



Influence of ultrasound modes on sonoelectrochemical degradation of Congo red and palm oil mill effluent

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ARTICLE INFO

Keywords:

Electrochemical oxidation
Sonoelectrochemical
Congo red
Palm oil mill effluent
Energy consumption

ABSTRACT

Sonoelectrochemical oxidation (SEO) treatment is a competitive technology for the degradation of organic pollutants in water. The operation modes of ultrasound (continuous and pulse) not only affect the pollutant degradation efficiency but also the energy consumption of SEO. In this study, the influence of ultrasound modes on SEO degradation of Congo red (CR) and real wastewater – palm oil mill effluent (POME) were investigated. The SEO was operated in two modes: continuous ultrasound throughout the whole process and intermittent ultrasound at a cycle of 15 min of ultrasound and 5 min without ultrasound. It was found that the intermittent SEO gave a higher degree of degradation of CR at 95% as compared to continuous SEO and electrochemical oxidation (EO) at 85% and 64%, respectively. The improved performance could be attributed to the supply of ultrasound that minimized electrode passivation and promoted mass transfer and production of hydroxyl radicals. The intermittent supply of ultrasound diminished the interference of ultrasound on the electrochemical process. A similar observation was also observed where the highest COD reduction of POME was recorded by intermittent SEO at about 65%. In terms of energy consumption, degradation of CR by SEO only required half of the energy consumed by the analogous purely electrochemical process at 250–265 kWh/kg dye removed. Surprisingly, the energy consumption for SEO degradation of POME only reduced from 32.82 (electrochemical) to 25.91 and 30.78 kWh/kg COD removed for continuous and intermittent SEO, respectively. Such contrast in energy saving highlights the need for further study as the complex constituents of real effluents will result in different SEO treatment performance. Nonetheless, the capability of SEO in reducing the COD indicates its potential to be used as pre- or post-treatment for other advanced processes in POME handling.

Introduction

Rapid industrialization has introduced a large number of hazardous pollutants into the environment, which pose an adverse risk to local ecosystems and living organisms. Conventional wastewater treatment methods have often struggled to efficiently remove emerging and persistent organic pollutants [1–6]. The presence of these pollutants has been reported to cause health problems [7]. To address these issues, advanced oxidation processes (AOPs) which rely on the generation of highly reactive and oxidable free radicals have received an increasing prevalence in wastewater treatment due to their oxidizing power. Among AOPs, electrochemical oxidation (EO) processes have attracted a great deal of attention attributed to their mild operational conditions, efficient functioning at room temperature, no requirement for additional chemicals, and complete mineralization/degradation of organic

pollutants [8,9]. For instance, EO processes have been proven capable of the partial degradation or even complete mineralization of dyes and phenol pollutants by the electrogeneration of hydroxyl radicals with great oxidizing power [10].

Despite their promising pollutant degradation performance, EO processes alone usually require a long reaction time to achieve satisfactory degradation efficiency. This is due to electrode surface passivation by reaction by-products which limits the available surface for the oxidation reaction to occur [11]. Another factor hampering EO processes is the slow mass transport of reactants to the electrode surface where the hydroxyl radicals that are generated accumulate [12]. The combination of EO with ultrasound irradiation (US), so-called sonoelectrochemical oxidation (SEO), could compensate for the weaknesses of the EO process by keeping the electrode clean and activated, as well as enhancing the mass transport rates of reactants to the electrode surface

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<https://doi.org/10.1016/j.rechem.2023.100880>

Received 30 July 2022; Accepted 2 March 2023

Available online 6 March 2023

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[13,14]. Many researchers have reported that there was an obvious improvement on the pollutant degradation efficiency by SEO as compared to standalone EO or US process [15]. For example, the mineralization kinetics of Allura Red and Erythrosine B dyes were improved from 0.08 to 0.11 min⁻¹ and from 0.03 to 0.04 min⁻¹, respectively, when the EO process was assisted with US [11]. The efficiency of reduction of chemical oxygen demand (COD) of cosmetic industry wastewater was also improved from 60.2 to 80.9% with the presence of US [16]. These positive enhancements could be attributed to the increased generation of hydroxyl radicals and mass transfer afforded by SEO as well as the minimization of electrode passivation.

