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A proof of concept study for wastewater reuse using bioelectrochemical processes combined with complementary post-treatment technologies

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Abstract

This article describes a proof-of-concept study designed for the reuse of wastewater using microbial electrochemical cells (MECs) combined with complementary post-treatment technologies. This study mainly focused on how the integrated approach works effectively for wastewater reuse. In this study, microalgae and ultraviolet C (UVC) light were used for advanced wastewater treatment to achieve site-specific treatment goals such as agricultural reuse and aquifer recharge. The bio-electrosynthesis of H₂O₂ in MECs was carried out based on a novel concept to integrate with UVC, especially for roust removal of trace organic compounds (TOrcs) resistant to biodegradation, and the algal treatment was configured for nutrient removal from MEC effluent. UVC irradiation has also proven to be an effective disinfectant for bacteria, protozoa, and viruses in water. The average energy consumption rate for MECs fed acetate-based synthetic wastewater was 0.28±0.01 kWh per kg of H₂O₂, which was significantly more efficient than are conventional electrochemical processes. MECs achieved 89±2% removal of carbonaceous organic matter (measured as chemical oxygen demand) in the wastewater (anolyte) and concurrent production of H₂O₂ up to 222±11 mg L⁻¹ in the tapwater (catholyte). The nutrients (N and P) remaining after

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Conflicts of interest

There are no conflicts of interest to declare.

MECs were successfully removed by subsequent phycoremediation with microalgae when aerated (5% CO₂, v/v) in the light. This complied with discharge permits that limit N to 20 mg L⁻¹ and P to 0.5 mg L⁻¹ in the effluent. H₂O₂ produced on site was used to mediate photolytic oxidation with UVC light for degradation of recalcitrant TORCs in the algal-treated wastewater. Carbamazepine was used as a model compound and was almost completely removed with an added 10 mg L⁻¹ of H₂O₂ at a UVC dose of 1000 mJ cm⁻². These results should not be generalized, but critically discussed, because of the limitations of using synthetic wastewater.

Keywords

hydrogen peroxide; microbial electrochemical cells; phycoremediation; advanced oxidation process; trace organic compounds

1. Introduction

Wastewater reclamation is of the utmost concern today to overcome the current water shortage that is aggravated by climate change and increasing population. High-pressure membrane technologies have been coupled with post-disinfection for the direct reuse of secondary effluent from municipal wastewater treatment plants,¹ despite the major drawbacks of high operating cost (derived from high energy input) and refractory concentrate production. Alternatively, domestic wastewater properly treated could be recharged to suitable aquifers for subsequent recovery (indirect reuse) after holding the water for a time.² Such managed aquifer recharge is a natural water treatment process by which pollutants are removed by taking surface water or well-treated domestic wastewater into an aquifer for a long time and recovering it as drinking water or for irrigation purposes *via* a production well. This technique is considered to be environmentally friendly and cost-effective, but there are trace organic compounds (TORCs) that are incompletely removed or not removed in the aquifer.³

Biological processing for domestic wastewater treatment generally focuses on removing biodegradable organic carbon and inorganic nutrients, and a broad range of TORCs are removed with various degrees of success during the treatment.⁴ Thereby, this can lead to accumulation of non- or slowly biodegradable compounds and their persistent metabolites in the effluent. Non-regulated TORCs, including pharmaceuticals, illicit drugs, and personal-care products, are ubiquitous in the aquatic environment, mainly derived from the discharge of secondary effluent from municipal wastewater treatment plants.⁵ This constitutes a major concern for wastewater reuse, associated with the possible ecological impact on biota within the environment. A review of the relevant literature demonstrates that the application of advanced oxidation processes (AOPs) is required to effectively remove TORCs. Of the processes studied, only the commercially available AOPs can be considered for full-scale treatment, and they typically include UV- and O₃-based technologies.⁶ Lee *et al.* (2016)⁷ investigated several oxidation processes at a bench-scale level and demonstrated their effectiveness in increasing the removal of persistent organic contaminants from wastewater effluents. A similar conclusion was also drawn by Liu *et al.* (2018).⁸ In the context of minimizing the contaminants of emerging concerns, it is important not to form toxic

oxidation byproducts as effectively as removing TOrCs from wastewater. The formation of toxic byproducts is typically less of an issue for UV/H₂O₂. Despite the advantage of UV/H₂O₂, its application is often limited because H₂O₂ is a relatively expensive agent for the treatment of large volumes of water and not readily used at wastewater treatment plants. In order to overcome such limitation, an alternative strategy is proposed and evaluated in a later section of this paper.

