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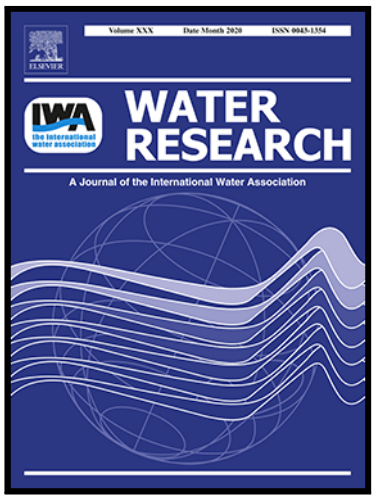

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Highlight

- A 20 L microbial electrochemical ultraviolet photolysis cell (MEUC) was developed.
- Fast and efficient removal of carbamazepine was achieved only with power input.
- UV intensity, voltage, HRT and aeration rate can affect MEUC system performance.
- Inferred probable transformation pathway and kinetics of carbamazepine by MEUC.
- MEUC proved to be a promising technology with non-biotoxicity in its effluent.

An innovative microbial electrochemical ultraviolet photolysis cell (MEUC) for efficient degradation of carbamazepine

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Abstract

Discharge of recalcitrant pharmaceuticals into aquatic environments can lead to serious negative environmental effects. While traditional wastewater treatment plants (WWTPs) are efficient for a wide range of non-toxic pollutants (i.e. ammonia), some wastewater streams contain recalcitrant toxic trace micropollutants such as pharmaceuticals that cannot be removed by the treatment processes that are typically employed in common WWTPs. Herein, an innovative 20 L microbial electrochemical ultraviolet photolysis cell (MEUC) was developed for the first time by the integration of a UV irradiation and a bioelectrochemical system, which exhibited efficient treatment of carbamazepine-a model pharmaceutical compound. Notably, neither the UV irradiation nor the bioelectrochemical system alone could effectively eliminate carbamazepine. The effect of operational parameters including applied voltage, cathodic aeration rate, UV intensity, and hydraulic retention time were evaluated. The obtained results elucidated that the degradation of carbamazepine was consistent with pseudo-first-order reaction kinetics, and required a lower energy input than traditional advanced oxidation processes. Five main transformation products were identified, and probable transformation pathways were established. Furthermore, the eco-toxicity as tested by *Vibrio fischeri* showed no significant bioluminescence inhibition by the treated carbamazepine effluent. Finally, the MEUC system was further tested with a real wastewater matrix, which again exhibited effective removal of carbamazepine. This paper provides a proof-of-concept verification of the novel MEUC system, which contributes insight for the subsequent vigorous development of the application of such efficient and cost-effective technologies for the treatment of trace pharmaceuticals wastewater.

Keywords: Microbial electrochemical systems; H_2O_2; UV Photolysis; Pharmaceuticals wastewater treatment; Transformation pathways; Eco-toxicity

1. Introduction

Nowadays, the extensive worldwide use of pharmaceuticals has lead to the appearance of residual pharmaceuticals ranging from ng L^{-1} to μg L^{-1} in various aquatic environments including ocean, municipal sewage, surface and ground water, and even drinking water (Bouissou-Schurtz et al., 2014; Buffle et al., 2006; Monteil et al., 2019). The trace pharmaceuticals that remain in the environment could seriously affect the ecosystem and pose risks to human health (Ganzenko et al., 2018; Simazaki et al., 2015). However, secondary biological treatment process applied in traditional wastewater treatment plants (WWTPs) and natural decomposition processes can not effectively eliminate many of these pharmaceuticals (Behera et al., 2011; Hu et al., 2018; Laurencé et al., 2014). For instance, carbamazepine, a widely used anti-epileptic drug with an annual global consumption of more than 1,014 tons, is notoriously difficult to be removed with conventional WWTPs (typically less than 10% removal efficiency) (Calisto et al., 2011; Mohapatra et al., 2012; Zhang et al., 2008). Carbamazepine is considered a model compound for residual pharmaceuticals, as it is widely found within WWTPs effluent, and has the potential to negatively impact on aquatic organisms and human beings (Appavoo et al., 2014; Mcdowell et al., 2005; Mohapatra et al., 2012). Moreover, carbamazepine has low phototransformation efficiency in nature, and its half-life is as high as 100 days, which was much longer than other pharmaceuticals (e.g., antibiotic sulphamethoxazole only has a half-life of 2.4 days) (Andreozzi et al., 2003a). Several treatment approaches such as adsorption, membrane process and electrocoagulation have met with very limited success at removing such trace pharmaceuticals from WWTPs (Monteil et al., 2019; Zaied et al., 2020). Therefore, the development of efficient and cost-effective technologies for such treatment are still urgently required.

Recently, advanced oxidation processes (AOPs) that can in-situ generate strong oxidants, especially hydroxyl radicals (• OH) and sulfate radicals (• SO_4^-), have been demonstrated as efficient treatment methods for pharmaceutical wastewaters (Feng et al., 2013; Kanakaraju et al., 2018; Olmez-Hanci and Arslan-Alaton, 2013). In particular, the electro-Fenton (EF) process which combines the conventional Fenton reaction with an electrochemical process has been intensively studied due to its good environmental compatibility, high removal rates, complete mineralization capacity, and mild operating conditions (Martinez-Huitle et al., 2015; Nidheesh et al., 2018; Plakas et al., 2016). More recently, in order to further save the electric energy consumption, a combination of emerging bioelectrochemical process and traditional EF technology, namely the bio electro Fenton (BEF) process, has been developed and received increasing attention (Li et al., 2018; Monteil et al., 2019; Nadais et al., 2018). However, some challenges with this technology still remain, and more extensive research is needed for its widespread application. Firstly, the generation of cathodic iron sludge needs to be further treated in time, otherwise, it will affect the system performance. Secondly, the iron catalyst added during the treatment process needs to be further treated before discharging into natural water bodies. Thirdly, the pH of the wastewater becomes acidic as a side effect of the process and therefore needs to be neutralized before being able to discharge it in an environmentally safe manner. This imposes both high treatment cost and a number of safety issues due to the chemicals used. In contrast, ultraviolet (UV) based AOPs like UV/H_2O_2, UV/O_3, UV/H_2O_2/Fe^{3+}, UV/chlorine, and UV/monochloramine have been used individually to remove various pollutants like dyes and pharmaceuticals efficiently, which could overcome the drawbacks of EF and BEF mentioned above (Andreozzi et al., 2003b; Doll and Frimmel, 2005; Pan et al., 2017).

Herein, an innovative microbial electrochemical ultraviolet photolysis cell (MEUC) system which integrated UV irradiation and BEF was developed for pharmaceutical-contaminated wastewater treatment. Carbamazepine was selected as a model pharmaceutical to investigate the feasibility and applicability of this novel MEUC system. The effects of key parameters including applied voltage, hydraulic retention time (HRT), cathodic aeration rate, UV intensity, and water matrix on system performance were investigated. Furthermore, the transformation products and potential transformation pathways of carbamazepine were identified. Finally, the eco-toxicity test of the treated effluent was assessed.

2. Materials and methods

2.1 Chemicals

Carbamazepine (99.5% purity), Na_2SO_4 (99% purity), Tert-butanol ($C_4H_{10}O$, 98.0%), and hydrogen peroxide (H_2O_2, 30% w/w solution) were purchased from Sigma-Aldrich, Denmark. Dried Vibrio fischeri bacteria for the eco-toxicity assay were purchased from ABOATOX, Finland.

2.2 MEUC reactor setup and operation

A 20 L two-chamber (40 cm × 10 cm × 25 cm for each chamber) MEUC reactor was established (Fig.1). Each chamber contained 10 electrodes and had a total volume of 10 L and a working volume of 9 L. The two chambers were separated by a cation exchange membrane (CEM, CMI 7001, Membrane International, NJ), which can transfer protons produced by the anodic exoelectrogens to the cathode and prevent cathode aeration from affecting the performance of the anodic microorganism. The electrode material of the anode was a carbon fiber brush (diameter 5.9 cm, length 6.9 cm, Mill-Rose, USA), which was pretreated prior to use, as previously described (Li et al., 2017b; Zhang et al., 2015). As for the cathode electrode material, a

commercial graphite plate (4.5 cm × 4.5 cm for each) was used. In addition, an Ag/AgCl reference electrode (+0.197 V vs SHE, Pine Instrument Company, USA) was placed in the cathode chamber near the graphite plate cathode.

Fig.1 is here

For the enrichment of electrogenic biofilm, 1.6 g L^{-1} of sodium acetate was added to the domestic wastewater from the primary sedimentation tank (Lyngby WWTP, Denmark) as anodic inoculum and substrate. During the enrichment period, the MEUC reactor was operated in microbial fuel cell (MFC) mode and the external resistance was 1000 Ω. In the cathode chamber, 50 mM phosphate buffer solution (PBS) at pH 7 was used as a catholyte and renewed every 4 days to avoid the impact of proton generation on the power generation of the system. After 2 months of operation, a stable and repeatable voltage was produced. Afterward, the reactor was switched to run in the microbial electrolysis cell (MEC) mode with a 0.1 Ω external resistance for the experiments described within this paper, unless otherwise indicated.

In this manuscript, the main objective was to study the degradation of carbamazepine in the cathode chamber. Therefore, to eliminate the impact of the fluctuating properties of real domestic wastewater on the anode reactions, a widely adopted synthetic nutrient medium was used to replace the domestic wastewater and the HRT was set to 58 h for continuous feeding in the subsequent experiments. The detailed composition of the synthetic nutrient medium is described within previous studies (Li et al., 2018; Nadais et al., 2018). Synthetic pharmaceuticals wastewater amended with 500 μg L^{-1} carbamazepine and 50 mM Na_2SO_4 was used for the tests. Two low-pressure mercury UV lamps (Hanovia GPH180T5L, 10 W, 254 nm) were submerged in the cathode chamber. The UV lamp needs to be warmed up before use, and the time is set to

30 mins. In addition, the corresponding UV irradiance was calibrated as 24 μW cm^{-2} based on a previous study (Bolton and Linden, 2003).

Batch experiments were first performed to verify the feasibility of the MEUC concept with the following conditions: UV photolysis, open circuit, without UV photolysis, and MEUC process. Thereafter, continuous experiments were performed to investigate the effect of several key operational parameters on MEUC system performance including cathodic aeration rate, UV intensity, and HRT. Moreover, in this paper, the actual wastewater picked up from secondary biological treatment effluent (Lyngby WWTP, Copenhagen, Denmark) was used to investigate its influence on carbamazepine removal during the MEUC process. The characteristics of the actual wastewater used within this investigation were listed in Table S1. A peristaltic pump (BT100-2J, Longer, China) was used for aeration in the cathode chamber. The applied voltage (0.1, 0.2, 0.3, 0.4, and 0.5 V) of the MEUC system and the corresponding current and cathode potential were provided and monitored by the battery test system (CT-4008W, Neware, China). Both chambers were stirred at a rate of 200 rpm. All the duplicated experiments were operated at room temperature (25 $\pm$ 5 ^{o}C).

