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Simultaneous degradation of some pharmaceuticals by anodic oxidation in different supporting electrolytes

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ABSTRACT

In the current paper, we investigated the electrochemical degradation of some pharmaceuticals, including an antioxidant (vitamin E), anti-coronavirus and anti-skin diseases and supplements (vitamin B1 or thiamin HCL), anti-inflammatories (caffeine, ibuprofen, acetaminophen), and antidepressants antipsychotic medications (quetiapine fumarate). For this purpose, we employed an advanced electrochemical oxidation process using Ti/nano SnO_2-α-Fe_2O_3 electrode by Na_2SO_4 or NaCl as a supporting electrolyte. We also evaluated the effects of pH and supporting electrolytes. On the degradation of pharmaceuticals and optimized the process. Results showed that the best conditions for supporting electrolytes were a pH of 7 for Na_2SO_4 or NaCl with a concentration of 1 g/L. Under optimum conditions, we achieved about 100% efficiency in the removal of pharmaceuticals. The total organic carbon (TOC) removal of 98.57% and 99.37% were also obtained, after 270 min of treatment with Na_2SO_4 and NaCl, respectively. In addition, in the same condition, the removal efficiency of pharmaceuticals after 150 min, was about 80% and TOC removal was equal to 90.21% and 80.74% with Na_2SO_4 and NaCl, respectively. It was shown that NaCl was stronger than Na_2SO_4 stronger Ti/nano SnO_2-α-Fe_2O_3 electrode is applicable for the electrochemical treatment of pharmaceutical pollutants simultaneously.

Keywords: Electrochemical degradation; Pharmaceuticals; Ti/nano SnO_2-α-Fe_2O_3 electrode; Supporting electrolyte

1. Introduction

The past decades, have witnessed a growth in production and demand for pharmaceuticals, which have intensified concerns about the potential risks to the ecosystems and human's health. The waste components are discharged to the environment without any limitation or processing. As a result, they remain in the environment due to their difficult degradability or continuous-release [1]. Electrochemical advanced oxidation processes (EAOPs), which use electrons for a clean, and inexpensive reagent and do not require chemicals, have received a great deal of attention as a promising green technology to degrade hazardous pharmaceutical elements in the aqueous environment [1–4]. The versatility, simplicity of control, good energy efficiency, potential cost-effectiveness, environmental compatibility, fast reaction rate, total mineralization ability, and high oxidation performance are only a few of the advantages of EAOPs [2,5–8]. Furthermore, studies have indicated that the electrochemical oxidation efficiency of organic pollutants containing pharmaceutical compounds depends on various parameters, such as type of anode and electrolyte used, pH, anode base material, anode coating and composition, applied power (current and voltage), anode preparation method, and types and concentration of pollutants [7,8]. Herein, a Ti/nano SnO_2-α-Fe_2O_3 composite electrode, which was fabricated in our previous work and had a good performance in color degradation, was used as an anode for the electrocatalytic degradation of pharmaceutical compounds [9,10]. During the degradation process,

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we needed to add salts as electrolytes in the pharmaceutical effluent wastewater before carrying out the electrochemical treatment to increase the efficiency of removing the pharmaceutical [11–13]. The selected Pharmaceutical compounds were including quetiapine fumarate, vitamin E, vitamin B1, ibuprofen, acetaminophen, and caffeine, which are commonly used in high-consumption drugs [12,14] (Fig. 1). Several studies on the elimination of these pharmaceuticals individually have been published in recent years using different methods [15–17]. However, there are no studies about removing these six drugs simultaneously or from a commercial drug. The present research aimed to degrade some pharmaceuticals using a process of electrochemical oxidation with a Ti/nano SnO_2-α-Fe_2O_3 composite electrode in various electrolytes as a support solution. We examined the parameters of the pharmaceutical degradation efficiency, like the types of supporting electrolytes and pH. The technique efficiency was measured using (UV–Vis) spectrophotometer and total organic carbon (TOC) measurements. The results showed an abundance of pharmaceutical compounds in aquatic solutions.

2. Materials and methods

2.1. Materials

Pharmaceuticals quetiapine fumarate from Hetero Drugs (India), vitamin E and vitamin B1 from Royal DSM (The Netherlands), ibuprofen from IOL CP (India), acetaminophen from Temad (Iran), and caffeine from CSPC Pharmaceutical Group (China), were purchased and used with no extra purification stage. The stock solutions were 2, 10, 7, 12, 5, and 1 mg/L of quetiapine fumarate, vitamin E, vitamin B1, ibuprofen, acetaminophen, and caffeine prepared with a suitable volume of deionized water, which was increased to 250 mL measuring flask. Using deionized water, we made preparations of 1 g/L NaCl and 1 g/L Na_2SO_4 solutions (p.a. grade, Merck, Germany) until the completion of the volume to 250 mL measuring flask. We adjusted the pH employing adequate diluted hydrochloric acid and sodium hydroxide solution. The solutions were enhanced using ultrapure water supplied by a Millipore Milli-Q (Germany) system (resistivity > 18 mU/cm).

