

Ultrasonically Facilitated Electrochemical Degradation of Acetaminophen Using Nanocomposite Porous Cathode and Pt Anode



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R. Darvishi Cheshmeh Soltani* and M. Mashayekhi

Department of Environmental Health Engineering,
School of Health, Arak University of Medical Sciences,
Arak, Iran

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In the present research study, an electrochemical process (EC) equipped with a porous cathode was combined with ultrasound (US) to efficiently degrade acetaminophen (ACE) as the target pollutant. The carbonaceous porous cathode was used for in situ generation of hydrogen peroxide. The generation of hydrogen through the cathodic reduction was current-dependent. As a result, the combination of US with EC resulted in the highest degradation efficiency (%) of 74.6 %. Increasing the concentration of Na₂SO₄ (as supporting electrolyte) from 0.01 to 0.1 M led to enhanced ACE degradation efficiency (%) from 50.6 to 75.7 %, respectively, while a significant drop in ACE removal efficiency from 93.0 to 22.0 % occurred when the initial concentration of ACE increased from 1 to 10 mg L⁻¹, respectively. The operation of US/EC with pulse mode of US irradiation led to a slight increase in ACE degradation efficiency (%) (79.0 %). The presence of halide compounds (chloride ions) significantly enhanced the removal of ACE (96.1 %), while alcoholic compounds, especially methanol, produced a substantial suppressive effect on the treatment of ACE.

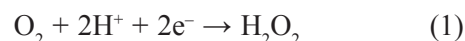
Keywords:

In situ H₂O₂, pharmaceutically active compounds (PhACs), air-permeable cathode, ultrasound, carbon black nanoparticles

Introduction

Pharmaceutical compounds discharged into aquatic environments such as lakes and rivers are toxic to aquatic life^{1,2}. Among various pharmaceutical compounds, acetaminophen (ACE) is one of the most widely consumed drugs. It is a non-narcotic analgesic drug which is typically used for treating fever, pain, and minor aches^{3,4}. ACE (i.e., N-acetyl-*p*-aminophenol) is detected in natural water resources, sewage, landfill leachate, and wastewater treatment plant effluents, producing potential environmental and health threats at trace concentrations^{3,5}. Among multiple adverse effects of ACE, lipid peroxidation, DNA damage, and protein denaturation have been reported. Moreover, the ACE molecules can cause toxicity to living organisms in aquatic systems⁶. This pharmaceutical compound is difficult to be treated by means of conventional treatment technologies. Therefore, the application of advanced treatment techniques, such as advanced oxidation processes (AOPs), has been considered for treating and degrading low-biodegradable target

organic compounds such as ACE. The utilization of AOPs results in the generation of hydroxyl free radical ([•]OH) destroying target organic pollutants in the aquatic solutions^{7,8}. Electrochemical AOPs (EAOPs) have gained more attention for decontamination of pharmaceutical compounds-polluted solutions via direct anodic oxidation. Moreover, the application of dimensionally stable anodes such as Pt leads to the generation of [•]OH because of the dissociation of water molecules⁹. To generate more oxidizing agents in the electrochemical process (EC), in the present research, a carbonaceous porous cathode was used for in situ generation of hydrogen peroxide through cathodic reduction, as shown in the following reaction¹⁰:



In addition, the combination of ultrasound (US) with the aforementioned EC was considered in order to synergistically generate radical species in the solution. The US waves bring about the generation of [•]OH in water via the formation, growth, and collapse of the “cavitation bubbles” as a result of the high pressure and temperature^{11–13}. In summary, porous cathode-equipped EC was combined with US for decomposing ACE in the aqueous solution. The

*Corresponding author:

E-mail address: darvishi@arakmu.ac.ir (rezadarvish86@yahoo.com)

Tel.: +98 86 33662024; Fax: +98 86 33686443

carbonaceous porous cathode was comprised of a carbon paper covered with carbon black nanoparticles to improve the electrical properties of the porous cathode.

