



Comparison of COD removal from pharmaceutical wastewater by electrocoagulation, photoelectrocoagulation, peroxi-electrocoagulation and peroxi-photoelectrocoagulation processes

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ABSTRACT

This work makes a comparison between electrocoagulation (EC), photoelectrocoagulation, peroxi-electrocoagulation and peroxi-photoelectrocoagulation processes to investigate the removal of chemical oxygen demand (COD) from pharmaceutical wastewater. The effects of operational parameters such as initial pH, current density, applied voltage, amount of hydrogen peroxide and electrolysis time on COD removal efficiency were investigated and the optimum operating range for each of these operating variables was experimentally determined. In electrocoagulation process, the optimum values of pH and voltage were determined to be 7 and 40 V, respectively. Desired pH and hydrogen peroxide concentration in the Fenton-based processes were found to be 3 and 300 mg/L, respectively. The amounts of COD, pH, electrical conductivity, temperature and total dissolved solids (TDS) were on-line monitored.

Results indicated that under the optimum operating range for each process, the COD removal efficiency was in order of peroxi-electrocoagulation > peroxi-photoelectrocoagulation > photoelectrocoagulation > electrocoagulation. Finally, a kinetic study was carried out using the linear pseudo-second-order model and results showed that the pseudo-second-order equation provided the best correlation for the COD removal rate.

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1. Introduction

Wastewater produced from the pharmaceutical factories is hazardous and toxic, and also often has intensive color and disgusting odor. The high concentration of chemical oxygen demand (COD) and low concentration of biological oxygen demand (BOD) in wastewater present a challenge for biological treatment technologies, because the components that are refractory in wastewater may greatly inhibit the activities of microorganisms [1]. Many researchers have been seeking suitable methods to treat pharmaceutical wastewater [2]. Physical–chemical and biological methods are the main treatment processes with their own characters. Biological treatment is economical, but not so effective in refractory organic wastewater. Physical–chemical treatment can obtain

high efficiency and is stable with a high quality effluent, but the treatment cost is relatively high [3]. In addition, neither single physical–chemical nor biological method is recommended as the most effective processes in the treatment of this highly concentrated wastewater [4].

Recently, thanks to the development of new electrode materials and more compact reactors, electrochemical technologies have reached a promising stage of development and can now also be effectively used for the destruction of toxic or biorefractory compounds. The electrochemical oxidation of organics for wastewater treatment can be obtained by direct electrolysis, where the pollutants are oxidized after adsorption on anode surface without the involvement of substances other than electron, which is a clean reagent. Direct electro-oxidation is theoretically possible at low potentials, before oxygen evolution, but the reaction rate usually has slow kinetics and above all during the process there is a decrease in the catalytic activity, commonly called the poisoning effect, due to the formation of a polymer layer on the anode surface [5–7]. This electrode deactivation can be avoided by performing the oxidation at high potentials, in the region of water discharge, due to the participation of intermediates of oxygen evolution [8,9].

Another approach to the electrochemical treatment of organic pollutants is the indirect electrolysis generating in situ

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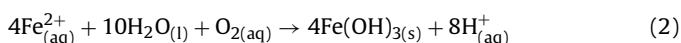
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chemical oxidizing agents to react with the pollutants, such as chlorine and/or hypochlorite and hydrogen peroxide [10].

Advanced oxidation processes (AOPs) are emergent technologies for wastewater treatment, mostly taking advantage of the strong oxidant power of the generated hydroxyl radical (species with an extremely high oxidation potential, $\bullet\text{OH}/\text{H}_2\text{O} = +2.73\text{ V}$) [11]. Recently, in a comprehensive review, Tekin et al. [12] indicate that Fenton oxidation is very effective method in the removal of many hazardous organic pollutants from pharmaceutical wastewaters. The Fenton system employs ferrous ions and hydrogen peroxide (H_2O_2) under acidic pH conditions, which results in strong oxidative hydroxyl radical is produced and the ferrous ions are oxidized to ferric ions and ferric hydroxo complexes that account for the coagulation capability of Fenton reagents [13]. Then suspended solids are captured and precipitated out. The $\bullet\text{OH}$ attacks organic compounds and thus causes chemical decomposition of these compounds in a short time. The Fenton process can therefore have the dual functions of oxidation and coagulation in the treatment process [14]. The coagulation step acts as a polishing step, and removes the remaining after Fenton's oxidation. Hence, Fenton system is one of the most interesting promising oxidative techniques for the abatement of refractory and/or toxic organic pollutants in waste and wastewater [15]. A comparison of various processes for COD removal from pharmaceutical wastewater was given in Table 1.