Considering SEO is an integration of both EO and US into a single treatment process, the factors influencing the performance of individual EO or US processes are also applicable to SEO. The important factors that directly or indirectly affect the SEO process performance include electrode materials, reactor design, and operating conditions (e.g., US power, US frequency, current density, applied voltage, solution pH, and electrolyte and electrolyte concentration), where the interaction between these factors and process performance have been thoroughly discussed in literature [15]. On the other hand, if operated inappropriately, the use of US could undermine the performance of the SEO process. It is known that the acoustic streaming and micro jetting produced by US can disrupt the directional movement of charged ions to the electrodes and the large number of bubbles produced can reduce the conductivity of electrolytes [17]. This could compromise the performance of SEO on top of the additional energy consumption due to the fact that both US and EO processes require power for operation.

The concerns stated above have driven some studies to look into the energy consumption of SEO. Some studies reported that the energy consumption of the SEO was improved as compared to standalone EO. For instance, the energy consumption for the degradation of Reactive Red 195 dye was reduced from 72.3 to 65.7 kWh/kg of COD removal while the degradation of Reactive Blue 19 dye showed a reduction of energy consumption from 1.2 to 0.75 kWh/L when US was applied to the EO process [18,19]. On the other hand, contradictory observations were also reported by researchers. Shestakova et al. observed that the energy consumption required for 90% degradation of formic acid increased from 675 to 1785 kWh/m³ when the treatment processes were conducted as EO and SEO, respectively [20]. This reflects that the US power requirement could be several orders of magnitude higher than that of the EO system. To improve the energy consumption efficiency of SEO without compromising the degradation performance, SEO operated under pulse mode was proposed. Interestingly, the energy consumption for *p*-nitrophenol degradation was halved (from 0.7336 to 0.3639 kWh/L) when the US was switched from continuous mode to pulse mode, with additional improvement of degradation efficiency from 89 to 94% [21]. This finding indicates the potential to achieve energy savings for SEO when the US supply is operated creatively.

Even though pulsed SEO appears to be promising in term of degradation performance and energy consumption, study related to this has been scarce, not to mention the use of real wastewater for SEO operated under different US modes. In this study, SEO operated under continuous and intermittent mode for palm oil mill effluent (POME) treatment was evaluated. POME is the largest agricultural wastewater in Malaysia, and contains abundant organic matter that contributes to the high COD value [22]. Proper treatment of POME is required to remove the organic compounds before treated effluent can be safely discharged to waterways. Hence, SEO could play a role in assisting the reduction of COD in POME. Prior to the use of POME for SEO study, the synthetic azo dye solution (Congo Red in Na₂SO₄ electrolyte) was used as the testing solution to understand the influence of US mode and operating conditions (solution pH, current, and inter-electrode distance) on the degradation efficiency. As a commonly found persistent pollutant, Congo red dye is used as the control pollutant in the operational parameter study to investigate the potential of SEO and EO technology in degrading recalcitrant pollutant. Fig. 1 shows the chemical structure of the dye,

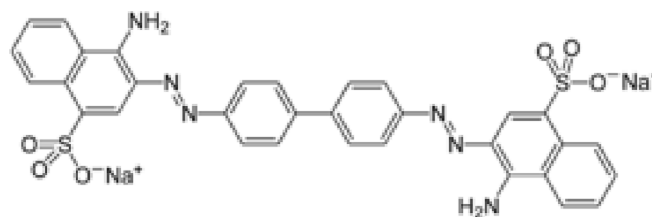


Fig. 1. Congo red dye chemical structure.

composing of -NH₂ and -SO₃ functional groups as well as other electron-withdrawing functional groups. The findings from the synthetic dye solution were then used to suggest conditions for the SEO treatment of POME.

Methodology

Chemicals and materials

Congo red (Sigma-Aldrich) was used to prepare the synthetic pollutant solution. Hydrochloric acid (R&M Chemicals) and sodium hydroxide (Sigma-Aldrich) were used for adjusting the pH. Sodium sulfate (R&M Chemicals) was used as the electrolyte for the synthetic wastewater. Boron doped diamond (BDD) anode was obtained from Boromond, China. Aerobically treated palm oil mill effluent (POME) was taken from a nearby palm oil mill. The sample was stored immediately at 4 °C to reduce or prevent any additional biological and chemical degradation. Before being used in the experiment, POME was centrifuged for 4 h to remove the large suspended solids.