2.2. Equipment

We used a DC power supply for the pharmaceutical solution electrolysis (MEGATEK MP-3005, Iran). The DC power terminals were connected to the anode and cathode electrodes with cables. Employing a spectrophotometer (Shimadzu UV-1800, Japan), the samples were scanned at 200–500 nm. The pH values of the solution were adjusted before electrochemical treatment and read using a Metrohm 913 pH Meter (Switzerland). The total organic carbon (TOC) variation was checked utilizing a Shimadzu analyzer. The weight was measured employing a sensitive analytical balance (Sartorius AZ124, Germany) with an accuracy of 0.0001. Also, the electrodes were a Ti/nano SnO_2-α-Fe_2O_3 electrode as an anode and a stainless-steel plate electrode as a cathode. The Ti/nano SnO_2-α-Fe_2O_3 electrode was developed following our previous work [9].

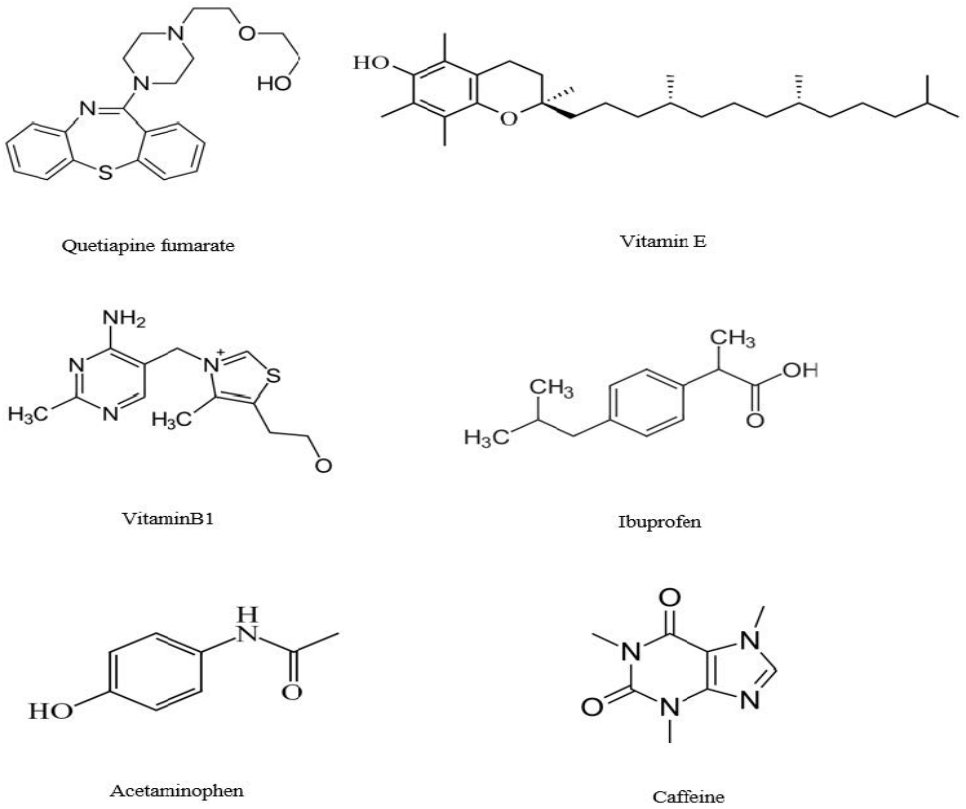

Fig. 1. Chemical structure of pharmaceuticals (quetiapine fumarate, vitamin E, vitamin B1, ibuprofen, acetaminophen, caffeine).

2.3. Procedure

We performed the electrochemical degradation process of some pharmaceuticals using a cylindrical glass electrochemical cell and 250 mL of electrolyte. To do so, we employed quetiapine fumarate, vitamin E, vitamin B1, ibuprofen, acetaminophen, caffeine, NaCl, and/or Na_2SO_4 in deionized water to prepare the electrolyte. During 270 min the electrochemical treatment was done utilizing Ti/nano SnO_2-α-Fe_2O_3 and a stainless-steel plate as the anode and the cathode, respectively. We fixed the electrodes at an equal distance from the opposite sides of the cell and kept their distance unchanged at 2 cm. In addition, the effective area of the anode and cathode were 4 and 5 cm^2, respectively (Fig. 2). During the electrocatalytic degradation, the solution was stirred at a constant speed of 300 rpm to achieve a better mass transport process and solution homogenization. We removed 5 mL of solution using a pipette to conduct UV–Vis spectral analysis and measured TOC. Employing deionized water for 3 min, we washed the electrodes before being fixed in the cell. The (degradation percentage (removal efficiency) was calculated through Eq. (1).

$$\text{Removal efficiency}\,\% = \frac{\left(A_0 - A_t\right)}{A_0} \times 100 \tag{1}$$

where A_0 and A_t represent the initial absorbance at the given wavelength and the absorbance at time with the given wavelength, respectively.