Electrocoagulation has been reported to successfully treat wastewater of different kinds, containing oil [16], fluoride [17], arsenic [18], dyes [19], suspended particles [20], surfactants [21], chromium ions [22], phosphate [23] and so on. Electrocoagulation is an electrochemical technology of treating polluted water whereby sacrificial anodes dissolve due to an applied potential, thus producing active coagulant precursors. Electrocoagulation is a complicated process with a multitude of mechanisms operating synergistically to remove the pollutants in wastewaters. It offers the possibility of anodic oxidation and in situ generation of active adsorbents (such as hydrous ferric oxides, hydroxides of aluminum). At the same time, cathodic reactions occur and the evolution of hydrogen gas is involved, causing flotation of the adsorbents. Chen [24], Mollah et al. [25] and Holt et al. [26] gave good reviews of electrocoagulation. In the study of iron anodes, two mechanisms for the production of the metal hydroxides have been proposed [27]:

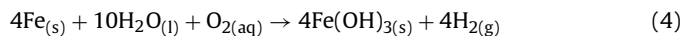
Mechanism 1: Anode:



Cathode:



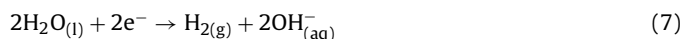
Overall:



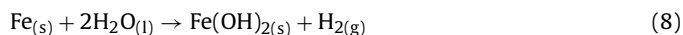
Mechanism 2: Anode:



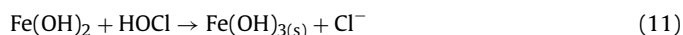
Cathode:



Overall:



Oxidation:



During electrocoagulation process, metal hydroxides formation occurs, these flocs have a large surface area, which are beneficial for a rapid adsorption of soluble organic compounds and trapping of colloidal particles. Finally, these flocs are removed easily from aqueous medium by sedimentation or flotation. The hypochlorous acid and hypochlorite ion can decompose organism because of their high oxidative potentials. Meanwhile, if the anode potential is high enough, other reactions such as direct oxidation of organic compounds may occur at the anode.

Presently, advanced oxidation processes (AOPs) have been used for wastewater treatment, particularly in cases where the contaminant species are difficult to remove by biological or physicochemical processes [28,29]. AOPs are based on the generation of a powerful oxidant, the hydroxyl radical ($\bullet\text{OH}$), which can react with most organic pollutants and then degrade them [30].

The peroxi-electrocoagulation method is efficient and less expensive. In this method, hydrogen peroxide was added into the electrocoagulation system, so Fenton reactive was formed in the process. In the peroxi-electrocoagulation, H_2O_2 is externally applied while a sacrificial Fe anode is used as Fe^{2+} source. Moreover, Fe^{2+} may be continuously regenerated at cathode depending on the setup of electrolytic cell. This process was applied to detoxifying herbicide, pesticide and insecticide containing wastewaters, and polishing biological effluent of a petrochemical wastewater as well [31].

Table 1
Comparison of some COD removal technologies from pharmaceutical wastewater.

Method	Initial COD (mg/L)	COD removal efficiency (%)	Optimum conditions	Literature
Combined PFS coagulation, Fenton and sedimentation	3279	96.9	[PFS] = 200 mg/L; [FeSO ₄] = 120 mg/L; [H ₂ O ₂] = 150 mg/L; pH, 4; HRT, 1 h	[36]
Ozonation	1555	10–20	[O ₃] = 2.8 g/(L h) pH, 11.5; HRT, 60 min	[3]
Fenton	362,000	56.4	[H ₂ O ₂] = 3 M; [FeSO ₄] = 0.3 M; pH, 4; HRT, 20 min	[3]
Photo-Fenton	670	67	COD/H ₂ O ₂ /Fe ²⁺ = 1/2.5/0.125; pH, 3; HRT, 30 min	[3]
Coagulation/flocculation	2700	24–28 70	[FeSO ₄] = 400 mg/L; [Al(SO ₄) ₃] = 250 mg/L;	[3]
Extended aeration	2100	88–98	HRT, 20 h	[3]
Oxidation ditch	2000–3000	86–91	HRT, 1–3 day; SRT, 8–16 day; MLVSS, 3000–4800 mg/L;	[3]
Anaerobic biological treatment	7320	62	Temp. 30 °C; two stages process	[3]
Anaerobic filter	1000–16,000	93.7–97.8	OLR, 0.37–3.52 kgCOD/m ³ ; HRT, 2 day	[3]

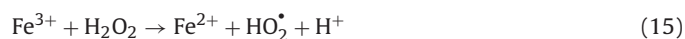
Table 2
Quantities of the pharmaceutical wastewater.

Parameter	COD (mg/L)	BOD (mg/L)	Conductivity ($\mu\text{S cm}^{-1}$)	TDS (mg/L)	Phosphate (mg/L)	Nitrate (mg/L)
Concentration	200–1000	50–300	1000–2500	500–1300	10–20	5–10

During Fenton process reaction, hydrogen peroxide is catalyzed by ferrous ions to produce hydroxyl radicals,



This reaction is propagated from ferrous ion regeneration mainly by the reduction of the produced ferric species with hydrogen peroxide,

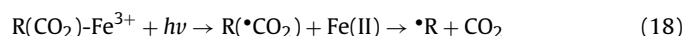


Ferrous ions are consumed more rapidly than they are produced. In addition, ferrous ions can be rapidly destroyed by hydroxyl radicals with the rate constant in the range of $3.2\text{--}4.3 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$ [32]



Therefore, more ferrous ion dosage is needed to keep the moderate hydroxyl radicals production. This results in the large amount of ferric hydroxide sludge during neutralization stage of Fenton process, which requires additional separation process and disposal [33]. The capability of the peroxi-electrocoagulation process has been confirmed by Everim Yuksel et al. [34], with more than 80% sodium dodecyl sulfate (SDS) removal.

