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The performance of electrosynthesised ferrate (VI) ion, electrocoagulation and peroxi-electrocoagulation processes for degradation of cholesterol-lowering drug atorvastatin

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ABSTRACT

The degradation of atorvastatin (ATV) by electrosynthesised ferrate (VI) ion, electrocoagulation (EC) and peroxi-electrocoagulation (p-EC) were compared in this study. The effects of pH, Fe (VI) dose, electrode type, current density, supporting electrolyte concentration (SEC) and hydrogen peroxide concentration were investigated. All processes were affected by pH. Acidic pH values showed better efficiencies for each process, which was related to the drug's solubility properties and dominant produced species with acidic values. Hybrid electrodes were found to be the most efficient electrode pairs. In EC, optimum pH value, current density and SEC were determined to be 3, 2.5 mA/cm^2 and 200 mg/L, respectively. The preferred pH and H_2O_2 concentration in the p-EC process were found to be 3 and 250 mg/L, respectively. Eighty-two per cent specific drug removal and 77% TOC removal were achieved. The performance of the processes for ATV degradation were found to be in the order of peroxi-electrocoagulation > Fe (VI) > electrocoagulation.

Keywords: Atorvastatin; Cholesterol-lowering drugs; Electrocoagulation; Ferrate (VI); Peroxi-electrocoagulation

1. Introduction

Pharmaceuticals are often used in veterinary medicine, human health and agricultural practice groups for chemicals [1–3]. Among these pharmaceuticals, cholesterol-lowering drugs are widely consumed [4]. Atorvastatin (ATV) is a synthetic lipid reducer, and it inhibits 3-hydroxy-3-methylglutaryl-coenzyme A (HMG-CoA) reductase enzyme. ATV was the target agent in this study because it is extensively produced and used worldwide for the treatment of hypercholesterolemia [5]. Its molecular structure is shown in Fig. 1.

It has been reported that statins have a high adverse effect on a plant called Lemna gibba [6]. Additionally, fish appear to be the most sensitive group of aquatic organisms. It has been documented that statin groups contribute to destroying some fish species even at low concentrations [7,8]. Recent studies have shown that pharmaceuticals in drinking water even at low concentrations affect human embryonic kidney cells [9] and blood cells [10].

Large amounts of pharmaceuticals escape from wastewater treatment plants without any degradation due to their solubility properties, and highly polar micropollutants, such as lipid-reducing drugs, cannot

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be removed by biological or conventional chemical processes. Therefore, they may reach significant concentrations in the environment. To destroy the undesirable residuals of active agents and metabolites, which are mostly from treatment plants, improved wastewater treatment systems, such as advanced oxidation processes (AOPs), activated carbon or UV, should be actualised. Thus, recent research is related to pharmaceuticals removal through AOPs, such as anodic oxidation processes [11–13], ozonation [14,15], photo-Fenton processes [16,17], adsorption [18], photocatalysis [19–21], electrochemically produced adsorbents [22,23] and membrane technologies [24].

Among AOPs, ferrate (VI) could be considered a promising technology due to its ability to remove pharmaceutical residuals through its oxidant and coagulant functions. Ferrate (VI) has been effectively applied in water and wastewater treatment due to its high redox potential under acidic conditions [25–27].

Electrocoagulation (EC) has been reported to remove pollutants effectively [28–33]. The removal mechanism is quite complex in the EC process. The production of active adsorbents (e.g. ferric oxides, aluminium hydroxides) removes pollutants. Coagulation, adsorption and precipitation caused by these adsorbents eliminate contaminants from water and wastewater. At the same time, flotation due to hydrogen evolution in the cathode side could improve pollutants removal.

The main aim is the production of a powerful oxidant, the hydroxyl radical (·OH), in AOPs. This radical reacts with the pollutants and then causes degradation

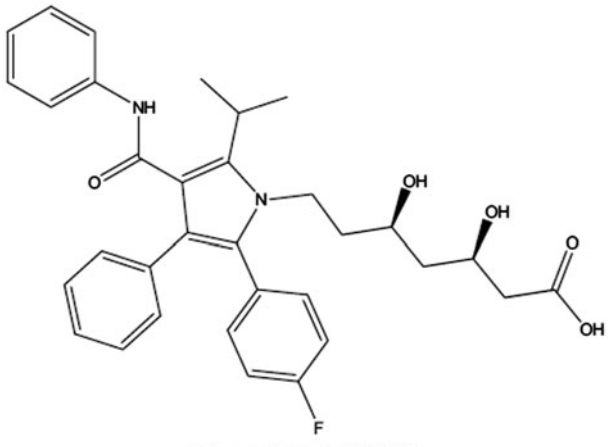

Fig. 1. Chemical structure of atorvastatin (CAS number: 134523-00-5 and IUPAC name: (3R,5R)-7-[2-(4 fluorophenyl)-3-phenyl-4-(phenylcarbamoyl)-5-(propan-2-yl)-1H-pyrrol-1-yl]-3,5 dihydroxy heptanoic acid).