Materials and methods

Chemicals and preparations

ACE ($C_8H_9NO_2$, $pK_a = 9.5$) was obtained from Sigma-Aldrich (USA). VULCAN[®] XC72R carbon black nanoparticles were purchased from Cabot Co., (USA). Carbon cloth and PTFE binder were purchased from ElectroChem, Inc (USA). All other chemicals were purchased from Merck (Germany). The porous cathode was synthesized by means of a carbon cloth covered with carbon black nanoparticles according to our previous research study¹⁰. Briefly, a mixture of 0.1 g carbon black, 1 mL PTFE, and 1.5 mL *n*-butanol in 50 mL deionized water was magnetically stirred (30 min), and then sonicated in an ultrasonic bath for 90 min. The carbon cloth was then coated with the aforementioned homogeneous mixture. The coated carbon cloth was oven-dried until it reached constant weight. Finally, it was sintered at 300 °C for 60 min.

Experimental set-up

The degradation of ACE was performed using an electrochemical cell equipped with Pt anode, carbonaceous porous cathode, and DC power supply. High-purity sulfate sodium was applied as supporting electrolyte. During the treatment process, the porous cathode was fed with oxygen gas supplied by an oxygen concentrator. The flow rate of oxygen gas was adjusted to the minimum value of 0.1 L min⁻¹. The electrochemical reactor with working volume of 200 mL was placed in an ultrasonic bath (Elma, P30H, Germany) for ultrasonication. The applied power and frequency of the ultrasonic bath were 320 W and 37 kHz, respectively. In fact, the US was generally irradiated by the ultrasonic bath in which the electrochemical cell containing ACE molecules was immersed.

Analysis

After the treatment process, the residual target pharmaceutical compound was analyzed by means of high performance liquid chromatography (KNAUER HPLC, Model: AZURA, Germany). An RP Amide column and a UV detector (wavelength of 243 nm) were used for the analysis. Methyl alcohol was mixed with deionized water (volumetric ratio: 60:40) and used as mobile phase. The mobile phase was injected into the HPLC with flow rate of 1 mL min⁻¹. *In situ* generated hydrogen peroxide

was measured as follows: 3 mL buffer solution (0.1 M potassium biphthalate) and 3 mL iodide reagent (10⁻⁴ M ammonium molybdate, 0.4 M potassium iodide and 0.06 M NaOH) were added to the withdrawn 4-mL sample. The spectrophotometer (UV-Vis spectrophotometer, Hach Co., USA) with wavelength of 351 nm was then implemented for measuring the concentration of hydrogen peroxide based on a calibration curve with high correlation coefficient^{10,14}. A TESCAN microscope (Mira 3, Czech Republic) was used for the scanning electron microscopy (SEM). The surface morphology of the samples was evaluated on the basis of the obtained SEM images.

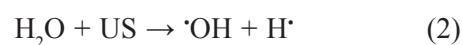
Results and discussion

SEM results

SEM analysis was conducted on uncoated carbon cloth and carbon black-coated carbon cloth, and the results are presented in Fig. 1. The surface morphology of the bare carbon cloth is given in Fig. 1(a). The image showed suitable structure of the bare carbon cloth to be used as the base of the porous cathode for oxygen diffusion and subsequently its reduction to hydrogen peroxide. The porous and interconnected structure of the carbon black was appropriate for the immobilization and enmeshment of carbon black nanoparticle. Fig. 1(b), (c), and (d) exhibit the successful immobilization and incorporation of carbon black nanoparticles into the carbon cloth matrix. Obviously, the covering of microstructured carbon cloth with nanostructured carbon black led to the production of a nanocomposite structure with higher surface area and consequently more reaction sites for the enhanced reduction of oxygen molecules to hydrogen peroxide.

Results from preliminary experiments

Considering a reasonable strategy, the contribution of each process involved in the degradation of ACE by the combined process of US/EC was determined separately. The results are given in Fig. 2. At reaction time of 60 min, the efficiency (%) of US alone in degrading ACE was 11.8 %, which was negligible. The US resulted in the generation of $\cdot OH$ in the solution by pyrolysis of water molecules^{11,15}:



However, the US irradiation led to the generation of limited amounts of $\cdot OH$; thus, the efficiency of US alone for the removal of ACE was insignificant. Similar results have been obtained and reported by Cihanoğlu *et al.* in their study on the degrada-