The efficiency of this process can be improved by using UV or visible light illumination in a process known as the peroxi-photoelectrocoagulation process. This improvement is due to the higher production rate of $\bullet\text{OH}$ from the photoreduction of $\text{Fe}(\text{OH})^{2+}$ (Eq. (17)) and the photodecomposition of complexes from Fe^{3+} reactions (Eq. (18)) [35]:



In the past few years, many experiments have been carried out to remove COD from industrial wastewater by combined coagulation and Fenton's reactions [36]. However, the performances of hydrogen peroxide (H_2O_2) and UV in electrocoagulation cell for COD removal from pharmaceutical wastewater were not evaluated. This study attempted to examine the possibility of COD removal from pharmaceutical wastewater by combined electrocoagulation with H_2O_2 and UV. The influence of several process parameters such as initial pH, current density, voltage, hydrogen peroxide concentration on COD removal were evaluated. Then, the performance of electrocoagulation, photoelectrocoagulation, peroxi-electrocoagulation and peroxi-photoelectrocoagulation were compared. Finally the adsorption kinetics and energy consumption of the processes were analyzed.

2. Materials and methods

2.1. Experimental method

The batch experimental setup is schematically shown in Fig. 1. A constant voltage was maintained using a potentiostat in intensiostat mode. Magnetic stirring at 400 rpm was maintained a homogenous solution in the batch reactor which contains 2.0 L of wastewater sample. The main function of stirring speed is to transfer efficiently the coagulant matter which is formed by the solution of electrodes to reactor. If coagulant matter does not disperse in the reactor efficiently, content of the reactor cannot be homogenous and regional differences can be seen. The chosen stirrer speed

(400 rpm) was found to be suitable to provide good mixing in the electrolyte cell and yet was not strong enough to break up the flocs formed during the processes. In this investigation, samples from pharmaceutical wastewater were used, which was taken from Osvah Pharmaceutical Company located in Tehran, Iran. Table 2 summarizes the characteristics of the produced wastewater. Experiments were carried out, at laboratory scale, in cell equipped by 2 Fe electrodes (anode and cathode with 150 cm^2 area) in addition with 2 extra Fe plates in order to improving coagulation. In other words, placing iron plates could result in producing more coagulant precursors which improves the treatment process. For the photoelectrocoagulation and peroxi-photoelectrocoagulation processes, irradiation was carried out with a 125-W (UV-C) mercury lamp (Philips), which was put above the cell. The distance between solution and UV source was constant, 15 cm, in all experiments. The light intensity of UV lamp at the surface of the solution was 0.315 W/cm^2 . In each run, 2.0 L pharmaceutical wastewater was fed to the electrolytic cell. At the end of each experiment, the solution was filtered before analysis. The membrane filter used in this method was $0.2 \mu\text{m}$. The COD of the wastewater was measured using a Hach spectrophotometer (Diar 5000) and a Hach COD reactor. The temperature and solution pH were monitored using the ultrameter II from Myron L Company in the electrolysis. Conductivity and TDS were recorded on a Sension378 Conductivity Meters (Hach). The reported concentration for each sample was the average of 3 times measurement.

3. Results and discussion

3.1. Factors affecting the performance of electrocoagulation process

3.1.1. Effect of initial pH

It has been established that pH is an important parameter influencing the performance of the EC process. The kinetics of Fe^{2+} conversion to Fe^{3+} are strongly affected by the pH; the surface charge of the coagulating particle also varies with pH. To examine the effect of initial pH, the pharmaceutical wastewater was adjusted to the desired pH (in the range 3–9) with diluted aqueous

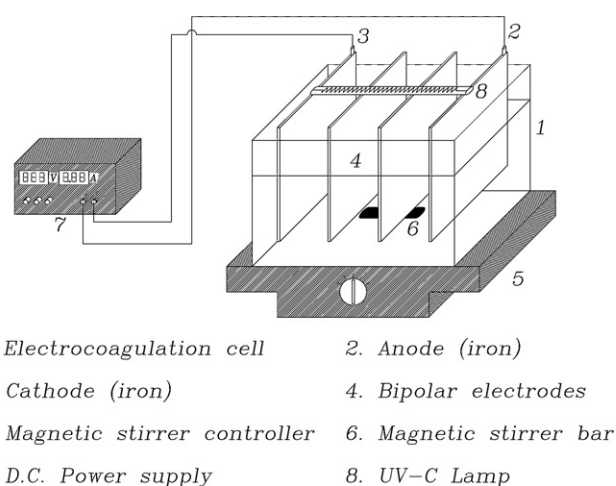


Fig. 1. The schematic experimental setup in the study.

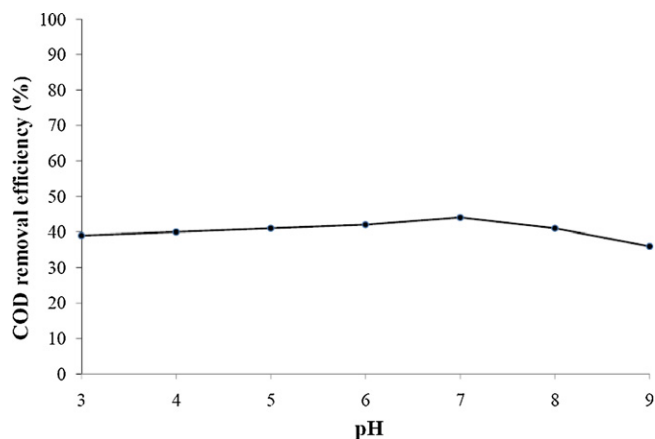


Fig. 2. Effect of initial pH on COD removal efficiency (electrocoagulation process; initial COD, 420 mg/L; HRT, 30 min; voltage, 30 V; current density, 1.7–1.9 mA cm⁻²; initial conductivity, 1514 μS cm⁻¹; distance between plates, 25 mm).