[34]. Hydrogen peroxide is added into the electrocoagulation reactor in this method for the formation of a Fenton reaction. The Fe anode is used as a Fe^{2+} source. The peroxi-electrocoagulation (p-EC) method is effective and less expensive compared with the other AOPs. According to Farhadi et al., the peroxi-electrocoagulation process had the minimum energy consumption compared with electrocoagulation, photoelectrocoagulation and peroxi-photoelectrocoagulation systems [35].

In this study, the performance of electrosynthesised ferrate (VI) and electrocoagulation and peroxi-electrocoagulation processes were investigated for the removal of atorvastatin. The comparison of the processes with regard to the efficiency and operating cost was also evaluated.

2. Experimental methods

2.1. Materials and methods

Atorvastatin (≥98%, HPLC grade) was purchased from Sigma-Aldrich and used without any treatment. The pH was adjusted with buffers, including $C_8H_5KO_4$–HCl solution (pH 3 and 4); $C_8H_5KO_4$–NaOH solution (pH 5); KH_2PO_4–NaOH solution (pH 6, 7 and 8); and $Na_2B_4O_7{\cdot}10H_2O$–NaOH solution (pH 9). Stock solutions (50 mg/L ATV) were prepared weekly in high-quality pure water using the Millipore Water Purification System and stored at 4°C.

2.2. Experimental procedures

Ferrate (VI) was synthesised via the electrochemical method. Details of the preparation, stability and optimum conditions of ferrate (VI) synthesis can be found in our previous study [36]. The concentration of ferrate (VI) was analysed utilising a Hach Lange DR5000 UV/vis Spectrophotometer at 505 nm using a pre-calibration curve. After electrolysis, the synthesised ferrate (VI) concentration in the electrochemical reactor was 240 ± 1 mg/L. Ferrate (VI) was synthesised freshly before each ATV degradation experiment and immediately dosed to the reactor. The pH was then adjusted to the chosen values (4, 5, 6, 7, 8 and 9). Ferrate (VI) was added to the solutions in volume ratios of 10/1; 8/1; 5/1; 3/1 and 1/1. Fast mixing for 30 s at 400 rpm and slow mixing for 10 min at 40 rpm were applied by a mechanic stirrer. Sedimentation took place for 60 min.

In each run, 600mL of ATV solutions were placed into the rectangular reactor for the EC and p-EC processes. The EC and p-EC reactors were made of plexiglass material. Four electrodes (two anodes and two

cathodes) in connection with a monopolar mode were used in each experiment, and the distance between the electrodes was 0.5 cm. Aluminium and iron electrodes were used in the EC process. The electrodes' active surface area was 150 cm^2. A constant direct current was provided by a TT Technic RXN 3010D DC power source. The current was constant in each experiment. During the EC and p-EC processes, ATV-containing solution was stirred with a magnetic stirrer at a speed of 120 rpm.

The initial atorvastatin concentrations were 1 and 5 mg/L in the ferrate (VI) process. For the EC and p-EC processes, they were set to 1 mg/L. The concentration level was chosen to assess the process efficiency for real-scale applications in the future, because wastewater from manufacturers may contain pharmaceutics at the mg/L level [37].

All experiments were conducted at room temperature in triplicate.

2.3. Analytical methods

After sedimentation, the samples were taken and filtered through 0.45-μm cellulose acetate membrane syringe filters (VWR) for UV–vis and TOC measurements.

The equilibrium ATV concentrations were determined via a UV–vis spectrophotometer (Hach Lange DR5000) at the wavelength of 241 nm. The coefficient of regression (R^2) was 0.9990, and the mean linear regression equation was $y = 0.0338x + 0.0045$. TOC measurements were performed by a TOC analyser (TOC-VCPH, Shimadzu, Japan) calibrated with standard potassium hydrogen phthalate solutions.

3. Results and discussion

3.1. Degradation of ATV by electrosynthesised Fe (VI)

3.1.1. Effect of pH

Fig. 2(a) shows the evaluation of ATV removal with the pH at initial concentrations of 1 and 5 mg/L. The results show that the performance of ferrate (VI) was affected by the pH of the solution. While 77.6% removal efficiency was obtained at pH 4, the efficiency was reduced to 62.0% at pH 9 for 1 mg/L initial drug concentration. The pH increment caused less efficient degradation for ATV. In other words, ferrate (VI) showed poor reactivity with ATV at alkaline pH values. When its initial concentration was 5 mg/L, the degradation of ATV was reduced to 54.3% at pH 4, and a similar trend was observed for other pH values. Ferrate (VI) was capable of degrading lower concentrations of ATV.

A total of 71.4% TOC removal efficiency for 1 mg/L was obtained at pH 4; the removal degree was 64.3% for the 5-mg/L initial drug concentration. As expected, alkaline pH values, such as pH 9, showed a lower degradation rate (58.3% for 1 mg/L and 46.8% for 5 mg/L at initial ATV concentrations) (see Fig. 2(b)). The TOC removal efficiencies were lower compared with specific drug removal, as expected. This may have been due to half-finished degradation and/or the formation of refractory primary degradation products.