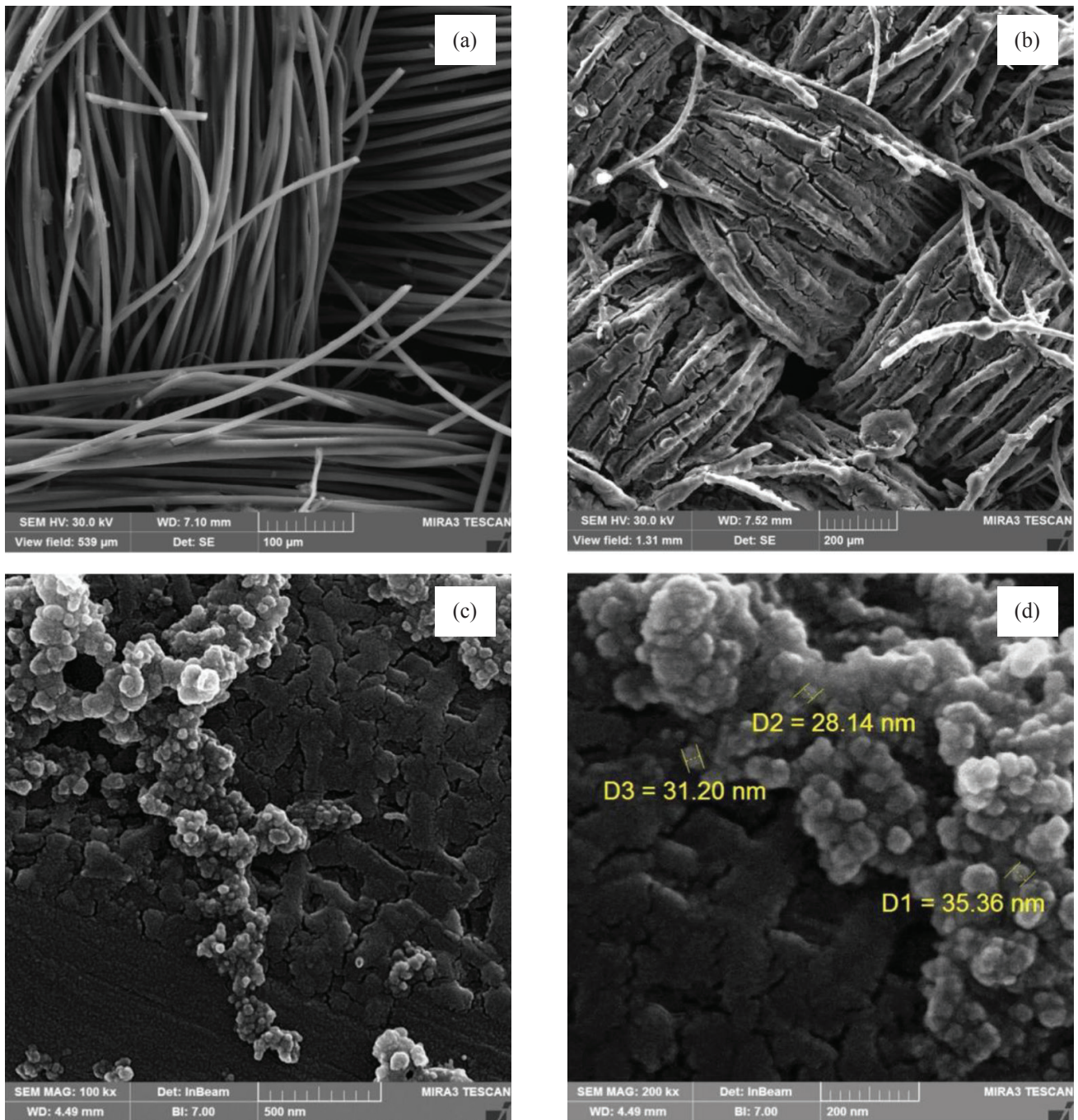
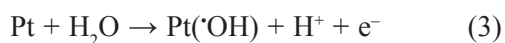


Fig. 1 – SEM image of uncoated carbon cloth (a), and carbon black-coated carbon cloth at different magnifications (b, c, and d)

tion of acetic acid by the hybrid process of US/Fenton¹⁶. The efficiency of EC in degrading and removing ACE was about 50 % within the reaction time of 60 min. The utilization of a dimensionally stable anode like Pt resulted in both direct oxidation of ACE molecules and its decomposition by the as-generated $\cdot\text{OH}$ in the bulk liquid, as displayed in the following equation^{17,18}:



The above reaction is heterogeneous, and the electro-generated $\cdot\text{OH}$ are adsorbed on the surface

of Pt anode. In the case of active anodes like Pt, the as-generated radicals are usually chemically adsorbed and are less obtainable¹⁹. Interestingly, the US irradiation of electrochemical cell containing ACE molecules resulted in a substantial increase in the degradation efficiency (74.6 %). As an explanation, it can be stated that the US irradiation cleans and reactivates the anode surface intensifying direct anodic oxidation¹⁵. It has been reported that the reactivation of anode surface would be helpful for the “cavitation phenomenon” and the generation of $\cdot\text{OH}$. Moreover, the US increases mass transfer of

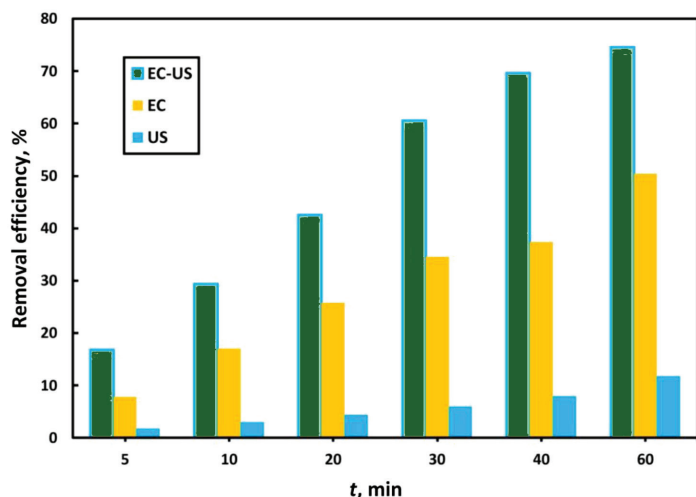
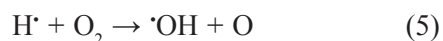


Fig. 2 – Comparison of US alone, EC alone, and US/EC processes in degrading ACE molecules. Experimental conditions: c : 5 mg L^{-1} , $[\text{Na}_2\text{SO}_4]_0$: 0.05 M , t : 60 min , pH : natural, f : 37 kHz , and I : 0.03 A .

the reactants inside the electrochemical cell^{20,21}. In agreement with our results, Souza *et al.* reported that the combination of US with electrolysis had a very positive effect on the degradation of herbicide 2,4-D²². Specifically, in the present study, the application of US in the presence of in situ electro-generated hydrogen peroxide led to the production of more $\cdot\text{OH}$ in the bulk solution for decomposing ACE, as exhibited in the following equation^{11,14,23,24}:



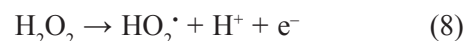
Coupling US with EC could result in increasing mass transfer rate of the reactants and enhancing the degradation of water molecules generating $\cdot\text{OH}$ ²². Meanwhile, the formation of new radical species and the “electrohydraulic cavitation” phenomenon could also be expected²⁵. For instance, non-converted oxygen molecules that have passed through the porous cathode could react with hydrogen radicals, producing more $\cdot\text{OH}$ for the enhanced degradation of ACE molecules. Non-converted oxygen molecules could also be converted to oxygen radicals (O^{\cdot}), producing extra $\cdot\text{OH}$ in the liquid phase, as shown in the following equations^{26,27}:



To conclude, the combination of US with porous cathode-equipped EC caused a substantial degradation of ACE in comparison with the individual processes of US and EC.

Current intensity

Fig. 3(a) exhibits the increase in the removal of ACE with increasing current intensity. At the reaction time of 10 min, increasing the current from 0.01 to 0.05 A resulted in increased ACE degradation efficiency (%) from 12.6 to 43.2 %, respectively. Clearly, increasing the reaction time resulted in intensifying the degradation efficiency. At the reaction time of 60 min, increasing the current from 0.01 to 0.05 A led to a significant increase in the removal of ACE from 39.6 to 94.8 %, respectively. In agreement with the present study, Zavala and Estrada reported that high current intensities favored the electrochemical degradation of ACE. However, they indicated that the effect of current intensity on the reactor performance is pH-dependent⁶. Actually, high current intensities produce large amounts of oxidizing agents in the electrochemical cell for degrading ACE^{18,28}. The difference in the efficiencies was significant at higher current intensities. In the case of the combination of US with EC, it is reported that when EC was operated at high current densities, the synergistic results could be associated with EC only, indicating that the effect of US alone was negligible at high current intensities¹⁵. The results represented in Fig. 3(b) indicate the increase in the generation of hydrogen peroxide when high current intensities were applied. As presented, the amount of in situ generated hydrogen peroxide was low, which was due to its self-decomposition in the electrochemical cell:



The current intensity, and consequently the amount of electro-generated hydrogen peroxide during the US/EC treatment process should be optimized considering economic viewpoint and applicability. In fact, the energy consumption rate is proportional to the applied current intensity²⁹.

