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Synergistic effect for efficient oxidization of refractory organics with high chroma by an innovative persulfate assisted microbial electrolysis ultraviolet cell

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Abstract

UV based advanced oxidation processes including the newly developed microbial electrolysis ultraviolet cell (MEUC) are easy to operate, but always exhibit an ineffective treatment of wastewater with high chroma due to the low UV transmittance. Herein, an innovative persulfate-assisted MEUC process (MEUPS) was developed to treat such wastewaters. The MEUPS can achieve complete decolorization of the selected model compound (40 mg L\(^{-1}\) of methylene blue, MB) within 140 min and a mineralization degree of 97% within 5 h under optimal operating conditions. The hybrid MEUPS process showed a much better treatment performance than that of the individual process and the synergy factor was quantified as 6.42. ‘SO\(_4\)\(^{-}\)’, ‘OH’, and ‘O\(_2\)\(^{-}\)’ were proved to be the major reactive radicals involved in MB degradation, and the degree of contribution was ranked as ‘SO\(_4\)\(^{-}\)’, ‘OH’, and ‘O\(_2\)\(^{-}\)’. Correspondingly, the working mechanism of the MEUPS process was inferred, in which the boosted above listed major reactive radicals can be attributed to the catalytic effect of bioelectrons and UV irradiation, thus the synergistic effect on the efficient treatment of MB-contaminated wastewater. Additionally, the treated effluent exhibited non-toxic by using aquatic plant *Lemna minor* as an indicator. This research provides a new perspective for the efficient and cost-effective treatment of industrial wastewater with high chroma and refractory organics over a broad pH range together with catalyst-free conditions by using PS-assisted microbial photoelectrochemical technologies.

**Keywords:** Microbial electrochemistry; UV irradiation; Persulfate activation; Synergy; Advanced oxidation processes;
1. Introduction

As the number of emerging pollutants is constantly increasing, their negative effects on the environment and living organisms is posing a large concern. Among them, the discharge of industrial wastewater with high chroma and refractory organics (e.g. dye-containing wastewater) has aroused continuous and intense attention all over the world due to its toxicity, difficulty in biodegradability, and persistence in water bodies [1]. It has been reported that more than 10,000 types of dyes are used globally with a total mass of over 700,000 tons each year, of which 280,000 tons are discharged with the resulting dye-containing wastewater, accounting for up to 20% of the total industrial wastewater [2]. Moreover, the concentration of azo dyes in wastewater from the textile industry has been reported to be between 5 and 1,500 mg L$^{-1}$, which can lower light penetration, gas solubility, and then further affect aquatic organisms [3]. Due to the persistence of synthetic dyes and the high salinity (approximately 5% of NaCl and Na$_2$SO$_4$), traditional biological treatment methods are invalid, and under certain conditions, they may even produce potentially dangerous aromatic amines via anaerobic treatment [2]. Hence, looking for efficient and cost-effective treatment methods for such industrial dyes wastewater is of importance.

In recent years, a variety of methods have been successfully developed for the treatment of dye-containing wastewater, which can be divided into three categories including physical (e.g. adsorption) [4], chemical (e.g. advanced oxidation processes (AOPs)) [5] and biological (e.g. bacterial) [6]. Among others, AOPs, a typical representative of chemical methods, has gained widespread attention due to the ability to efficiently degrade various dye-containing wastewaters. As one of the eco-friendly AOPs, electrochemical based AOPs (EAOPs) such as the electro-Fenton (EF) process can effectively remove and even completely mineralize target pollutants by the in-situ generation of a large number of reactive radicals (e.g. $\cdot$OH), [5]. Nevertheless, the high energy consumption of conventional EAOPs including EF is indeed a challenge for practical application [5]. To further lower the energy input of EF, an emerging EAOP called bio-electro-Fenton (BEF) process was recently
developed by combining traditional EF with microbial electrochemical technology [7]. In particular, for a typical two-compartment BEF, the organics from municipal wastewater could be decomposed by electrochemically active microorganisms attached to produce electrons, protons and carbon dioxide via Eq. (1) [8]. Thereafter, the produced electrons and protons are respectively transferred to the cathode and combine with oxygen molecules on the cathode surface to form H$_2$O$_2$ via a two-electron reduction reaction (Eq. (2)) [8].

\[
\begin{align*}
C_aH_bO_c + (2a-c)H_2O & \rightarrow aCO_2 + (b+4a-2c)H^+ + (b+4a-2c)e^- \\
O_2 + 2H^+ + 2e^- & \rightarrow H_2O_2
\end{align*}
\]

(1) (2)

For example, it has been reported that electric energy consumed by using the BEF process for the treatment of dyes-containing wastewater is far below (26 vs. 865 kWh kg$^{-1}$ TOC$^{-1}$) than that of the conventional EF process [9]. Moreover, the unique advantages of the BEF system include the possibility of in-situ removal of residual H$_2$O$_2$ by switching the system to the microbial fuel cell (MFC) mode [10]. Though promising, several challenges still need to be addressed before the wide application of EF and BEF technologies. More specifically, the remaining iron and the produced iron sludge need to be further removed, which will improve the overall treatment cost. Besides, both EF and BEF processes need to be operated at acidic conditions (pH of 2-3), and thus, pH adjustment is required before and after operation periods. It will not only increase the operating cost but also limit its scope of application. Hence, for addressing the above-mentioned challenges, combining the BEF process with other chemical oxidation methods could be an effective solution [11].

Alternatively, ultraviolet (UV) based AOPs such as UV/H$_2$O$_2$, UV/persulfate (PS) processes have been also proven to effectively remove emerging pollutants including dye-containing wastewaters [12-14]. The powerful reactive radicals including ‘OH ($E^0 = 1.9$-2.7 V) and ‘SO$_4^-$ ($E^0 = 2.5$-3.1 V) activated by UV irradiation are well-known to play a major role in the degradation of pollutants [14, 15]. Thus, the removal of remaining iron and iron sludge will not be required in such processes. Furthermore, there is no strict requirement on the operating pH, while better removal is obtained
under neutral and slightly alkaline (pH at 9) conditions corresponding to UV/H$_2$O$_2$ and UV/PS processes, respectively [15, 16]. Recently, the hybrid UV/H$_2$O$_2$/PS process that combines UV/H$_2$O$_2$ and UV/PS has also been proposed, which has shown a certain degree (around 10%) of synergistic improvement for the removal of target pollutants compared to the individual technologies [11]. Nevertheless, the major challenge of the UV/H$_2$O$_2$ and UV/H$_2$O$_2$/PS process is the cost of H$_2$O$_2$, and the need to remove residual H$_2$O$_2$ which is up to 80% of the initial dosage remains in the effluent. It costs approximately 22 € to remove one kilogram of H$_2$O$_2$ [17]. To solve the above shortcomings, a microbial electrolysis ultraviolet cell (MEUC) was recently proposed by combining the UV photolysis and bioelectrochemical system to achieve an in-situ synthesis of H$_2$O$_2$ and further catalyse conversion to ‘OH for efficient and cost-effective removal of pollutants [18]. However, to be noted, a common challenge of above UV/H$_2$O$_2$, UV/PS, UV/H$_2$O$_2$/PS, and MEUC processes is the low transmission of UV light when treating the wastewater with dark color, which in turn affects the conversion efficiency to free radicals like ‘OH and ‘SO$_4$− and ultimately leads to the reduction of treatment efficiency. Thus, alternative means to first activate H$_2$O$_2$ or PS and remove the color for efficient UV transmission should be pursued.

Taking together, a novel PS-assisted MEUC (MEUPS) process, which combines the advantages of BEF, UV, and PS based AOPs while overcoming the shortcomings of the individual processes, was developed in this study to significantly improve the dyes-containing wastewater treatment efficiency. In particular, considering that dye-containing wastewaters generally have a dark color with a pH value ranging from 6 to 10 [19], the new MEUPS process could be a more suitable treatment technology than the individual processes. Methylene blue (MB), a cationic dye belonging to the heterocyclic aromatic group, has dominated the market for decades and is widely used in the textile industry, such as for coloring in the paper, cotton, silk, and wool industries [20]. In addition, because of its anti-fungal and anti-malaria potential, it is also widely used in clinical medicine [21]. However, the corresponding MB containing wastewater produced due to the excessive use of MB not only poses a
serious threat to the ecological environment but also human health, such as causing serious diseases including central nervous system toxicity and gastrointestinal infections [20, 21]. In addition, considering that MB is difficult to remove by traditional treatment approaches including photodegradation (UV irradiation) together with its simple detection method, it was used as a model pollutant in this study [14]. Firstly, the feasibility of the MEUPS system for MB removal was verified. Subsequently, the influence of operating parameters such as input voltage, cathodic aeration velocity, initial catholyte pH, and initial PS dosage on MB degradation was investigated. Furthermore, the treatment cost of MEUPS was calculated and compared with other technologies. Lastly, use *Lemna minor* (*L. minor*) to evaluate the ecotoxicity of treated wastewater. This work not only offers an efficient and cost-effective treatment approach of dyes-containing wastewater but also potentially provides a versatile platform technology for the elimination of other emerging pollutants.