2.3 Analysis methods

At a given sampling point, 10 ml samples were taken, of which 6 ml was used to determine the H_2O_2 concentration and pH value immediately. A PHM 210 pH meter (Radiometer) was used for pH measurement. Conductivity and dissolved oxygen (DO) were measured by a CDM 83 meter (HACH, USA). The turbidity was tested by a Turb 430 IR/T turbidity meter (WTW, Germany). A sparOmeter electricity meter (Type NZR230, S.L. Energitekinik, Denmark) was used for recording the electrical energy consumption of the MEUC system. The method for determining the concentration of H_2O_2 was followed as previously described (Nadais et al., 2018).

Concentrations of carbamazepine and its transformation products were detected using a high-performance liquid chromatography, HPLC (Agilent 1290 Infinity, USA) coupled with a triple quadrupole tandem mass spectrometer, MS/MS (Agilent 6470 series, USA). The detailed method was described in Supporting Information (SI).

The eco-toxicity was assessed using a standard Micro Tox® toxicity test system (Carlsbad, CA, USA) (Libralato et al., 2010; Parvez et al., 2006). To eliminate the interference of Cl^-, additional NaCl was added into each sample before testing to maintain the same Cl^- concentration (2%). All eco-toxicity tests were carried out in duplicate.

3. Results and discussion

3.1 System feasibility verification under batch mode

To verify the feasibility of the MEUC concept, the system was first tested in batch mode with applied voltages from 0.1 to 0.5 V. The initial carbamazepine concentration of 500 μg L^{-1}, Na_2SO_4 of 50 mM, airflow rate at 0.022 mL min^{-1} mL^{-1}, UV intensity of 48 μW cm^{-2} and without pH adjustment were adopted as operating parameters for the test. As shown in Fig.2, the removal efficiency of carbamazepine in 2 hours was only about 10%, showing the characteristic resistance of carbamazepine to UV photolysis alone. The results were consistent with previous findings where carbamazepine showed low degradation under UV photolysis (Bu et al., 2018; Deng et al., 2013; Wang et al., 2016). When operated in an open circuit or without UV irradiation, the removal efficiency of carbamazepine was less than 4% after 2 h operation. This suggests that carbamazepine was neither readily absorbed by reactor materials, nor oxidized by H_2O_2 alone (Liu et al., 2018). In contrast, rapid removal of carbamazepine was observed in the MEUC reactor with UV photolysis in a closed circuit, resulting in a removal efficiency of

approximately 98% after 1 h and complete removal within 2 h. The fast removal of carbamazepine was mainly due to the effective conversion of in-situ electrochemically synthesized H_2O_2 to strong • OH through UV photolysis via Eq. (1), where the generated ·OH was further responsible for the degradation of carbamazepine.

$$H_2O_2 \xrightarrow{hv} \cdot OH \quad (1)$$

The feasibility of this novel MEUC system was successfully verified based on the results obtained from the control experiments. As such, it was then necessary to explore the effect of operating parameters that can affect system performance.

The applied voltage is a well-known key parameter affecting H_2O_2 production in the traditional BEF process (Li et al., 2018; Nadais et al., 2018). Thus, the effect of different applied voltages (0.1, 0.2, 0.3, 0.4, and 0.5 V) on the carbamazepine removal in the MEUC system was investigated. It can be seen that the MEUC system reached approximately 100% degradation of carbamazepine within 2 h for all of the applied voltages that were tested (Fig.2). As a result, the degradation efficiency of carbamazepine showed no significant difference with selected applied voltages, where the residual H_2O_2 concentrations varied between 7 and 9 mg L^{-1} (Fig. S1). Hence, the similar removal efficiencies that were observed at the selected applied voltages in the first 2 h may be due to sufficient H_2O_2 being produced under these applied voltages. Nevertheless, it is worth noting that the MEUC system with an applied voltage of 0.2 V showed relatively faster degradation of carbamazepine than the other applied voltages. Higher applied voltages correlated with higher pH being observed in the cathode (Fig. S1). The drop in removal rate with increasing applied voltage could be attributed to H_2O_2 decomposition, which reduced the H_2O_2 level during the treatment. Furthermore, the degradation of carbamazepine observed in the MEUC system fits with pseudo-first-order kinetics, and the related k_{app} values were calculated to be 4.84 (R^2 = 0.98),

6.07 (R^2 = 0.96), 4.76 (R^2 = 0.99), 5.07 (R^2 = 0.98) and 4.10 (R^2 = 0.99) h^{-1} for the corresponding applied voltages of 0.1, 0.2, 0.3, 0.4, and 0.5 V, respectively (Table S2).

The batch mode experiments were able to directly demonstrate the feasibility of this novel MEUC system, as an effective platform technology for carbamazepine removal. From these results, an applied voltage of 0.2 V was selected for the subsequent continuous experiments by taking removal efficiency and energy consumption into account.

Fig.2 is here

3.2 System performance under continuous mode

3.2.1 Effect of cathodic aeration rate

The cathodic dissolved oxygen (DO) concentration and the gas-liquid transfer are the typical limiting factors for electrochemical synthesis of H_2O_2 via Eq. (2) (Li et al., 2018; Monteil et al., 2019; Nadais et al., 2018), which may further affect •OH production. Therefore, the effect of the cathodic aeration rate (in terms of airflow rate) on the treatment performance of the MEUC system was investigated.

$2H^+ + O_2 + 2e^- \rightarrow H_2O_2$ (2)

Five airflow rates of 0, 0.011, 0.022, 0.033, and 0.044 mL min^{-1} mL^{-1} (on the basis of cathodic working volume) corresponding to 0, 0.0024, 0.0048, 0.0072, 0.0096 mL O_2 min^{-1} mL^{-1} were adopted for the experiment. Notably, the airflow rates investigated in this study were much lower than those previously reported in EF and BEF processes, and thus, lower energy consumption in current work could be expected (Chen and Lin, 2009; Nadais et al., 2018). As shown in Fig.3a, the MEUC system with a cathodic airflow rate of 0.033 mL min^{-1} mL^{-1} exhibited the highest carbamazepine removal efficiency (with a value above 98%). The k_{app} values were 1.86 (R^2 =

0.99), 2.43 (R^2 = 0.99), 2.63 (R^2 = 0.99), 2.93 (R^2 = 0.99) and 2.66 (R^2 = 0.99) h^{-1} in the reactors with airflow rates of 0, 0.011, 0.022, 0.033, and 0.044 mL min^{-1} mL^{-1}, respectively (Table S2). The MEUC reactor at an airflow rate of 0.033 mL min^{-1} mL^{-1} also showed the fastest removal (Fig. S2). A similar phenomenon was observed within previous studies related to the traditional BEF system (Li et al., 2017a; Nadais et al., 2018; Zhou et al., 2018). The increased removal efficiency with increasing of cathodic aeration rate was due to the increased DO level which can promote the electrochemical synthesis of H_2O_2 and subsequent $\bullet OH$ production (Li et al., 2017a). However, when the airflow rate was further increased to 0.044 mL min^{-1} mL^{-1}, the observed removal efficiency of carbamazepine decreased slightly, which probably due to saturated DO and gas collapsing to big bubbles and thereby decreasing the oxygen availability with the cathode electrode (Li et al., 2017a; Liu et al., 2007; Moreira et al., 2017). In addition, a high aeration rate will reduce the irradiation volume in the MEUC system, thereby reducing the generation of $\bullet OH$, and ultimately leading to a decrease in system performance (Moreira et al., 2017). The trend of removal performance was consistent with that of the residual H_2O_2 concentration, circuit current, and cathode potential exhibited in Fig.S2. These results were also consistent with previous EF and BEF studies (Fig. S2)(Li et al., 2017b; Zhou et al., 2013). When the cathode was not aerated, the carbamazepine removal efficiency was 94% after the first HRT and then continuously decreased to 92% after the second HRT. The cathodic DO concentration remained high after the first HRT and there was sufficient oxygen available for H_2O_2 production. In the second HRT, the further consumption of DO led to a decreased generation of H_2O_2, which subsequently resulted in a drop in removal efficiency. The results indicated that long-term operation without aeration may reduce treatment efficiency due to insufficient oxygen. In fact, running EF and BEF systems, like the traditional Fenton process, usually require adjusting the

pH to below 3 in order to avoid iron precipitation (Zhou et al., 2017). However, acidic pH can also lower the production of H_2O_2 due to the higher concentration of H^+ can not only lower the solubility of oxygen, but also further consume the generated H_2O_2 and the pumped oxygen to produce H_2O via Eq.(3) and (4), respectively, thereby leading to reduced efficiencies (Oturan et al., 2018; Yu et al., 2015). Thus, more intensive aeration may be required for these systems when compared to our MEUC system operated at neutral pH.

$$2H^+ + H_2O_2 + 2e^- \rightarrow 2H_2O \quad (3)$$

$$4H^+ + O_2 + 4e^- \rightarrow 2H_2O \quad (4)$$

3.2.2 Effect of UV intensity

UV intensity was another key parameter for UV-catalyzed AOPs like UV/chlorine and UV/H_2O_2 oxidation processes, whereby it can affect the amount of electron-hole pairs that were produced (Linsebigler et al., 1995; Somathilake et al., 2018; Wang et al., 2016). Herein, the effect of UV intensity on the performance of the MEUC system was studied by changing the number of UV lamps (0, 1, and 2). For this test, the initial carbamazepine concentration of 500 μg L^{-1}, applied voltage of 0.2 V, Na_2SO_4 of 50 mM, HRT of 2 h, and airflow rate of 0.033 mL min^{-1} mL^{-1} were adopted. As shown in Fig.3b, the increased number of UV lamps (and hence increased UV irradiation) led to the enhancement of carbamazepine removal, which is likely due to the increased •OH production with increasing UV irradiation. The k_{app} obviously increased from 2.14 (R^2 = 0.98) to 2.93 (R^2 = 0.99) h^{-1} with the doubling of UV lamp number from 1 to 2 (corresponding to increasing UV intensity from 24 to 48 μW cm^{-2}). In the MEUC system without UV irradiation, it was found that carbamazepine was barely degraded, which was in agreement with previous studies that have found H_2O_2 alone cannot efficiently oxidize carbamazepine (Somathilake et al., 2018; Wang et al., 2016). Interestingly, residual H_2O_2 was

detected in both conditions with the UV intensity of 24 and 48 μW cm^{-2} (4.9 and 2.5 mg L^{-1}, respectively) (Fig. S3). The incomplete conversion of H_2O_2 to • OH could probably be improved by the better arrangement of the position of the cathode electrodes. This is because part of the reverse side of the cathode electrodes was not sufficiently irradiated with UV light in the current setup. This issue could be addressed by better system design and thus improved conversions of H_2O_2 can be expected in the future study.