Sonoelectrochemical system

Electrochemical oxidation (EO) and sonoelectrochemical oxidation (SEO) processes were conducted in a cylindrical glass beaker containing 500 mL of testing solution. BDD was used as the anode while a stainless steel plate was used as cathode. Both the anode and cathode were rectangular in shape with a geometric area of 48 cm². For the SEO processes, the electrochemical cell was placed in an ultrasound generator (Elmasonic S60H, Elma) at 37 kHz as shown in Fig. 2. The temperature of the water bath was kept below 30 °C by continuously replacing the water to remove the heat produced during sonication. The pH value was measured throughout the experiment by immersing the pH probe (HI 2550, HANNA instrument) in the solution.

The performance of the EO and SEO processes was evaluated by

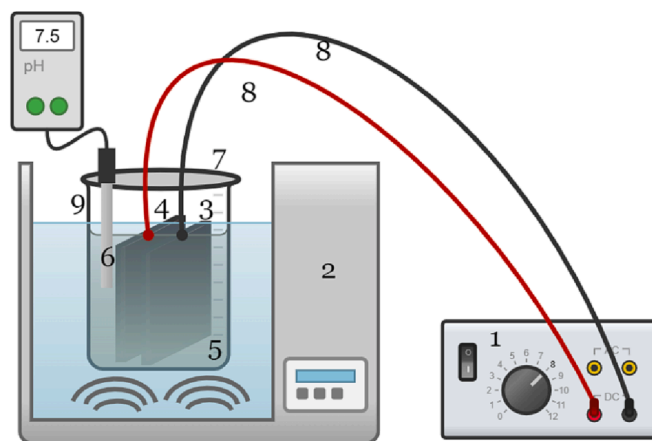


Fig. 2. Set up for SEO process: (1) DC power supply, (2) Ultrasound generator, (3) BDD anode, (4) Stainless steel cathode, (5) POME, (6) pH probe, (7) cover, (8) electric cables, (9) 600 mL beaker.

using two solutions: synthetic dye solution consisting of Congo red (CR) at 20 ppm in 0.05 M Na₂SO₄ (electrolyte) and real wastewater – aerobically treated palm oil mill effluent (POME). The characteristics of the POME are displayed in Table 1. The EO experiment was started by investigating the influence of solution pH (5, 7, 9, and 11), current (0.1, 0.15, and 0.2 A), and distance between the electrodes (1–4 cm) on the degradation of the dye. The pH, current, and distance values giving the best dye degradation performance were then used in the subsequent testing of different ultrasound modes. SEO with the synthetic dye solution was subjected to two operating modes: continuous ultrasound for 2 h and intermittent ultrasound at a cycle of 15 min of ultrasound and 5 min without ultrasound for 2 h. The EO and SEO processes were then repeated with POME. The extent of degradation of the EO and SEO processes was determined based on the reduction of UV-absorbance (for CR) and chemical oxygen demand (COD) and colour (for POME) using Equation (1):

$$X = \frac{c_0 - c_t}{c_0} \times 100\% \quad (1)$$

where X is the degree of degradation, c_0 is the initial value of the parameter of concern (absorbance, COD, and colour), and c_t is the value of the parameter of concern at a given time.

Analytical techniques

The variation of the concentration of CR was determined by a UV-VIS spectrophotometer (DR3900, Hach) at 497 nm wavelength [23]. Concentration of CR was quantified from absorbance reading by injecting 2 mL of CR sample into a 10 mm rectangular cuvette before inserted into the spectrophotometer at the mentioned wavelength. COD was analysed with USEPA-approved Hach method 8000. High range COD vials (20–1500 mg/l) were utilised in combination with reactor digestion method using the digital reactor (DRB200, Hach) that complements the Hach reagents. The colour change of POME was measured using a UV-VIS spectrophotometer (DR3900, Hach) at 455 nm wavelength [24]. POME sample was injected into a 10 mL, square sample cell for this colour analysis. The employed Hach method 8025 complied with the Platinum-Cobalt standard method of measuring colour of water. In addition, the amount of suspended solids before and after treatment of POME was measured by a UV-VIS spectrophotometer (DR3900, Hach) based on the Hach method 8006 using the same square sample cell as per colour analysis. The pH value and conductivity were measured by a two-channel logging micro-processor-based meter (HI-2550, HANNA instrument).