NaOH_(aq) or H₂SO_{4(aq)}. Fig. 2 demonstrates the COD removal at different initial pH. The optimal initial pH of this process was 7.0. A slight drop in COD removal was observed at pH values <7 or >7. This result can be explained by the distribution of iron ionic species [37].

The mechanism of electrochemical process in aqueous system is quite complex. However, the COD removal process may involve precipitation and adsorption. Each of the mechanism is applicable at different pH ranges. At low pH values, metal species like Fe²⁺ generated at the anode bind to the anionic colloidal particles present in the wastewater, thus, neutralizing their charge and reducing their solubility. This process of removal is termed precipitation.

The adsorption mechanism operates at higher pH range (>7) and involves adsorption of organic substances on amorphous metal hydroxide precipitates [38]. In the present case, for pH < 7, the primary mechanism is charge neutralization by monomeric cationic iron species, while for higher pH, sweep coagulation with amorphous iron hydroxide explains the results [39].

3.1.2. Effect of current density and voltage

One of the most important parameters that can affect the removal or destruction efficiency in the electrochemical process is the current density or the voltage.

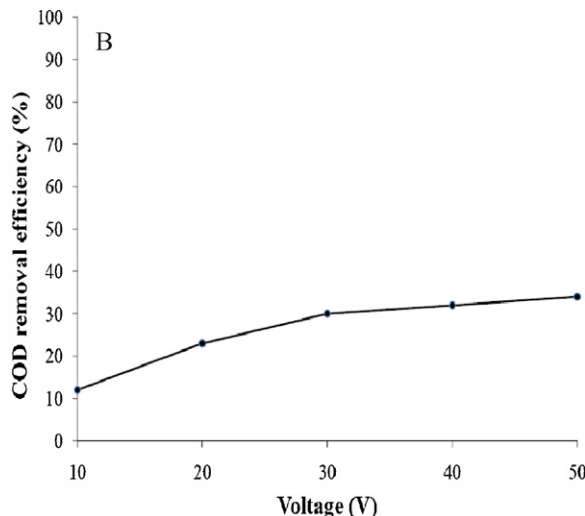
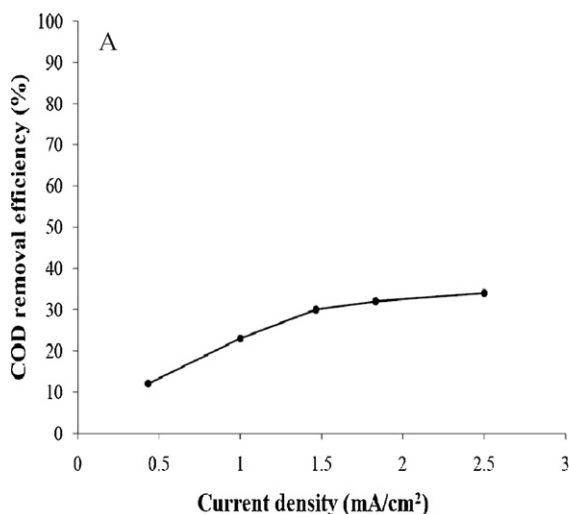


Fig. 3. Effect of (a) current density and (b) voltage on COD removal efficiency (initial COD, 488 mg/L; HRT, 30 min; initial pH, 7; initial conductivity, 1514 μS cm⁻¹; distance between plates, 25 mm).

Current density was calculated as the applied current divided by the projected surface area of the studied electrode. According to Faraday's formula (Eq. (19)), it is obvious that Fe²⁺ dose released from anode depends on the electrolysis time and current:

$$C_{Fe} = \frac{M_w I t_{EC}}{Z F V} \quad (19)$$

where C_{Fe} , Z , F , V , and M_w are the theoretical concentration of Fe²⁺ (g/m³), the chemical equivalence, Faraday's constant (96,487 C/mol), volume of reactor (m³), and molecular weight of iron (g/mol), respectively [34]. According to Faraday's law, When 1 F (26.8 Ah) passes through the electric circuit, 0.0224 Nm³ hydrogen gas will be evolved, which is much greater than the volume of gas released in traditional DAF. Consequently, increasing current density will give rise to an increase in charge loading and leading to increased removal of pollutants. The influence of the current density on the COD removal during the electrolysis with the iron electrodes is reported in Fig. 3a.