Electrolyte concentration

The electrolyte type and concentration play important roles in the removal of target pollutants by means of electrochemical-based treatment systems. Therefore, the efficiency of the combined US/EC treatment system was recorded as a function of the concentration of Na_2SO_4 as supporting electrolyte. Fig. 3(c) shows that increasing the concentration of Na_2SO_4 (as supporting electrolyte) from 0.01 to 0.1 M led to enhanced ACE degradation efficiency (%) from 50.6 to 75.7 %, respectively. The higher the electrolyte concentration, the more mass transfer and current produced for the effective oxidation reaction.

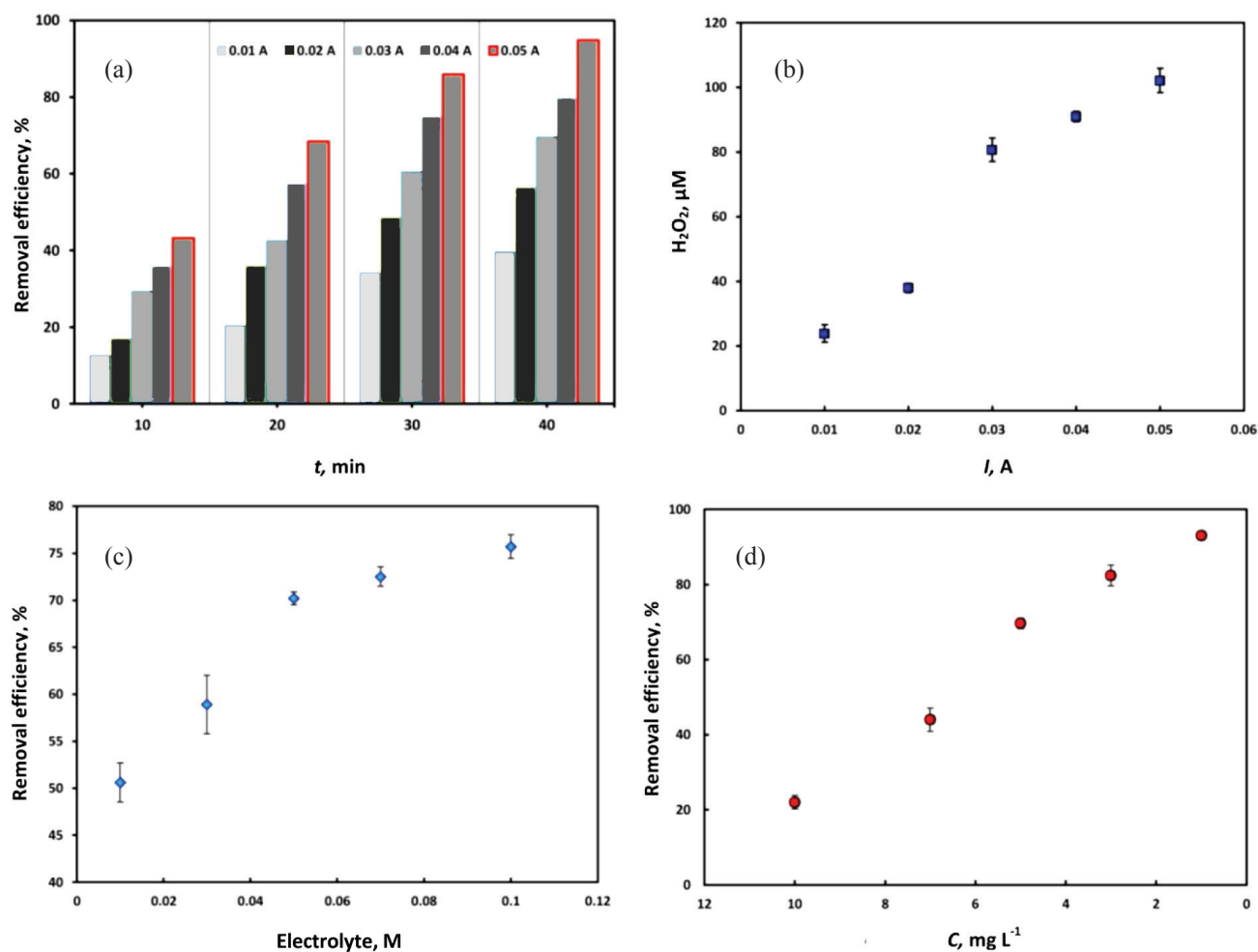


Fig. 3 – Effect of applied current (a), together with the variations of electro-synthesized H₂O₂ (b), electrolyte concentration (c), and initial ACE concentration (d) on ACE degradation efficiency. Experimental conditions: I: 0.01–0.05 A, c: 1–10 mg L⁻¹, [Na₂SO₄]₀: 0.01–0.1 M, t: 40 min, pH: natural.

ACE concentration

The initial solute concentration was varied in the range of 1–10 mg L⁻¹ in order to assess the efficacy of the US/EC treatment system under different pollutant concentrations. The results exhibited a rapid increase in ACE removal efficiency from 22.0 to 93.0 % as the initial concentration of ACE decreased from 10 to 1 mg L⁻¹, respectively (Fig. 3(d)). Decreased efficiency of the US/EC treatment process with increasing initial concentration of the target compound might be ascribed to the generation of limited amounts of oxidizing agents in the bulk solution under constant operating conditions for treating higher concentrations of the target compound. On the other hand, the decomposition of higher concentrations of ACE molecules by the treatment process is difficult when the constant amount of oxidizing agents is present in the solution⁹.