The energy consumption for the degradation of the dye was calculated using Equation (2) [25] while the energy consumed per unit COD removal (POME) was determined with Equation (3) [26].

$$E_D : \frac{U \times I \times t}{C_0(0.01d\%)V} \quad (2)$$

$$E_P : \frac{1000 \times U \times I \times t}{C \times V} \quad (3)$$

Here, E_D is the energy consumption for dye degradation (kWh/kg dye removed), U is the mean cell voltage (V), I is current (A), t is reaction time (h), C_0 is dye initial concentration (g/L), $d\%$ is the dye degradation

Table 1
Characteristics of POME.

Parameter	Value
pH	8.0–8.5
COD	600–700 mg/L
Suspended solid	60–62 mg/L
Conductivity	8.2–8.3 mS
Turbidity	4.7–4.9 NTU

percentage (%), V is the electrolyte volume (L), E_p is the energy consumption per unit COD removed from POME (kWh/kg COD removed), and C is the reduction of COD (mg/L).

The rate constants for the US, EO, and SEO processes were calculated using the following equation [20]:

$$\ln C(t) = \ln C_0 - kt \quad (4)$$

where C_0 is the initial concentration of pollutant, C is the concentration of pollutant at time t , and k is the first-order rate constant which is estimated from the slope by plotting $\ln C$ vs. t (not shown in this manuscript).

The combination of US and EO is expected to have higher efficiency as compared to the sum of the efficiencies of the two individual processes. The synergism of SEO is represented by a synergistic index, which was calculated by the following equation [27]:

$$\text{SynergyIndex} = \frac{R_{SEO}}{R_{US} + R_{EO}} \quad (5)$$

where R_{US} , R_{EO} , and R_{SEO} denote the degradation rates of US, EO, and SEO, respectively. A synergy index of 1 means the overall rate is merely the sum of the addition of the individual rates whereas a synergy index greater than 1 means there is a positive synergetic effect (and vice versa).

Results and discussion

Degradation of dye

Effect of solution pH

Fig. 3 shows the degree of degradation of CR dye at different pH values (5, 7, 9, and 11) using an EO process for 2 h. The condition of pH 3 was not conducted as the dye compounds were found to be unstable and tended to settle down at the bottom of beaker naturally. It was found that the degradation percentage increased from 24 to 44% when the solution pH was raised from 5 to 9. This degradation trend aligned with the finding reported by other researchers, where the degradation of Reactive Blue 19 dye was improved by greater than 40% with an increase of pH from 3 to 8 [18]. Such improvement could be attributed to more hydroxyl anions being in the electrolyte, which can be oxidized to hydroxyl radicals at the anode surface under alkaline conditions as shown in equation 6–7 [28]. Hence, more dye pollutants could be degraded in alkaline solution. However, the degradation percentage decreased significantly to 21% once the dye solution was adjusted to pH 11. The decline in performance could be due to the production of more free sulfate radical scavengers that reduce the amount of hydroxyl radicals available for dye degradation. This phenomenon has also been

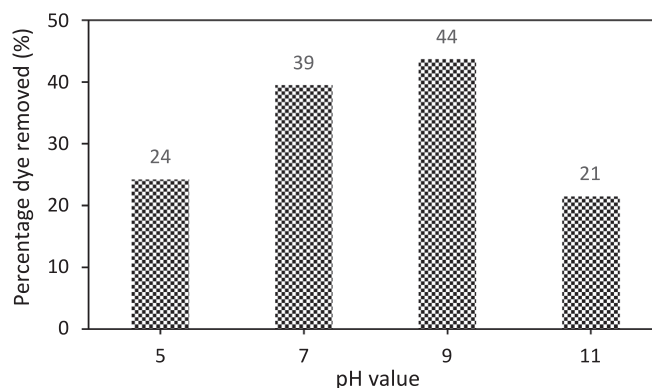


Fig. 3. Effect of pH on the degradation of CR pollutant (operating conditions: 0.1 A, 500 mL of 20 ppm CR solution in 0.05 M Na₂SO₄, distance between electrodes is 2 cm).

observed in other studies where the production of scavengers such as hydroperoxide ion and carbonate ion diminished the amount of hydroxyl radicals in the alkaline solution [16,18,21,28]. Hence, the optimal pH chosen for subsequent tests was pH 9.