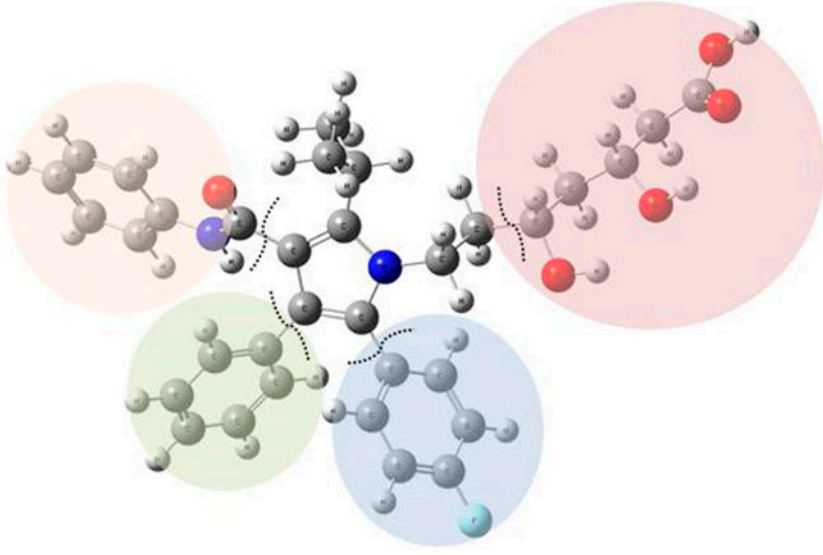

Fig. 2. Optimised ATV structure and the most probable points of the bonds breakup and fragments formation.

ATV is dissolved better at a pH value equal to or greater than the dissociation constant (pK_a) values of the ATV molecule (pK_a = 4.33), and all forms of ATV are dissolved at a much faster rate [38]. The increase in the solubility of the drug leads to less electrochemical reactivity and less degradation efficiency. This indicates that ATV degradation by electrosynthesised ferrate (VI) ion was favoured in acidic conditions, which is in close agreement with the experimental results.

In addition to the solubility of the ATV molecule, ferrate (VI) speciation according to pH should be considered for a better understanding of the pH effect. Ferrate (VI) can be found in aqueous media in different forms. The formation of these species depends on pH. The species are $H_3FeO_4^+$, H_2FeO_4, $HFeO4^-$ and FeO_4^{2-}, and their pK_a values are 1.6, 3.5 and 7.23, respectively [39]. Among them, $HFeO_4^-$, which is present in acidic and mildly acidic conditions, has a higher oxidation potential and is the most reactive species of ferrate (VI). Thus, lower pH values mean an increase of the $HFeO_4^-$ fraction, and this leads to improved degradation of the target agent.

In an alkaline solution, degradation of the tetrahedral form, $[FeO_4]^{2-}$, is slower than that of $HFeO_4^-$ [40,41]. In the light of this, ferrate (VI) showed better performance in acidic/mildly acidic conditions for ATV removal.

In Fig. 3, at the base of the electron structure calculations, the weakest bonds of a molecule are shown, which can possibly be broken. These bonds are the most polarised ones, and they have a minimal electron density relative to the rest of the bonds. In an acidic environment (pH ~4), the fragments that are being formed can be coordinated with the ions of Fe(III). They form chelate compounds and are deleted from the solution together with the sediment afterwards.

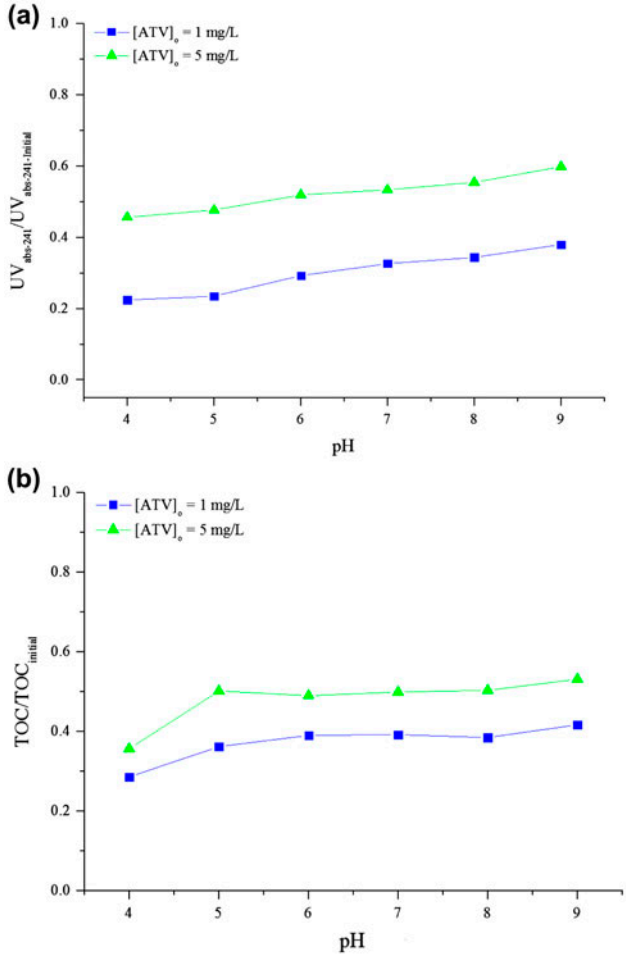

Fig. 3. Effect of pH on atorvastatin degradation (a) specific drug removal and (b) TOC removal at two different initial concentrations (experimental conditions: Fe (VI) dose 1/1 in volume ratio).