2.4. Analysis and calculations

Following ISO 20236:2018, the TOC values were measured (water quality—dissolved organic carbon (DOC), total bound nitrogen (TNb), TOC, and dissolved bound nitrogen (DNb) following catalytic oxidative combustion at a high temperature). Five-milliliter specimens were handled using glass test vials (Shimadzu) before and after the electrochemical process. In addition, we added two TOC digestion solution reagents: hydrochloric acid solution (1 M) and phosphoric acid solution (3 M). The samples were digested into a TOC furnace (Shimadzu) for 7 min at 600°C and measured using the TOC analyzer to measure the extent of pharmaceuticals degradation. The level of removing TOC was determined as follows:

$$\text{TOC Removal}\,\% = \frac{\left(\text{TOC}_0 - \text{TOC}_t\right)}{\text{TOC}_0} \times 100 \tag{2}$$

where TOC_0 is before electrochemical treatment, and TOC_t is after electrochemical treatment.

3. Results and discussion

Among the key factors in the electrochemical degradation pathway, the pharmaceutical compounds are the nature and the presence of the supporting electrolytes. They can improve the electric conductivity and solution ionic strength and decrease the resistance. They also enhance the degradation efficiency [18]. Some of the most supporting electrolytes for the electrochemical degradation of pharmaceutical compounds are Na_2SO_4 and NaCl. The former improves hydroxyl radicals ($OH^{\bullet}$) generation, which is oxidizing agents. In addition, it is inert and generates no reactive species during electrolysis except for a few special conditions, in which it produces $S_2O_3^{2-}$ ions. The latter is a stronger electrolyte and can generate strong oxidants like

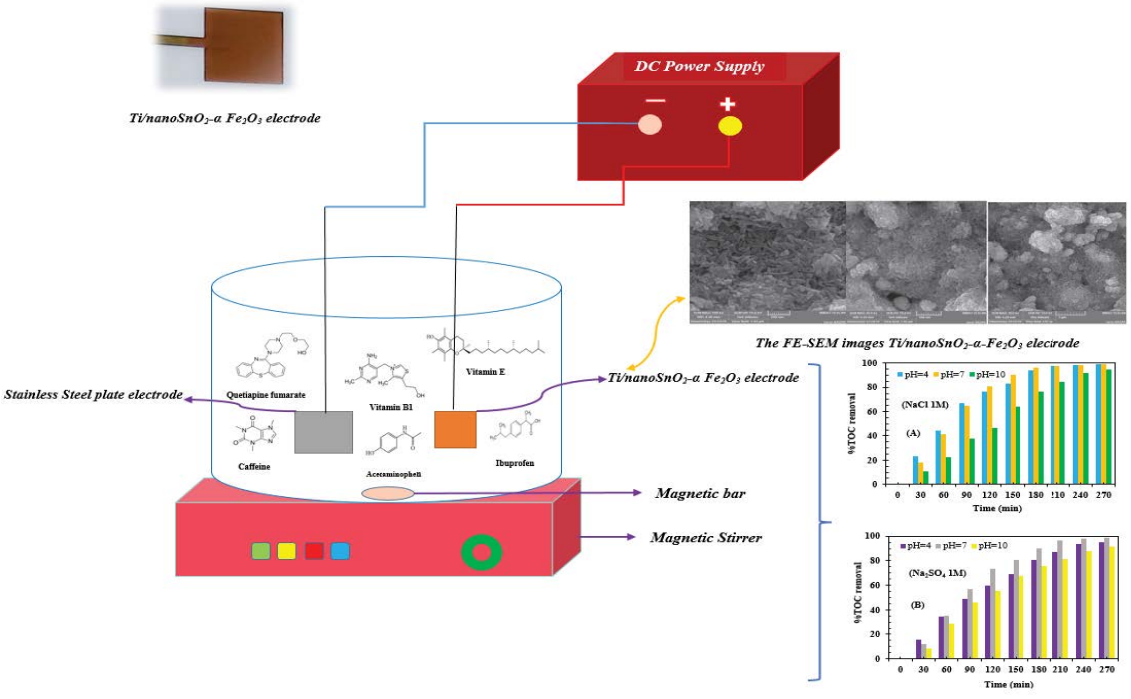

Fig. 2. Set-up of the electrochemical cell used for pharmaceutical treatment.

Cl_2, HOCl, and OCl^-. The degradation of some pharmaceuticals, such as quetiapine fumarate, vitamin E, vitamin B1, ibuprofen, acetaminophen, and caffeine, are followed based on spectrophotometric measurements at wavelengths of 312, 291, 278, 239, 267, and 207 nm, respectively. The main factors in the process are as follows:

3.1. pH

The optimum pH level is an important factor in the degradation of pharmaceuticals, whose role in Na_2SO_4 was examined with diverse pH levels in the 4–10 range, shown in Fig. 3. Moreover, the degradation of drugs changed with the change in pH, which means that the process depends on pH. The highest degradation was with pH = 7, followed by pH = 4 and pH = 10 after 270 min. In the acidic medium, $OH^{\bullet}$ radicals were generated by water anodic discharge of water through indirect electrochemical oxidation of organic pharmaceuticals at the anode. These $OH^{\bullet}$ radicals were adsorbed onto the anode [MO_x], and the organic material [*R*] was oxidized [19,31]:

$$MO_x + H_2O \rightarrow MO_x\left(OH^{\bullet}\right) + H^+ + e^- \quad (3)$$

$$R + MO_x\left(OH^{\bullet}\right) \rightarrow MO_x + RO + H^+ + e^- \quad (4)$$

It has been shown that with a higher pH, a higher quantity of OH will be expected, which results in a stronger degradation efficiency [20,21]. However, the finding demonstrated that the ionization level of pharmaceutical compounds is pH-dependent, which leads to a decrease in the mass transfer resistance with a higher pH. With neutral pH, a higher solubility of ionization degree happened. Thus, electrolytes were extensively consumed, and the solution conductivity decreased due to the lack of electrolytes at alkaline pH [22].