2. Materials and methods

2.1 Reactor setup and operation

In this paper, a 20 L MEUPS reactor composed of anode and cathode chambers was constructed using polycarbonate material. The two chambers were separated by a cation exchange membrane (CEM, CMI 7001, Membrane International, NJ). The size of each chamber was 40 cm in length, 10 cm in width, and 20 cm in height. Correspondingly, the total and effective volumes of each chamber were 10 and 9 L, respectively. 10 electrodes were installed in each chamber, and the anode and cathode were made of commercial carbon brush (diameter 5.9 cm, length 6.9 cm, Mill-Rose, USA) and graphite plate (length and width are all 4.5 cm), respectively. The carbon brushes need to be pretreated according to the method described in our published study before use [10]. Moreover, an Ag/AgCl reference (+0.197 V vs SHE, Pine Instrument Company, USA) was also installed in the cathode chamber to monitor the cathode potential. The cathode chamber was also equipped with two microporous aerators with pore size ranged from 5 to 100 µm for aeration. Besides, the cathode chamber was equipped with two low-pressure UV lamps (Hanovia GPH180T5L, 10 W, 254 nm) with
a calibrated irradiation intensity of 24 µW cm⁻² of each. Because of the mercury lamp used, it was necessary to turn on the UV lamps to preheat for 30 minutes before each operation. The specific arrangement of electrodes, aerators, and UV lamps was shown in Fig. 1.

The detailed operation of the reactor enrichment stage refers to our recent work [22]. In the actual experiment process, the configuration of synthetic methylene blue wastewater includes mixing of 40 mg MB and 50 mM Na₂SO₄ into 1 L of deionized water, except as otherwise noted. A battery tester/cycle instrument (CT-4008W, Neware, China) was employed to provide the input voltage and monitor the current and cathode potential. The experiment was repeated twice for each condition and run at room temperature (20 ± 2 °C).

Fig.1 is here

2.2 Chemicals, analytical methods and calculations

Methylene blue (C₁₆H₁₈ClN₃S · xH₂O, MB, ≥ 97%), sodium persulfate (Na₂S₂O₈, PS, ≥ 99%), methanol (≥ 99.9%), sodium sulfate (Na₂SO₄, ≥ 99%), sulfuric acid (H₂SO₄, 95-98%), sodium thiosulfate (Na₂S₂O₃, ≥ 98%), potassium titanium oxide oxalate dihydrate (C₄K₂O₉Ti· 2H₂O) hydrogen peroxide solution (H₂O₂, 30 wt. %) and sodium hydroxide (NaOH, ≥ 99%) were obtained from Sigma Aldrich (Denmark).

The pH of the sample was measured by a pH meter (PHM 210, radiometer). The concentration of MB, cathodic electrosynthesis of H₂O₂ and total organic carbon (TOC) in each sample was monitored as previously described [22]. 10 mL samples were taken each time from each sampling point and then 100 µL of Na₂S₂O₃ solution (50 mM) was immediately added to quench the reaction, before testing the remaining MB concentration and TOC in the samples.

In addition, the decolorization and mineralization of MB during the MEUPS, MEUC and UV/PS processes were all following pseudo-first-order kinetic and the corresponding calculation methods of the kinetic rate constant values were based on our previous study [22]. Since the MEUPS system studied in this work was a hybrid system, thus synergetic factors (f) were determined via Eq. (3).
Besides, the consumed electrical energy and total operating cost were described using electrical energy per order \( (E_{EO}) \) value and total cost per order \( (\text{Cost/O_{total}}) \). For the MEUPS process, the calculation of \( E_{EO} \) value can be divided into two parts, one was the electrical energy consumed by UV lamps and the other was the electrical energy consumed by the reactor including direct voltage supplied, aeration and stirring. The detailed calculation was made as previously described [23].

2.3 Eco-toxicity test

As a kind of aquatic plant, fronds of duckweed of \( L. \ minor \) was extensively used to determine the ecotoxicity of water bodies after various technical treatments because of its fast growth and high sensitivity to various water pollutants [24]. The \( L. \ minor \) was collected from the Lyngby lake, Copenhagen, Denmark. The fetched \( L. \ minor \) was disinfected and washed with 0.5% v/v sodium-hypochlorite and distilled water, and then cultured in the medium as described previously [25]. Thereafter, the treatment of dye-containing wastewater was conducted in the MEUPS process under optimal conditions. 10 mL of samples were taken from the reactor at a reaction time of 0, 60, 100, 120, 140, and 160 min. Next, 10 mL of nutrient medium was added into the above samples, and the conversions in the frond color after 1 day and 14 days of cultivation were compared with the control group. The changes of fronds were observed by using a stereomicroscope (Olympus szx9 Olympus, Japan).

3. Results and discussion

3.1 The performance of the MEUPS for MB degradation

The proof-of-concept experiments were firstly carried out to validate the feasibility of this novel MEUPS process, followed by the comparison with controls including individual PS, individual UV photolysis, MEUPS (UV light off), MEUC (UV light on/off), UV/PS, EUPS (without microorganisms), EU (without microorganisms and without PS), and EC (without microorganisms, without PS and without UV). The results presented in Fig.2a indicated that only around 12.35% and
11.90% of MB can be removed within 160 min under conditions of only PS addition and MEUC (UV light off), respectively. In the MEUC (UV light off) process, H₂O₂ produced via Eq. (4) was the only oxidant which has weak oxidation ability \((E^0 = 0.88 \text{ V})\), and thus, led to the ineffective removal of MB [26].

\[
2H^+ + O_2 + 2e^- \rightarrow H_2O_2 \quad (4)
\]

Similar phenomena have also been found in previous BEF and photo-Fenton studies treating MB [22, 27]. Moreover, the H₂O₂ concentration in the cathode varied with the reaction time (Fig. S1). Likewise, the wastewater with only PS addition has also been shown to have weak oxidation ability [16]. Thus, the observed MB removal in the control tests could be mainly due to the adsorption effect of the dye on the reactor (e.g. electrodes, CEM and polycarbonate inner wall, etc.), which was also consistent with the findings regarding the MB degradation in a scaled-up BEF system [22]. Besides, after 160 min of UV irradiation, approximately 15% of MB was removed, and the whole process was in line with pseudo-first-order kinetics, with a \(k_{app}\) value of \(1.1 \times 10^{-3} \text{ min}^{-1} \) \((R^2 = 0.99)\) (Fig. 2b). According to the molecular structure of MB, it contains aromatic rings and heteroatoms of nitrogen, sulfur and chlorine, which can form electron excited state MB* under UV (254 nm) irradiation via Eq. (5), and then further decompose into intermediate products via Eq. (6) [28, 29].

\[
MB \rightarrow MB^* \quad (5)
\]

\[
MB^* \rightarrow \text{intermediate products} \quad (6)
\]

Relatively low MB removal efficiencies (25.60% and 23.03%) were obtained by MEUC (UV light on) and UV/PS processes within 160 min, respectively (Fig. 2b). Similarly, the removal process conformed to pseudo-first-order kinetics with the corresponding \(k_{app}\) values of \(1.9 \times 10^{-3} \text{ min}^{-1} \) \((R^2 = 0.98)\) and \(1.7 \times 10^{-3} \text{ min}^{-1} \) \((R^2 = 0.98)\), respectively. The low removal efficiency could be attributed to the heavy color of MB solution which had a shielding effect on UV light and thus only a small part of PS and synthetic H₂O₂ were activated by UV to generate free radicals including ‘OH and ‘SO₄⁻ via Eq. (7) and (8), respectively [14, 15].
H$_2$O$_2$ $\xrightarrow{hv}$ 2·OH \hspace{1cm} (7)

S$_2$O$_8^{2-}$ $\xrightarrow{hv}$ 2·SO$_4^{2-}$ \hspace{1cm} (8)

In addition, previous studies on the BEF technology found that anodic microorganisms have a significant impact on system performance [30]. Therefore, several corresponding control experiments (EUPS, EU and EC) were carried out, and the results showed that without anodic microorganisms, the removal efficiency of MB at the cathode was significantly reduced (corresponding to 24.17%, 12.52% and 8.19%, respectively). The absence of anodic microorganisms that drive the electrons flow from substrates to the anode led to an extremely low system current (below 0.05 mA). It subsequently reduced the efficiency of PS activation by the cathodic electron and stopped the H$_2$O$_2$ synthesis, and finally reduced the production of ·OH and ·SO$_4^{2-}$.