The COD removal efficiency was increased to 32% at 1.83 mA cm⁻² from 12% at 0.43 mA cm⁻² after 30 min reaction. The removal efficiency of COD at higher current densities than 1.83 mA cm⁻² stayed at the constant value. At a high current density, the extent of anodic dissolution of iron increases, resulting in a greater amount of Fe²⁺ and Fe(OH)_{n(s)}. In addition, the increasing concentration of ferrous iron could enhance the reaction, producing hydroxyl radicals. Moreover, the rate of bubble-generation increases and the bubble size decreases with increasing current density; both of these trends are beneficial in terms of high pollutant-removal efficiency by H₂ floatation. In evaluating batch electrocoagulation as a technology to provide a low cost, low maintenance local wastewater treatment, this set of experiments clearly demonstrates two important results. First, that operating current density is the key operational parameter, affecting not only the system's response time, but also strongly influencing the dominant mode of pollutant separation. Second, these results indicate that running the reactor at the highest allowable current density may not be the most efficient mode of operation. For any specific application, the optimal current density will invariably involve a trade-off between operating costs and efficient use of the introduced coagulant.

Voltage is the only operational parameter which can be controlled directly because current will change with time. In other word, due to increase of ohmic resistance electric current would change. Moreover, generation of salt sediments like carbonate salts

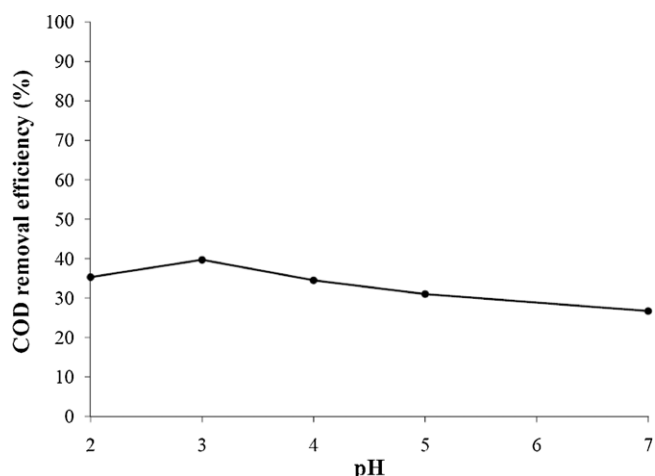


Fig. 4. Effect of initial pH on COD removal efficiency (peroxi-electrocoagulation process; initial COD, 482 mg/L; hydrogen peroxide, 100 mg/L; HRT, 30 min; voltage, 40 V; current density, 1.7–1.9 mA cm⁻²; initial conductivity, 1514 μS cm⁻¹; distance between plates, 25 mm).

on iron plates could affect the electrical current. In this system electrode spacing is fixed and voltage is a continuous supply. Voltage directly determines both coagulant dose and bubble generation rates, as well as strongly influencing both solution mixing and mass transfer at the electrodes. Thus a set of experiments was carried out to quantify the impact of operating voltage on reactor performance. Fig. 3b shows the COD removal as a function of voltage. It can be seen from Fig. 3b that COD removal efficiency was raised with the application of voltage on the reactor. The removal efficiency of COD from the pharmaceutical wastewater was still low, only 12% when applying 10 V. When the applied voltage was raised to 20 V, the removal efficiency rose to about 23% because a larger amount of Fe²⁺ and Fe³⁺ was produced via anodic metal dissolution, causing coagulation, and more bubbles formed at the cathode, causing flotation. Although the removal efficiency of COD increased to 32% and 34% with increasing the applied voltage to 40 V and 50 V. Therefore, the voltage 40 V was chosen for all the processes.

3.2. Factors affecting the performance of peroxi-electrocoagulation process

3.2.1. Effect of initial pH

The pH effect was particularly studied in Fenton process. Fig. 4 shows the influence of initial pH on the COD removal from this wastewater. These results also reveal that Fenton's reagent is a highly pH sensitive process. Fig. 4 depicts that COD removal performance declined for pH values greater than 3.0. This occurs due to the formation of the ferric hydroxo-complexes, namely the precipitation of Fe³⁺ as Fe(OH)₃, hindering the reaction between Fe³⁺ and H₂O₂, and therefore the regeneration of Fe²⁺. Besides, Fe(OH)₃ catalyzes the self-decomposition of H₂O₂ (particularly unstable in basic media) to oxygen molecular and water, resulting in a decline of its oxidative capacity [40]. When pH is higher than 8.0 the ferric complexes would further form Fe(OH)₃ with the generation of flakes and consequent precipitation [41]. This formation of flakes contributes to a small reduction of COD which occurs for pH 9.0. It is also possible that the precipitation occurs with Fe³⁺ as oxyhydroxide amorphous (Fe₂O₃·nH₂O) at pH greater than 3 [42].

On the other hand, for pH values lower than 2.0 the reaction of hydrogen peroxide with Fe²⁺ is seriously affected due to the formation of complex species [Fe(H₂O)₆]²⁺, which reacts slower with peroxide when compared to that of [Fe(OH)(H₂O)₅]²⁺. In addition, the peroxide gets solvated in the presence of high concentration