As displayed in Fig. 3A, at pH = 4 and 60 min after the removal process, caffeine, ibuprofen, acetaminophen, and vitamin E showed a better performance than other drugs in the presence of electrolyte sodium sulfate. The removal efficiency was about 80% for these three drugs in 150 min and 90% in 270 min, nevertheless, it was 80% for other drugs. Fig. 3B depicts that, at pH = 7 and the time of 60 min, almost all drugs except caffeine, which worked better, were removed in the same proportion. In 90 min, caffeine, acetaminophen, and ibuprofen had a better removal performance than other drugs. In 150 min, the removal efficiency of these three drugs was about 80%, and that of other drugs was up to 50%. In 210 and 240 min the energy system was focused on degrading quetiapine fumarate, vitamin B1, and vitamin E. Finally, caffeine, acetaminophen, and ibuprofen were removed up to 95% in 270 min, although this percentage was 85% for other drugs. From Fig. 3C it is evident that at pH = 10, the three drugs, named ibuprofen, acetaminophen, and caffeine, had a better removal efficiency, while other drugs were removed by less than 70%. In the neutral environment and the presence of sodium sulfate, the performance of all drugs was better than that in the acidic and alkaline environment. For the former, alkaline environment, acetaminophen, caffeine, and ibuprofen performances were better. For the latter, acidic environment, the removal efficiency of drugs was good too.

In addition, Fig. 4 demonstrates the role of pH in the degradation of pharmaceuticals with NaCl electrolyte,

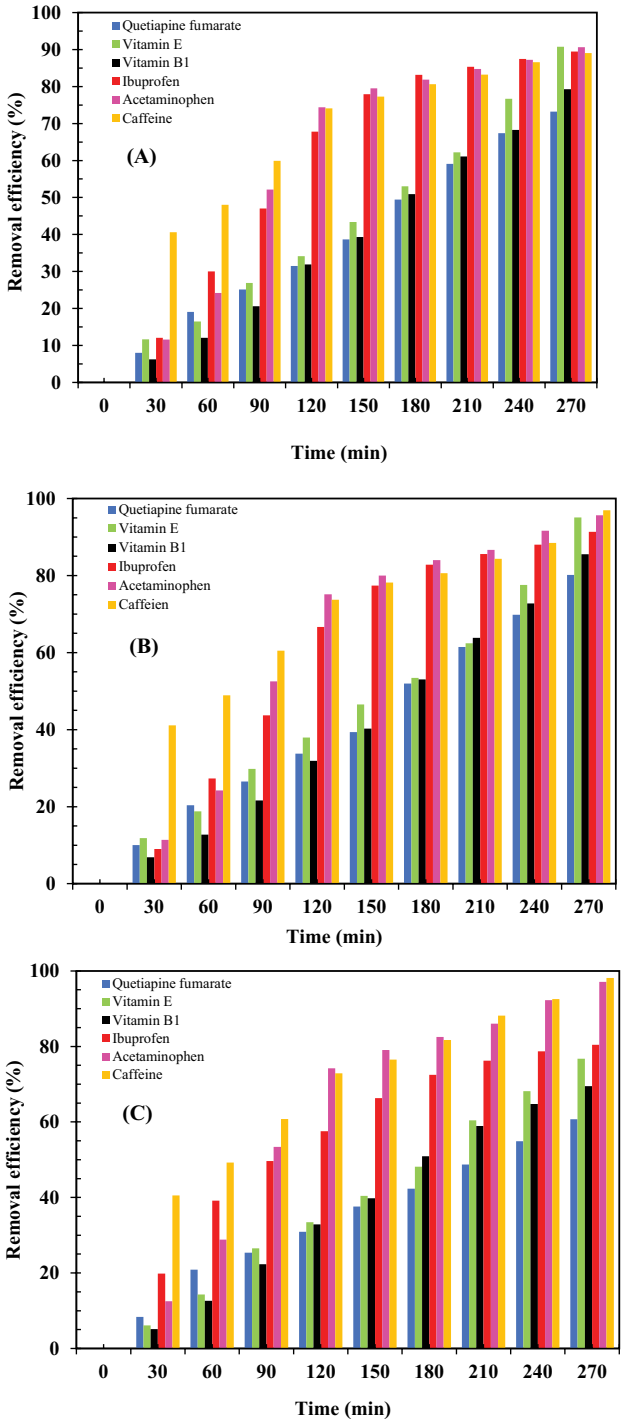

Fig. 3. Effects of supporting electrolyte and pH on 2, 10, 7, 12, 5, and 1 mg/L of quetiapine fumarate, vitamin E, vitamin B1, ibuprofen, acetaminophen, and caffeine, respectively, mixed with Na_2SO_4 1 g/L at pH (*A* = 4, *B* = 7, *C* = 10). The experiments were conducted for 270 min at 0.01 A/cm² using a Ti/nano SnO_2-α-Fe_2O_3 electrode.