However, when MEUC (UV light on) and UV/PS processes were combined into the novel MEUPS process, a more significant improvement in MB removal was observed (100% removal within 140 min). The MB removal in the MEUPS also followed pseudo-first-order kinetics and the corresponding $k_{app}$ values were as high as 2.67×10$^{-2}$ min$^{-1}$ ($R^2 = 0.99$). Based on Eq.(1), the synergetic factor was calculated as 6.42 (Fig. 2c), which demonstrated that the MEUPS process had a better synergy compared to the individual MEUC (UV light on) or UV/PS process. The high removal efficiency could be explained by the production of more free radicals, mainly ·OH and ·SO$_4^{2-}$.

Firstly, it is well-known that both ·OH and ·SO$_4^{2-}$ can be produced via UV activation (Eq. (7) and (8)) [14, 15]. Besides, the H$_2$O$_2$ not only can be activated by UV to produce ·OH, but it would also participate in the activation of PS to produce free radicals including ·SO$_4^{2-}$ and ·HO$_2$ via Eq. (9) [11].

H$_2$O$_2$ + S$_2$O$_8^{2-}$ $\rightarrow$ ·SO$_4^{2-}$ + ·HO$_2$ + HSO$_4^{-}$ \hspace{1cm} (9)

Furthermore, PS can also act as an electron acceptor in the cathode chamber to generate ·SO$_4^{2-}$ through single-electron reduction (Eq. (10)) [31].

e$^- + S_2O_8^{2-}$ $\rightarrow$ ·SO$_4^{2-}$ + SO$_4^{2-}$ \hspace{1cm} (10)
Lastly, the addition of PS and its final product \( \text{SO}_4^{2-} \) can also increase the conductivity of catholyte and thereby increasing the circuit current density (Fig. S1) and accelerating the in-situ production of \( \text{H}_2\text{O}_2 \) and single-electron reduction of PS \([9, 31]\), which subsequently improve the production of \( ^\cdot \text{OH} \) and \( ^\cdot \text{SO}_4^- \).

In addition, in order to further verify the effect of UV radiation on the removal of high chroma wastewater (e.g., 40 mg L\(^{-1}\) MB containing wastewater) in the MEUPS system, a set of control experiment (MEUPS (UV light off)) was carried out. Correspondingly, it can be seen in Fig. 2a, compared to the MEUPS process (UV light on), the removal efficiency of MB in the control MEUPS process (UV light off) only reaches 61.85% under the same conditions. This could be due to the low UV transmittance caused by the darker color of the MB solution in the initial stage of the reaction, so that the removal rates of MB in the MEUPS (UV light on) and MEUPS (UV light off) processes are not much different. However, as the reaction progressing, the color of the MB solution became light, and accordingly, the UV transmittance continues to increase, and more \( ^\cdot \text{OH} \) and \( ^\cdot \text{SO}_4^- \) are continuously generated via Eq. (7) and (8), thereby significantly improving the removal efficiency \([14, 15]\). In addition, with the increase in UV transmittance, the role of UV radiation itself in the degradation of MB via Eq. (5) and (6) is also expected to continue to increase \([28, 29]\). Therefore, UV radiation can significantly affect the treatment efficiency of the MEUPS system for the treatment of refractory organics with high chroma. However, considering energy consumption, in the future treatment of high-chroma wastewater, the treatment cost of the MEUPS process can be reduced by optimizing the on and off time of the UV lamp (e.g., turning off the UV lamp in the initial stage of the treatment process).

Notably, the relatively high and stable system current and cathode potential were obtained in both MEUC and MEUPS processes which also indicated the stability of bio-anode and further proved the feasibility of the future application of this MEUPS. It should be noted that the MEUPS process exhibited much better treatment performance in terms of the MB removal than that of lab-scale and
scaled-up BEF processes, which required more than 12 and 22 h for the complete removal of 50 mg L⁻¹ of MB, respectively [10, 22]. Significantly shortened treatment time can greatly reduce the overall costs including the capital, operating, and maintenance costs in the future for a full-scale application [32].

In summary, from the treatment point of view, the system performance of the above technologies was ranked as follows: MEUPS (UV light on) > MEUPS (UV light off) > MEUC (UV light on) > EUPS ≈ UV/PS > EU ≈ UV photolysis > MEUC (UV light off) ≈ only PS addition > EC. Continued with the proof-of-concept, the following experiments were carried out to explore the effect of key operating parameters on the system performance of MEUPS.

3.2 Effect of key operating parameters on the MEUPS process

3.2.1 Effect of input voltage

As depicted in section 3.1 and also found in the EF and BEF systems [33, 34], the system current can directly affect the H₂O₂ synthesis at the cathode. Thus, the effect of the input voltage (0.1, 0.3, 0.5, 0.6, and 0.7 V) on the MB removal in the MEUPS system was investigated. As shown in Fig. 3a, the complete removal of MB was obtained within 140 min when the applied voltage was 0.6 V, followed by 92.49%, 86.50%, 70.56%, and 35.35% of MB removal (within 160 min) with the applied voltage of 0.7, 0.5, 0.3, and 0.1 V, respectively. Likewise, the MB degradation process under various input voltages was in line with pseudo-first-order kinetics and the calculated kₐₚₚ values were 2.67×10⁻² min⁻¹ (R² = 0.99), 1.72×10⁻² min⁻¹ (R² = 0.99), 1.29×10⁻² min⁻¹ (R² = 0.99), 8×10⁻³ min⁻¹ (R² = 0.99), and 3×10⁻³ min⁻¹ (R² = 0.98), respectively. Moreover, the circuit current density increased from 6.64 to 12.67 A m⁻² with the increasing of the input voltage, while the recorded variation trend of cathode potential was the opposite, ranging from -0.44 to -0.62 V (Fig. S2). The same phenomena have also been found previously in the BEF and MEUC processes treating various pollutants such as pharmaceuticals and dyes [18, 22]. The enhanced system performance with the increase of applied
voltages from 0.1 to 0.6 V could probably be due to an increase in current for the synthesis of more H\textsubscript{2}O\textsubscript{2} and thereby increasing the formation of ‘OH and ‘SO\textsubscript{4}\textsuperscript{−} via Eq (4), (7), (8) and (9), respectively. Moreover, the increased voltage made more electrons involving in activating PS for the production of ‘SO\textsubscript{4}\textsuperscript{−} via Eq (10). Therefore, the MB removal efficiency was improved due to the generation of more ‘OH and ‘SO\textsubscript{4}\textsuperscript{−}. However, when the input voltage was further raised to 0.7 V, a relatively high current will cause a series of parasitic reactions according to Eq. (11) and (12) and thereby reducing the amount of H\textsubscript{2}O\textsubscript{2} synthesized, which eventually resulted in the reduction of ‘OH and ‘SO\textsubscript{4}\textsuperscript{−} [35, 36]. The previous study on the synthesis of H\textsubscript{2}O\textsubscript{2} using the same reactor has also demonstrated that H\textsubscript{2}O\textsubscript{2} production decreased when the applied voltage was further increased from 0.6 to 0.7 V or higher [8].

\begin{equation}
\text{H}_2\text{O}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow 2\text{H}_2\text{O} \quad (11)
\end{equation}

\begin{equation}
2\text{H}_2\text{O}_2 \rightarrow 2\text{H}_2\text{O} + \text{O}_2 \quad (12)
\end{equation}