Microbial electrochemical cells (MECs) have a dual function of contaminant removal and resource recovery from organic-rich wastewater and are considered to be a sustainable method for energy-efficient wastewater treatment.⁹ In MECs producing H₂O₂, the organic substrates are oxidized by anode-respiring bacteria at the anode to produce electrons. The produced electrons can be transferred through an external circuit to the air-permeable cathode where oxygen is reduced to H₂O₂. Several studies have demonstrated the H₂O₂-producing MECs.^{10–12} H₂O₂ produced by a cathodic reaction in MECs can be directly used in a variety of applications in wastewater treatment, such as odor control, membrane cleaning, and sludge pretreatment.^{13–15} Moreover, the decomposition of H₂O₂ has been successfully used as a significant source of hydroxyl radicals in numerous studies of AOPs (e.g., UVC/H₂O₂, O₃/H₂O₂, and Fe(II)/H₂O₂). Hydroxyl radicals are produced from H₂O₂ *via* different pathways and with different efficiencies that depend on the nature of the catalyst involved.¹⁵ This paper discusses the use of ultraviolet C (UVC) to catalyze production of high-powered hydroxyl radicals from H₂O₂ produced on site in MECs. This approach could achieve greater reliability for removal of TOrCs that are resistant to biological degradation. Carbamazepine is hardly removed by biological activities during slow bio-filtration,^{3, 16} bioelectrochemical treatment,¹⁷ or algal treatment.¹⁸ Carbamazepine, diclofenac, clofibric acid, and gembrozil are known to be recalcitrant toward biodegradation in the nitrification/denitrification of wastewater,^{19, 20} and among these, carbamazepine requires the highest UVC dose to be degraded by > 90%.²¹ In this study, carbamazepine was used as an effectiveness indicator of oxidation capacity in AOPs using UVC/H₂O₂.

Conventional biological processes involve the production of an activated mass of microorganisms capable of aerobic stabilization of organic substrates in wastewater. These processes require a robust aeration to sustain the microorganisms actively in the system, typically accounting for 45–75% of total energy consumption.²² In contrast, microbial electrochemical treatment is arguably the most energy efficient strategy to stabilize biodegradable organic compounds from a wide range of wastewaters. The main advantages of using MECs in wastewater treatment come from the savings of aeration energy and biomass disposal.²² Microbial electrochemical systems convert carbonaceous organic matter in wastewater into an electric current using bioanodes under the given conditions. Thus, they are generally efficient for meeting the limit of organic removal (depending on biochemical or chemical oxygen demands), but are ineffective for removing nutrients (N and P) from the wastewater unless there is an additional cathodic reaction. Some investigators have reported that nitrogen can also be decreased to some extent by the migration of ammonium ions (NH₄⁺) across the cationic exchange membrane to the catholyte.²³ For a full-scale treatment system, nutrient-rich wastewater should be properly treated before it is discharged into the receiving water bodies. The microbial electrochemical system is a highly promising technology for the treatment of organic-rich wastewater and can be beneficially combined

with microalgae for nutrient removal from MEC effluent. The algal-mediated treatment is considered to be a promising alternative for the removal of inorganic nutrients, organic components, metallic ions, and emerging contaminants from a wide range of wastewaters.²⁴ To date, we have screened diverse algal species to assess their adaptability in the context of phycoremediation, selected the best candidates based on several criteria, and applied them to the treatment of a wide range of refractory wastewaters.²⁵ This paper discusses the feasibility of using phycoremediation with microalgae to achieve greater reliability for compliance with nutrient goals, especially by replacing conventional biological nutrient removal (BNR) processes.