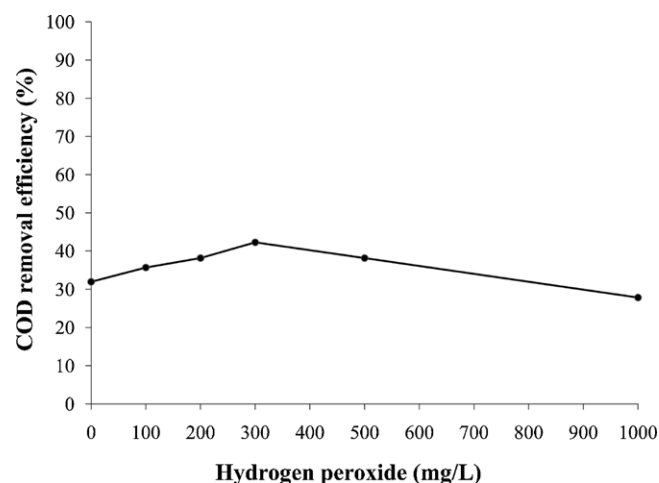


Fig. 5. Effect of hydrogen peroxide on COD removal efficiency (peroxi-electrocoagulation process; initial COD, 330 mg/L; HRT, 30 min; pH, 3; voltage, 40 V; current density, 1.7–1.9 mA cm⁻²; initial conductivity, 1514 μS cm⁻¹; distance between plates, 25 mm).

of H⁺ ion to form stable peroxone ion [H₃O₂]⁺. The peroxone ion it leads to an electrolytic behavior on the part of hydrogen peroxide improving its stability and substantially reducing the reactivity with ferrous ion [40].

Therefore, the initial pH value has to be in the acidic range (2.5–3.5) to generate the maximum amount of •OH and oxidize the organic compounds. In particular the optimal value of pH is 3, which is in agreement with previous results obtained in other studies using Fenton's reagent [43].

3.2.2. Effect of hydrogen peroxide (H₂O₂)

It is important to optimize the amount of H₂O₂ in the Fenton method because the main cost of the method is the cost of H₂O₂ and excessive dose of H₂O₂ trigger adverse effects. The amount of H₂O₂ required for efficient COD removal is demonstrated in Fig. 5. From the results observed that the maximum removal rate was nearly 42.2% for optimum 300 mg/L H₂O₂ after 30 min electrolysis time for voltage of 40 V. The COD removal can be attributed to the fact that the system suffered both reactions simultaneously, electrocoagulation and also Fenton process.

When the dosage of H₂O₂ increased from 100 mg/L to 300 mg/L, the COD removal increased from 35.6% to 42.2%. However, when

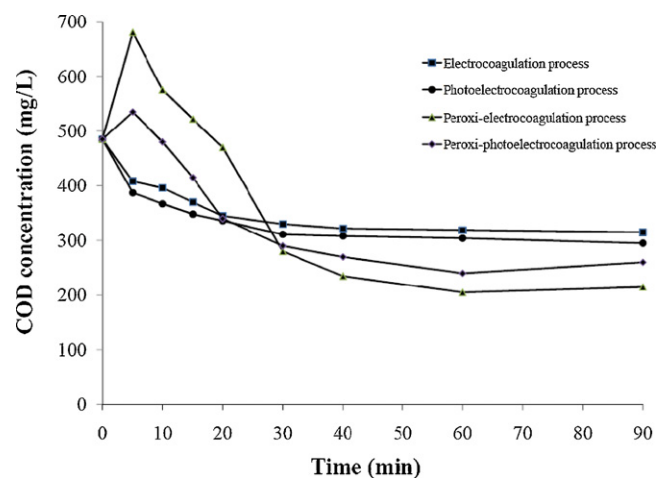


Fig. 6. Effect of HRT on COD removal efficiency (initial COD, 485 mg/L; voltage, 40 V; current density, 1.7–1.9 mA cm⁻²; initial conductivity, 1514 μS cm⁻¹; distance between plates, 25 mm).

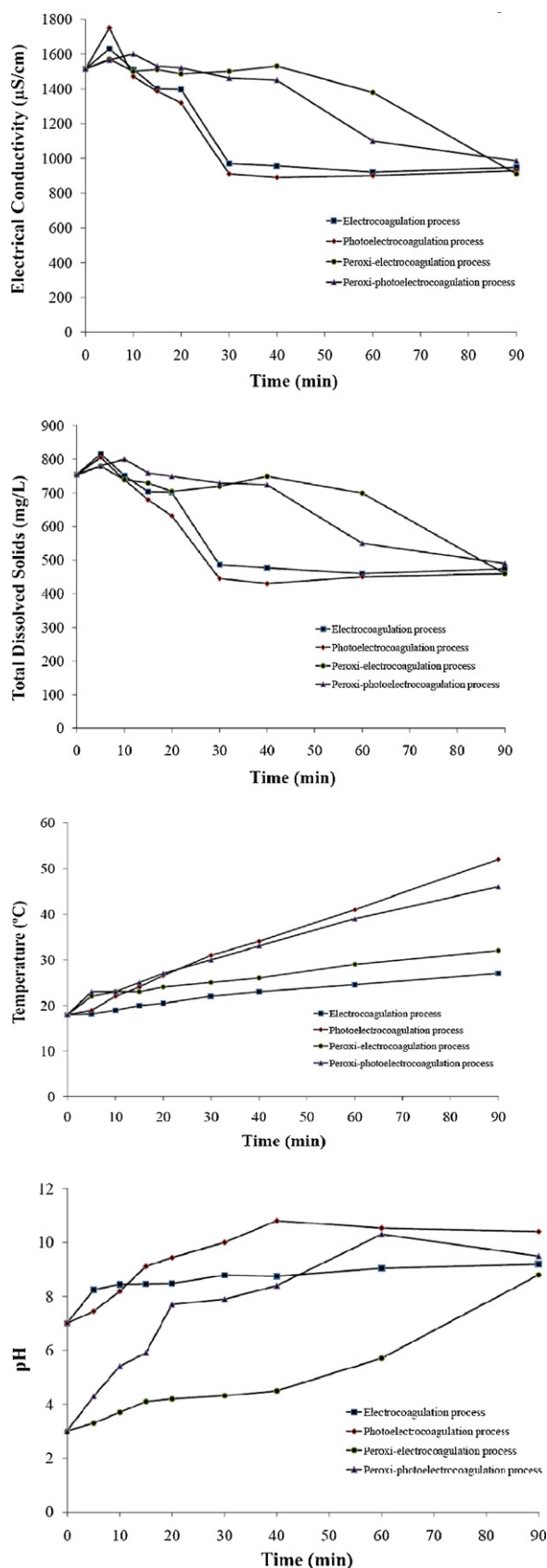
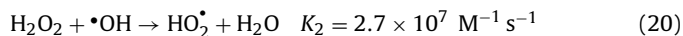