It was also possible that the generated H\textsubscript{2}O\textsubscript{2} first increased with the increase of current. After reaching a certain level, excess H\textsubscript{2}O\textsubscript{2} and ‘OH were generated, which would trigger the well-known "quenching effect" according to Eq. (13)-(17), and thereby reducing the removal efficiency [11].

\begin{equation}
\text{H}_2\text{O}_2 + \cdot\text{OH} \rightarrow \cdot\text{HO}_2 + \text{H}_2\text{O} \quad (13)
\end{equation}

\begin{equation}
\text{H}_2\text{O}_2 + \cdot\text{SO}_4\textsuperscript{−} \rightarrow \cdot\text{HO}_2 + \text{SO}_4^{2−} + \text{H}^+ \quad (14)
\end{equation}

\begin{equation}
\text{H}_2\text{O}_2 + \cdot\text{OH} \rightarrow \cdot\text{O}_2\textsuperscript{−} + \text{H}^+ + \text{H}_2\text{O} \quad (15)
\end{equation}

\begin{equation}
\cdot\text{HO}_2 + \cdot\text{OH} \rightarrow \text{O}_2 + \text{H}_2\text{O} \quad (16)
\end{equation}

\begin{equation}
\cdot\text{HO}_2 + \cdot\text{SO}_4\textsuperscript{−} \rightarrow \text{O}_2 + \text{SO}_4^{2−} + \text{H}^+ \quad (17)
\end{equation}

### 3.2.2 Effect of cathodic aeration velocities

Apart from the input voltage, oxygen supply (corresponding to cathodic aeration velocity) was another crucial parameter that can affect the mass transfer of oxygen to electrodes for H\textsubscript{2}O\textsubscript{2} production according to Eq. (4) [22]. In this context, cathodic aeration velocity would not only influence the removal efficiency of MB but also affect the operating costs of the MEUPS process in
terms of electrical energy consumption. Thus, the effect of different aeration velocities (0.0056, 0.011, 0.022, 0.033, and 0.056 mL min\(^{-1}\) mL\(^{-1}\)) on the system performance was investigated. As shown in Fig.3b, the removal efficiency of MB was improved when the aeration velocity was increased from 0.0056 to 0.056 mL min\(^{-1}\) mL\(^{-1}\), which verified the importance of oxygen supply to the MEUPS process. The calculated \(k_{\text{app}}\) values corresponding to the aeration velocities ranged from 0.056 to 0.0056 mL min\(^{-1}\) mL\(^{-1}\) were as follows: 2.67×10\(^{-2}\) min\(^{-1}\) (\(R^2 = 0.98\)), 1.83×10\(^{-2}\) min\(^{-1}\) (\(R^2 = 0.99\)), 1.23×10\(^{-2}\) min\(^{-1}\) (\(R^2 = 0.99\)), 6.8×10\(^{-3}\) min\(^{-1}\) (\(R^2 = 0.99\)) and 3.6×10\(^{-3}\) min\(^{-1}\) (\(R^2 = 0.98\)). The observed results were consistent with the previous studies regarding the treatment of emerging pollutants such as dyes by using EF and BEF technologies [22, 37]. Moreover, the circuit current density (Fig. S3) was raised (10.02 to 11.90 A m\(^{-2}\)) with the increase of aeration velocity, which could be due to the enhanced mass transfer of oxygen to the electrode [38]. Noticeably, a negative effect on the removal efficiency of MB was obtained when the system current density reached 11.90 A m\(^{-2}\) (Fig. S2). This could be due to that the increase of bubbles increased the internal resistance of the system and disturbed the contact between the bubbles and the active sites of the electrode [34, 39].

### 3.2.3 Effect of PS dosage

As a source of \(\cdot\text{SO}_4\)\(^-\), PS dosage would not only affect the removal efficiency but also affect the overall operating cost. Thus, the impact of PS dosage (5-25 mM) on the removal of MB by the MEUPS process was studied. As shown in Fig.3c, the degradation of MB followed the pseudo-first-order kinetics model. With the increase in the dose of PS from 5 to 25 mM, the \(k_{\text{app}}\) of MB monotonously raised from 2.8×10\(^{-3}\) to 2.67×10\(^{-2}\) min\(^{-1}\). It was worth noting that when the dose of PS was more than 20 mM, the \(k_{\text{app}}\) increased much slower than that with the dose of PS ranged from 5 to 20 mM. Similar results were also observed in the UV/PS and UV/H\(_2\)O\(_2\)/PS processes [11, 29]. The main reason for the continuous increase in \(k_{\text{app}}\) could be attributed to the production of more free radicals under UV irradiation, mainly \(\cdot\text{SO}_4\)\(^-\), as the PS dosage increased. Besides, as explained in the previous section, higher PS dosage means higher conductivity, correspondingly higher system circuit
current density (Fig. S4) and promoting the in-situ production of H\textsubscript{2}O\textsubscript{2} and single-electron reduction of PS [9, 31, 40], which further enhance the production of \textquote{•}OH and \textquote{•}SO\textsubscript{4}\textsuperscript{2−}. As for the slow increase of \(k_{\text{app}}\) as the PS dosage increased from 20 to 25 mM, it could be due to the quenching effect caused by excessive PS and the self-consumption of \textquote{•}SO\textsubscript{4}\textsuperscript{2−} through Eq.(18)-(20) [11, 29].

\[
\textquote{•}SO\textsubscript{4}\textsuperscript{2−} + S_{2}O_{8}^{2−} \rightarrow \textquote{•}S_{2}O_{8}^{−} + SO_{4}^{2−} \quad (18) \\
\textquote{•}OH + S_{2}O_{8}^{2−} \rightarrow \textquote{•}S_{2}O_{8}^{−} + SO_{4}^{2−} \quad (19) \\
\textquote{•}SO\textsubscript{4}\textsuperscript{2−} + \textquote{•}SO\textsubscript{4}\textsuperscript{−} \rightarrow S_{2}O_{8}^{2−} \quad (20)
\]

3.2.4 Effect of catholyte pH

Although the pH value of dye wastewater is generally at around 6-10 [19], it may turn to be acidic under some specific conditions. Therefore, to comprehensively evaluate the MEUPS system, further experiments were conducted using synthetic MB wastewater with different pH values (3, 5, 7, 9 and 11). A slightly pH-dependent effect was observed for the abatement of MB in the MEUPS system when the initial pH was between 3 and 7. The highest removal efficiency was obtained at pH 3 (see Fig. 3d). Then, the relative low MB removal efficiency (approximately 15% decreased in terms of MB removal within 160 min compared to pH 3) was achieved when the initial pH further raised to 9. In contrast, when the pH was further increased to 11, the removal efficiency of MB drops significantly to 65.15%. The results were in agreement with a previous study regarding the removal of aniline via UV/H\textsubscript{2}O\textsubscript{2}/PS process [11]. Additionally, the \(k_{\text{app}}\) values under corresponding pH conditions were calculated to be 3.25×10\textsuperscript{−2} (\(R^2 = 0.99\)), 2.67×10\textsuperscript{−2} (\(R^2 = 0.98\)), 2.53×10\textsuperscript{−2} (\(R^2 = 0.98\)), 2.09×10\textsuperscript{−2} (\(R^2 = 0.99\)), 1.26×10\textsuperscript{−2} min\textsuperscript{−1} (\(R^2 = 0.98\)) and 8×10\textsuperscript{−3} min\textsuperscript{−1} (\(R^2 = 0.98\)), respectively. Besides, the eventually pH reached to around 5, 6, 7, 9, 11 and 11.3, respectively (E-supplementary data of this work can be found in online version of the paper). The effect of pH on MB removal efficiency can be explained from the following aspects. Firstly, the pKa value of MB (5.85) was within the pH range between 3 and 11, which may affect the direct UV degradation of MB by shifting its form in the
solution [41]. Specifically, when the catholyte pH was higher than the pKa of MB, MB existed in a deprotonated state. Thus, the increase in pH promoted the formation of more deprotonated MB, which was beneficial to direct UV photolysis [16]. In addition, the increase in pH value may enhance the UV activation of PS to generate ‘SO₄⁻’, and the deprotonated MB could be more easily degraded by ‘SO₄⁻’, thereby promoting the degradation of MB [16]. Moreover, ‘SO₄⁻’ could react with H₂O and OH⁻ to generate ‘OH according to Eq. (21) and (22), which could enhance MB removal due to the higher oxidation ability of ‘OH compared to ‘SO₄⁻’ in the alkaline conditions [29]. Moreover, when pH higher than 10.5, the reaction of ‘SO₄⁻’ and OH⁻ became very important and may lead to the formation of •OH via Eq. (21) [29]. However, the redox potential of •OH decreased continuously as the pH increased, which in turn might lead to a decrease in its oxidation capacity [42]. Therefore, this can explain the reduced effect of MB removal at pH=11.

\[
\text{‘SO}_4^- + \text{OH}^- \rightarrow \text{‘OH} + \text{SO}_4^{2-} \quad (21)
\]

\[
\text{‘SO}_4^- + \text{H}_2\text{O} \rightarrow \text{‘OH} + \text{SO}_4^{2-} + \text{H}^+ \quad (22)
\]

Secondly, the self-decomposition of electro-synthesized H₂O₂ may occur via Eq. (12) under the alkaline conditions, which could be promoted as pH increased and resulted in less ‘OH generation [13].