Effect of current density

Fig. 4 depicts that the increase in current from 0.1 to 0.2 A led to the enhancement of CR degradation efficiency from 44 to 64%. This observation is expected as with the increase in current, the amount of hydroxyl radicals generated is also increased, which is expected to result in a greater extent of pollutant degradation [29]. Further increase in current had only limited improvement on the degradation performance as the additional charge was passed in performing parasitic water oxidation (oxygen evolution) rather than to oxidize and degrade the pollutants [15,16,30]. Hence, to minimize the oxygen evolution reaction, subsequent EO and SEO tests were conducted at 0.2 A.

Effect of distance between electrodes

The relationship between extent of CR dye degradation and electrode distance of EO process is shown in Fig. 5. It is observed that the degree of degradation peaked at an inter-electrode distance of 2 cm. The reduction in the percentage of degradation when the distance between the electrodes increased from 2 to 4 cm could be attributed to the increase of the solution resistance with enlarged inter-electrode distance. This resulted in lower current density and subsequently led to a smaller amount of electrochemically-generated oxidative species for the degradation of CR. A similar performance trend was also reported by Dietrich et al., where the degradation of bisphenol A declined from 27 to 15% when the electrode distance was adjusted from 2 to 3 cm [31]. Surprisingly, an inter-electrode distance of 1 cm showed a low degradation value of 36% despite the fact that the shorter electrode distance should incur lower solution resistance. It was hypothesized that the short distance favoured the accumulation of CR dye contaminants adsorbed on the electrode surface during the oxidation process and could potentially block and reduce the active sites on the electrode surface. This condition is known as electrode poisoning [27]. Hence, an inter-electrode distance of 2 cm was chosen for the subsequent ultrasound modes study.

Effect of ultrasound modes

Overall, it was found that intermittent SEO process shows the highest degree of degradation of 95%, followed by continuous SEO (85%) and EO (64%) after 2 h of degradation (Fig. 6). The results reveal that both

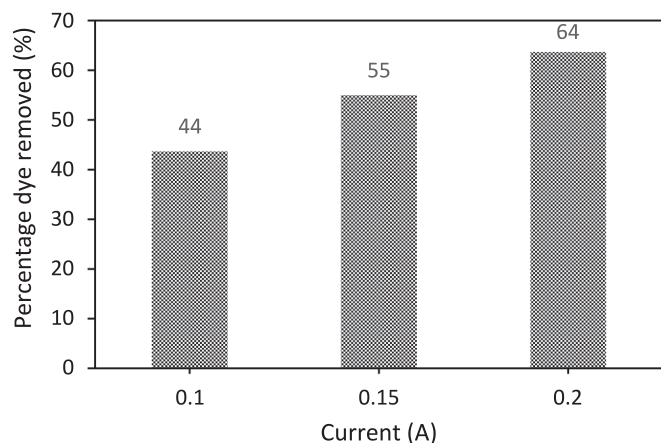


Fig. 4. Effect of current on the degradation of CR pollutant (operating conditions: 500 mL of 20 ppm CR solution in 0.05 M Na₂SO₄, solution pH at 9, distance between electrodes is 2 cm).

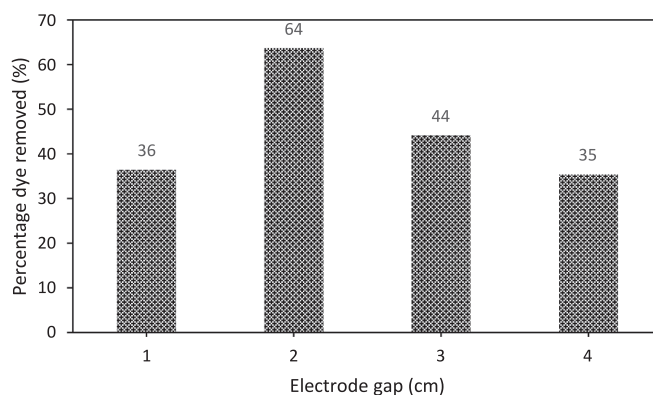


Fig. 5. Effect of electrode distance on the degradation of CR pollutant (operating conditions: 0.2 A, 500 mL of 20 ppm CR solution in 0.05 M Na₂SO₄, solution pH at 9).