which had a better efficiency in neutral pH than in acidic or alkaline systems. The degradation percentage was about 100% in 270 min at pH = 7, whereas it was lower at the same time at pH = 4 and pH = 10. The findings indicated that effective pharmaceutical degradation depends on the solution's pH. As shown, hypochlorous acid was mostly an active species in the degradation of pharmaceuticals [18]. Hypochlorous acid in an acidic solution is the key product of the hydrolysis of chlorine, which results in a high degradation efficiency after a neutral medium. The concentration of hypochlorous acid reduces by increasing the pH of the solution because of the dissociation to hypochlorite. It is also possible to explain the reaction mechanism by the formation of chlorine on the anode and the immediate formation of HOCl. The HOCl partially reacts with pharmaceuticals and is partially dissociated with ClO^- depending on pH. Moreover, dissociation happens faster with high pH, which leads the slowing down the degradation. However, some pharmaceuticals, such as acetaminophen and caffeine, can achieve 100% degradation in an alkaline environment due to the natural pH of each pharmaceutical compound.

$$2Cl^- \rightarrow Cl_2(aq) + 2e^- \quad (5)$$

$$Cl_2(aq) + H_2O \rightarrow HClO + Cl^- + H^+ \quad (6)$$

$$HClO \rightarrow +ClO^- + H^+ \quad (7)$$

The species types depend on the pH level of the solution. With a pH close to 4, Cl_2(aq) was predominant. On the other hand, for pH ranging from 4 to 7, HClO was predominant. For pH above 7, ClO^- was noticeable [23,24]. An acidic medium is not an ecologically viable work condition, so the best pH for pharmaceutical degradation is the neutral medium (pH = 7) [18]. In this analysis, all the pharmaceuticals used at neutral pH were the best degradation performance. Oxidation of pharmaceuticals was faster in neutral to acidic conditions compared to the alkaline one given the higher standard potential of Cl_2(aq) ($E°$ = 1.36 V vs. SHE), HClO ($E°$ = 1.49 V vs. SHE) in comparison to ClO^- ($E°$ = 0.89 V vs. SHE) [25]. In addition, Fig. 4 illustrates that a good degradation level (100%) was achieved after 270 min with a trivial change in pH in the treatment course.

As shown in Fig. 4A, at pH = 4, vitamin E, acetaminophen, and caffeine had a better performance in the presence of electrolyte sodium chloride 30 min after the removal process. In 60 min, the removal efficiency of these drugs was about 50%. In 150 min, this efficiency was about 85% for ibuprofen and caffeine, 80% for vitamin E, 90% for acetaminophen, and 60% for the other two drugs. Moreover, in 240 min, about 75% and 85% of quetiapine fumarate and vitamin B1 were eliminated, respectively. The removal efficiency of other drugs was up to 95%. This efficiency for 270 min was 99% of vitamin E and acetaminophen, 97% of ibuprofen and caffeine, 90% of vitamin B1, and 80% of quetiapine fumarate. From Fig. 4B it is obvious that the removal efficiency at pH = 7 was around 50% of vitamin E, caffeine, and other drugs with almost the same proportions in 60 min. Furthermore, about 60% of vitamin E, caffeine, and acetaminophen were removed in 90 min, and around 50% for the other drugs. In regard to 150 min, about 90% of acetaminophen, 85% of ibuprofen and caffeine, and 80%, 65%,

