the amounts more than 200 mg/L (due to the destabilization of the clots), and also the increase of the H_2O_2 concentration in the amounts more than 2000 mg/L (due to the radical abduction of ●OH by the Excess H_2O_2) was observed. It was also observed that increasing the pH of the oxidation 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, is 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.

Acknowledgments

References

1   Wei X, Wang Z, Fan F, Wang J, Wang S (2010) Advanced treatment of a complex pharmaceutical wastewater by nanofiltration: Membrane foulant identification and cleaning. Desalination 251: 167-175.

2   Oktem YA, Ince O, Sallis P, Donnelly T, Ince BK (2008) Anaerobic treatment of a chemical synthesis-based pharmaceutical wastewater in a hybrid upflow anaerobic sludge blanket reactor. Bioresour Technol 99: 1089-1096.

3   Madukasi EI, Dai X, He C, Zhou J (2010) Potentials of phototrophic bacteria in treating pharmaceutical wastewater. Int J Environ Sci Techno 7: 165-174.

4   Andreozzi R, Canterino M, Marotta R, Paxeus N (2005) Antibiotic removal from wastewaters: the ozonation of amoxicillin. J Hazard Materi 122: 243-250.

5   Rosario-Ortiz FL, Wert EC, Snyder SA (2010) Evaluation of UV/H_2O_2 treatment for the oxidation of pharmaceuticals in wastewater. Water Res 44: 1440-1448.

6   Shalini K, Anwer Z, Sharma PK, Garg VK, Kumar N (2010) A review on pharma pollution. Int J PharmTech Res 2: 2265-2270.

7   Chelliapan S, Wilby T, Sallis P (2010) Treatment of Pharmaceutical Wastewater Containing Tylosin in an Anaerobic—Aerobic Reactor System. Water Pract Technol p. 5.

8   Clara M, Strenn B, Gans O, Martinez E, Kreuzinger N, et al. (2005) Removal of selected pharmaceuticals, fragrances and endocrine disrupting compounds in a membrane bioreactor and conventional wastewater treatment plants. Water Res 39: 4797-4807.

9   Chang CY, Chang JS, Vigneswaran S, Kandasamy J (2008) Pharmaceutical wastewater treatment by membrane bioreactor process–A case study in southern Taiwan. Desalination 234: 393-401.

10 Babu BR, Venkatesan P, Kanimozhi R, Basha CA (2009) Removal of pharmaceuticals from wastewater by electrochemical oxidation using cylindrical flow reactor and optimization of treatment conditions. J Environ Sci Health 44: 985-994.

11 Serrano D, Suarez S, Lema JM, Omil F (2011) Removal of persistent pharmaceutical micropollutants from sewage by addition of PAC in a sequential membrane bioreactor. Water Res 45: 5323-5333.

12 Rosal R, Rodríguez A, Perdigón-Melón JA, Mezcua M, Hernando MD, et al. (2008) Removal of pharmaceuticals and kinetics of mineralization by O_3/H_2O_2 in a biotreated municipal wastewater. Water Res 42: 3719-3728.

13 Klavarioti M, Mantzavinos D, Kassinos D (2009) Removal of residual pharmaceuticals from aqueous systems by advanced oxidation processes. Environ Int 35: 402-417.

14 Melero JA, Martínez F, Botas JA, Molina R, Pariente MI (2009) Heterogeneous catalytic wet peroxide oxidation systems for the treatment of an industrial pharmaceutical wastewater. Water Res 43: 4010-4018.

15 Akyol A, Can OT, Demirbas E, Kobya M (2013) A comparative study of electrocoagulation and electro-Fenton for treatment of wastewater from liquid organic fertilizer plant. Sep Purif Technol 112: 11-19.

16 Bautista P, Mohedano AF, Gilarranz MA, Casas JA, Rodriguez JJ (2007) Application of Fenton oxidation to cosmetic wastewaters treatment. J Hazard Materi 143: 128-134. Desalin Water Treat.

17 Pirsaheb M, Azizi E, Almasi A (2015) Evaluation of the efficiency of the electrochemical process in removal of COD and $NH_4–N$ from landfill leachate. Desalin Water Treat.

18 Aquino JM, Rocha-Filho RC, Bocchi N, Biaggio SR (2013) Electrochemical degradation of the Disperse Orange 29 dye on a β-PbO_2 anode assessed by the response surface methodology. J Environ Chem Engin 1: 954-961.

19 Feng JW, Sun YB, Zheng Z, Zhang JB, Shu LI, et al. (2007) Treatment of tannery wastewater by electrocoagulation. J Environ Sci 19: 1409-1415.

20 Fernandes A, Spranger P, Fonseca AD, Pacheco MJ, Ciríaco L, et al. (2014) Effect of electrochemical treatments on the biodegradability of sanitary landfill leachates. Appl Catal B 144: 514-520.

21 Pallier V, Feuillade-Cathalifaud G, Serpaud B (2011) Influence of organic matter on arsenic removal by continuous flow electrocoagulation treatment of weakly mineralized waters. Chemosphere 83: 21-28.

22 Rguiti MM, Baddouh A, Elmouaden K, Bazzi LH, Hilali M, et al. (2018) Electrochemical oxidation of olive mill waste waters on tin oxide electrode. J Mater Environ Sci 9: 551-558.

23 Garcia-Segura S, Ocon JD, Chong MN (2018) Electrochemical oxidation remediation of real wastewater effluents—a review. Proc Saf Environ Protec 113: 48-67.

24 Enick OV, Moore MM (2007) Assessing the assessments: Pharmaceuticals in the environment. Environ Impa Assess Rev 27: 707-729.

25 Umar M, Aziz HA, Yusoff MS (2010) Trends in the use of Fenton, electro-Fenton and photo-Fenton for the treatment of landfill leachate. Waste Manag 30: 2113-2121.

26 Ben W, Qiang Z, Pan X, Chen M (2009) Removal of veterinary antibiotics from sequencing batch reactor (SBR) pretreated swine wastewater by Fenton's reagent. Water Res 43: 4392-4402.

27 Dutta K, Mukhopadhyay S, Bhattacharjee S, Chaudhuri B (2001) Chemical oxidation of methylene blue using a Fenton-like reaction. J Hazard Mat 84: 57-71.

28 Yang Y, Wang P, Shi S, Liu Y (2009) Microwave enhanced Fenton-like process for the treatment of high concentration pharmaceutical wastewater. J Hazard Mat 168: 238-245.

29 Choi KJ, Kim SG, Kim SH (2008) Removal of antibiotics by coagulation and granular activated carbon filtration. J Hazard Mat 151: 38-43.

30 Carranzo IV (2012) Standard methods for examination of water and wastewater. In Anales De Hidrología Médica. Universidad Complutense de Madrid 5: 185.

31 Al-Mutairi NZ, Hamoda MF, Al-Ghusain I (2004) Coagulant selection and sludge conditioning in a slaughterhouse wastewater treatment plant. Biores Technol 95: 115-119.

32 Ghosh P, Samanta AN, Ray S (2011) Reduction of COD and removal of Zn^{2+} from rayon industry wastewater by combined electro-Fenton treatment and chemical precipitation. Desalination 266: 213-217.

33 Atmaca E (2009) Treatment of landfill leachate by using electro-Fenton method. J Hazard Mat 163: 109-114.