SEO processes performed much better than EO for CR dye removal. The supply of US (continuous or intermittent mode) minimized or even alleviated the shortcomings of the EO process, such as electrode passivation and slow mass transport at the electrode-electrolyte interface [15]. US also helps in producing and dispersing more hydroxyl radicals from cavitation bubble splitting, which can accelerate the degradation of pollutants, as supported by observations reported in other studies [32–34]. On the other hand, the intermittent mode SEO possessed a better degradation efficiency compared to continuous mode SEO, which could be explained by referring to other SEO systems operated under pulsed US mode [35,36]. Xia et al. (2014) & Xie et al. (2016) reported that the pulse mode diminished the interference of the US on the EO process, which then slightly enhanced the degradation efficiency of pollutants by 3–5% [21,37]. Indeed, proper operation of pulsed US could enhance the diffusion of the pollutant molecules to the bubble interface, where the degradation reaction is held to take place [30]. The degradation efficiency of intermittent SEO also resulted in a more complete discoloration of CR compounds, as depicted in Fig. 7.

The first-order kinetic rate constants for US, EO, continuous SEO, and intermittent SEO were obtained from the kinetic behaviour (Fig. 8) and tabulated in Table 2. As can be seen, the US process shows the slowest kinetics for CR degradation with a rate constant of 0.0003 min⁻¹ in comparison to 0.0056 min⁻¹ for the EO process. The combination of US and EO has substantially increased the rate of CR degradation to 0.0173 and 0.0264 min⁻¹ for continuous SEO and intermittent SEO, respectively. This can be explained by the enhanced mass transfer in the EO process resulting from the supply of US. Hence, the CR degradation rate was accelerated giving a higher kinetic rate constant.

It is known that energy consumption is one of the deciding factors for a treatment process to be economically feasible. Table 2 displays the energy consumption and synergistic index calculated for the CR degradation operated under different modes. The energy consumption here considered is only the energy required for the EO process due to limitations in obtaining the energy consumption of the US process. Apparently, the incorporation of US successfully reduced the electrochemical energy consumption by roughly 50%. This is a positive improvement that resonates well with other studies, where not only does the SEO improve the treatment efficacy but also enables cost savings from reduced energy consumption [38–41]. Unexpectedly, the energy consumed for continuous and intermittent SEO were more or less the same. Further study is required to optimize the operation of intermittent SEO such that the full potential energy savings can be obtained. The synergistic index reflects the effect arising between US and EO that produces an effect greater than the sum of the individual effects. A positive value of synergistic index indicates that the combination of US and EO performs better than the standalone processes. The synergistic index of continuous and intermittent SEO was found to be greater than 1

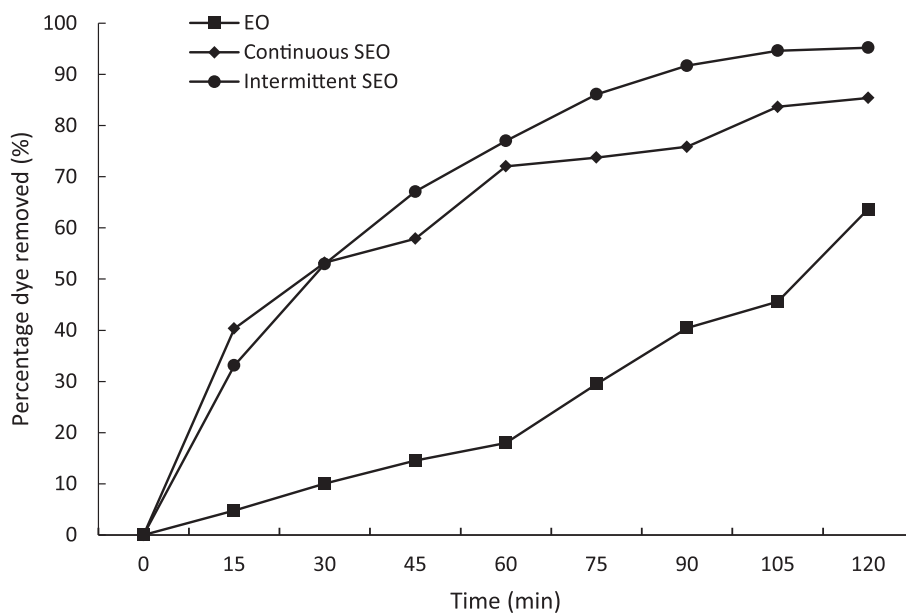


Fig. 6. Effect of ultrasound modes on the degradation of CR dye (operating conditions: 0.2 A, 500 mL of 20 ppm CR solution in 0.05 M Na_2SO_4 , solution pH at 9, electrode distance at 2 cm).