Various integrated treatment strategies combined with complementary technologies for removing the compounds of emerging concern should be considered and investigated to minimize the adverse effects on the environment that are associated with wastewater reuse. Therefore, the objective of this research was to investigate a novel process configuration for wastewater reuse to achieve the following goals during treatment of synthetic domestic wastewater: (1) consistent bioelectrosynthesis of H_2O_2 and concurrent removal of carbonaceous organic matter; (2) photochemical oxidation of recalcitrant TOrCs using UVC/ H_2O_2 ; (3) increased biodegradability of effluent organic matter prior to artificial aquifer recharge; (4) robust removal of inorganic nutrients (N and P) when required to comply with the discharge permit standards. For these purposes, this study integrated MECs, photolytic oxidation, and algal treatment. To the best of our knowledge, the process configuration investigated in this study has not been proposed for wastewater reuse, which typically requires membrane-based tertiary treatment. One could say that extensive studies have already been carried out with each of the elements of this treatment processes. However, this work connects them with one another systematically to complement each other and maximize system performance. This is significant, as our strategy produces a useful chemical for the purpose of on-site use (e.g., advanced oxidation and disinfection), employs living components that are capable of reproduction and substrate uptake, and is designed to be operated with high flexibility to meet diverse desires of the end user.

2. Materials and methods

Experiments were conducted in three phases (see Fig. 1): (1) MECs were constructed and operated to assess the effectiveness of H_2O_2 production and organic removal from synthetic domestic wastewater; (2) MEC effluent was further treated with microalgae for evaluation of nutrient removal; (3) the algal-treated wastewater was then subjected to photolytic oxidation (UVC/ H_2O_2) for removal of non- or slowly biodegradable compounds. The performance of the hybridized processes was evaluated in terms of the removal of chemical oxygen demand (COD), total nitrogen (TN), total phosphorus (TP), dissolved organic carbon (DOC), UV absorbance at 254 nm (UV_{254}), and TOrCs. The MEC performance was also quantified by H_2O_2 productivity, energy consumption, Coulombic efficiency, and conversion efficiency (from Coulombs to H_2O_2). Multi-spectroscopic characterization of effluent organic matter was done to assess the biodegradability of dissolved organic matter during wastewater treatment.

2.1. MEC configuration and operation

Unless specified otherwise, all chemicals used in this study were of analytical grade and were supplied by Sigma-Aldrich (St. Louis, MO, USA). Each chamber of the MECs was made from plexiglass with cubical and cylindrical shapes from the inner side (effective volume 29 mL). Heat-treated carbon brushes supplied by Mill-Rose Co. (25 mm diameter $\times$ 25 mm length) were used as an anode.²⁶ The air-diffusion cathodes (surface area 7 cm²) were made from 30% wet-proofed carbon cloths (Fuel Cell Earth, LLC., USA) containing four diffusion layers on the air-exposed side.²⁷ The diffusion layers were made by brushing a 60% polytetrafluoroethylene solution onto the cathode surface, followed by drying and heating at 370 °C for 10 min. No catalyst layer was applied on the liquid-exposed side for H₂O₂ production.

The biofilm on the anode carbon brush was pre-acclimated at 1 kΩ in single-chamber microbial fuel cells (MFCs) with the inoculum collected from a wastewater treatment plant in Jeju City. The medium used in the inoculation step was composed of (per L of deionized water) 1.5 g CH₃COONa, 0.31 g NH₄Cl, 0.13 g KCl, 4.57 g Na₂HPO₄, and 2.45 g NaH₂PO₄·2H₂O. Trace minerals and vitamins were also added to the medium as previously reported.²⁸ Once the voltage of the MFCs, measured using a Keithley 2700 multimeter, showed consistent trends over the course of fed-batch cycles, the single-chamber MFCs were restructured into dual chambers, separated by a cation-exchange membrane (CEM) (Neosepta CMX, ASTOM Corp., Japan), and three replicate reactors were operated as an MEC mode for H₂O₂ production. The anodic chamber of the dual MECs was fed with synthetic domestic wastewater, of which the composition was (per L of deionized water) 0.250 g CH₃COONa, 0.153 g NH₄Cl, 0.13 g KCl, and 0.0267 g NaH₂PO₄·2H₂O along with trace minerals and vitamins.²⁸ In addition to these substrates, 50 mM NaHCO₃ was also used as a buffer to consistently maintain pH (initial pH: 7.3 $\pm$ 0.1). The anode medium was purged with N₂ (99.99%) for 10–15 min prior to initiating the test, and the cathodic chamber was filled with tapwater. Ag/AgCl reference electrodes (RE-1B, ALS Co., Ltd., Japan) were placed in the anodic and cathodic chambers to fix anode potential at –0.4 V (relative to the Ag/AgCl reference electrode) and measure cathode potential using an Ivium-n-Stat potentiostat (Ivium Technologies B.V., The Netherlands) (see ESI† Fig. S1). All electrode potentials are given here vs Ag/AgCl.