Irradiation pattern and frequency

The efficiency of the US/EC system in degrading ACE was checked under three different irradiation

patterns, including normal, sweep, and pulse modes. Accordingly, the pulse mode (79.0 %) was the most efficient irradiation pattern for the degradation of ACE compared to the normal (70.2 %) and sweep (68.5 %) modes (Fig. 4). The pulse mode of US used in the EC could decrease ultrasonic cavitation erosion on the surface of electrodes, leading to a longer service life of the applied electrodes in the electrochemical cell. Thus, the pulsed irradiation of US in the EC not only saves energy, but also improves the generation of free radical species in the solution³⁰. Actually, the increase in the efficiency of the treatment system was not significant when the pulse mode was operated (below 9 % increase in efficiency). However, the operation of ultrasonic bath in pulse mode led to the lower consumption of energy than that in the normal mode, which increased cost-efficiency of the treatment technique. It is demonstrated that the pulse mode of US irradiation could reduce the energy consumption of the process by 20 % over normal mode of operation (continuous US)³¹. Two different frequencies of 37

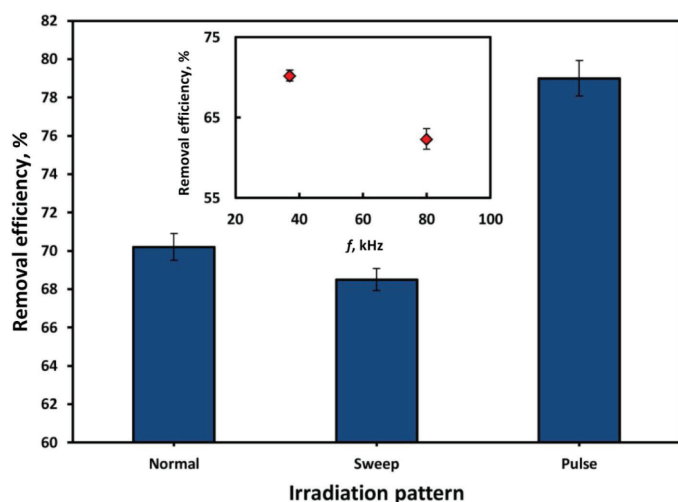


Fig. 4 – Effect of irradiation pattern and US frequency on degradation of the target pollutant. c : 5 mg L^{-1} , $[\text{Na}_2\text{SO}_4]_0$: 0.05 M , I : 0.03 A , t : 40 min , pH : natural, f : 37 and 80 kHz .