3.2.3 Effect of HRT

HRT is an important parameter in continuous flow reactors, which could affect the degree of target pollutant removal and expenditure across the whole treatment process. Thus, four HRTs (2, 2.5, 3, and 5 h) were employed to elucidate the impact of HRT on the system performance. The initial carbamazepine concentration of 500 μg L^{-1}, applied voltage of 0.2 V, Na_2SO_4 of 50 mM, UV intensity of 48 μW cm^{-2}, and airflow rate of 0.033 mL min^{-1} mL^{-1} were chosen for the test based on the results obtained in the above sections. As shown in Fig. 3c, the carbamazepine removal efficiency was observed to increase with longer HRT and reached 100% removal at HRT of 5 h within the first HRT period. However, after one full HRT period, the removal rate of carbamazepine had slightly decreased to 98%. The variation in effluent pH under different HRT conditions showed the same trend as current (Fig.S4). Therefore, the decrease of carbamazepine removal efficiency after one HRT period in the reactor with HRT of 5 h could again be due to the H_2O_2 decomposition as a result of the increased pH (above 9) (Kuo, 1992). Corresponding to the removal efficiency, the k_{app} values were 2.93 (R^2 = 0.99), 3.05 (R^2 = 0.99), 3.24 (R^2 = 0.99), and 5.89 (R^2 = 0.99) h^{-1} with HRT of 2, 2.5, 3, and 5 h, respectively (Table S2). This indicated that the complete removal of carbamazepine in the MEUC system can be achieved by extending

the HRT. Although the carbamazepine degradation profile increased from 98% to 100% when the HRT was gradually extended from 2 to 5 h, the long HRT may significantly lower the treatment capacitance and increase energy consumption. Thus, HRT of 2 h was chosen as proper HRT for the following experiments.

Fig.3 is here

3.3 Transformation products identification and degradation pathway proposed

The above results successfully demonstrate the feasibility of the novel MEUC system for pharmaceutical-containing wastewater treatment without pH adjustment and the addition of oxidants or catalysts. To better understand the system, the transformation products and potential transformation pathways of carbamazepine were further explored. The initial carbamazepine concentration of 500 μg L^{-1}, UV intensity of 48 μW cm^{-2}, airflow rate of 0.033 mL min^{-1} mL^{-1} applied voltage of 0.2 V, Na_2SO_4 of 50 mM, and HRT of 2 h was chosen for the test. Total ion chromatography under MS2 scan (Fig.S5) revealed that carbamazepine at an elution time of 7.765 mins was efficiently degraded by the MEUC system. Five main transformation products with mass-to-charge ratios (m/z) were produced over the test period with elution times at 0.068 (m/z 118.1), 0.479 (m/z 164.9 and 226.9), 6.628 (m/z 253) and 6.953 (m/z 258) mins (Fig.S5). The shorter elution times of these transformation products compared to that of the carbamazepine, indicating that the polar of transformation products were higher than that of carbamazepine. A previous study on the photocatalytic oxidative degradation of carbamazepine also reported similar results (Ding et al., 2017). It should be pointed out that only some major transformation products of carbamazepine were able to be identified in this study, as only tandem triple quadrupole mass spectra was used. Possible molecular structures corresponding to each of these transformation products were inferred based on the combination of observed m/z

with the associated abundance according to previous literature related to carbamazepine degradation with AOPs.

Based on the elution time (Table S3) and variation in the abundance of each potential intermediate (Fig.S6), a probable transformation pathway of carbamazepine through the MEUC system was proposed. The •OH generated in-situ first attacked the N-heterocyclic ring of the parent carbamazepine, transforming it to monohydroxylated carbamazepine (m/z 253) (Fig.4). This can exist as a number of different molecular structures (P1-P4) and are some of the most common transformation products found from carbamazepine degradation within conventional advanced oxidation studies (Begum and Ahmaruzzaman, 2018; Bo et al., 2017; Bu et al., 2018; Ding et al., 2017; Divyapriya et al., 2018; Wang et al., 2016; Zhang et al., 2019). The reason for the formation of various monohydroxylated carbamazepine isomers has been suggested to be due to the symmetrical structure of carbamazepine (Pearce et al., 2002). Then, the P1-P4 was further degraded to P5 by the loss of its amide group and cleavage of the azepine ring. The same degradation pathway has also been observed in conventional advanced oxidation studies (Ding et al., 2017; Zhang et al., 2019). Thereafter, the further transformation of P5 underwent two different pathways. On the one hand, P7 was produced via a hydroxylation reaction of P5 (Bo et al., 2017; Ding et al., 2017). On the other hand, both P5 and P7 could be further degraded into P6 through a hydroxylation reaction between •OH and the aromatic ring. This has previously been demonstrated to be a key step for the cleavage of the heterocycle ring (Bo et al., 2017; Vogna et al., 2004; Zhang et al., 2019). Finally, the observed signal with the smallest m/z at 118.1 could be ascribed to the short-chain carboxylic acid P8, brought about through the cleavage of the benzene ring of P6. This has also been observed to occur within photocatalytic processes (Bo et al., 2017; Wang et al., 2017). The speculated transformation products P8 was further verified by

comparing mass spectra and retention time of samples to that of the commercial standard from Sigma-Aldrich. The transformation products P8 was confirmed to be succinic acid, according to the retention time and MS/MS spectra (m/z=118.1) (see SI Fig. S7 for details). Moreover, m/z=118.1 was also one of the major fragments in the MS/MS spectra at retention time at 0.479 mins, also indicating that transformation product P8 was the standard succinic acid. To the best of our knowledge, this is in line with a number of photocatalytic degradation studies that have reported the cleavage of benzene ring into low molecule weight fragments production from carbamazepine. The obtained results demonstrated that this novel MEUC system has a great potential as the AOPs system for mineralization of carbamazepine (Begum and Ahmaruzzaman, 2018; Bo et al., 2017; Wang et al., 2017).

Fig.4 is here

3.4 Application to real wastewater

The performance of the MEUC system on carbamazepine removal in WWTPs secondary effluent was further investigated under varied applied voltages (0.2 and 0.3 V), HRTs (2, 4, and 5 h) and cathodic aeration rates (0 and 0.033 mL min^{-1} mL^{-1}). The applied parameters used were as follows: the initial concentration of carbamazepine in the wastewater was 500 µg L^{-1} and UV intensity of 48 µW cm^{-2}. As shown in Fig.5, when 0.2 V was applied, the removal efficiency of carbamazepine reached a steady-state after five full cycles (10 h operation with HRT of 2 h) and reached about 60%, which was significantly lower than the 98% removal efficiency obtained with synthetic wastewater. This could be mainly attributed to the consumption of •OH by the natural organic matter presented in the real wastewater (Kang et al., 1999). In addition, the lower conductivity (782 µs cm^{-1}) of the real wastewater could also decrease the current and thereby reducing the electrochemical generation of H_2O_2 (Fig.S8) (Brillas et al., 2009). Furthermore, the

inorganic ions such as bicarbonate may also act as $^{\bullet}OH$ scavengers (Olmez-Hanci et al., 2015). Notably, chloride ions present in wastewater are generally considered to be one of the quenchers of $^{\bullet}OH$ according to Eq. (5) in the UV based AOPs. However, when the pH value of the solution was greater than 7.2 (see Fig. S8), the generated $\cdot HOCl^-$ can be further dissociated to form ·OH again via Eq. (5) (Kläning and Wolff, 1985; Liao et al., 2001; Zhang et al., 2018).

$$^{\bullet}OH + Cl^- \leftrightarrow {}^{\bullet}HOCl^- \quad (5)$$

Therefore, the scavenging of $^{\bullet}OH$ by chloride ions is not important in the MEUC system treating trace pharmaceuticals-contaminated WWTPs secondary effluent at neutral pH.

Taking into account the low carbamazepine removal efficiency observed when the applied voltage was 0.2 V, the applied voltage was further increased to 0.3 V, but the removal efficiency of carbamazepine did not show any obvious increase after three full cycles (6 h operation with HRT of 2 h). The current density increased only slightly compared to 0.2 V (17 mA vs. 20 mA), which could explain the insignificant increase of removal after switching the voltage from 0.2 to 0.3 V (Fig.S8). Therefore, to further improve the carbamazepine removal, the HRT was extended to 4 h. As a result, the carbamazepine removal efficiency increased to around 78% and reached a steady state after an operation time equal to three times of HRTs. Then, when the HRT was further extended to 5 h, the final carbamazepine removal efficiency increased to approximately 81% and reached a steady-state after an operation time equal to three times of HRT, indicating that carbamazepine can be efficiently removed in a real wastewater matrix with a proper HRT. Finally, we evaluated the effect of stoping of cathodic aeration on the removal of carbamazepine in the real wastewater matrix, and the results showed that the overall removal efficiency of carbamazepine slightly decreased from 81% to 77% after a time equal to three times of full

HRTs (HRT of 5 h). Similar results were also obtained in the earlier experiments using the synthetic wastewater. This could be because the cathodic electrochemically synthesized H_2O_2 decreased without cathodic aeration (Nadais et al., 2018). Furthermore, it was observed that the system current and DO in cathodic effluent decreased correspondingly but stabilized at around 18.5 mA and 4 mg L^{-1} (27 ℃), respectively (Fig. S8). Previous studies on the BEF system for the degradation of the azo dyes also reported similar results (Li et al., 2017a). Since the cathodic aeration rate can significantly affect the overall energy consumption and there was a still good removal efficiency without cathodic aeration, thus the MEUC system can become an energy-efficient technology for tertiary treatment in WWTPs. Apart from the above parameters, we also monitored the common parameters of the treated effluent including turbidity, COD, NH_4-N, and conductivity to comprehensively evaluate the MEUC system (Fig.S8). Besides, recent reports on the successful operation of the pilot-scale MFC system using real municipal wastewater to power the bio-anode can provide valuable experiences for future practical applications of the MEUC system in the real wastewater treatment plant (Hiegemann et al., 2019; Rossi et al., 2019).

Fig.5 is here

3.5 Eco-toxicity test

To further assess the safety quality of effluent from the MEUC system, eco-toxicity tests were performed by using a *Vibrio Fischeri* assay. Samples were collected at various times (0-8 h) from the MEUC reactor under certain operation conditions (real wastewater with the initial carbamazepine concentration of 500 μg L^{-1}, UV intensity of 48 μW cm^{-2}, airflow rate of 0.033 mL min^{-1} mL^{-1}, and HRT of 2 h). Fig.6 shows the bioluminescence inhibition percentage of *Vibrio Fischeri* in each sample after 10- and 20-min exposure. As expected, the bioluminescence inhibition percentage for each sample showed no clear difference and were all less than 15%

during 8 hours of operation. It should be noted that the inhibition below 20% was generally considered to be no significant harmful effects. Thus, it can be concluded that the toxic effect of the treated effluent from the MEUC could be neglected. Similar results were also reported in the catalyst-activated peroxymonosulfate process for carbamazepine removal (Deng et al., 2017). In contrast to this, some reaction intermediates have been found to be more toxic than the parent carbamazepine during UV photolysis (Donner et al., 2013). Furthermore, acridine, a degradation product commonly found in photocatalytic degradation of carbamazepine, showed strong acute and chronic toxicity (Zhu et al., 2019). However, considering no obvious increase of bioluminescence inhibition observed in the eco-toxicity test, acridine could be formed but was not a major byproduct in the MEUC system. To conclude, the MEUC system was not only efficient but also can be a safer and more eco-friendly wastewater treatment technology.