Three replicate MEC reactors were operated in batch mode for 24 h, and the H₂O₂ concentration of the catholyte was measured at 0, 6, 12, and 24 h using the vandate method.²⁹ We ran the reactors in a temperature-controlled room at 30 °C as previously reported.^{12, 30, 31} The current density was calculated from the charge production (current over time) divided by the projected surface area of the air-diffusion cathode. The performance of the MECs was evaluated in terms of Coulombic efficiency, H₂O₂ conversion efficiency, and energy input as previously described (see ESI† eqn (S1) – (S3)).¹⁰ The H₂O₂ solution in the cathodic chamber was collected at the end of the MEC runs to be used in further UVC treatment, as described in section 2.3.

2.2. Phycoremediation of MEC effluent with microalgae

2.2.1. Preparation of synthetic bio-effluent—In order to obtain enough test wastewater for algal treatment, the MEC effluent was artificially prepared by manipulating the composition of synthetic domestic wastewater designed for MEC runs. Identical chemicals were used except for the organic substrate. Humic acid (30%) was blended with dextran (70%) to simulate wastewater effluent organic matter based on the findings reported by Vakondios *et al.* (2014).³² The organic mixture was then used to prepare a synthetic bio-effluent instead of using sodium acetate. Dextran has been frequently used as a good surrogate for polysaccharide-like substances that are present in secondary effluent,³³ and humic-like substances are typically refractory to microbial degradation, biogenic, and yellow-colored organic acids. The COD, TN, TP, DOC, and UV₂₅₄ in the synthetic bio-effluent were 19 ± 1 mg L⁻¹, 35 ± 2 mg L⁻¹, 5.6 ± 0.8 mg L⁻¹, 6.48 ± 0.52 mg L⁻¹, and 0.27 ± 0.03 cm⁻¹, respectively. The final concentrations of those parameters were selected based on the removal of organic and inorganic components with MECs, similar to previously reported observations with an anaerobic biofilm reactor for domestic wastewater treatment.³⁴

Dichromate, persulfate digestion, and acid persulfate digestion were employed to measure the COD, TN, and TP in the water samples using a DR/5000 spectrophotometer. The DOC was measured (TOC-V CPN, Shimadzu, Japan) to obtain the specific UV absorbance (SUVA) value, which is calculated from the UV₂₅₄ divided by the DOC of the water sample. SUVA has been adopted to estimate the condensation degree of organic structures, which is strongly correlated with the extent of electron-rich sites, such as aromatic functional groups and double-bonded carbon groups in an organic molecule.³⁵ The fluorescence spectra were collected using a Shimadzu RF-5301PC fluorescence spectrometer with a 150 W xenon lamp source. Three dimensional spectra was obtained by repeatedly measuring the emission (Em) spectra within a range of 280–600 nm, with excitation (Ex) wavelengths from 200 to 400 nm spaced at 10 nm intervals in the excitation domain. Spectra were then concatenated into an excitation–emission matrix (EEM). The EEM components determined in this study were humic-like components such as Ex/Em 230–260/ 400–450 nm and Ex/Em 300–340/400–450 nm.³ The analytical conditions have been reported in detail elsewhere.³⁶ The water samples were manually filtered with hydrophilic 0.45 µm polyethersulfone microfilters prior to measuring the water quality parameters. Each measurement was carried out at least in triplicate, and the average and standard deviation values were reported.