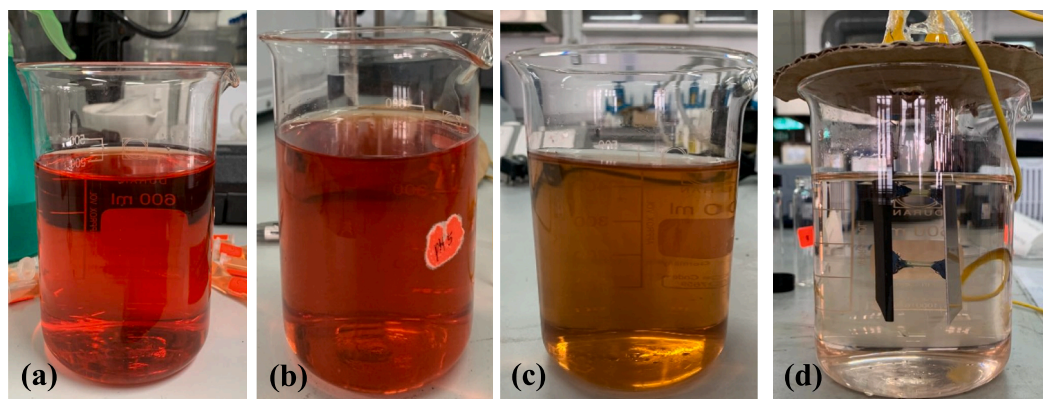


Fig. 7. Physical observation of synthetic dye solutions: (a) pristine dye solution, (b) dye solution after EO treatment for 2 h, (c) dye solution after continuous ultrasound SEO treatment for 2 h, (d) dye solution after intermittent ultrasound SEO treatment for 2 h.

at 2.93 and 4.47, respectively. This confirms that the supply of US led to positive improvement in CR degradation efficiency, and the US supplied intermittently to the SEO delivered better removal percentage for the reasons discussed earlier. Generally, the SEO should obtain a positive synergistic index as the intention of incorporating US with EO is to enhance the performance of the whole process [40–42].

Degradation of POME

The EO and SEO processes were then investigated for use on real wastewater – POME. Fig. 9 and Fig. 10 show the COD and colour removal trend of POME when subjected to EO and SEO (continuous and intermittent modes) treatment processes. After 4 h of treatment, both continuous and intermittent SEO recorded a better removal efficiency as compared to EO alone. This observation is similar to the previous testing using CR dye, where the improvement is mostly due to the enhanced mass transfer, cleaning of electrodes, and production of more hydroxyl radicals that accelerate the degradation of organic compounds in POME. The intermittent SEO also recorded a better degree of removal of organic compounds in POME as compared to SEO operated in continuous US mode, where the former achieved relatively 10% higher removal. The

physical observation of POME before and after treatment is depicted in Fig. 11. The images clearly show the POME changed colour from milky dark brown to a clear brown solution after the treatment process, indicating the removal of material from POME.

In the past decade, different AOPs have been tested for POME treatment. These include Fenton oxidation, photo-Fenton, electro-Fenton, and photocatalysis [43–45]. The working mechanism of these AOPs is similar to EO and SEO, which rely on the generation of hydroxyl radicals for the degradation of organic compounds in POME. The COD reduction efficiencies ranged from 40 to 100%, with the starting COD of POME (diluted or fresh anaerobically or aerobically treated) around 50 to 32,000 mg/L [44]. Despite the similarity in the degradation principle, the majority of past studies were conducted under extreme acidic conditions (pH 2–3), since Fenton-based AOPs can only perform satisfactorily within this pH range. As compared to these past AOPs studies, SEO does not encounter the challenges often associated with other AOPs, such as production of iron sludge, operation at extreme pH condition, and poor photooxidation due to the limited light penetration of turbid POME [44]. Hence, SEO appears to be a potential treatment process for POME given its promising degradation efficiency and fewer challenges than for other AOPs. In spite of that, another acceptance factor that