Thirdly, the conjugation reaction of H₂O₂ was promoted to form HO₂⁻ according to Eq. (23) under the alkaline conditions, which can consume ‘OH (Eq. (24)), H₂O₂ (Eq. (25)) and UV photons and ultimately lead to the reduction of ‘OH and ‘SO₄⁻’ generation [43, 44];

\[
\text{H}_2\text{O}_2 \rightarrow \text{H}^+ + \text{HO}_2^- \quad (23)
\]

\[
\text{‘OH} + \text{HO}_2^- \rightarrow \text{H}_2\text{O} + \text{‘O}_2^- \quad (24)
\]

\[
\text{H}_2\text{O}_2 + \text{HO}_2^- \rightarrow \text{H}_2\text{O} + \text{O}_2 + \text{OH}^- \quad (25)
\]

Fourthly, in the pH range of 9-11, it may be attributed to the quenching effect of OH⁻ and ‘SO₄⁻’ on ‘OH via Eq. (26) and (27) [29];

\[
\text{‘OH} + \text{OH}^- \rightarrow \text{‘O}^- + \text{H}_2\text{O} \quad (26)
\]
\[2 \cdot \text{OH} + 2 \cdot \text{SO}_4^- \rightarrow 2 \text{HSO}_4^- + \text{O}_2 \] (27)

Fifthly, carbonate and bicarbonate may be formed through the following series of reactions (Eq. (28), (29) and (30)). Especially under alkaline conditions (pH > 8.3), the dissolved carbon dioxide mainly existed in the form of bicarbonate and carbonate in the solution, and as the pH continued to rise, the carbonate content may increase, which could also have a quenching effect on free radicals including ‘\text{SO}_4^-’ and ‘\text{OH}’ [11].

\[\text{CO}_2 (\text{aq}) + \text{H}_2\text{O} \rightarrow \text{H}_2\text{CO}_3 \] (28)

\[\text{H}_2\text{CO}_3 \rightarrow \text{H}^+ + \text{HCO}_3^- \] (29)

\[\text{HCO}_3^- \rightarrow \text{H}^+ + \text{CO}_3^{2-} \] (30)

In summary, it can be seen that the MEUPS process could overcome the challenges of low operating pH (between 2-3) encountered by the traditional EF and BEF technologies.

**Fig.3 is here**

### 3.2.5 Effect of inorganic ions

The actual dye-containing wastewater may contain several inorganic ions (e.g., \(\text{Cl}^-\), \(\text{HCO}_3^-\), \(\text{NO}_3^-\), and \(\text{NO}_2^-\)), which has been demonstrated to have varying degrees of influence on the application of ‘\text{SO}_4^-’ and ‘\text{OH}’ based AOPs [14, 29]. Therefore, it was essential to study the effect of these inorganic ions on MB degradation during the MEUPS treatment process. Four different inorganic ions including \(\text{Cl}^-\), \(\text{HCO}_3^-\), \(\text{NO}_3^-\) and \(\text{NO}_2^-\) that are widely existing in different types of wastewater were selected in this section. Although the actual dye-containing wastewater usually contains high \(\text{Cl}^-\) content and low \(\text{NO}_3^-\) and \(\text{NO}_2^-\) content, it may be relevant when the MEUPS technology is further applied in the future for the treatment of various types of wastewater such as industrial wastewater from electronic components production and landfill leachate, as well as the above-mixed wastewater, which usually contains high concentrations of \(\text{NO}_3^-\) and \(\text{NO}_2^-\) [45]. Therefore, the initial concentration of each ion was set as 1-20 mM. As shown in Fig. 4, the four selected inorganic anions all showed more or less suppression effect on the abatement of MB during the MEUPS process.

#### 3.2.5.1 Chloride
On the whole, the presence of Cl\(^-\) has a relatively low impact on the system performance. Specifically, as the concentration of Cl\(^-\) continued to rise to 20 mM, the removal efficiency of MB only slightly decreases to 95.67%. The less suppression effect of Cl\(^-\) could be explained as follow. Firstly, while Cl\(^-\) can quench ‘OH to generate ‘HOCl\(^-\)\), and ‘HOCl\(^-\) can be further decomposed to generate ‘OH via Eq. (31) [18]. Therefore, the addition of Cl\(^-\) has little effect on the concentration of ‘OH, and thus has a relatively lower effect on the removal efficiency of MB.

\[
\text{‘OH} + \text{Cl}^- \leftrightarrow \text{‘HOCl}^- \quad (31)
\]

Secondly, Cl\(^-\) can react with ‘SO\(_4\)\(^-\)\) to form reactive radicals like ‘Cl and ‘Cl\(_2\)\) via Eq. (32) and (33), in which ‘Cl\(_2\) has a weak oxidation capacity. With the increasing concentration of Cl\(^-\) added, more generated ‘Cl\) was further transformed into ‘Cl\(_2\)\), which may lead to the reduction of removal efficiency of MB [46].

\[
\text{‘SO}_4^- + \text{Cl}^- \rightarrow \text{‘Cl} + \text{SO}_4^{2-} \quad (32)
\]

\[
\text{‘Cl} + \text{Cl}^- \rightarrow \text{‘Cl}_2^- \quad (33)
\]

However, a recent study has found that the generated ‘Cl and ‘Cl\(_2\) were believed to easily react with electron-rich compounds such as MB [47]. Moreover, it has even been discovered that the addition of Cl\(^-\) could promote the degradation of another electron-rich compound propranolol during the UV/PS process [47]. Thus, in this study, the scavenging effect of Cl\(^-\) on free radicals including ‘OH and ‘SO\(_4\)\) can be ignored.

### 3.2.5.2 Nitrate

In contrast, the inhibitory effect of NO\(_3^-\) on MB removal is obvious. When the concentration of NO\(_3^-\) gradually increased from 1 to 20 mM, the MB removal efficiency first decreased from 100% to 94.26% and then continuously decreased to 79.79%. This result could be because the produced ‘OH and ‘SO\(_4^-\) can be consumed by the NO\(_3^-\) and generate reactive radicals like ‘NO\(_2\) and ‘NO\(_3\) with lower oxidizing ability via Eq. (34)-(40) [46, 48]. Among them, it is worth noting that although ‘O\(^-\) and derivative product ‘OH generated by direct UV irradiation of NO\(_3^-\) can promote the degradation of MB, in fact,
NO₃⁻ may first react with 'OH and 'SO₄⁻ first [49]. As a result, the removal efficiency of MB was greatly reduced due to the presence of NO₃⁻.

\[ \text{NO}_3^- \xrightarrow{hv} '\text{NO}_2 + '\text{O}^- \]  
\[ 2\text{NO}_3^- \xrightarrow{hv} 2\text{NO}_2^- + \text{O}_2 \]  
\[ '\text{O}^- + \text{H}_2\text{O} \rightarrow \text{OH}^- + '\text{OH} \]  
\[ '\text{SO}_4^- + \text{NO}_3^- \rightarrow '\text{NO}_3 + \text{SO}_4^{2-} \]  
\[ '\text{OH} + \text{NO}_3^- + \text{H}^+ \rightarrow '\text{NO}_3 + \text{H}_2\text{O} \]  
\[ '\text{SO}_4^- + \text{NO}_2^- \rightarrow '\text{NO}_2 + \text{SO}_4^{2-} \]  
\[ '\text{OH} + \text{NO}_2^- \rightarrow '\text{NO}_2 + \text{OH}^- \]  