Fig. 7. Comparison between various processes on (a) electrical conductivity, (b) total dissolved solids, (c) temperature and (d) pH change (voltage, 40 V; current density, 1.7–1.9 mA cm^{-2} ; initial conductivity, 1514 $\mu\text{S cm}^{-1}$; distance between plates, 25 mm).

the dosage of H_2O_2 varied from 300 mg/L to 1000 mg/L, the COD removal decreased to 27.8%, demonstrating that most of organic pollutants in the wastewater could be oxidized by hydroxyl radical. Although the $\cdot\text{OH}$ was generated by H_2O_2 , which could enhance the oxidation ability of treatment along with increment of H_2O_2 dosage, the degressive trend indicated that the over-abundant H_2O_2 could also consumed $\cdot\text{OH}$ and become the elimination reagent of hydroxyl radical (Eq. (20)) [44].



3.3. Comparison between various processes

3.3.1. Effect of time on COD removal efficiency

Reactive time influences the treatment efficiency of the electrochemical process. Electrolysis time determines the production rate of Fe^{2+} or Fe^{3+} ions from iron electrodes. To explore the effect of operating time, the optimal conditions of these processes were used and all processes were started, simultaneously. As be shown in Fig. 6, the concentration of COD in electrocoagulation process and photoelectrocoagulation process decreased with increasing electrolysis time and after 30 min the concentration of COD decreased to 330 and 311 mg/L with removal efficiency of 31.96% and 35.88%, respectively. After this time, the COD removal reached a plateau. The COD removal by electrocoagulation and photoelectrocoagulation could be due to the removal of suspended solids and precipitation of dissolved COD by electrocoagulation, electroflotation, direct anodic oxidation and indirect oxidation by chloride ions. Moreover, COD removal may also involve electrochemical oxidation and adsorption by electrostatic attraction and physical entrapment. It is obvious that the use of UV had a positive effect on the performance of electrocoagulation process and improved the COD removal efficiency because of the enhancement of available photoactive sites.

The concentration of COD in peroxi-photoelectrocoagulation process and peroxi-electrocoagulation process increased in the first 5 min to 535 and 680 mg/L, respectively. It is probably due to the degradation of some complex compounds in the wastewater, which were broken into degradable compounds. UV light had a strong effect on the performance of peroxi-photoelectrocoagulation and enhanced the COD removal efficiency in the first 5 min. However, the removal efficiencies for COD in the peroxi-photoelectrocoagulation process and the peroxi-electrocoagulation process were 40.21% and 42.27%, respectively, after 30 min of reaction. The removal of COD was due to the formation of $\cdot\text{OH}$ via Eq. (14). Moreover, Fe^{3+} in the solution was able to regenerate inside the reactor when electric discharge and UV irradiation were used, allowing numerous Fe^{2+} react with H_2O_2 to generate $\cdot\text{OH}$. Ferrous ions were not depleted during the oxidation reaction, as shown in Eqs. (15)–(18). Therefore, the dosage of H_2O_2 could enhance the performance of electrocoagulation process and photoelectrocoagulation process.

3.3.2. Change in the characteristics of the solution

The change in the electrical conductivity of the solution, total dissolved solids (TDS), temperature and pH along with the electrolysis time in the study are shown in Fig. 7. The solution

Table 3

Comparison between calculated q_e and k_2 for COD in pseudo-second-order equation (voltage, 40 V; distance between plates, 25 mm).

Kind of process	q_e (mg)	k_2 ($\text{g mg}^{-1} \text{ min}^{-1}$)	R^2
Electrocoagulation process	188.68	6.59×10^{-4}	0.996
Photoelectrocoagulation process	204.08	7.55×10^{-4}	0.999
Peroxi-electrocoagulation process	312.50	2.66×10^{-4}	0.978
Peroxi-photoelectrocoagulation process	263.16	3.32×10^{-4}	0.970

Table 4
Energy consumption in the various processes.