Fig.6 is here

3.6 Economic analysis

Electrical consumption was the sole treatment expenditure of the MEUC system, which was consisted of two parts, one from the MEUC reactor and the other from the pump for aeration, agitation, and continuous feeding of the wastewater into the reactor, respectively. Therefore, the electrical energy per order (EE/O) was used to assess the cost-effectiveness of this novel technology (Bolton et al., 2001). Regarding a continuous-flow reactor, the EE/O can be calculated via Eq.(6) (Behnajady et al., 2009).

$$\mathrm{EE/O} = \frac{P}{V_0 \times \log(C_0/C)} = \frac{P}{V_0 \times \mathrm{k}} \quad (6)$$

Where P is power input (kW), V_0 is the volumetric flow rate ($m^3\ h^{-1}$), C_0 and C are initial and final concentrations of carbamazepine ($\mu g\ L^{-1}$), respectively, k is rate constant (h^{-1}). The

electricity price in Denmark was 0.25 € kWh^{-1} and the corresponded total cost per order ($Cost/O_{total}$) can be calculated via Eq.(7).

$Cost/O_{total} = Cost/O_{MEUC} + Cost/O_{pump} = (EE/O_{MEUC} + EE/O_{pump}) \times$ electricity price (7)

According to the Eq.(6) and (7), the corresponding values under optimized conditions obtained above were calculated and listed in Table S4. As shown in Table S4, the total energy consumption by the MEUC system was 6.069 kWh m^{-3}. 75% of the energy (4.551 kWh m^{-3}) was consumed by the pump for aeration (2.275 kWh m^{-3}), agitation (0.360 kWh m^{-3}), and continuous feeding of the wastewater into the reactor (1.916 kWh m^{-3}), while only 1.518 kWh m^{-3} was required by the MEUC system (0.001 kWh m^{-3} as direct voltage supply and 1.517 kWh as for UV lights). It was found that the removal efficiencies were not significantly affected without cathode aeration using both the synthetic and real wastewaters (see Fig.3 and Fig.5). On the contrary, according to Eq.(6), the E/EO value was related to the volumetric flow rate (corresponding to HRT). Thus, shortening HRT can further reduce the E/EO values. Given the fact that the concentration of the residual pharmaceuticals in the WWTPs secondary effluent is usually lower than 500 μg L^{-1} used in this study and many residual pharmaceuticals can be directly removed with UV irradiation (De la Cruz et al., 2012; Loos et al., 2013), the treatment performance should be ensured in the continuous operation without aeration and with shorter HRT. Thus, the overall energy consumption could be reduced when the MEUC technology is applied as the tertiary treatment process of WWTPs on a full scale in the future. Furthermore, it should be noted that the agitation and continuous feeding of the wastewater into reactors are common processes that are also required by AOPs and other wastewater treatment technologies. They could be omitted during continuous flow operation. Thus, these costs are normally not included in the calculation and comparison of energy consumption (Miklos et al., 2018). Thus,

even without optimization, the energy consumption of the lab-scale MEUC (1.518 kWh m^{-3}) was lower than most of the AOPs (Table 1). Though the median E/EO values of some AOPs such as UV/H_2O_2, UV/Cl_2 and UV/persulfate processes are usually less than 1 kWh m^{-3}, these processes need a big amount of chemicals and catalysts (e.g., H_2O_2 and persulfate) which costs are several times higher than the energy.

The energy consumption by the MEUC is nearly as same as the energy required by reverse osmosis (1-2 kWh m^{-3}) (Peñate and García-Rodríguez, 2012; Voutchkov, 2018). However, the reverse osmosis process can not eliminate pollutants. Instead, it typically produces a concentrate of 15-25% of the feedwater flow rich in nutrients, salts, microorganisms, and refractory organic compounds, and thus, requires further treatment by other means (Bagastyo et al., 2011; Lee et al., 2012). Much more energy consumption (usually more than 2 kWh m^{-3}) was reported to further degrade such pollutants (Arola et al., 2019) after the reverse osmosis. For example, the energy consumption for treating reverse osmosis concentrate was 2.43 kWh m^{-3} via an electrochemical oxidation process by using a 240 mL electrochemical cell in batch mode (Bagastyo et al., 2011). Additionally, it has been demonstrated that the E/EO value can be reduced when up-scaling the processing capacity from lab-scale (2.2 kWh m^{-3}) to pilot-scale (0.68 kWh m^{-3}) or even full scale (0.5 kWh m^{-3}) during UV/H_2O_2 process (Miklos et al., 2018). In addition, the reactor configuration can be further optimized to reduce the number of UV lamps used to further lower energy consumption in the future. Thus, the MEUC could be even competitive after scaling up for practical application. Notably, the carbamazepine removal efficiency of the MEUC system explored in this study was significantly higher compared to those biological processes. Additionally, the acetate (0.46 € kg^{-1}) was fed into the bio-anode continuously, which add the treatment cost of 0.016 € m^{-3}.

Apart from operational expenditure, the capital expenditure of the MEUC system was also one of the key factors for the implementation of this technology at a large-scale in the future. The capital expenditure of the MEUC system was about 930 € m^{-3} in Denmark (Zhang and Angelidaki, 2016). In the future industrial application, the sewage with high COD content could be used instead of acetate solution to further reduce the total treatment cost. To conclude, the MEUC system was expected to be a cost-effective technology for the treatment of trace pharmaceuticals-contaminated wastewater.

Table.1 is here

3.7 Significance and Perspective

The MEUC system has the following advantages over the traditional AOPs. Firstly, no additional H_2O_2 is required due to the H_2O_2 is in-situ electrochemically synthesized at the cathode. Thus, compared with the conventional Fenton and UV/H_2O_2 processes that rely on the external dose of H_2O_2, it can greatly reduce the costs associated with chemical production, transportation, storage, safety, and procurement. Secondly, the challenge of removing residual H_2O_2 (up to 70-80% of the H_2O_2 dose) could be addressed since the residual H_2O_2 could be in-situ converted into H_2O by changing the MEUC system into the MFC mode (Zhang et al., 2015). The reported cost of removing residual H_2O_2 is approximately 22.02 € kg^{-1} (Wu and Englehardt, 2012). Besides, unlike the typical EF and BEF processes, no additional chemicals (e.g., iron) are needed by the MEUC, which could greatly reduce the treatment cost and address the problem of iron sludge. Furthermore, compared with the biological treatment processes (Table 1), the MEUC system exhibits significantly higher treatment efficiency regarding carbamazepine removal.

Nevertheless, some challenges still need to be addressed before the large-scale application. Firstly, membrane fouling could occur in the MEUC system after long-term operation. To date,

there are several approaches or achievements in the field that could be adopted in future research. For instance, the potential membrane fouling issue in the MEUC system could be effectively reduced by the development of hybrid membrane-like sulfonated poly(arylene ether sulfone)/polyimide nanofiber composite membrane (Park et al. 2017), functional nanomaterials modified membrane (Li et al. 2013, Meng et al. 2017), Nafion modified membrane (Angioni et al. 2016), and ionic liquid-containing membranes (Koók et al. 2019). In addition, due to the cleaning effect of H_2O_2 and ·OH on the cathode side of the membrane (Meng et al. 2017), choosing suitable wastewater sources (e.g., low solid content and salinity) in the anode can also retard the membrane fouling of anode side and eventually extend the life of the membrane. Secondly, the cost of materials like electrodes should be further reduced. Future work could be dedicated to developing cost-effective electrodes such as using biochar (Huggins et al., 2014). Thirdly, Ca^{2+} and Mg^{2+} precipitation on the cathode electrode surface may occur when the presence of a high amount of Ca^{2+}, Mg^{2+} in real wastewater during long-term operation of the MEUC system. Thus, the acid can be added regularly to eliminate the precipitation. Fourthly, regarding of micropollutants removal, HRTs (2-5 h, 94% removal of carbamazepine within 1 h) applied in this study was higher than that applied in some AOPs at full-scale such as O_3 (13-43 min) (Bourgin et al., 2018), UV/H_2O_2 (5-15 min) (Kim et al., 2009), and Fenton (0.5-2 h) (Bae et al., 2015; Chen et al., 2019). Since HRT can strongly affect the overall costs including the capital, operating, and maintenance costs in a full-scale water treatment system (Shemer et al., 2006), efforts should be made to shorten HRT in the future. Thus, the following measures could be taken to achieve the goal: i) since the remaining H_2O_2 can still be observed in continuous flow (see Fig. S2 and S3), the reactor configuration could be further optimized to improve the conversion efficiency of H_2O_2 into • OH; ii) medium-pressure UV lamps could be used to

replace the low-pressure UV lamps to improve removal efficiency and shorten HRT (Shu et al., 2013); iii) the materials and geometry of the cathode electrode can be further optimized to improve removal efficiency and thereby shortening the HRT. For instance, 3D electrodes with a higher surface area (Chen et al., 2014) or composite cathode involving carbon nanotube (CNT)/γ-FeOOH (Feng et al., 2010) could be adopted in the future study.

4. Conclusions

In this paper, a novel 20 L MEUC system was designed and constructed for the removal of trace pharmaceuticals, such as carbamazepine. The results obtained from batch experiments indicated that carbamazepine can be efficiently removed through the MEUC system. Several key operating parameters including applied voltage, cathodic aeration rate, and HRT were optimized in continuous experiments. Under optimized operating parameters (0.2 V voltage, cathodic aeration rate of 300 mL min^{-1} and HRT of 2 h), fast and efficient removal of carbamazepine was observed in one HRT (98%). Furthermore, the removal of carbamazepine in the MEUC system conformed to pseudo-first-order kinetics and a probable carbamazepine transformation pathway was proposed. Finally, the successful application of the MEUC system to actual wastewater treatment and non-obvious eco-toxicity test results of the effluent during the treatment process also provides feasibility for future commercialization of such technology.

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References

Andreozzi, R., Raffaele, M. and Nicklas, P. 2003a. Pharmaceuticals in STP effluents and their solar photodegradation in aquatic environment. Chemosphere, 50(10), 1319-1330.

Andreozzi, R., Caprio, V., Marotta, R., Vogna, D., 2003b. Paracetamol oxidation from aqueous solutions by means of ozonation and H_2O_2/UV system. Water Res., 37, 993–1004.

Angioni, S., Millia, L., Bruni, G., Tealdi, C., Mustarelli, P. and Quartarone, E. 2016. Improving the performances of Nafion™-based membranes for microbial fuel cells with silica-based, organically-functionalized mesostructured fillers. J. Power Sources, 334, 120-127.

Appavoo, I.A., Hu, J., Huang, Y., Li, S.F.Y., Ong, S.L., 2014. Response surface modeling of Carbamazepine (CBZ) removal by Graphene-P25 nanocomposites/UVA process using central composite design. Water Res., 57, 270–279.

Arola, K., Van der Bruggen, B., Mänttäri, M. and Kallioinen, M. 2019. Treatment options for nanofiltration and reverse osmosis concentrates from municipal wastewater treatment: A review. Crit. Rev. Environ. Sci. Technol., 49(22), 2049-2116.

Bagastyo, A.Y., Radjenovic, J., Mu, Y., Rozendal, R.A., Batstone, D.J. and Rabaey, K. 2011. Electrochemical oxidation of reverse osmosis concentrate on mixed metal oxide (MMO) titanium coated electrodes. Water Res., 45(16), 4951-4959.

Bae, W., Won, H., Hwang, B., de Toledo, R.A., Chung, J., Kwon, K. and Shim, H. 2015. Characterization of refractory matters in dyeing wastewater during a full-scale Fenton process following pure-oxygen activated sludge treatment. J. Hazard. Mater., 287, 421-428.