3.2.5.3 Nitrite

Similar to the results obtained by adding NO₃⁻, the presence of NO₂⁻ had an even more negative effect on the system performance. Specifically, when the concentration of NO₂⁻ gradually increased from 1 to 20 mM, the MB removal efficiency first decreased from 100% to 91.02% and then continuously decreased to 75.91%. The negative effect caused by NO₂⁻ is mainly attributed to its quenching effect on 'OH and 'SO₄⁻ via Eq. (39), (40) and (41) [47, 50].

\[ '\text{OH} + '\text{NO}_2 \rightarrow \text{HO}_2\text{NO} + \text{OH}^- \]  

3.2.5.4 Biocarbonate

Fig. 4 shows that HCO₃⁻ also has a significant negative effect on system performance, and the negative effect continued to increase as the concentration increased. When HCO₃⁻ was added to the catholyte, a hydrolysis reaction first occurred to form CO₃²⁻ via Eq. (30). Thereafter, both of HCO₃⁻ and CO₃²⁻ can greatly participate in the competitive consumption of 'OH and 'SO₄⁻ to form transformation reactive radicals (e.g., 'CO₃⁻ and 'HCO₃⁻) with lower reactivity via Eq. (42)-(45) [47, 50]. In addition, it is worth noting that the addition of HCO₃⁻ will increase the pH of the catholyte. Consequently, the initial pH corresponding to different HCO₃⁻ dosages (1, 5, 10 and 20 mM) are 6.71, 7.76, 8.13 and 8.24, respectively. As we found in the previous section that the increase in the
catholyte pH can lead to a decrease in the MB removal efficiency. Therefore, the increase in the catholyte pH caused by the addition of HCO$_3^-$ would also lead to a decrease in the removal efficiency of MB. As the dosage of HCO$_3^-$ increases, the negative effect is expected to be more obvious.

\[
\begin{align*}
\cdot SO_4^--HCO_3^- & \rightarrow \cdot HCO_3^- + SO_4^{2-} \quad (42) \\
\cdot OH + HCO_3^- & \rightarrow \cdot CO_3^- + H_2O \quad (43) \\
\cdot SO_4^- + CO_3^{2-} & \rightarrow \cdot CO_3^- + SO_4^{2-} \quad (44) \\
\cdot OH + CO_3^{2-} & \rightarrow \cdot CO_3^- + OH^- \quad (45)
\end{align*}
\]

Lastly, both of the selected anions and their transformation reactive radicals may also compete with H$_2$O$_2$, PS, and MB for UV photons, and thereby reducing the amounts of radicals for MB removal [14]. Similar results were also observed in the previous study regarding MB degradation through VUV/UV/PS process [14].

Fig.4 is here

3.2.6 Contribution of reactive species

Based on the foregoing introduction, ‘OH, ‘SO$_4^-$, and ‘O$_2^-$ were considered to be the main reactive species in the MEUPS process [51]. As previously reported, the rate constants of the reactions between isopropanol (IPA) and ‘OH and ‘SO$_4^-$ were not much different (2.8 × 10$^9$ M$^{-1}$ s$^{-1}$ and 6 × 10$^7$ M$^{-1}$ s$^{-1}$, respectively), whereas tert-butyl alcohol (TBA) reacted at a higher rate with ‘OH ((3.8–7.6) × 10$^8$ M$^{-1}$ s$^{-1}$) and at a lower rate with ‘SO$_4^-$ ((4.0–9.1) × 10$^5$ M$^{-1}$ s$^{-1}$) [52, 53]. Consequently, TBA reacted at a rate about 870 times faster with ‘OH than ‘SO$_4^-$, while the reaction of IPA with ‘OH was only around 47 times faster than ‘SO$_4^-$. Besides, 1,4-benzoquinone (BQ) could react with ‘O$_2^-$ at a high rate constant of 9.6 × 10$^8$ M$^{-1}$ s$^{-1}$ [54]. Thus, TBA, IPA, and BQ, which were capable of quenching ‘OH, both ‘OH and ‘SO$_4^-$, and ‘O$_2^-$, respectively, were chosen to determine the involvement of each reactive species in the MEUPS [51]. We also use scavengers with a dose (IPA or TBA of 20 and 200 mM) equivalent to or higher than the oxidant (PS) to ensure inhibition of MB removal.
degradation. As for BQ, its dosage of 20 mM was determined according to the previous literature [55].

It can be seen in Fig. 5 that after adding TBA or IPA, the removal of MB was significantly inhibited (45.88%, 32.90% of TBA and 38.88%, 21.51% of IPA at dosage of 20 and 200 mM, respectively). The result confirmed the existence of ‘OH and ‘SO₄⁻ and their major role in the degradation of MB during the MEUPS process. Comparatively, the removal efficiency of MB still reached 88.02% within 160 min after adding 20 mM BQ, indicating that ‘O₂⁻ played a minor role during the MEUPS process. To conclude, in the MEUPS process, the reactive radicals species that played a major role in the treatment of MB were considered to be ‘OH and ‘SO₄⁻, while ‘O₂⁻ acted a minor role.

Fig.5 is here

3.2.7 Proposed the working mechanism of the MEUPS process

In the previous section, the main types of reactive radicals (‘SO₄⁻, ‘OH, and ‘O₂⁻) generated in the cathode chamber of the MEUPS system were determined, and on this basis, the working mechanism of the MEUPS system was proposed, as shown in Fig. 6. The synergistic effect on the treatment of MB-contaminated wastewater can be explained as the fact that more reactive radicals (‘SO₄⁻, ‘OH, and ‘O₂⁻) were generated through the catalysis of both PS and H₂O₂ by UV irradiation, electrons and H₂O₂. More specifically, in the anodic compartment, the anodic electrochemically active biofilm could ultilize organic substances in municipal wastewater firstly and convert them into electrons, protons and carbon dioxide. Notably, we also monitored the COD concentration of anodic effluent, which showed that the COD removal efficiency by the anodic microorganisms was about 85.12 ± 0.55%. Then, the generated electrons and protons entered the cathodic compartment through the wire and the CEM respectively, and some of the electrons combined with the aerated oxygen and protons to synthesize H₂O₂ in-situ on the electrode surface via Eq. (4). The other part of the electron binded to PS, the electron acceptor, to form the ‘SO₄⁻ via Eq. (10) [31]. In addition, as described in the previous section, the in-situ synthesis of H₂O₂ can also activate PS and produce the ‘SO₄⁻ via Eq. (9).
Under UV irradiation, the generated H$_2$O$_2$ and dosed PS were well known to be activated to produce \( \text{SO}_4^{2-} \) and \( \cdot\text{OH} \) via Eq. (7) and (8) \cite{14, 15}. In addition, the generated \( \text{SO}_4^{2-} \) may also trigger the radical conversion reaction via Eq. (21) and (22), thus forming \( \cdot\text{OH} \) with stronger oxidation ability \cite{29}. As for the formation of \( \text{O}_2^- \), which had a low contribution to the overall treatment efficiency, its generation was mainly due to the direct combination of electrons and aerated oxygen via Eq. (46) \cite{56}. Moreover, the reaction of \( \cdot\text{OH} \) and H$_2$O$_2$ under alkaline conditions will also generate a small amount of \( \text{O}_2^- \) via Eq. (24) \cite{44}.

\[
e^- + \text{O}_2 \rightarrow \text{O}_2^- \quad (46)
\]

Notably, the produced \( \text{O}_2^- \) can further convert into \( \cdot\text{OH} \) and \( \text{SO}_4^{2-} \) via Eq. (47) and (48), thus enhancing the treatment performance of the MB-contaminated wastewater \cite{56, 57}.

\[
\text{O}_2^- + \text{H}_2\text{O} \rightarrow \cdot\text{OH} \quad (47)
\]

\[
\text{O}_2^- + \text{S}_2\text{O}_8^{2-} \rightarrow \text{SO}_4^{2-} + \cdot\text{SO}_4^{2-} + \text{O}_2 \quad (48)
\]