In experiments for evaluating the degradation capacity in treatment processes, carbamazepine was prepared in methanol and then spiked at 8.06 ± 0.28 µg L⁻¹ into the synthetic MEC effluent. This study focused mainly on the degradability of carbamazepine by UV/H₂O₂, but did not investigate the behavior of carbamazepine during the course of MECs. The removal efficiency of carbamazepine with hydrophobic neutral properties can be largely biased by an abiotic removal due to a small volume of acrylic MEC reactor in which the anode electrode with a large surface area is located. Carbamazepine was analyzed using an Agilent 1200 high-performance liquid chromatograph, and mass spectrometry detection was performed on an Agilent 6460 triple-quadrupole mass spectrometer equipped with a

dual jet-stream electrospray ionization source (see ESI† Fig. S2). The details have been described in our previous work.¹⁸

2.2.2. Batch experiment using microalgae—The stock culture of *Scenedesmus quadricauda* strain (AG 10003) was prepared as described in our prior work.³⁵ *Scenedesmus* is a dominant genus of algae commonly found in wastewater ponds.³⁷ Briefly, the algal cells in the exponential growth phase were collected *via* centrifugation (3000 rpm, 10 min), washed by mineral bottled water, and inoculated at an optical density (OD) of 0.4 cm⁻¹ (680 nm) into a flask containing 800 mL of synthetic bio-effluent (see ESI† Fig. S3). The flask was incubated under continuous light illumination with an intensity of 150 μmol photons m⁻² s⁻¹ at 25 °C while shaking at 130 rpm for 36 h. The light intensity was measured using an MQ-500 quantum meter (Apogee Instruments, Inc., USA). The flask was aerated with a gas mixture of 95% air and 5% CO₂ at a flow rate of 45±5 mL min⁻¹. *S. quadricauda* can engage in mixotrophic growth in addition to the common photoautotrophic growth using CO₂ as its sole carbon source, thus consuming organic carbon (measured as COD) in the growth medium. During incubation, 50 mL of mixed liquor was collected from the flask every 12 h to measure the removal of COD, TN, and TP. The cell growth was also measured by monitoring the OD at 680 nm (OD₆₈₀). This batch test was performed for 36 h in triplicate. The supernatant was collected from the flask at the end of the test, filtered using glass-fiber microfilters, and stored in a refrigerator at 4 °C until use in further UVC treatment.

2.3. Collimated UVC beam test

The UVC treatment of algal-treated wastewater was carried out at 254 nm using a collimated beam apparatus (see ESI† Fig. S4) with a 20 W low-pressure monochromatic mercury lamp (UVP XX-20S, Analytik Jena Co., Germany). The batch experiments were conducted at neutral pH, and 40 mL of water samples was placed in an open crystalline Petri dish (90 mm diameter) containing a small stir bar to achieve homogeneous treatment. The UVC light traveled in a cylindrical tube (ID=8cm, H=25 cm) treated with unglazed black paint to minimize any internal scattering. Incident UVC intensity was measured at the same height as the water level in the Petri dish using a calibrated UVX radiometer (Analytik Jena Co., Germany). The petri factor (0.854), reflection factor (0.975), and water factor (0.918) were applied to correct the UVC intensity, and the UVC dose was then calculated using the average intensity (0.474 mW cm⁻²) and exposure time.³⁸

The H₂O₂ solution collected from the cathodic chamber immediately after MEC runs was injected (< 5%, v/v) into algal-treated wastewater to achieve 10 mg L⁻¹ of H₂O₂ in the mixture prior to UVC irradiation. UVC photolysis was also investigated using algal-treated wastewater without added H₂O₂. For both UVC/H₂O₂ and UVC photolysis, the UVC treatment was performed in duplicate at doses of approximately 0, 500, 1000, and 2000 mJ cm⁻². The raw and treated water samples were collected and characterized using the same analytical methods as described above. If needed, H₂O₂ remaining in the samples was quenched using bovine liver catalase prior to the analyses of the water samples.