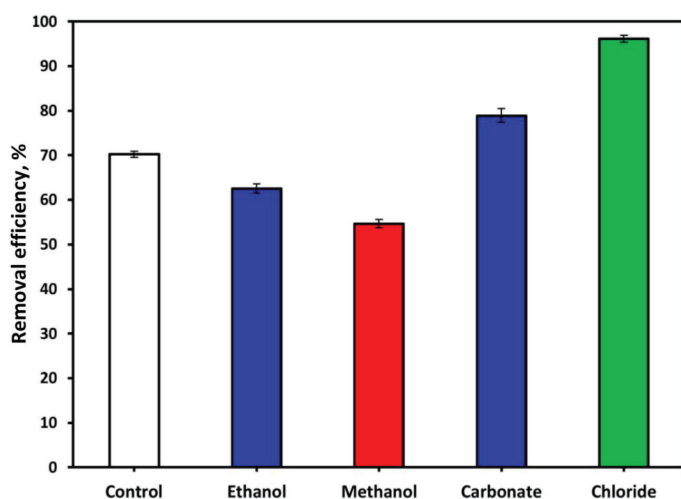
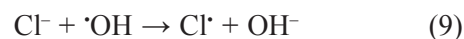


Fig. 5 – Effect of co-existing compounds on the degradation of ACE by US/EC process. [co-existing compounds]: 0.05 M , c : 5 mg L^{-1} , $[\text{Na}_2\text{SO}_4]_0$: 0.05 M , I : 0.03 A , pH : natural, f : 37 kHz , t : 40 min .

and 80 kHz were applied to determine the role of this parameter in the decomposition of ACE by means of the US/EC treatment system. As a result, lower value of the frequency (37 kHz) favored the degradation of ACE (70.2%). The removal efficiency (%) of 62.4% was obtained when US irradiation with the frequency of 80 kHz was applied.

Co-existing compounds

The effect of the presence of co-existing compounds was evaluated, and the results are presented in Fig. 5. Surprisingly, ACE degradation efficiency (%) substantially increased in the presence of chloride ions. The interaction of chloride ions with hydroxyl radicals resulted in the generation of chlorine radical, as represented in Eq. (9)³²:



It was demonstrated that the concentration of $\cdot\text{OH}$ remained unchanged in the presence of chloride ions. On the other hand, chlorine radicals had a high reaction potential with ACE where the $\cdot\text{OH}$ was still the main oxidizing agent in the solution³. This led to the enhanced degradation of ACE in the presence of chloride ions. Additionally, the interaction of chloride ions with water molecules produced hypochlorous acid (HClO), promoting the oxidation process^{18,33}. The degradation efficiency increased from 70.2 to 96.1% when chloride ions with molarity of 0.05 M were added to the reactor. Similar results were obtained in the case of the addition of carbonate ions to the US/EC reactor. The addition of carbonate ions led to a slight increase in the ACE degradation efficiency (%) from 70.2 to 78.9% . Regarding the presence of organic co-existing compounds, the addition of ethanol and methanol caused an obvious reduction in the degradation of ACE from 70.2 to 62.5 and 54.6% , respectively. The addition of ethanol and methanol to the solution led to the quenching of $\cdot\text{OH}$, which led to the considerable reduction of reactor performance in degrading ACE molecules³⁴. The scavenging properties of the studied alcoholic compounds are represented in the following equations¹⁷:



Regardless of the aforementioned results, the decreased efficiency of the reactor in the presence of organic scavenging compounds indicated the significant role of radical species in the decomposition of ACE³⁵.

Conclusions

The combination of US irradiation with an EC equipped with a porous cathode was considered for degrading ACE molecules in an aquatic medium. A porous cathode comprising a carbon cloth coated with carbon black nanoparticles was utilized for in situ generation of hydrogen peroxide in the electrochemical cell. The results indicated the highest efficiency of the combined US/EC process in terms of ACE degradation compared with the individual processes due to the formation of more radical species in the solution. The variations in current intensity significantly influenced the efficiency of the treatment system as well as the amount of electro-generated hydrogen peroxide. The combined process was inefficient at high concentrations of the target pollutant. The pulse mode operation of the ultrasonic bath with low frequency resulted in the highest deg-

radiation efficiency. The presence of inorganic co-existing compounds, such as chloride and carbonate led to increased efficiency, while the addition of alcoholic quenching compounds resulted in a significant reduction in ACE degradation. Overall, the US-assisted EC was an effective treatment technique in decontamination of ACE-polluted aquatic environments.

CONFLICT OF INTEREST

The authors declare that they have no conflict of interest.

ACKNOWLEDGEMENT

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List of symbols

- c* – concentration of acetaminophen, mg L⁻¹
t – reaction time, min
f – frequency of ultrasonic irradiation, kHz
I – current intensity, A

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