3.1.2. Effect of Fe (VI) dose

To evaluate the effect of applied ferrate (VI) dosage for the removal of ATV, different ferrate (VI) doses in terms of volume ratio were used. The pH was kept constant at 4 for the duration of the experiments. The initial concentration of ATV was 1 mg/L. Fig. 4(a) shows the degradation of ATV at various applied ferrate (VI) doses. According to Fig. 4(a), ATV degradation occurred in all applied ferrate (VI) doses; the degradation rate improved with the increasing ferrate (VI) dose.

A significant change was seen from the 5/1 (v/v) ferrate (VI) dose. The drug concentration was reduced to 0.22 mg/L with the 1/1 (v/v) ferrate (VI) dose.

According to Fig. 4(b), the change of pH did not affect TOC removal for the ATV samples except at pH 4, where removal efficiency improved for 1 and 5 mg/L initial concentrations, achieving 71.4 and 64.3% TOC removal, respectively.

A comparison of Fig. 4(a) and (b) shows a similar trend for TOC removal with specific drug removal. TOC was reduced to 1.02 mg/L with 64.5% removal.

3.2. Degradation of ATV by EC process

3.2.1. Effect of electrode type

Aluminium, iron and hybrid (Al–Fe) electrodes were used to evaluate the effect of electrode type on ATV degradation. The current was set to 2.5 mA/cm^2, and the initial pH value was 4. As seen from Fig. 5(a), the highest specific drug removal efficiency was gained with hybrid electrodes (62% removal) at 30 min of process time. The Al electrodes showed less

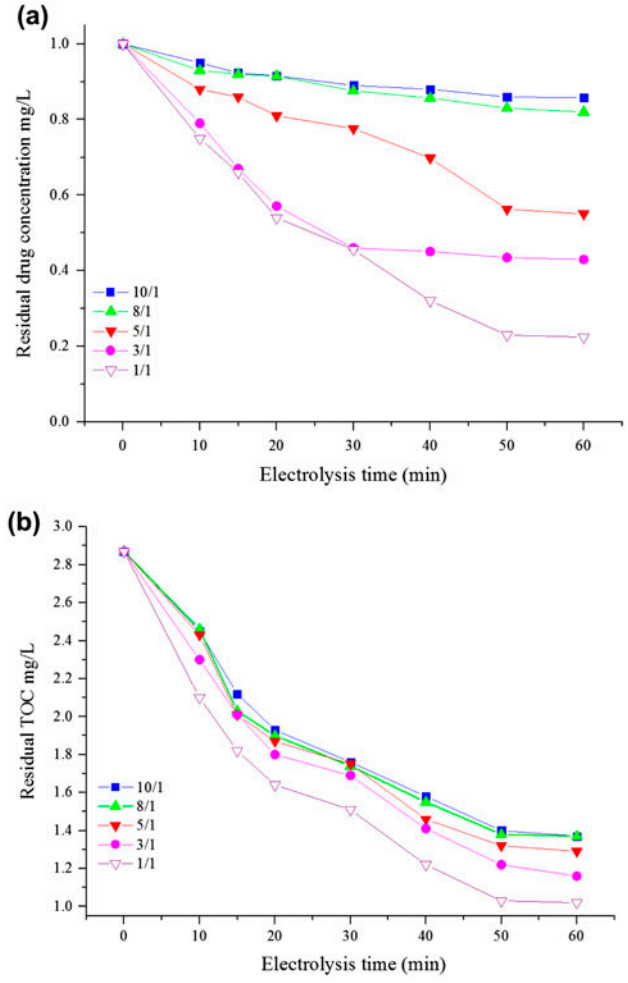

Fig. 4. Effect of ferrate (VI) dose on atorvastatin degradation (a) specific drug removal and (b) TOC removal (experimental conditions: pH 4 and initial drug concentration 1 mg/L).

efficient performance compared with the Fe electrodes. It can be said that hybrid electrodes and Fe electrodes provided faster degradation, as the specific drug removal efficiencies were 34 and 22% at 5 min of process time for hybrid and Fe electrodes, respectively. Only 6.2% ATV degradation was obtained by Al electrodes at the same operating time. Fig. 4(b) shows the TOC removal efficiencies for hybrid, Fe and Al electrodes. As expected, after the results of specific drug removal, the hybrid electrode type was the most suitable electrode pair for ATV degradation. Therefore, the EC process was conducted with hybrid electrodes for the evaluation of other parameters.