Time (min)	Kind of process	COD removal efficiency (%)	Energy consumption (kWh/kg COD)
30th min	Electrocoagulation process	31.96	34.84
	Photoelectrocoagulation process	35.88	90.80
	Peroxi-electrocoagulation process	42.27	21.95
	Peroxi-photoelectrocoagulation process	40.21	74.36
40th min	Electrocoagulation process	33.61	44.17
	Photoelectrocoagulation process	36.49	100.19
	Peroxi-electrocoagulation process	51.54	24.00
	Peroxi-photoelectrocoagulation process	44.33	74.42
60th min	Electrocoagulation process	34.22	65.06
	Photoelectrocoagulation process	37.32	119.34
	Peroxi-electrocoagulation process	54.73	32.14
	Peroxi-photoelectrocoagulation process	50.52	77.55

conductivity in electrocoagulation, photoelectrocoagulation, peroxi-electrocoagulation and peroxi-photoelectrocoagulation process decreased from the original $1514 \mu\text{S cm}^{-1}$ to 948, 928, 910 and $985 \mu\text{S cm}^{-1}$, respectively, and the TDS from 755 mg/L to 474, 460, 460 and 490 mg/L, respectively, after 90 min of reaction, indicating some species in the wastewater were removed. As be shown in Fig. 7(c), the solution temperature increased from 18°C to 27, 52, 32 and 46°C in electrocoagulation, photoelectrocoagulation, peroxi-electrocoagulation and peroxi-photoelectrocoagulation process, due to the input of electrical energy and light energy. Fig. 7(d) shows the pH change of the solution along with the electrolysis time. The pH of a solution is one of the most important parameters, but controlling the pH is very difficult because the reactions involved change the pH. It could be seen that in both electrocoagulation and photoelectrocoagulation, pH increases from 7 to 8.75 and 10.8, respectively, in first 40 min and then remains relatively constant. In peroxi-electrocoagulation and peroxi-photoelectrocoagulation, solution pH increased and reached to 8.8 and 9.5, respectively, at the end of 90 min.

3.4. Kinetic studies of the COD removal

The removal of COD can be presented by the following the linear pseudo-second-order equation:

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (21)$$

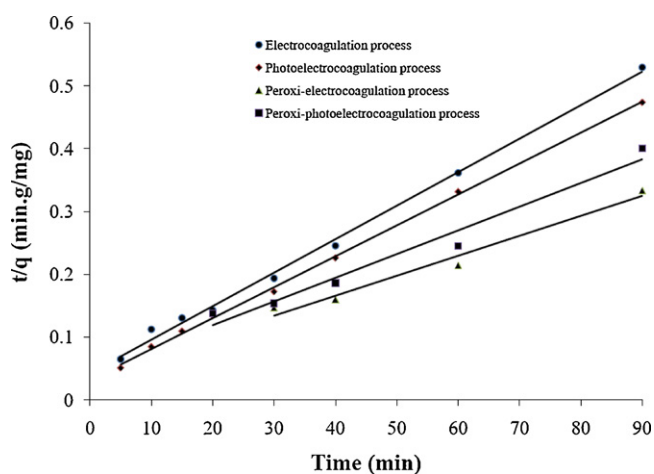


Fig. 8. The pseudo-second-order equation plot with electrolysis time (initial COD, 485 mg/L; voltage, 40 V; current density, $1.7\text{--}1.9 \text{ mA cm}^{-2}$; initial conductivity, $1514 \mu\text{S cm}^{-1}$; distance between plates, 25 mm).

where k_2 ($\text{g mg}^{-1} \text{ min}^{-1}$) is the rate constant of the pseudo-second-order equation, q_e (mg) is the maximum adsorption capacity and q_t is the amount of adsorption at time t . The straight line in plot of linear pseudo-second-order equation (Fig. 8) shows good agreement of experimental data with the pseudo-second-order kinetic model for different removal rates. The values of q_e and k_2 were calculated from the slope and intercept of these plots. Correlation coefficients for the pseudo-second-order kinetic model obtained in bipolar reactor studies were above 0.97. Table 3 demonstrates the computed result obtained from the second-order kinetic model. These results indicate that the adsorption system of all processes belongs to the pseudo-second-order kinetic model.

3.5. Electric energy consumption

It is clear that a technically efficient process must also be feasible economically. The major operating cost of EC is associated with electrical energy consumption during process. Electrical energy consumption was calculated using the Eq. (22):

$$E = UIt_{\text{EC}} \quad (22)$$

where E is the electrical energy in Wh, U the cell voltage in volt (V), I the current in ampere (A) and t_{EC} is the time of EC process in per hour [45]. According to the results presented in Table 4, the minimum energy consumption belonged to peroxi-electrocoagulation process.

4. Conclusion

In this research, performance of electrocoagulation, photoelectrocoagulation, peroxi-electrocoagulation and peroxi-photoelectrocoagulation processes with iron electrodes were investigated for the removal of COD from pharmaceutical wastewater originated from Osvah Pharmaceutical Company. Effect of various parameters like pH, voltage, hydraulic retention time (HRT), hydrogen peroxide concentration were studied and. At optimal conditions, the COD removal efficiency and power requirement of electrocoagulation, photoelectrocoagulation, peroxi-electrocoagulation and peroxi-photoelectrocoagulation processes were obtained 34.2%, 65.06 kWh/kgCOD, 37.3%, 119.34 kWh/kgCOD, 57.7%, 32.14 kWh/kgCOD, and 50.5%, 77.55 kWh/kgCOD, respectively, after 60 min of reaction. Also, the amounts of pH, electrical conductivity, temperature and total dissolved solids were determined during processes. The adsorption kinetic data of COD were analyzed using pseudo-second-order equation. The results showed that pseudo-second-order equation model was found to be in good agreement with the experimental results.

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