Begum, S., Ahmaruzzaman, M., 2018. CTAB and SDS assisted facile fabrication of SnO_2 nanoparticles for effective degradation of carbamazepine from aqueous phase: A systematic and comparative study of their degradation performance. Water Res., 129, 470–485.

Behera, S.K., Kim, H.W., Oh, J.-E., Park, H.-S., 2011. Occurrence and removal of antibiotics, hormones and several other pharmaceuticals in wastewater treatment plants of the largest industrial city of Korea. Sci. Total Environ., 409, 4351–4360.

Behnajady, M.A., Modirshahla, N., Shokri, M. and Vahid, B. 2009. Design equation with mathematical kinetic modeling for photooxidative degradation of CI Acid Orange 7 in an annular continuous-flow photoreactor. J. Hazard. Mater., 165(1-3), 168-173.

Bo, L., He, K., Tan, N., Gao, B., Feng, Q., Liu, J., Wang, L., 2017. Photocatalytic oxidation of trace carbamazepine in aqueous solution by visible-light-driven $Znln_2S_4$: performance and mechanism. J. Environ. Manage., 190, 259–265.

Bolton, J.R., Bircher, K.G., Tumas, W. and Tolman, C.A. 2001. Figures-of-merit for the technical development and application of advanced oxidation technologies for both electric- and solar-driven systems (IUPAC Technical Report). Pure. Appl. Chem., 73(4), 627-637.

Bolton, J.R. and Linden, K.G. 2003. Standardization of methods for fluence (UV dose) determination in bench-scale UV experiments. J. Environ. Eng., 129(3), 209-215.

Bouissou-Schurtz, C., Houeto, P., Guerbet, M., Bachelot, M., Casellas, C., Mauclaire, A.-C., Panetier, P., Delval, C., Masset, D., 2014. Ecological risk assessment of the presence of pharmaceutical residues in a French national water survey. Regul. Toxicol. Pharmacol., 69, 296–303.

Bourgin, M., Beck, B., Boehler, M., Borowska, E., Fleiner, J., Salhi, E., Teichler, R., von Gunten, U., Siegrist, H. and McArdell, C.S. 2018. Evaluation of a full-scale wastewater treatment plant upgraded with ozonation and biological post-treatments: Abatement of micropollutants, formation of transformation products and oxidation by-products. Water Res., 129, 486-498.

Brillas, E., Sirés, I., Oturan, M.A., 2009. Electro-Fenton process and related electrochemical technologies based on Fenton's reaction chemistry. Chem. Rev., 109, 6570–6631.

Bu, L., Zhou, S., Zhu, S., Wu, Y., Duan, X., Shi, Z., Dionysiou, D.D., 2018. Insight into carbamazepine degradation by UV/monochloramine: Reaction mechanism, oxidation products, and DBPs formation. Water Res., 146, 288–297.

Buffle, M.-O., Schumacher, J., Salhi, E., Jekel, M., Von Gunten, U., 2006. Measurement of the initial phase of ozone decomposition in water and wastewater by means of a continuous quench-flow system: application to disinfection and pharmaceutical oxidation. Water Res., 40, 1884–1894.

Calisto, V., Domingues, M.R.M., Erny, G.L., Esteves, V.I., 2011. Direct photodegradation of carbamazepine followed by micellar electrokinetic chromatography and mass spectrometry. Water Res., 45, 1095–1104.

Chen, J.-y., Li, N. and Zhao, L. 2014. Three-dimensional electrode microbial fuel cell for hydrogen peroxide synthesis coupled to wastewater treatment. J. Power Sources, 254, 316-322.

Chen, W.-S., Lin, S.-Z., 2009. Destruction of nitrotoluenes in wastewater by Electro-Fenton oxidation. J. Hazard. Mater., 168, 1562–1568.

Chen, Y., Cheng, Y., Guan, X., Liu, Y., Nie, J. and Li, C. 2019. A Rapid Fenton treatment of bio-treated dyeing and finishing wastewater at second-scale intervals: kinetics by stopped-flow technique and application in a full-scale plant. Sci. Rep., 9(1), 1-11.

De la Cruz, N., Giménez, J., Esplugas, S., Grandjean, D., De Alencastro, L. and Pulgarin, C. 2012. Degradation of 32 emergent contaminants by UV and neutral photo-fenton in

domestic wastewater effluent previously treated by activated sludge. Water Res., 46(6), 1947-1957.

Deng, J., Cheng, Y., Lu, Y., Crittenden, J.C., Zhou, S., Gao, N., Li, J., 2017. Mesoporous manganese Cobaltite nanocages as effective and reusable heterogeneous peroxymonosulfate activators for Carbamazepine degradation. Chem. Eng. J., 330, 505–517.

Deng, J., Shao, Y., Gao, N., Xia, S., Tan, C., Zhou, S., Hu, X., 2013. Degradation of the antiepileptic drug carbamazepine upon different UV-based advanced oxidation processes in water. Chem. Eng. J., 222, 150–158.

Ding, Y., Zhang, G., Wang, X., Zhu, L., Tang, H., 2017. Chemical and photocatalytic oxidative degradation of carbamazepine by using metastable Bi^{3+} self-doped $NaBiO_3$ nanosheets as a bifunctional material. Appl. Catal. B Environ., 202, 528–538.

Divyapriya, G., Srinivasan, R., Nambi, I.M., Senthilnathan, J., 2018. Highly active and stable ferrocene functionalized graphene encapsulated carbon felt array-A novel rotating disc electrode for electro-Fenton oxidation of pharmaceutical compounds. Electrochim. Acta, 283, 858–870.

Doll, T.E., Frimmel, F.H., 2005. Cross-flow microfiltration with periodical back-washing for photocatalytic degradation of pharmaceutical and diagnostic residues–evaluation of the long-term stability of the photocatalytic activity of TiO_2. Water Res., 39, 847–854.

Donner, E., Kosjek, T., Qualmann, S., Kusk, K.O., Heath, E., Revitt, D.M., Ledin, A., Andersen, H.R., 2013. Ecotoxicity of carbamazepine and its UV photolysis transformation products. Sci. Total Environ., 443, 870–876.

Feng, L., Van Hullebusch, E.D., Rodrigo, M.A., Esposito, G., Oturan, M.A., 2013. Removal of residual anti-inflammatory and analgesic pharmaceuticals from aqueous systems by electrochemical advanced oxidation processes. A review. Chem. Eng. J., 228, 944–964.

Ganzenko, O., Trellu, C., Papirio, S., Oturan, N., Huguenot, D., Van Hullebusch, E.D., Esposito, G., Oturan, M.A., 2018. Bioelectro-Fenton: evaluation of a combined biological—advanced oxidation treatment for pharmaceutical wastewater. Environ. Sci. Pollut. Res., 25, 20283–20292.

García-Gómez, C., Drogui, P., Zaviska, F., Seyhi, B., Gortáres-Moroyoqui, P., Buelna, G., Neira-Sáenz, C., Estrada-Alvarado, M. and Ulloa-Mercado, R. 2014. Experimental design methodology applied to electrochemical oxidation of carbamazepine using Ti/PbO_2 and Ti/BDD electrodes. J. Electroanal. Chem., 732, 1-10.

Ghasemian, S., Nasuhoglu, D., Omanovic, S. and Yargeau, V. 2017. Photoelectrocatalytic degradation of pharmaceutical carbamazepine using Sb-doped Sn80%-W20%-oxide electrodes. Sep. Purif. Technol., 188, 52-59.

Hiegemann, H., Littfinski, T., Krimmler, S., Lübken, M., Klein, D., Schmelz, K.-G., Ooms, K., Pant, D. and Wichern, M. 2019. Performance and inorganic fouling of a submergible 255 L prototype microbial fuel cell module during continuous long-term operation with real municipal wastewater under practical conditions. Bioresour. Technol., 294, 122227.

H.R. Andersen, K.M.S. Hansen, T. Kosjek, E. Heath, P. Kaas, A. Ledin, Photochemical treatment of pharmaceuticals, in: 6th IWA World Water Congress and Exhibition, Vienna, Austria, 2008.

Hu, D., Li, X., Chen, Z., Cui, Y., Gu, F., Jia, F., Xiao, T., Su, H., Xu, J., Wang, H., 2018. Performance and extracellular polymers substance analysis of a pilot scale anaerobic

membrane bioreactor for treating tetrahydrofuran pharmaceutical wastewater at different HRTs. J. Hazard. Mater., 342, 383–391.

Huggins, T., Wang, H., Kearns, J., Jenkins, P. and Ren, Z.J. 2014. Biochar as a sustainable electrode material for electricity production in microbial fuel cells. Bioresour. Technol., 157, 114-119.

Kanakaraju, D., Glass, B.D., Oelgemöller, M., 2018. Advanced oxidation process-mediated removal of pharmaceuticals from water: A review. J. Environ. Manage. 219, 189–207.

Kang, J.-W., Hung, H.-M., Lin, A., Hoffmann, M.R., 1999. Sonolytic destruction of methyl tert-butyl ether by ultrasonic irradiation: the role of O_3, H_2O_2, frequency, and power density. Environ. Sci. Technol., 33, 3199–3205.

Kim, I., Yamashita, N. and Tanaka, H. 2009. Performance of UV and UV/H_2O_2 processes for the removal of pharmaceuticals detected in secondary effluent of a sewage treatment plant in Japan. J. Hazard. Mater., 166(2-3), 1134-1140.

Kläning, U.K. and Wolff, T. 1985. Laser Flash Photolysis of HClO, ClO^-, HBrO, and BrO^- in Aqueous Solution. Reactions of Cl-and Br-Atoms. Berichte Bunsenges. für Phys. Chem., 89(3), 243-245.

Koók, L., Bakonyi, P., Harnisch, F., Kretzschmar, J., Chae, K.-J., Zhen, G., Kumar, G., Rózsenberszki, T., Tóth, G. and Nemestóthy, N. 2019. Biofouling of membranes in microbial electrochemical technologies: Causes, characterization methods and mitigation strategies. Bioresour. Technol., 279, 327–338.

Kuo, W.G., 1992. Decolorizing dye wastewater with Fenton's reagent. Water Res., 26, 881–886.

Laurencé, C., Rivard, M., Martens, T., Morin, C., Buisson, D., Bourcier, S., Sablier, M., Oturan, M.A., 2014. Anticipating the fate and impact of organic environmental contaminants: a new approach applied to the pharmaceutical furosemide. Chemosphere, 113, 193–199.

Lee, C.O., Howe, K.J. and Thomson, B.M. 2012. Ozone and biofiltration as an alternative to reverse osmosis for removing PPCPs and micropollutants from treated wastewater. Water Res., 46(4), 1005-1014.

Li, J.-H., Shao, X.-S., Zhou, Q., Li, M.-Z. and Zhang, Q.-Q. 2013. The double effects of silver nanoparticles on the PVDF membrane: Surface hydrophilicity and antifouling performance. Appl. Surf. Sci., 265, 663-670.

Li, X., Chen, S., Angelidaki, I., Zhang, Y., 2018. Bio-electro-Fenton processes for wastewater treatment: Advances and prospects. Chem. Eng. J., 354, 492–506.

Li, X., Jin, X., Zhao, N., Angelidaki, I., Zhang, Y., 2017a. Novel bio-electro-Fenton technology for azo dye wastewater treatment using microbial reverse-electrodialysis electrolysis cell. Bioresour. Technol., 228, 322–329.