The better efficiency of hybrid electrodes could be explained by electrochemical reactions that occur at anode sides (Al and Fe) (Eqs. (1)–(3)) as well as cathode sides (Al and Fe) (Eqs. (4) and (5)):

$$Fe_{(s)} \rightarrow Fe^{2+} + e^- \quad (1)$$

$$Fe_{(s)} \rightarrow Fe^{3+} + 3e^- \quad (2)$$

$$Al_{(s)} \rightarrow Al^{3+} + 3e^- \quad (3)$$

$$2H_2O + 2e^- \rightarrow H_{2(g)} + 2OH^- \quad (4)$$

$$3H_2O + 3e^- \rightarrow 3/2H_{2(g)} + 3OH^- \quad (5)$$

When considering the equivalent masses of both Al and Fe electrodes, the released coagulants from the Fe electrodes were higher than those from Al electrodes. This might be one reason for the higher removal

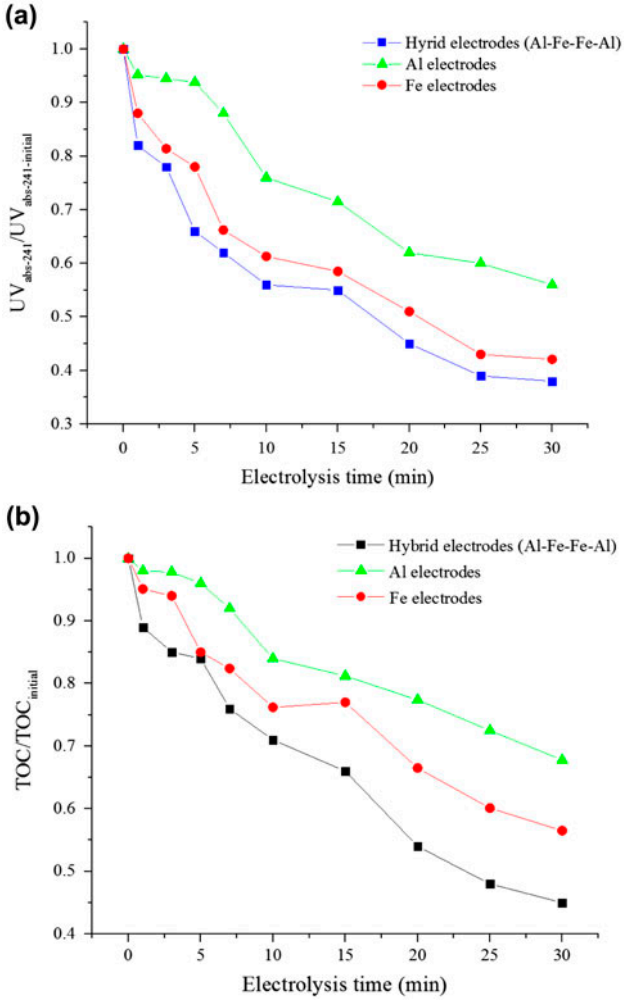

Fig. 5. Effect of electrode type on atorvastatin degradation (a) specific drug removal and (b) TOC removal (experimental conditions: current density 2.5 mA/cm^2; pH 4 and initial drug concentration 1 mg/L).

efficiencies when using hybrid electrodes in the EC process. Additionally, hydrogen bubbles that occur at the cathode side might be another reason for the better efficiency using hybrid electrodes. As a result, the combined effects of EC, electrooxidation and electroflotation when using the hybrid electrode type provided better performance for ATV removal.

3.2.2. Effect of pH

The studies showed that pH is an important operating factor that influences the EC process [32,35,42]. To investigate the effect of pH on ATV removal, the initial pH of ATV solutions was adjusted to the desired value in each run. The current density was kept constant at 2.5 mA/cm^2. The operating time was 30 min, and the initial ATV concentration was set to 1 mg/L. Fig. 6 shows the removal efficiency as a function of the solution pH. As seen from the figure, the highest removal efficiencies were obtained at pH ≤ 4. Increasing the pH resulted in less removal efficiency. It is clear that specific drug and TOC removal showed the same trend at the studied pH values. The pH effect can be explained by iron species and the form of ATV. At pH < 4.33, ATV was unionised, as mentioned before, and monomeric species, such as Fe^{3+} and $Fe(OH)^{2+}$, dominate the aquatic media. The removal mechanism might be the adsorption and then precipitation of ATV by these monomer species of iron. It can be said that the precipitation of deprotonated ATV molecules is easier at pH < 4.33, as the highest removal efficiencies (62% for UV_{abs} and 55% for TOC) were gained.

3.2.3. Effect of current density

Current density has a great significance in electrochemical processes. A high current density provides a fast dissolution rate in the anode side and therefore increases the growth of flocs. Additionally, bubble production in the cathode side improves the removal of pollutants. However, it should be noted that a higher current density does not always provide higher efficiency due to passive layer formation on the surface of the anode. Furthermore, energy consumption should be considered for the economical point of view. To assess the effect of current density on ATV removal, experiments were carried out with a 1-mg/L initial ATV concentration at pH 4. The range of current density was between 0.5 and 4 mA/cm^2. In Fig. 7, the specific drug removal was only 22.6% and the TOC removal efficiency was determined to be 15.5% at the lowest current density (0.5 mA/cm^2). The increasing current density provided higher removal efficiency for both parameters. The highest specific drug removal was gained at 2.5 mA/cm^2 with 62% removal efficiency. At the same current density, the TOC removal was 55%. However, a higher current density (4 mA/cm^2) provided less efficient removal of ATV with 44.8 and 22.6% for specific drug and TOC removal, respectively.

3.2.4. Effect of supporting electrolyte concentration (SEC)

The conductivity of the solution to be treated is another important parameter for EC process efficiency.