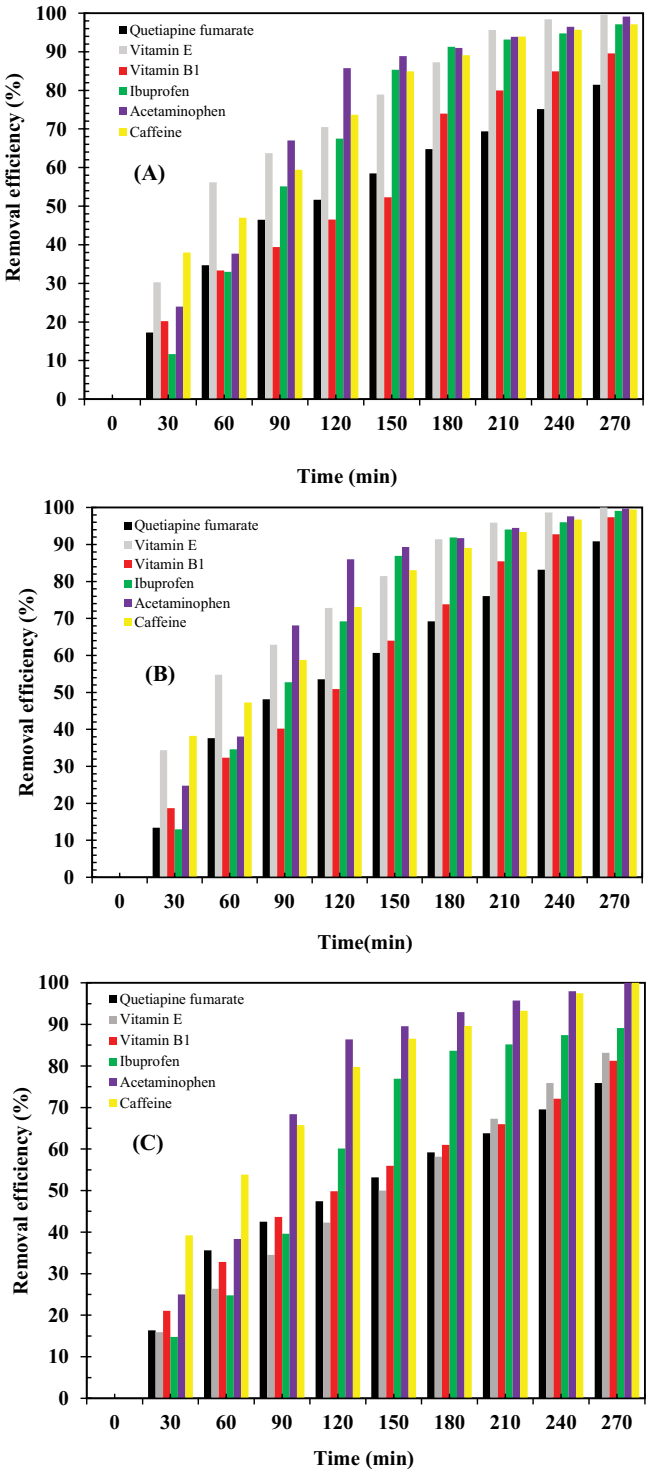

Fig. 4. Effects of supporting electrolyte and pH on 2, 10, 7, 12, 5, and 1 mg/L of quetiapine fumarate, vitamin E, vitamin B1, ibuprofen, acetaminophen, and caffeine mixed with NaCl 1 g/L at pH (A = 4, B = 7, C = 10). Experiments were conducted for 270 min at 0.01 A/cm^2 using a Ti/nano SnO_2-α-Fe_2O_3 electrode.

and 60% of vitamin E, vitamin B1, and quetiapine fumarate were removed, respectively. It can be said that there was an improvement in the elimination process gradually. Finally, after 270 min, 99% of acetaminophen, caffeine, and ibuprofen and 100%, 90%, and 97% of vitamin E, quetiapine fumarate, and vitamin B1, respectively, were wiped out. From Fig. 4C, it is evident that at pH = 10, acetaminophen and caffeine had a better removal performance. The removal efficiency was about 70% for acetaminophen and caffeine and 50% for other drugs in 90 min. Also, 90% of acetaminophen, 85% of caffeine, 75% of ibuprofen, and 50% of other drugs are removed in 150 min. In 210 min, the removal efficiencies of acetaminophen, caffeine, ibuprofen, quetiapine fumarate, vitamin E, and vitamin B1 were 95%, 95%, 90%, 65%, and 65%, respectively. The removal efficiency was 100% for acetaminophen and caffeine, 90% for ibuprofen, 75% for quetiapine fumarate, 80% for vitamin B1, and 85% for vitamin E in 270 min. In addition, acetaminophen and caffeine had better removal performance in an alkaline environment. All drugs showed a better removal performance in the presence of sodium chloride at pH = 7. Accordingly, the results showed that pH = 7 was the optimal pH for NaCl and Na_2SO_4 electrolytes.

3.2. Supporting electrolyte

In the current paper, we studied the role of the supporting electrolytes (Na_2SO_4 and NaCl) in the electrochemical degradation of some pharmaceuticals, including quetiapine fumarate, vitamin E, vitamin B1, ibuprofen, acetaminophen, and caffeine. From the results displayed in Figs. 3 and 4, it is evident that the pharmaceutical solutions were degraded in 270 min for Na_2SO_4 and NaCl with a concentration of 1 g/L. At the concentration of Na_2SO_4 (1 g/L), the removal rate relative to NaCl (1 g/L) was lower under the same conditions because available electrolyte ions increased the solution's electrical resistance and decreased the efficiency of the degradation. With 1 g/L of Na_2SO_4, the removal efficiency percentage of most drugs with pH = 7 and that of other ones reached about 95% and 85%, respectively. This shows a decline in the solution resistance and growth in $HO^{\bullet}$ radicals generation, which caused pharmaceuticals degradation, as depicted in Fig. 3B. Moreover, from Fig. 3A and at pH of 4, the efficiency of some pharmaceutical compounds reached 73.2%. Obviously, a further increase in the pH to 10 in Na_2SO_4 decreased the removal efficiency percentage of pharmaceutical compounds down to 76.73% (Fig. 3C).