Li, X., Jin, X., Zhao, N., Angelidaki, I., Zhang, Y., 2017b. Efficient treatment of aniline containing wastewater in bipolar membrane microbial electrolysis cell-Fenton system. Water Res., 119, 67–72.

Liao, C.-H., Kang, S.-F. and Wu, F.-A. 2001. Hydroxyl radical scavenging role of chloride and bicarbonate ions in the H_2O_2/UV process. Chemosphere, 44(5), 1193-1200.

Libralato, G., Annamaria, V.G., Francesco, A., 2010. How toxic is toxic? A proposal for wastewater toxicity hazard assessment. Ecotoxicol. Environ. Saf., 73, 1602–1611.

Linsebigler, A.L., Lu, G., Yates Jr, J.T., 1995. Photocatalysis on TiO_2 surfaces: principles, mechanisms, and selected results. Chem. Rev., 95, 735–758.

Liu, H., Wang, C., Li, X., Xuan, X., Jiang, C., Cui, H., 2007. A novel electro-Fenton process for water treatment: reaction-controlled pH adjustment and performance assessment. Environ. Sci. Technol., 41, 2937–2942.

Liu, K., Yu, J.C.-C., Dong, H., Wu, J.C.S., Hoffmann, M.R., 2018. Degradation and Mineralization of Carbamazepine Using an Electro-Fenton Reaction Catalyzed by Magnetite Nanoparticles Fixed on an Electrocatalytic Carbon Fiber Textile Cathode. Environ. Sci. Technol., 52, 12667–12674.

Liu, N., Zheng, M., Sijak, S., Tang, L., Xu, G. and Wu, M. 2015. Aquatic photolysis of carbamazepine by UV/H_2O_2 and UV/Fe (II) processes. Res. Chem. Intermed., 41(10), 7015-7028.

Loos, R., Carvalho, R., António, D.C., Comero, S., Locoro, G., Tavazzi, S., Paracchini, B., Ghiani, M., Lettieri, T. and Blaha, L. 2013. EU-wide monitoring survey on emerging polar organic contaminants in wastewater treatment plant effluents. Water Res., 47(17), 6475-6487.

Martínez-Huitle, C.A., Rodrigo, M.A., Sirés, I., Scialdone, O., 2015. Single and coupled electrochemical processes and reactors for the abatement of organic water pollutants: a critical review. Chem. Rev., 115, 13362–13407.

Mcdowell, D.C., Huber, M.M., Wagner, M., von Gunten, U., Ternes, T.A., 2005. Ozonation of carbamazepine in drinking water: identification and kinetic study of major oxidation products. Environ. Sci. Technol., 39, 8014–8022.

Meng, F., Zhang, S., Oh, Y., Zhou, Z., Shin, H.-S. and Chae, S.-R. 2017. Fouling in membrane bioreactors: an updated review. Water Res., 114, 151-180.

Miklos, D.B., Remy, C., Jekel, M., Linden, K.G., Drewes, J.E. and Hübner, U. 2018. Evaluation of advanced oxidation processes for water and wastewater treatment–A critical review. Water Res., 139, 118-131.

Mohapatra, D., Brar, S., Tyagi, R., Picard, P. and Surampalli, R. 2012. Carbamazepine in municipal wastewater and wastewater sludge: ultrafast quantification by laser diode thermal desorption-atmospheric pressure chemical ionization coupled with tandem mass spectrometry., Talanta 99, 247-255.

Monteil, H., Péchaud, Y., Oturan, N., Oturan, M.A., 2019. A review on efficiency and cost effectiveness of electro-and bio-electro-Fenton processes: application to the treatment of pharmaceutical pollutants in water. Chem. Eng. J., 376, 119577.

Moreira, F.C., Boaventura, R.A.R., Brillas, E., Vilar, V.J.P., 2017. Electrochemical advanced oxidation processes: a review on their application to synthetic and real wastewaters. Appl. Catal. B Environ., 202, 217–261.

Nadais, H., Li, X., Alves, N., Couras, C., Andersen, H.R., Angelidaki, I., Zhang, Y., 2018. Bio-electro-Fenton process for the degradation of Non-Steroidal Anti-Inflammatory Drugs in wastewater. Chem. Eng. J., 338, 401–410.

Nidheesh, P. V, Zhou, M., Oturan, M.A., 2018. An overview on the removal of synthetic dyes from water by electrochemical advanced oxidation processes. Chemosphere 197, 210–227.

Olmez-Hanci, T., Arslan-Alaton, I., 2013. Comparison of sulfate and hydroxyl radical based advanced oxidation of phenol. Chem. Eng. J., 224, 10–16.

Olmez-Hanci, T., Dursun, D., Aydin, E., Arslan-Alaton, I., Girit, B., Mita, L., Diano, N., Mita, D.G., Guida, M., 2015. $S_2O_8^{2-}$/UV-C and H_2O_2/UV-C treatment of Bisphenol A:

Assessment of toxicity, estrogenic activity, degradation products and results in real water. Chemosphere, 119, S115–S123.

Oturan, M.A., Sirés, I. and Zhou, M. 2018. Electro-Fenton Process: New Trends and Scale-Up, Springer.

Pan, Y., Cheng, S., Yang, X., Ren, J., Fang, J., Shang, C., Song, W., Lian, L., Zhang, X., 2017. UV/chlorine treatment of carbamazepine: Transformation products and their formation kinetics. Water Res., 116, 254–265.

Park, S.-G., Chae, K.-J. and Lee, M. 2017. A sulfonated poly (arylene ether sulfone)/polyimide nanofiber composite proton exchange membrane for microbial electrolysis cell application under the coexistence of diverse competitive cations and protons. J. Membr. Sci., 540, 165-173.

Parvez, S., Venkataraman, C., Mukherji, S., 2006. A review on advantages of implementing luminescence inhibition test (Vibrio fischeri) for acute toxicity prediction of chemicals. Environ. Int., 32, 265–268.

Pearce, R.E., Vakkalagadda, G.R., Leeder, J.S., 2002. Pathways of carbamazepine bioactivation in vitro I. Characterization of human cytochromes P450 responsible for the formation of 2- and 3-hydroxylated metabolites. Drug Metab. Dispos., 30, 1170–1179.

Peñate, B. and García-Rodríguez, L. 2012. Current trends and future prospects in the design of seawater reverse osmosis desalination technology. Desalination, 284, 1-8.

Plakas, K. V, Sklari, S.D., Yiankakis, D.A., Sideropoulos, G.T., Zaspalis, V.T., Karabelas, A.J., 2016. Removal of organic micropollutants from drinking water by a novel electro-Fenton filter: pilot-scale studies. Water Res., 91, 183–194.

Rossi, R., Jones, D., Myung, J., Zikmund, E., Yang, W., Gallego, Y.A., Pant, D., Evans, P.J., Page, M.A. and Cropek, D.M. 2019. Evaluating a multi-panel air cathode through electrochemical and biotic tests. Water Res., 148, 51-59.

Shemer, H., Kunukcu, Y.K. and Linden, K.G. 2006. Degradation of the pharmaceutical metronidazole via UV, Fenton and photo-Fenton processes. Chemosphere, 63(2), 269-276.

Shu, Z., Bolton, J.R., Belosevic, M. and El Din, M.G. 2013. Photodegradation of emerging micropollutants using the medium-pressure UV/H_2O_2 advanced oxidation process. Water Res., 47(8), 2881-2889.

Simazaki, D., Kubota, R., Suzuki, T., Akiba, M., Nishimura, T., Kunikane, S., 2015. Occurrence of selected pharmaceuticals at drinking water purification plants in Japan and implications for human health. Water Res., 76, 187–200.

Somathilake, P., Dominic, J.A., Achari, G., Langford, C.H., Tay, J.-H., 2019. Influence of UV dose on the UV/H_2O_2 process for the degradation of carbamazepine in wastewater. Environ. Technol., 40, 3031–3039.

Vasiliadou, I., Molina, R., Martínez, F. and Melero, J. 2014. Experimental and modeling study on removal of pharmaceutically active compounds in rotating biological contactors. J. Hazard. Mater., 274, 473-482.

Vogna, D., Marotta, R., Andreozzi, R., Napolitano, A., d'Ischia, M., 2004. Kinetic and chemical assessment of the UV/H_2O_2 treatment of antiepileptic drug carbamazepine. Chemosphere, 54, 497–505.

Voutchkov, N. 2018. Energy use for membrane seawater desalination–current status and trends. Desalination 431, 2-14.

Wang, L., Lu, W., Ni, D., Xu, T., Li, N., Zhu, Z., Chen, H., Chen, W., 2017. Solar-initiated photocatalytic degradation of carbamazepine on excited-state hexadecachlorophthalocyanine in the presence of peroxymonosulfate. Chem. Eng. J., 330, 625–634.

Wang, W.-L., Wu, Q.-Y., Li, Z.-M., Lu, Y., Du, Y., Wang, T., Huang, N. and Hu, H.-Y. 2017. Light-emitting diodes as an emerging UV source for UV/chlorine oxidation: carbamazepine degradation and toxicity changes. Chem. Eng. J., 310, 148-156.

Wang, W., Lu, Y., Luo, H., Liu, G., Zhang, R. and Jin, S. 2018. A microbial electro-fenton cell for removing carbamazepine in wastewater with electricity output. Water Res. 139, 58-65.

Werner, C.M., Hoppe-Jones, C., Saikaly, P.E., Logan, B.E. and Amy, G.L. 2015. Attenuation of trace organic compounds (TOrCs) in bioelectrochemical systems. Water Res., 73, 56-67.

Wu, T. and Englehardt, J.D. 2012. A new method for removal of hydrogen peroxide interference in the analysis of chemical oxygen demand. Environ. Sci. Technol. 46(4), 2291-2298.

Yu, X., Gocze, Z., Cabooter, D. and Dewil, R. 2020. Efficient reduction of carbamazepine using UV-activated sulfite: Assessment of critical process parameters and elucidation of radicals involved. Chem. Eng. J., 126403.

Yu X, Zhou M, Ren G, Ma L. 2015. A novel dual gas diffusion electrodes system for efficient hydrogen peroxide generation used in electro-Fenton. Chem. Eng. J., 263, 92-100.

Yuan, G.-E., Li, Y., Lv, J., Zhang, G. and Yang, F. 2017. Integration of microbial fuel cell and catalytic oxidation reactor with iron phthalocyanine catalyst for Congo red degradation. Biochem. Eng. J., 120, 118-124.

Zaied, B., Rashid, M., Nasrullah, M., Zularisam, A., Pant, D. and Singh, L. 2020. A comprehensive review on contaminants removal from pharmaceutical wastewater by electrocoagulation process. Sci. Total Environ., 138095.

Zhang, L., Zhao, X., Niu, C., Tang, N., Guo, H., Wen, X., Liang, C., Zeng, G., 2019. Enhanced activation of peroxymonosulfate by magnetic Co_3MnFeO_6 nanoparticles for removal of carbamazepine: Efficiency, synergetic mechanism and stability. Chem. Eng. J., 362, 851–864.