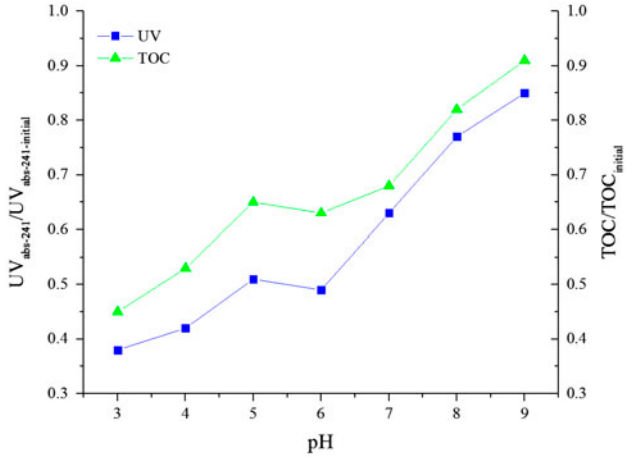

Fig. 6. Effect of pH in EC process in terms of specific drug and TOC removal (experimental conditions: current density 2.5 mA/cm^2 and initial drug concentration 1 mg/L).

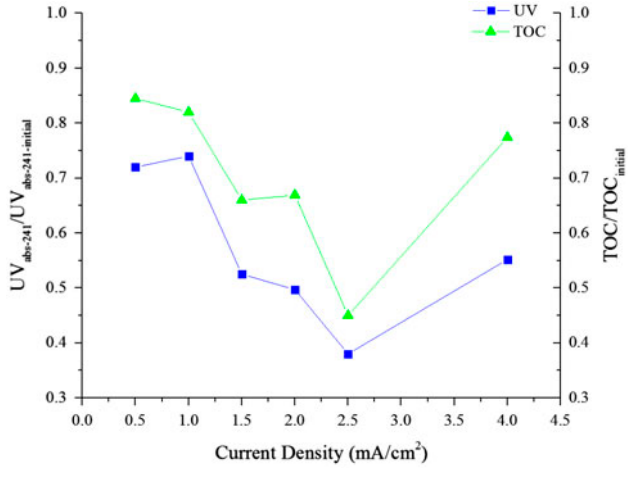

Fig. 7. Effect of current density in EC process in terms of specific drug and TOC removal (experimental conditions: pH 3 and initial drug concentration 1 mg/L).

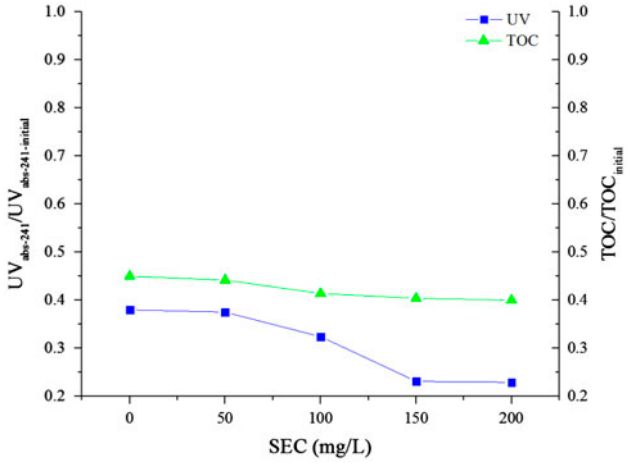

Fig. 8. Effect of SEC in EC process in terms of specific drug and TOC removal (experimental conditions: pH 3, initial drug concentration 1 mg/L and current density 2.5 mA/cm^2).

For this reason, the experiments were conducted with and without adding Na_2SO_4 as a supporting electrolyte in a range of 0–300 mg/L.

As seen from Fig. 8, there was no significant change in TOC removal with increasing supporting electrolyte concentration (SEC). Specific drug removal did not change when the SEC increased to 50 mg/L from 0 mg/L. However, specific drug removal increased with increasing SEC. The removal efficiency was 62% without using a supporting electrolyte. The efficiency increased to only 62.5% with 50 mg/L SEC. It then increased to 67.6, 76.9 and 77.1% with 100, 150 and 200 mg/L SEC, respectively.

3.3. Degradation of ATV by p-EC process

3.3.1. Effect of pH

The solution pH affects Fenton processes. The influence of pH on ATV removal through the p-EC process is illustrated in Fig. 9. As seen in Fig. 9, the performance of the process was significantly affected by the change in pH. The removal efficiencies were higher in acidic pH values (the specific drug removal efficiency was 82.4%, and the TOC removal efficiency was 77% at pH 3). When the pH increased through the alkaline values, the efficiencies decreased significantly. Specific drug removal decreased to 38 and 32% at pH 8 and 9, respectively. In the case of TOC removal efficiency, it was reduced to 32% at pH 8 and 25.5% at pH 9. This result can be explained by the formation of ferric hydroxo-complexes. The formation of those complexes, such as $Fe(OH)_3$, hinders the reaction between Fe^{3+} and H_2O_2, and as a result, the reproduction of Fe^{2+}. Moreover, $Fe(OH)_3$ causes the self-decomposition of H_2O_2 to molecular oxygen and water, and this reduces the oxidation capacity [43].