3. Results and discussion

3.1. Bioelectrochemical H₂O₂ production and organic removal

Acetate-based synthetic wastewater was used in evaluating the performance of the MECs, not only in terms of stabilization of carbonaceous organic compounds, but also to produce H₂O₂ that can be further used as a mediator for photolytic advanced oxidation with UVC light. The COD of the synthetic wastewater was $173 \pm 3 \text{ mg L}^{-1}$, like that observed for untreated domestic wastewater.³⁹ The results of the batch experiment with MECs are shown in Fig. 2, in which the current density and cathode potential are also plotted against time. The current density increased steeply for the first 2 h of the MECs run, reached a maximum value of $1.5 \pm 0.2 \text{ A m}^{-2}$, and then declined to $0.4 \pm 0.1 \text{ A m}^{-2}$ gradually. A reverse trend was observed for the cathode potential. Fig. 2a shows an almost linear production of H₂O₂ for 24 h *via* an oxygen reduction reaction (ORR), which proceeds in electron pathways on the cathode surface. Bioelectrochemical treatment of the synthetic wastewater with a dual-chamber reactor resulted in $89 \pm 2\%$ removal of COD in the anodic chamber (see Table 1) and concurrent production of up to $222 \pm 11 \text{ mg L}^{-1}$ of H₂O₂ with tapwater (as catholyte) for 24 h. Because the current density mainly accounts for H₂O₂ concentration, several previous studies using MECs fed with acetate-based media have reported higher production of H₂O₂ ($711\text{--}1447 \text{ mg H}_2\text{O}_2 \text{ L}^{-1}$) because of higher concentrations of substrate and its continuous supply.^{10, 30, 40}

On the other hand, high Coulombic efficiency and H₂O₂ conversion efficiency were obtained in this study. The Coulombic efficiency based on measured COD was $96 \pm 2\%$ in the MEC and the conversion efficiency (from Coulombs to H₂O₂) was $71 \pm 2\%$ (see Table 1). Similar conversion efficiencies ranging from 64% to 84% were obtained by others with synthetic wastewater.^{11, 40} The losses of electrons at the cathode could be due to H₂ gas formation at very negative cathode potentials and/or generated H₂O₂ can self-decompose or be further reduced to water at higher H₂O₂ concentration.^{11, 41} The pH of catholyte raised up to 11.5 at the end of MEC runs due to cathodic-hydroxide-ion generating reactions. Although protons generated at the anode should be migrated through the CEM for electroneutrality, pH imbalances developed probably due to anodic proton-generating oxidation reactions and the migration of cations other than protons for the charge balance.

The average energy consumption rate for the MECs examined in this study was $0.28 \pm 0.01 \text{ kWh per kg of H}_2\text{O}_2$, which was significantly more efficient than are conventional electrochemical processes.^{42, 43} Our energy input delivered by the potentiostat was also lower than that observed for previously reported work with synthetic media ($0.65\text{--}0.93 \text{ kWh per kg of H}_2\text{O}_2$).^{30, 40} It has been reported that the electrical-energy input for H₂O₂ production tends to be higher for MECs fed with actual wastewater ($2.2\text{--}8.3 \text{ kWh per kg of H}_2\text{O}_2$) than for those with synthetic media ($1.8\text{--}3.0 \text{ kWh per kg of H}_2\text{O}_2$).¹¹ Likewise, H₂O₂ conversion efficiency was relatively lower when using actual wastewater, indicating significant losses of H₂O₂ in the catholyte.¹⁰ Review of the literature indicates that the scaling up of MEC for only H₂O₂ production is still challenging,⁴⁴ but can be feasible for use of H₂O₂ *in situ* in advanced treatment process. Much work is still needed for further

improvement in the electrode materials that play a significant role in the ORR pathways and system performance.

3.2. Nutrient removal from MEC effluent

The phycoremediation of a synthetic MEC effluent with *S. quadricauda* was conducted using aeration with 5% (v/v) CO₂ in the light. Fig. 3 shows a gradual increase in the algal density during the entire period of cultivation (36 h) and the associated removal of organic carbon and inorganic nutrients from the MEC effluent. *S. quadricauda* removed carbonaceous organic compounds, decreasing COD from 19±1 to 6±2 mg L⁻¹. Given the integrated system proposed in this study, CO₂ released from the MECs will be also captured by *S. quadricauda* capable of mixotrophic growth as previously explained in Section 2.2.2. The algal treatment resulted in operational simplicity in the simultaneous removal of TN (69±9%) and TP (97±4%) in a single treatment process. In contrary, conventional BNR processes are composed of nitrification/denitrification and luxury phosphorus uptake under strictly controlled operating conditions.⁴⁵ BNR processes typically require some external carbon source for heterotrophic denitrification and phosphorus release under anoxic conditions and many coagulants for consistent removal of phosphorus in wastewater effluent to < 0.5 mg P L⁻¹.⁴⁶ In this study, bioelectrochemical treatment followed by phycoremediation complied with the discharge permit standards that limit TN to 20 mg L⁻¹ and TP to 0.5 mg L⁻¹ in the effluent without added organic chemicals and metallic coagulants. It is worthwhile to note that the removal of residual nutrients in the MECs effluent may not be required for agricultural irrigation in wastewater reuse.