Zhang, W., Zhou, S., Sun, J., Meng, X., Luo, J., Zhou, D. and Crittenden, J. 2018. Impact of chloride ions on UV/H_2O_2 and UV/persulfate advanced oxidation processes. Environ. Sci. Technol., 52(13), 7380-7389.

Zhang, Y. and Angelidaki, I. 2016. Microbial electrochemical systems and technologies: it is time to report the capital costs. Environ. Sci. Technol., 50 (11), 5432-5433.

Zhang, Y., Wang, Y., Angelidaki, I., 2015. Alternate switching between microbial fuel cell and microbial electrolysis cell operation as a new method to control H_2O_2 level in Bioelectro-Fenton system. J. Power Sources, 291, 108–116.

Zhang, Y., Geißen, S.-U., Gal, C., 2008. Carbamazepine and diclofenac: removal in wastewater treatment plants and occurrence in water bodies. Chemosphere, 73, 1151–1161.

Zhou, L., Zhou, M., Zhang, C., Jiang, Y., Bi, Z., Yang, J., 2013. Electro-Fenton degradation of p-nitrophenol using the anodized graphite felts. Chem. Eng. J., 233, 185–192.

Zhou, S., Huang, S., Li, X., Angelidaki, I., Zhang, Y., 2018. Microbial electrolytic disinfection process for highly efficient Escherichia coli inactivation. Chem. Eng. J., 342, 220–227.

Zhu, S., Dong, B., Wu, Y., Bu, L., Zhou, S., 2019. Degradation of carbamazepine by vacuum-UV oxidation process: Kinetics modeling and energy efficiency. J. Hazard. Mater., 368, 178–185.

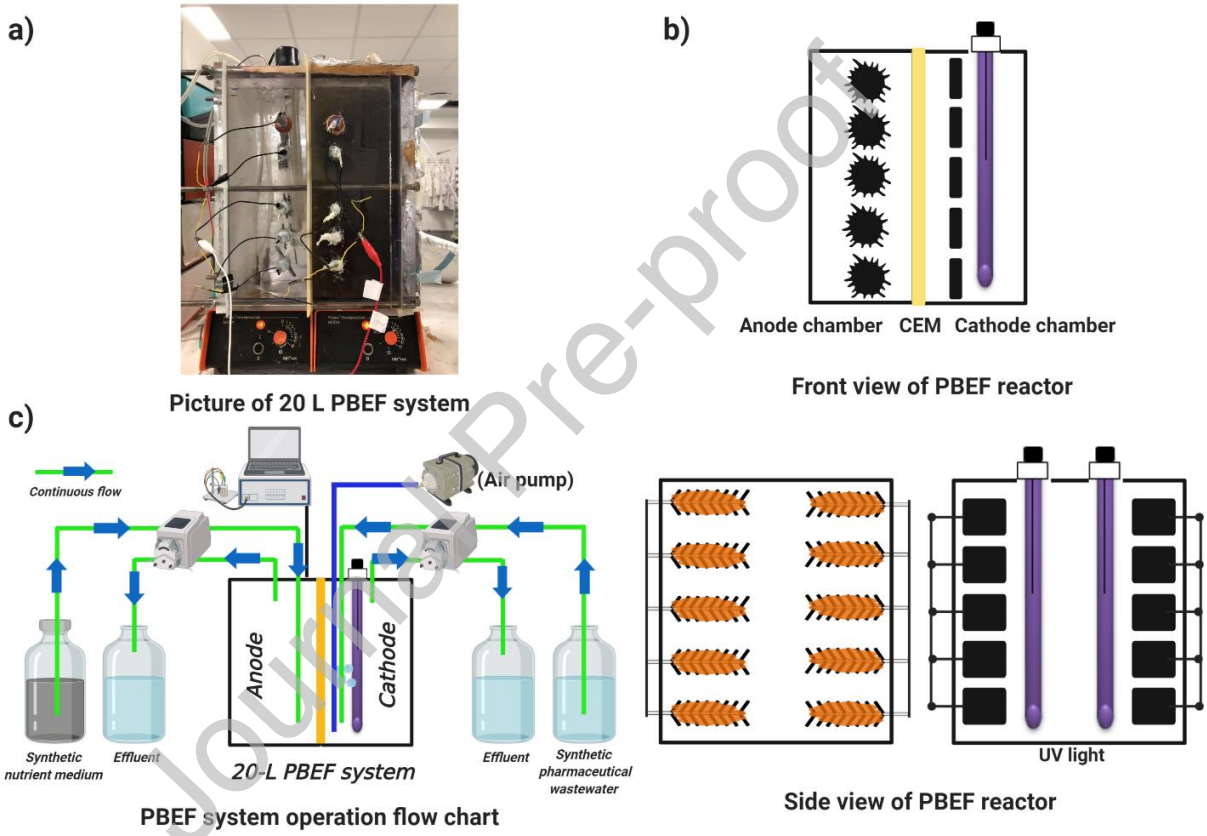

Fig.1. Schematic diagram and flowchart of the 20 L MEUC system. (a) Picture of 20 L MEUC system. (b) Schematic diagram of electrodes and UV lamps arrangement. (c) Flowchart of 20 L MEUC system.

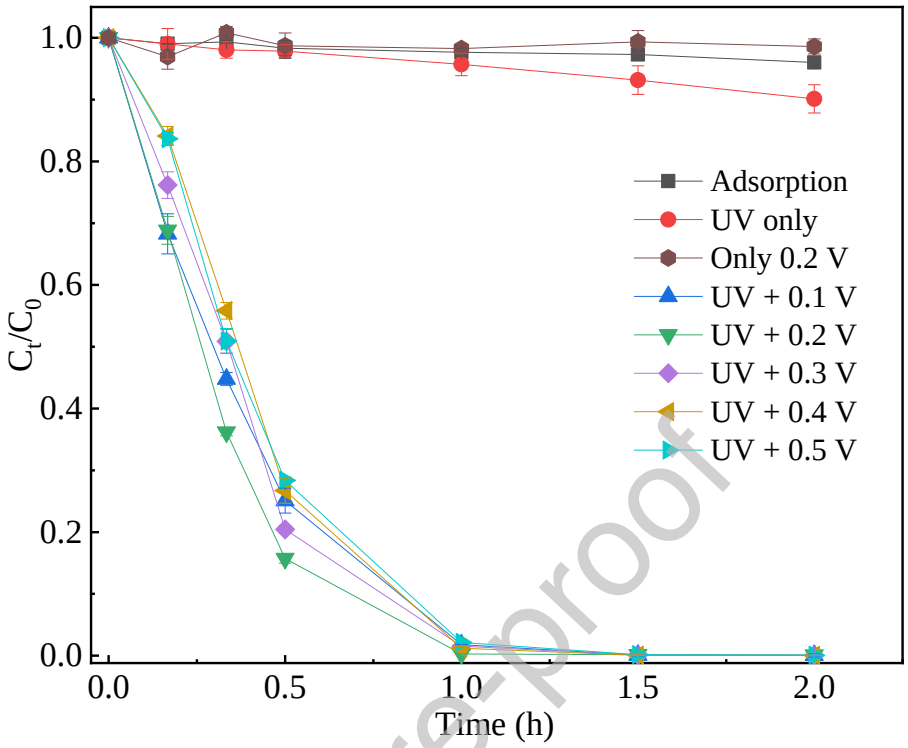

Fig.2. The MEUC system feasibility verification under batch mode. System operational parameters: carbamazepine of 500 μg L^{-1}, UV intensity of 48 μW cm^{-2}, Na_2SO_4 of 50 mM, applied voltage of 0.2 V (for the control experiment) and airflow rate of 0.033 mL min^{-1} mL^{-1}.

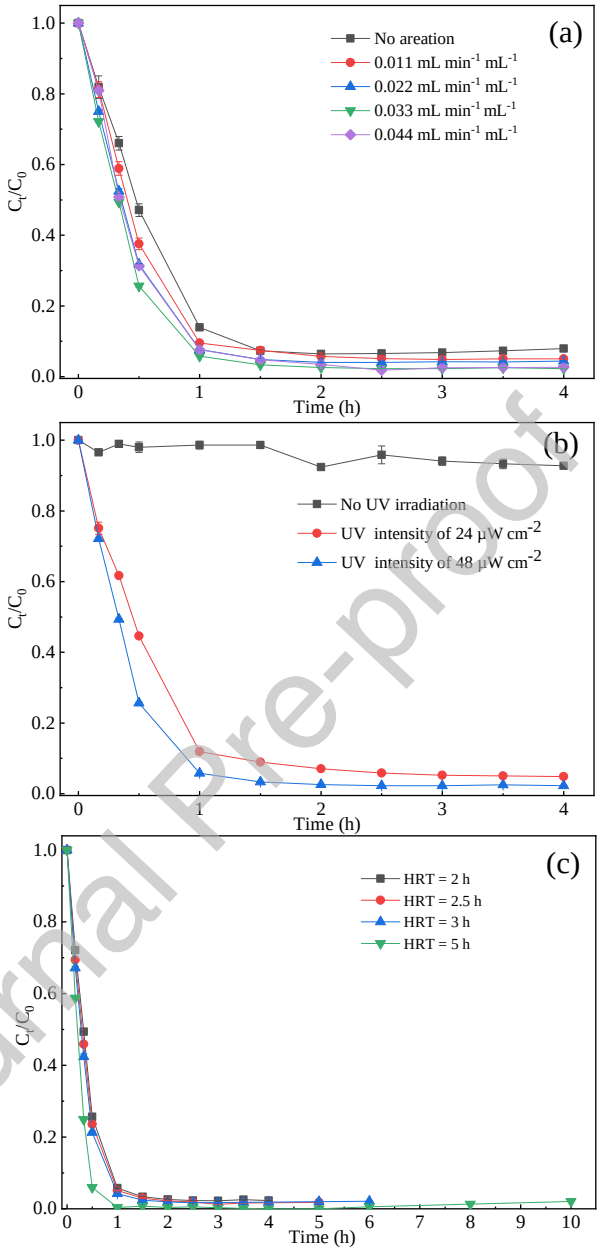

Fig. 3. The effect of operating parameters including (a) cathodic aeration rate, (b) UV intensity, and (c) HRT on system performance under continuous mode. System operational parameters: carbamazepine of 500 μg L^{-1}, airflow rate of 0, 0.011, 0.022, 0.033 and 0.044 mL min^{-1} mL^{-1}, UV intensity of 0, 24 and 48 μW cm^{-2}, Na_2SO_4 of 50 mM, applied voltage of 0.2 V and HRT of 2, 2.5, 3 and 5 h.