Therefore, for the treatment of MB-contaminated wastewater with high chromaticity, due to the influence of chromaticity on the UV transmittance in the initial treatment stage, a series of reactive radicals including \( \text{SO}_4^{2-} \), \( \cdot\text{OH} \), and \( \text{O}_2^- \) were generated by the electronic catalysis of PS and aerated oxygen and H$_2$O$_2$ activation of PS as describe above to involve the pollutants removal. Note that in the initial stage of the reaction, the darker color of the solution resulted in low UV transmittance, so UV radiation only played a very limited role on the degradation of MB in the MEUPS system. This inference has been verified in the previous series of control experiments (see Fig. 2). Subsequently, with the decrease of chromaticity, the participation of UV radiation can effectively activate H$_2$O$_2$ and PS to generate more reactive radicals (mainly were \( \text{SO}_4^{2-} \) and \( \cdot\text{OH} \)) to achieve rapid decolorization and mineralization of such wastewater. Besides, with the increase in transmittance, UV radiation was also believed to be more effective in participating in MB degradation directly. In conclusion, the boosted reactive radicals including \( \text{SO}_4^{2-} \), \( \cdot\text{OH} \), and \( \text{O}_2^- \) in this novel MEUPS process were mainly
responsible for the degradation of target pollutants and ultimately complete mineralization via Eq. (49).

\[ \cdot \text{SO}_4^- / \cdot \text{OH} / \cdot \text{O}_2^- + \text{target pollutants} \rightarrow \text{transformation products} \rightarrow \text{CO}_2 + \text{H}_2\text{O} \quad (49) \]

Fig.6 is here

3.3 Economic analysis

Since UV light was used, instead of traditional Fe (II), to activate PS and the in-situ generated H_2O_2, the operating cost of the MEUPS system can be mainly divided into two parts, one was electrical energy consumed by the UV lamp, stirring and the pumping for aeration and the other part was the consumption of PS as a chemical agent. The electricity price in Denmark was about 0.25 € kWh\(^{-1}\) and the industrial price of PS was approx. 0.54 € kg\(^{-1}\) [42]. Moreover, electrical energy consumption regarding the mineralization of MB was calculated (Fig. S6). The mineralization process accorded with pseudo-first-order kinetics and the \(k_{\text{app}}\) value was around 0.701 h\(^{-1}\) (\(R^2 = 0.98\)). As described previously, the electrical energy consumption in terms of \(E_{\text{EO}}\) value and the total operating cost per order (Cost/O\(_{\text{total}}\)) regarding on decolorization and mineralization of MB were calculated and presented in Table 1. The calculated \(E_{\text{EO}}\) value was considered reasonable, which was one order of magnitude from the median \(E_{\text{EO}}\) value of different AOPs [58]. UV lamps and aeration account for about 95% of the energy consumption, which could be further reduced by selecting a more efficient UV light source (such as a medium pressure UV lamp), adjusting the design of the aeration, and running the reactor in the continuous mode in the future. Moreover, because the selected MB was a heavier color dye, the future treatment of low-concentration or lighter-colored substances will also reduce energy consumption by reducing the filtering effect of UV [59].

Besides, as shown in Table 2, we also compared the treatment performance and operating cost (mainly electrical energy consumption) of MEUPS with other AOPs that are commonly used to treat MB-containing wastewaters. Although the UV/H_2O_2, UV/H_2O_2/TiO_2, sono-Fenton, and EF showed a faster decolorization rate of MB compared to the MEUPS, their \(E_{\text{EO}}\) values were indeed an order of
magnitude higher than that of the MEUPS process. It should be noted that higher pollutant concentration was applied in this study, thus the decolorization rate would be further accelerated and energy consumption would be further reduced when treating wastewater with a relatively lower concentration of MB. Compared to the MEUPS process, the UV or visible light-based photocatalysis processes like UV-LED/TiO$_2$ process and bioelectrochemical-based EF process like the BEF process showed higher energy consumption and lower treatment efficiency. Especially, for these processes, the catalyst activity cannot be guaranteed during long-term operation. In addition, it is worth noting that ozonation exhibited a very excellent MB decolorization effect (e.g., 50 mg L$^{-1}$ of MB achieved complete decolorization within 4min). Therefore, from the perspective of decolorization, the combination of ozonation and MEUPS process could achieve rapid decolorization and enhance mineralization capabilities. Lastly, it can be seen from Table 2 that the removal efficiency of the conventional biological treatment processes was far lower than that of the MEUPS process. Furthermore, the MEUPS process can operate over a wide pH range, whereas biological treatment processes and Fenton based AOPs were limited to a very narrow pH range. In this regard, the MEUPS process can be recognized as a low-cost and efficient treatment technology for treating dye-containing wastewater.

Table 1 and 2 are here

3.4 Ecotoxicity assessment

Based on the results above, the mineralization of MB required a longer time than the decolorization of MB. Therefore, discharging treated effluent based on the decolorization degree could significantly save the treatment cost. However, due to incomplete mineralization, the resulting intermediates may be toxic or even more toxic than parent MB and thus further assessing the aquatic toxicity of effluent before discharging is required. Therefore, in this study, *L. minor* was exposed to the reference solution, untreated MB solution, and MB solutions treated for 60, 100, 120, 140, and 160 min under the selected operating condition to study the ecotoxicological effect of MB and the generated
intermediate compounds during the MEUPS treatment process. As shown in Fig.7, *L. minor* exposed to the untreated solution had withered, indicating the toxicity of MB. Comparatively, the samples collected after 120 min of treatment in the MEUPS showed almost no toxic effect to *L. minor*. Thus, we can conclude that the toxic MB and probable intermediates were finally removed or converted to non-toxic compounds. The above results further prove and promote the proposed MEUPS as an appropriate water treatment technology for the outstanding removal of emerging pollutants.

**Fig.7 is here**

4. Conclusions

The proposed novel MEUPS process presented a remarkable enhancement in the treatment of MB-contaminated wastewater compared with the conventional processes. The effect of operating parameters including input voltage, cathodic aeration velocities, PS dosage, and initial catholyte pH on the treatment performance was systematically studied. It was found the decolorization and mineralization of MB conformed to pseudo-first-order kinetics and the rate constants were $2.67 \times 10^{-2}$ min$^{-1}$ and $7.01 \times 10^{-1}$ h$^{-1}$, respectively. $\cdot$SO$_4^-$, $\cdot$OH and $\cdot$O$_2^-$ were involved in the degradation of MB, among which $\cdot$SO$_4^-$ and $\cdot$OH played a key role. The common existing inorganic anions such as HCO$_3^-$, NO$_2^-$ and NO$_3^-$ influenced negatively the removal of MB, while the presence of Cl$^-$ did not significantly inhibit the degradation of MB in the MEUPS. In addition, compared to UV-LED/TiO$_2$, Visible light/BaFe$_{12}$O$_{19}$/H$_2$O$_2$, and BEF processes, the MEUPS process not only increased the removal rate but also greatly reduced the energy consumption for MB wastewater treatment. The eco-toxicity test showed that the effluent after 120 min of treatment in the MEUPS had no obvious toxicity. This proof-of-concept work demonstrated an innovative microbial electrochemically assisted UV/PS process for efficient and cost-effective treatment of emerging pollutants.

Acknowledgments

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References


**Highlight**

- PS assisted microbial electrolysis ultraviolet cell for wastewater treatment.
- The hybrid process has a significant synergy compared to the individual ones.
- This process was more efficient and cost-effective than common AOPs (e.g. UV/H$_2$O$_2$).
- MEUPS has much broader working pH range than typical (bio)electro-Fenton process.
- MEUPS process can effectively reduce the toxicity of MB via *L.minor* bioassays.