S. quadricauda removed carbamazepine by 1.9±0.5 µg L⁻¹ (24±6%) for 36 h of cultivation under the given conditions, which was consistent with our previous observations.¹⁸ Carbamazepine is known to be recalcitrant toward biodegradation, correlated to the non-polar hydrophobicity of the compound. Considering its high log K_{ow} value of 2.25 (octanol/water partition coefficient),¹⁶ hydrophobic sorption is proposed as the dominant mechanism for the removal of carbamazepine by microalgae. Likewise, hydrophobic sorption has previously been reported to be the dominant mechanism for attenuation of carbamazepine in MFCs and MECs.¹⁷ Thus, the combined use of MECs and algal treatment can efficiently reduce COD, TN, and TP in wastewater, but removal of TOxCs is limited mostly to an accidental sorption that occurred in the combined processes due to their resistance to biodegradation. The following section discusses a robust removal of the residual carbamazepine using UV/H₂O₂.

3.3. Post UVC treatment with on-site produced H₂O₂

UVC/H₂O₂ oxidation achieved almost complete removal of the residual carbamazepine after algal treatment (see Fig. 4a). The UVC dose applied was 1000 mJ cm⁻² at 10 mg L⁻¹ H₂O₂. Pereira *et al.* (2007)⁴⁷ reported similar observations using surface water with 74% UV transmission. Some investigators found 10 mg L⁻¹ to be an optimal concentration of H₂O₂ in order to produce enough OH radicals under UVC light for advanced treatment of surface water and wastewater effluent,^{48, 49} but others spiked higher H₂O₂ doses into a reverse osmosis concentrate with lower UV transmittance (~55%) prior to UVC irradiation.²¹ The ability of H₂O₂ to absorb UV light and then produce OH radicals can be limited by the UV-

absorbing materials in the wastewater,⁶ whereas H₂O₂ can also scavenge OH radicals that would otherwise be available to degrade the target compounds. Thus, such operating parameters for UVC/H₂O₂ oxidation will need to be optimized to achieve site-specific treatment objectives. Fig. 4a also shows a negligible change in carbamazepine when an identical dose of UVC was used without added H₂O₂. This is not surprising, because direct photolysis of the target compound could be significantly limited because of UVC absorption by the background components in the wastewater matrix. Wastewater effluent organic matter (measured as DOC) can absorb light in the UV/visible range. The concentration of DOC in this study was over three orders of magnitude higher than that of the carbamazepine to be degraded, even though the extinction coefficient of carbamazepine (6070 M⁻¹ cm⁻¹ at 254 nm) is much higher than that of organic components (464~965 M⁻¹ cm⁻¹ at 254 nm) found in wastewater effluent.^{50, 51}

The UVC/H₂O₂ examined in this study was not enough to completely mineralize the DOC in biologically treated wastewater (see ESI† Fig. S5). However, UVC irradiation with added H₂O₂ substantially decreased the SUVA for residual organic matter (see Fig. 4b), indicating the degradation of UV-absorbing moieties was much greater than was removal of DOC. UV-absorbing moieties can also be degraded by the oxidation of water by the excited triplet states (³DOC*) upon UVC irradiation.⁵² The OH radicals produced upon photolytic oxidation are electrophilic oxidants and attack the electron-rich sites of the organic molecules,⁵³ which coincided with the results shown for the SUVA and fluorescence measurements of this study (see Fig. 4c). The decrease in the fluorescence intensity of organic matter reflects the degradation or sometimes mineralization of the corresponding fluorophores or functional groups that are present in the chemical structure of the fluorescent organic matter. For wastewater reuse, the decreasing degree of condensation of the residual organic matter is of great significance for promoting biodegradation of refractory organic constituents during managed aquifer recharge (i.e., artificial recharge and recovery). In addition to the photolysis function of UVC producing OH radicals, UVC irradiation has also proven to be an effective disinfectant for water and wastewater treatment due to its germicidal effect. Given the typical UVC doses (~100 mJ cm⁻²) used for disinfection of secondary effluent, the UVC dose applied in this study is high enough to do inactivate bacteria, protozoa, and viruses in the biological treatment effluent.