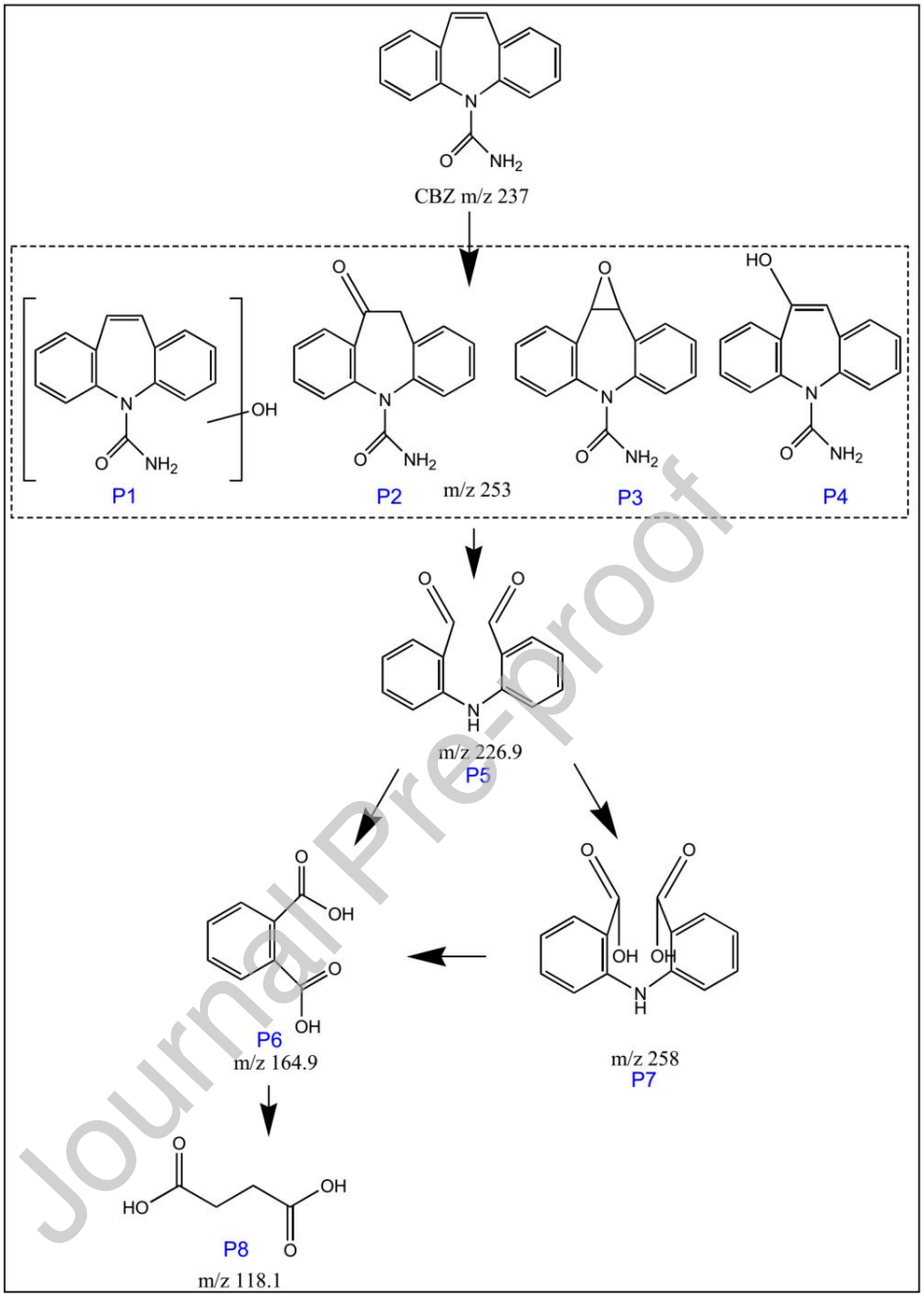

Fig.4. Proposed carbamazepine transformation pathway in the MEUC system.

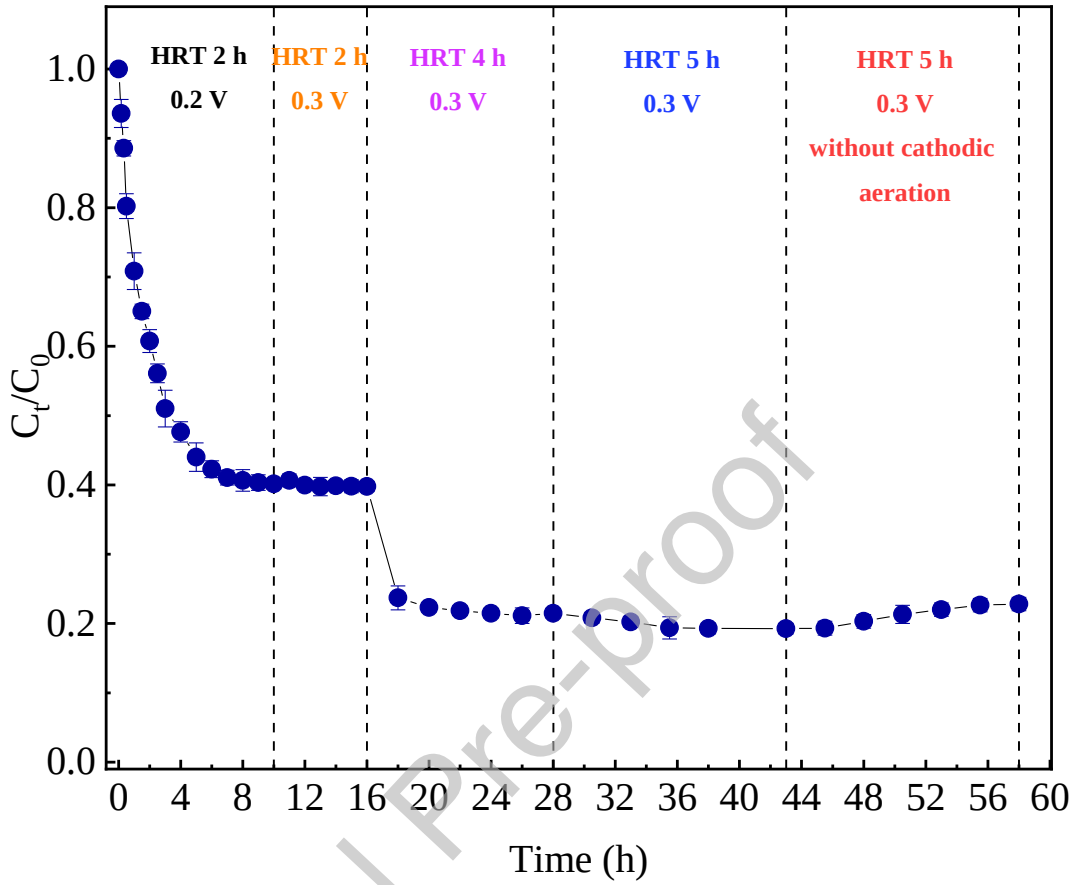

Fig.5. The effect of real wastewater on system performance under continuous mode. System operational parameters: carbamazepine of 500 µg L^{-1}, UV intensity of 48 µW cm^{-2}, applied voltage of 0.2 and 0.3 V, HRT of 2, 4 and 5 h and airflow rate of 0 and 0.033 mL min^{-1} mL^{-1}.

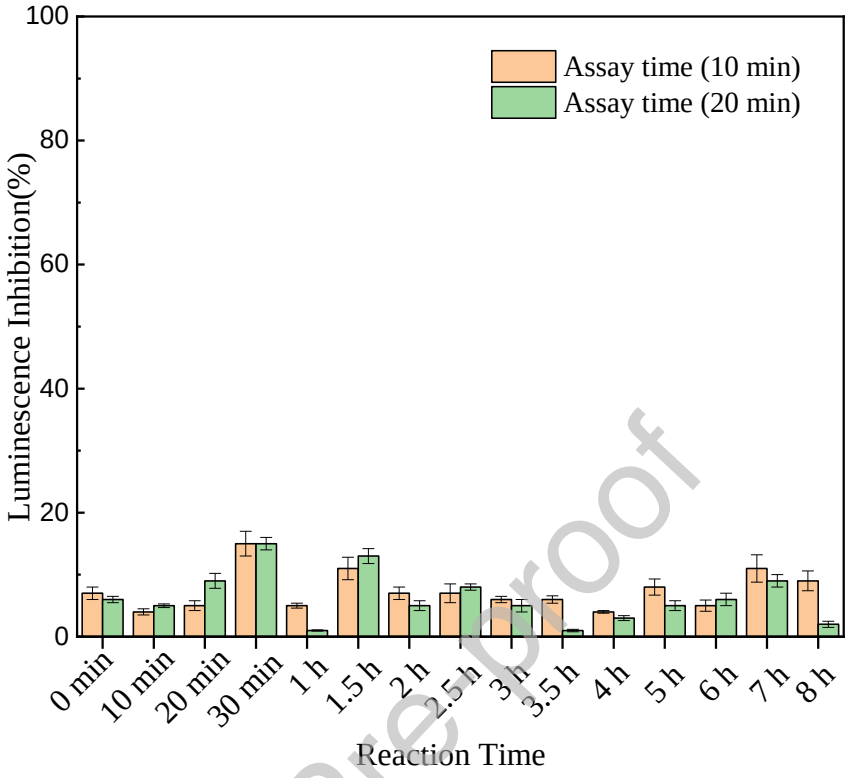

Fig.6. The eco-toxicity test at two assay times (10 and 20 min) in terms of inhibition (%) of the luminescence of bacteria Vibrio Fischeri during the degradation of carbamazepine by this MEUC system. System operational parameters: carbamazepine of 500 µg L^{-1} spiked in the real wastewater, UV intensity of 48 µW cm^{-2}, applied voltage of 0.2 V, HRT of 2 h and airflow rate of 0.033 mL min^{-1} mL^{-1}.

Table 1. carbamazepine degradation by using various treatment technologies in previous studies.

Treatment technologies	Initial concentration (μg L^{-1})	Degradation efficiency	Energy consumption (E/EO, kWh m^{-3})	Reactor volume (mL)	Operation mode	Reference
UV/Fe(II)	2000	100% in 60 min	576	80	batch	(Liu et al., 2015)
UV/sulfite	5000	100% in 20 min	10	800	batch	(Yu et al., 2020)
UV/NH_2Cl	1185	90%	2.5	_	batch	(Bu et al., 2018)
UV and UV/H_2O_2	10	90%	22.7 and 3.7	_	batch	(Andersen et al., 2008)
Photoelectrocatalytic process by using Sb-doped Sn80%-W20%-oxide electrodes	200	90%	32 (photolytic), 24 (photocatalytic), and 2 (photoelectrocatalytic)	900	batch	(Ghasemian et al., 2017)
Electrolysis with a boron-doped diamond electrode and PbO_2 electrode	10000	89.33% in 101 min and 81.52% in 120 min	40 and 44	650	batch	(García-Gómez et al., 2014)
LED UV/Cl_2	3351	96% in 10 min	1.5-1.6	50	batch	(Wang et al., 2017)
Fe_3O_4-NP@CNF catalyzed EF	1000	100% in 30 min	0.239	50	batch	(Liu et al., 2018)
Microbial electro-Fenton cell (MeFC) and EF	10000	90% (MeFC) and 62% (EF) in 24 h	4.15 (EF)	28	batch	(Wang et al., 2018)
non-sterile fungal bioreactor	5000	47% in 168 h	_	2000	continuous	(Zhang and Geißen, 2012)
Biological treatment using MFC	50	80% in 24 h	_	28	batch	(Werner et al., 2015)
Rotating biological contactors	20	85% in 240 h	_	24500	continuous	(Vasiliadou et al., 2014)
MEUC process	500	94% in 60 min and 98% in 120 min	6.069 (1.518[a])	20000	continuous	In this study

⁻ Not reported in the paper a-Only considering energy consumption of the MEUC reactor

Declaration of interests

☒ 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.

Graphical