The explanation for this result is the generation of fewer oxidants with a higher pH in the presence of Na_2SO_4, which is due to the deceleration of reactions (3) and (8) [1] and because of the Ti/nano SnO_2-α-Fe_2O_3 electrode and SnO_2 that function as non-active metal oxide (MO) anodes. The water oxidation at the beginning of these MO_x generates physisorbed MO_x ($OH^{\bullet}$) through reaction (3). At the non-active MO anode surface, the MO_{x+1} is generated more than MO_x ($OH^{\bullet}$). Thus, the organic matter is oxidized to a relatively low mineralization.

$$MO_x + H_2O \rightarrow MO_x\left(OH^{\bullet}\right) + H^+ + e^- \quad (8)$$

$$MO_x\left(OH^{\bullet}\right) \rightarrow MO_{x+1} + H^+ + e^- \quad (9)$$

According to Fig. 4, at pH = 10 in NaCl, the removal efficiency percentage decreased. Also, it was close to a complete degradation for some pharmaceuticals due to the natural pH of the drug (Fig. 4C). However, it reduced to 81.43% and 89.45% for some drugs at pH = 4 and in the neutral environment (Fig. 4A). The best degradation performance at pH = 7 was near 100% for all drugs (Fig. 4B).

In addition, an electrochemical degradation mechanism with NaCl was proposed. As mentioned, the NaCl mechanism was an indirect electro-oxidation of the pollutant, which happened between the electrogenerated chlorine/ClO^- and a pharmaceutical molecule. Also, $ClOH^{\bullet}$ was generated in the presence of Cl^- ions and adsorbed onto the anode surface [MO_x] and then oxidized the organic material [*R*] [19,31].

$$H_2O + MO_x + Cl^- \rightarrow MO_x\left[ClOH^{\bullet}\right] + H^+ + 2e^- \quad (10)$$

$$R + MO_x\left[ClOH^{\bullet}\right] \rightarrow MO_x + RO + H^+ + 2e^- \quad (11)$$

Furthermore, increasing pH in the NaCl higher than 7 led to a minor improvement of the degradation efficiency up to 100% for some pharmaceuticals, such as acetaminophen and caffeine, and resulted in the degradation efficiency to 75.86% and 94.40% for other ones (270 min) (Fig. 4C). This can be explained by the accumulation of OCl^-, which increased pH and then decreased the generation of chlorine/hypochlorite, due to the production of chlorate or perchlorate [26–28].

$$6HOCl + 3H_2O \rightarrow 2ClO_3 + 4Cl^- + 12H^+ + \frac{3}{2}O_2 + 6e^- \quad (12)$$

$$ClO_3 + H_2O \rightarrow ClO_4^- + 2H^+ + 2e^- \quad (13)$$

Moreover, increasing the pH in the NaCl electrolyte was not recommended, as it resulted in hazardous organ chlorine by-products [27,29,30]. In other words, as shown in Figs. 3 and 4, the pharmaceutical degradation and complete degradation were achieved in 270 min. In addition, there was a high pharmaceutical removal efficiency (>80%) in 150 min. By utilizing NaCl as the supporting electrolyte (Fig. 4), complete degradation of the pharmaceuticals occurred at pH = 7 (Fig. 4B), and pH = 4 and pH = 10 had a relatively lower reduction in adsorption (Fig. 4A and C). As observed under similar conditions for sodium chloride, by using Na_2SO_4 as the supporting electrolyte, it decreased with reduced degradation of the drugs (Fig. 3). When the level of pharmaceutical degradation with Na_2SO_4 or NaCl electrolyte was the same, the former was more desirable since it could work with nearly neutral pH condition and generate more degradation in 270 min. Therefore, pH = 7 was employed as the optimal pH, and NaCl as the optimal electrolyte [26].

3.3. TOC removal

Examining TOC led to more detailed examinations of electrochemical degradation. TOC is the amount of TOC after the organic compounds oxidized in the water so that

Table 1
Results of total organic carbon removal and removal efficiency for the electrochemical oxidation of various pharmaceuticals

Supporting electrolyte and pH	1 g/L NaCl, pH = 4	1 g/L Na_2SO_4, pH = 4	1 g/L NaCl, pH = 7	1 g/L Na_2SO_4, pH = 7	1 g/L NaCl, pH = 10	1 g/L Na_2SO_4, pH = 10
%TOC removal	99.12	95.05	99.37	98.57	94.40	91.65
			%Removal efficiency			
Quetiapine fumarate	81.43	73.20	90.88	80.16	75.86	60.72
Vitamin E	99.60	90.76	100	95.1	83.18	76.73
Vitamin B1	89.58	79.31	97.38	85.54	81.22	69.48
Ibuprofen	97.13	89.45	99.09	91.33	89.15	80.41
Acetaminophen	99.1	90.67	99.73	95.63	100	97.1
Caffeine	97.12	89.08	99.45	96.96	100	98.16