**Graphical abstract**
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.

☐ The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:
Fig. 1. Picture and schematic diagram of the MEUPS reactor. (a) Picture of 20 L MEUPS reactor; (b) Front view of MEUPS schematic; (c) Side view of MEUPS schematic; (d) Top view of MEUPS schematic.
Fig. 2. (a) Comparison of the decolorization of MB through different treatment methods. (b) Determination of decolorization kinetic constants of MB through different treatment methods. (c) Evaluation of the synergy factor for MEUPS with MEUC and UV/PS. Operating conditions: MB of 40 mg L\textsuperscript{-1}, Na\textsubscript{2}SO\textsubscript{4} of 50 mM, PS of 25 mM, cathodic aeration velocity of 0.056 mL min\textsuperscript{-1}, input voltage of 0.6 V, UV intensity of 48 µW cm\textsuperscript{-2} and without pH adjustment.
Fig. 3. Effect of operating parameters including (a) input voltage, (b) cathodic aeration velocities, (c) PS dosage, (d) initial catholyte pH on the decolorization of MB through the MEUPS process. Operating conditions: MB of 40 mg L^{-1}, Na_2SO_4 of 50 mM, input voltage of 0.1, 0.3, 0.5, 0.6 and 0.7 V, cathodic aeration velocity of 0.0056, 0.011, 0.022, 0.033 and 0.056 mL min^{-1} mL^{-1}, PS of 5, 10, 15, 20 and 25 mM, initial catholyte pH of 3, 5, 7, 9 and 11, UV intensity of 48 µW cm^{-2} and without pH adjustment.
Fig. 4. Effect of inorganic ions (Cl$^-$, NO$_3^-$, NO$_2^-$, and HCO$_3^-$) on the decolorization of MB through the MEUPS process. Operating conditions: MB of 40 mg L$^{-1}$, Na$_2$SO$_4$ of 50 mM, PS of 25 mM, cathodic aeration velocity of 0.056 mL min$^{-1}$ mL$^{-1}$, input voltage of 0.6 V, UV intensity of 48 $\mu$W cm$^{-2}$ and without pH adjustment.
Fig. 5. Effect of radical scavengers on the decolorization of MB through the MEUPS process. Operating conditions: MB of 40 mg L\(^{-1}\), \(\text{Na}_2\text{SO}_4\) of 50 mM, PS of 25 mM, cathodic aeration velocity of 0.056 mL min\(^{-1}\) mL\(^{-1}\), input voltage of 0.6 V, UV intensity of 48 µW cm\(^{-2}\) and without pH adjustment.
Fig. 6. Proposed working mechanism of the MEUPS process for the treatment of MB-contaminated wastewater
Fig. 7. Eco-toxicity assessment on the decolorization of MB through the MEUPS process by comparing the conversions in the frond color of duckweed of *L. minor* after 1 day and 14 days of cultivation. Operating conditions: MB of 40 mg L$^{-1}$, Na$_2$SO$_4$ of 50 mM, PS of 25 mM, cathodic aeration velocity of 0.056 mL min$^{-1}$ mL$^{-1}$, input voltage of 0.6 V, UV intensity of 48 µW cm$^2$ and without pH adjustment.

Table 1. Economic analysis for the removal of MB in the MEUPS process.
<table>
<thead>
<tr>
<th>Electrical energy-consuming components</th>
<th>$E_{EO}$ (Decolorization) (kWh m$^{-3}$ order$^{-1}$)</th>
<th>Cost/O (€ m$^{-3}$ order$^{-1}$)</th>
<th>$E_{EO}$ (Mineralization) (kWh m$^{-3}$ order$^{-1}$)</th>
<th>Cost/O (€ m$^{-3}$ order$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>UV lamp</td>
<td>1.553</td>
<td>0.095</td>
<td>11.190</td>
<td>2.798</td>
</tr>
<tr>
<td>Direct voltage supply</td>
<td>0.002</td>
<td>0.001</td>
<td>0.017</td>
<td>0.001</td>
</tr>
<tr>
<td>Cathodic aeration</td>
<td>2.218</td>
<td>0.532</td>
<td>15.980</td>
<td>3.995</td>
</tr>
<tr>
<td>Stirring</td>
<td>0.232</td>
<td>0.058</td>
<td>1.671</td>
<td>0.418</td>
</tr>
<tr>
<td>PS</td>
<td>0</td>
<td>3.213</td>
<td>0</td>
<td>3.213</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>4.005</strong></td>
<td><strong>3.899</strong></td>
<td><strong>28.858</strong></td>
<td><strong>10.428</strong></td>
</tr>
<tr>
<td>Treatment technologies</td>
<td>Operating conditions</td>
<td>Degradation efficiency</td>
<td>Energy consumption (E/EO, kWh m$^{-3}$)</td>
<td>Reactor volume (mL)</td>
</tr>
<tr>
<td>----------------------------------------</td>
<td>---------------------------------------------------------------------------------------</td>
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</tr>
<tr>
<td>UV/TiO$_2$/H$_2$O$_2$</td>
<td>20 mg L$^{-1}$ of MB, 100 mg L$^{-1}$ of H$_2$O$_2$ and 1 g L$^{-1}$ TiO$_2$</td>
<td>98% in 10 s</td>
<td>38.09</td>
<td>10</td>
</tr>
<tr>
<td>UV/H$_2$O$_2$</td>
<td>20 mg L$^{-1}$ of MB and 1.4 g L$^{-1}$ of H$_2$O$_2$</td>
<td>100% in 5 s</td>
<td>16.24</td>
<td>10</td>
</tr>
<tr>
<td>Visible light/BaFe$<em>{12}$O$</em>{19}$/H$_2$O$_2$</td>
<td>10 mg L$^{-1}$ of MB, 12 mM of H$<em>2$O$<em>2$ and 0.75 g L$^{-1}$ BaFe$</em>{12}$O$</em>{19}$</td>
<td>70.8% in 6 h</td>
<td>11.10</td>
<td>50</td>
</tr>
<tr>
<td>BEF</td>
<td>20 mg L$^{-1}$ of MB, pH of 2, 0.2 mM of Fe$^{2+}$, cathodic aeration velocity of 0.039 mL min$^{-1}$ mL$^{-1}$, and 0.4 V.</td>
<td>98% in 8 h</td>
<td>53.33</td>
<td>200</td>
</tr>
<tr>
<td>Sono-Fenton</td>
<td>10 mg L$^{-1}$ of MB, pH of 2.5, 1 g L$^{-1}$ of Fe$^{6+}$, ultrasound 120 W L$^{-1}$, 100 mg L$^{-1}$ of H$_2$O$_2$</td>
<td>100% in 5 min</td>
<td>40</td>
<td>100</td>
</tr>
<tr>
<td>EF using a self-doped TiO$_2$ nanotubes electrode</td>
<td>20 mg L$^{-1}$ of MB, pH of 3, and current density of 16.67 mA cm$^{-2}$.</td>
<td>Around 90% in 20 min</td>
<td>77.60</td>
<td>500</td>
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<tr>
<td>UV-LED/TiO$_2$</td>
<td>5 mg L$^{-1}$ of MB</td>
<td>61% in 300 min</td>
<td>3000</td>
<td>200</td>
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<tr>
<td>Ozonation</td>
<td>50 mg L$^{-1}$ of MB, pH of 5, ozone gaseous concentration of 3.6 mg L$^{-1}$</td>
<td>100% in 4 min</td>
<td>–</td>
<td>100</td>
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<tr>
<td>Biological treatment using $\text{Galactomyces geotrichum KL20A}$</td>
<td>50 mg L$^{-1}$ of MB and 35 $\text{°C}$</td>
<td>70% in 48 h</td>
<td>–</td>
<td>12</td>
</tr>
<tr>
<td>Packed bed bio-reactor (PBBR)</td>
<td>500 mg L$^{-1}$ of MB</td>
<td>87% in 240 h</td>
<td>–</td>
<td>251</td>
</tr>
<tr>
<td>MEUPS process</td>
<td>40 mg L$^{-1}$ of MB, 25 mM of PS, cathodic aeration velocity of 0.056 mL min$^{-1}$ mL$^{-1}$, without pH adjustment and 0.6 V</td>
<td>100% in 140 min</td>
<td>4.005</td>
<td>200</td>
</tr>
</tbody>
</table>

- Not reported in the paper

**Supporting Information**

**Synergistic effect for efficient oxidization of refractory organics with high chroma by an innovative persulfate assisted microbial electrolysis ultraviolet cell**

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Fig. S1. $\text{H}_2\text{O}_2$ synthesis (without PS dosing), comparison of current density, and the mineralization of MB during the MEUPS process.

Fig. S2. The effect of input voltage (current density and cathode potential) on the decolorization of MB through the MEUPS process.

Fig. S3. The effect of cathodic aeration velocities (current density and cathode potential) on the decolorization of MB through the MEUPS process.
Fig. S4. The effect of PS dosage (current density and cathode potential) on the decolorization of MB through the MEUPS process.

Fig. S5. The effect of catholyte pH (pH variation) on the decolorization of MB through the MEUPS process.
Fig. S1
Fig. S2
Fig. S3
Fig. S4
Fig. S5