4. Conclusions

This paper proposes a novel scheme integrating MECs, algal treatment, and post-photolytic oxidation for advanced wastewater treatment to achieve site-specific treatment objectives, such as agricultural reuse and aquifer recharge. Carbonaceous organic compounds were used as fuel for MECs to produce H₂O₂ via an oxygen reduction reaction, decreasing the COD from 173±3 to 20±2 mg L⁻¹ under the given conditions. The nutrient removal with microalgae, which can be optional depending on the purpose of wastewater treatment, complied with discharge permits of N and P in the effluent. Combined MECs and algal treatment demonstrated the efficient removal of organic matter and inorganic nutrients from domestic wastewater, but carbamazepine (as a model compound of refractory TOxCs) still remained. H₂O₂ was consistently produced up to 222±11 mg L⁻¹ by MECs with synthetic domestic wastewater and then it was used at a concentration of 10 mg L⁻¹ to mediate

photolytic oxidation with UVC light (1000 mJ cm^{-2}). This achieved an almost complete degradation of carbamazepine and also increased the biodegradability of residual organic matter in the final effluent. More research should be done using actual wastewater to establish the effectiveness of using our wastewater reclamation strategies, and more work of testing the integrated approach to lower temperatures should be also undertaken to increase the economic feasibility of this alternative.

Supplementary Material

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Fig. 1.

Conceptual schematics for advanced wastewater treatment to achieve site-specific treatment objectives using a hybrid system combining (i) bioelectrochemical treatment for COD removal and consequent H₂O₂ production, (ii) phycoremediation with microalgae for removal of residual inorganic nutrients, and (iii) UVC irradiation for advanced oxidation of non-biodegradable micropollutants with H₂O₂ produced on site.

Fig. 2.

The changes in H_2O_2 production (a), current density (b), and cathode potential (c) as a function of time. The performance of MECs was monitored using synthetic wastewater (anolyte) and tapwater (catholyte) at an anode potential of -0.4 V.

Fig. 3. The changes in water quality during algal growth in synthetic MEC effluent using aeration with 5% (v/v) CO₂ under continuous illumination for 36 h. The error bars represent the standard deviations of each parameter measured every 12 h.

Fig. 4.

Degradation of carbamazepine in synthetic MEC effluent with sequential algal treatment, UVC photolysis, and UVC/H₂O₂ oxidation (a). ND (not detected) means a concentration below the lowest level ($0.5 \mu\text{g L}^{-1}$) of carbamazepine among the standard solutions analyzed for a calibration curve. The SUVA (b) and fluorescent characteristics (c) of residual organic matter also changed after each treatment. Fluorescence EEM spectra of organic matter in synthetic MEC effluent (i), algal treated (ii), UVC treated (iii), and UVC/H₂O₂ treated (iv) wastewaters. Algal treatment was conducted in the light for 36 h. A UVC dose of 1000 mJ cm^{-2} was applied for UVC irradiation with and without an added 10 mg L^{-1} of H₂O₂.

Table 1.

Bioelectrochemical conversion of carbonaceous organic matter to H_2O_2 in a dual-chamber reactor and the relevant parameters.

Parameter	Value
pH of the anolyte (media) at the end of test	6.3 ± 0.2 (the initial pH = 7.3 ± 0.1)
Removal of COD in the anolyte	$89 \pm 2\%$ (the initial COD = $173 \pm 3 \text{ mg L}^{-1}$)
Coulombic efficiency	$96 \pm 2\%$
Conversion efficiency at the end of test	$71 \pm 2\%$
Energy consumption for H_2O_2 production	$0.276 \pm 0.007 \text{ kWh per kg of H}_2\text{O}_2$
pH of the catholyte (tapwater) at the end of test	11.5 ± 0.1 (the initial pH = 7.8 ± 0.1)
$^*[\text{HO}_2^-] / [\text{H}_2\text{O}_2]$ at the final pH	0.9 ± 0.2 (H_2O_2 fraction = $54 \pm 7\%$)

* Based on the pK_a value (≈ 11.6) of H_2O_2 , the ratio of [Base]/[Acid] was calculated from the determined pH.