3.3.2. Effect of H_2O_2 concentration

H_2O_2 concentration is a very important parameter in the p-EC process because the amount of H_2O_2 determines the cost-effectiveness. Fig. 10 shows the removal efficiencies according to H_2O_2 dosage. The results demonstrate that the maximum specific drug removal and TOC removal were gained using 250 mg/L of H_2O_2 after 30 min of operating time at

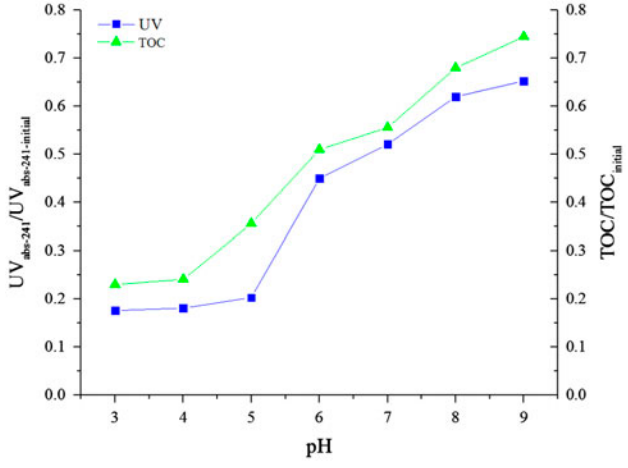

Fig. 9. Effect of pH in p-EC process in terms of specific drug and TOC removal (experimental conditions: current density 2.5 mA/cm^2 and initial drug concentration 1 mg/L).

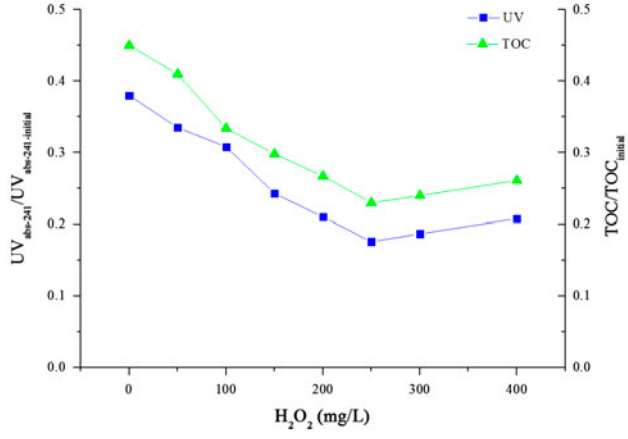

Fig. 10. Effect of H_2O_2 concentration in p-EC process in terms of specific drug and TOC removal (experimental conditions: pH 3, initial drug concentration 1 mg/L and current density 2.5 mA/cm^2).

pH 3. The specific drug and TOC removal were 62 and 55%, respectively, in the absence of H_2O_2 (in other words, for the EC process alone). Higher levels of specific drug and TOC removal were observed with increasing H_2O_2 concentrations. A total of 82.4% specific drug removal and 77% TOC removal efficiency were obtained with 250 mg/L of H_2O_2. The removal of ATV can be attributed to electrocoagulation together with the Fenton process. However, when extent concentrations (300 and 400 mg/L) of H_2O_2 were used, a slight decrease was observed for both specific drug and TOC removal. This demonstrates that the ATV molecules were oxidised by the hydroxyl radical, which was generated by H_2O_2, but overabundant H_2O_2 also consumed the produced hydroxyl radical.

3.4. Overall assessment of the processes

Three different processes were used for the removal of the cholesterol-lowering drug atorvastatin. The processes were assessed considering the removal efficiency and the operating cost. According to the findings, for the optimum conditions of each process, the specific drug removals were 77.6, 77.1 and 82.4% for Fe (VI), EC and p-EC, respectively. Additionally, the TOC removal efficiencies were 71.4, 55 and 77% for Fe (VI), EC and p-EC, respectively. The p-EC process was the most efficient for ATV degradation.

In the literature, many AOPs have been applied for the degradation of specific pharmaceuticals and the treatment of pharmaceutical wastewater, including electro-Fenton, photocatalytic oxidation, EC, p-EC and

Table 1
The comparison of AOPs for pharmaceutical removal

Refs.		Target pharmaceutic	Matrix	Initial concentration	Process	Results
[11]	Analgesics	Diclofenac	Ultra-pure water	30 mg/L	Electro-oxidation with BDD	72% mineralisation degree after 4 h with the bias potential of 4 V
[44]		Ibuprofen	Ultra-pure water	10 μg/L	Ferrate (VI)	55.5 ± 1.2% removal with 1 mg/L Fe (VI) dose at pH 4
[45]		Flurbiprofen	Ultra-pure water	1 mg/L	Ferrate (VI) and EC	Complete degradation was achieved by 1/1 Fe (VI) dose in volume ratio at pH 4.82% removal was provided by EC at pH 6.5 with 2.5 mA/cm^2
[46]	Antibiotics	Amoxicillin	Ultra-pure water and secondary treated effluent	2.5–30 mg/L	UV-A/TiO_2 photocatalysis	93% mineralisation was achieved after 25 and 90 min of reaction, respectively at 10 mg/L AMX and 250 mg/L titania. Degradation in treated effluent was partly impeded compared to pure water. Increasing solution pH from 5 to 7.5 had no effect on degradation
[47]		Ciprofloxacin	Ultra-pure water	100 mg/L	Electron-ionising energy	The degradation efficiency of CFX after irradiation was 38% at 1 kGy, 80% at 5 kGy, and 97% at 10 kGy
[37]		Penicillin	Wastewater effluent	600 mg/L initial COD	Ozonation	82% COD removal at pH 7.9 with 120 min ozonation time at 1,440 mg/h O_3 feed
[48]	Cholesterol-lowering drugs	Clofibric acid	Ultra-pure water	179 mg/L	Anodic oxidation with Pt and BDD anodes	Complete mineralisation with BDD at pH range of 2–12 at 7 h. Pt anode provided more rapidly degradation
Present study		Atorvastatin	Ultra-pure water	1 mg/L	EC, p-EC and Ferrate (VI)	The specific drug removal efficiencies were found as 77.6, 77.1 and 82% for Fe (VI), EC and p-EC processes, respectively