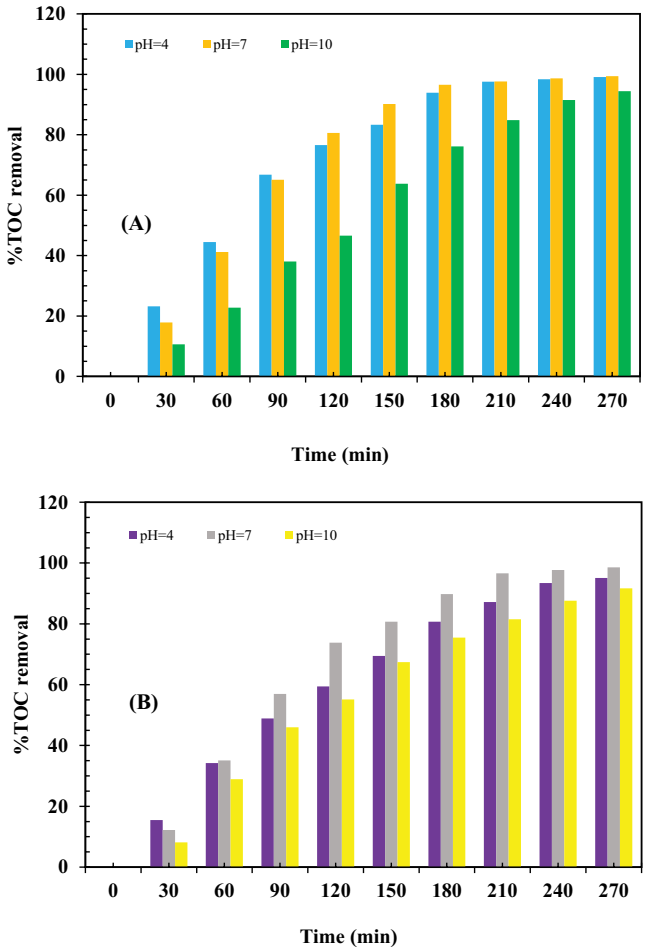

Fig. 5. Total organic carbon removal as a function of the electrolysis time on mixed 2, 10, 7, 12, 5, and 1 mg/L of quetiapine fumarate, vitamin E, vitamin B1, ibuprofen, acetaminophen, and caffeine, respectively, with (A) NaCl at pH = 4, 7, 10, and (B) Na_2SO_4 (1 g/L) at pH = 4, 7, 10. Experiments were conducted for 270 min at 0.01 A/cm^2 using a Ti/nano SnO_2-α-Fe_2O_3 electrode.

the amount of carbon remaining is measured. Table 1 lists the TOC removal percentage resulting in 270 min, as determined from the electrochemical oxidation experiments of pharmaceuticals using the Ti/nano SnO_2-α-Fe_2O_3 electrode under proper conditions. According to Fig. 5 and Table 1, the best results in removal efficiency, the highest reduction in TOC value, and the best removal percentage of TOC were obtained in optimal conditions with NaCl as the supporting electrolyte (1 g/L) and pH = 7. For the pharmaceuticals removal, including quetiapine fumarate, vitamin E, vitamin B1, ibuprofen, acetaminophen, and caffeine, TOC were 90.88%, 100%, 97.38%, 99.09%, 99.73%, 99.45%, and 99.37%, respectively. Although there was a high pharmaceutical removal (>90%), the TOC removal percentage was almost the same. In addition, according to Figs. 3–5, in optimal conditions and after 150 min, TOC removal was 90.21%, and the removal efficiency of pharmaceuticals was about 80%.

The degradation of the pharmaceutical compound achieved complete mineralization. The presence of NaCl as a supporting electrolyte resulted in a higher removal efficiency and formation of Na_2SO_4.

4. Conclusions

The results indicated that pharmaceuticals, including quetiapine fumarate, vitamin E, vitamin B1, ibuprofen, acetaminophen, and caffeine, were electrochemically degraded using a Ti/nano SnO_2-α-Fe_2O_3 electrode, with Na_2SO_4 or NaCl as supporting electrolytes. The best conditions were pH = 7 for Na_2SO_4 or NaCl. Moreover, the UV–Vis spectrophotometric measurements confirmed that absorbance decay was a function of the electrolysis time, indicating the degradation of pharmaceuticals. There was complete mineralization for the degradation of the pharmaceutical compound. In supporting electrolytes, NaCl was more desirable than Na_2SO_4, so the degradation method had a better performance with NaCl at pH = 7. The removal efficiency in 270 min was 90.88%, 100%, 97.38%, 99.09%, 99.73%, 99.45%, and 99.37% for quetiapine fumarate, for vitamin E, vitamin B, ibuprofen, acetaminophen, caffeine, respectively. In addition, TOC removal in optimum conditions was equal to 99.37%. In the same conditions and after 150 min, the removal efficiency of pharmaceuticals and the percentage of TOC removal were 80% and 90.21%, respectively. Because it is not essential to adjust the pH, these results show that the AO application is suitable for the removal of organic pollutants that are a growing source of concern, such as

pharmaceuticals. Given the production of some intermediate products during the electro-oxidation process, liquid chromatography coupled with high-resolution mass spectrometry (LC-HRMS) and ion exclusion chromatography can be used by future works to investigate the mineralization ratio of pharmaceutical compounds.

CRediT authorship contribution statement

Sepideh Ghasemi: Investigation, Resources, Data curation, Writing - original draft, Writing - review & editing.

Farideh Nabizadeh Chianeh: Conceptualization, Methodology, Formal analysis, Resources, Data curation, Writing - review & editing, Supervision, Project administration.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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