Table 2
Overall assessment of the processes for ATV removal

Assessment parameters	Fe (VI)	EC[a]	p-EC
Current density, I_d (mA/cm^2)	1.47	2.5	2.5
Current, i (A)	0.12	0.2	0.2
pH	4	3	3
Fe (VI) dose (in volume ratio)	1/1	–	–
SEC (mg/L)	–	200	–
H_2O_2 dose (mg/L)	–	–	250
Process time, $t_{process}$ (h)	1.5	0.5	0.5
Average voltage, V_{ave} (V)	1.716	3.88	4.12
Energy consumption, C_{energy} (kwh/m^3)	1.0296	1.293	1.373
Electrode consumption, $C_{electrode}$ (kg/m^3)	0.627	0.0121	0.013
Chemicals consumption, $C_{chemicals}$ (€/kg)	15.04	0.01	0.057
Overall cost for ATV removal, OC (€/m^3)	15.64	0.106	0.159
Specific drug removal efficiency (%)	77.6	77.1	82.4
TOC removal efficiency (%)	71.4	55	77

[a]Calculated for hybrid electrodes.

ferrate (VI) processes. A comparison of the processes, including the present study, is shown in Table 1.

The operating cost (OC) is also essential for real-scale applications. In this study, the OC was calculated by considering electrode consumption ($C_{electrode}$), electrical energy utility (C_{energy}) and chemicals ($C_{chemicals}$) as €/m^3 of ATV containing wastewater.

The electrical energy need was calculated in terms of kWh/m^3 using the equation below:

$$C_{energy} = \frac{Uit_{process}}{V} \quad (6)$$

where U is the average cell potential (V) in the reactor, i is the current (A) passed during the operating time ($t_{process}$) (h) and V is the volume (m^3) of the solution.

Electrode consumption was calculated according to Eq. (7):

$$C_{electrode} = \frac{it_{process}M_w}{zFV} \quad (7)$$

where M_w is the atomic weight of the anode material (55.85 g/mol in this case), z is the number of electrons involved in the oxidation/reduction reaction (zFe = 2) and F is the Faraday constant (96,485 C/mol).

For the whole assessment, the total OC was calculated according to Eq. (8):

$$\begin{aligned}&\text{Operating cost (OC, €/m}^3\text{)}\\&= aC_{energy}\ (\text{kWh/m}^3) + bC_{electrode}\ (\text{kg/m}^3)\\&\quad + cC_{chemicals}\ (\text{kg/m}^3)\end{aligned} \quad (8)$$

Unit prices a, b and c were given for the Turkish Market in July 2015: "a" is the electrical energy price (0.066€/kWh), "b" is the electrode material price for Fe (0.85€/kg) and Al (0.92€/kg) and "c" is the chemical price for NaOH (0.0188€/kg) in the Fe (VI) process, Na_2SO_4 (0.05€/kg) in the EC process and H_2O_2 (0.228 €/kg) in the p-EC process.

The OC for each process was calculated by considering the equations and prices given above. The comparison of the processes is summarised in Table 2. According to Table 2, the most economic process was EC. However, there was only a 0.053€ difference between the EC and p-EC processes for the treatment of 1 m^3 of ATV-containing wastewater.

In the application of the Fe (VI) process, the operating cost is derived by electrochemical synthesis only. The OC was very high due to the need for highly alkaline media (20 M of NaOH) for Fe (VI) synthesis and the usage of the volume ratio (1/1) to obtain the highest removal efficiency of ATV. In our previous study, greywater treatment by Fe (VI) was found to be a cost-effective process because the needed volume ratio was lower (100/1) [49]. It should be noted that the optimum volume ratio should be taken into account when the practical use of ferrate (VI) is considered.

4. Conclusion

This study demonstrates the comparison of three different processes—namely, electrosynthesised ferrate (VI), electrocoagulation and peroxi-electrocoagulation —for the cholesterol-lowering drug atorvastatin.

Various experimental parameters, such as pH, Fe (VI) dose, current density, SEC and hydrogen peroxide concentration, were employed to investigate the performance of the processes. pH was found to be effective in all processes. Acidic pH values provided better performance in removing atorvastatin. The specific drug removal efficiencies were 77.6, 77.1 and 82% for the Fe (VI), EC and p-EC processes, respectively. While the p-EC process provided the highest removal efficiency, the EC process was found to be the most economic process.

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