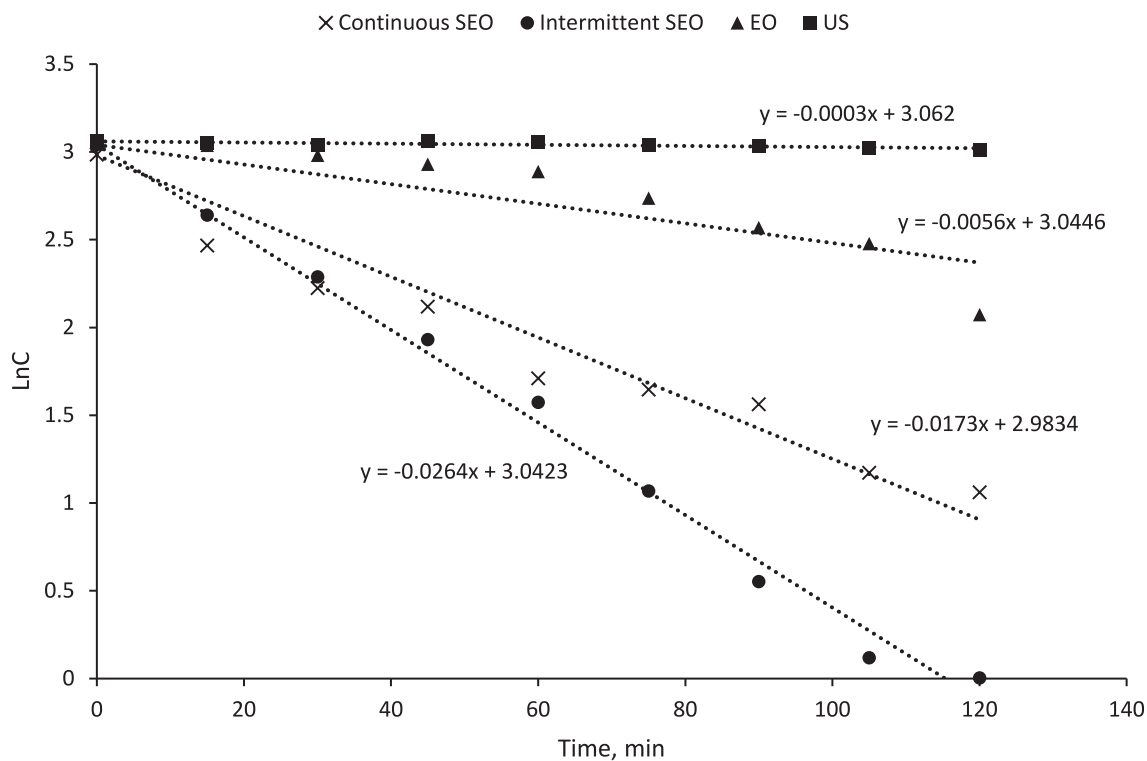


Fig. 8. Kinetics of the CR degradation operated under different modes.

Table 2

Energy consumption and synergistic index of the CR degradation process operated under different modes.

Process	Energy consumption (kWh/kg dye removed)	The first-order kinetic rate constant, k , min^{-1}	Synergistic Index
US	–	0.0003	–
EO	556.96	0.0056	–
Continuous mode SEO	251.59	0.0173	2.93
Intermittent mode SEO	264.10	0.0264	4.47

would need to be considered for wastewater treatment processes is energy consumption (operating cost).

The energy consumption of EO, continuous SEO, and intermittent SEO is tabulated in Table 3. The energy consumption of SEO processes was not significantly reduced as compared to the study conducted with CR dyes. This unanticipated finding reveals that the potential energy saving caused by SEO might not be so significant due to the complex constituents of real wastewater. It also signifies the need for further optimization study and to employ real effluents in SEO studies such that a more comprehensive insight of its performance can be obtained. Due to the limited information reported on energy consumption for AOP degradations of POME, direct comparison between this finding with other studies could not be done. For instance, the electrical energy per order of photo-oxidation of POME was about 3217 kWh/($\text{m}^3 \cdot \text{order}$) for

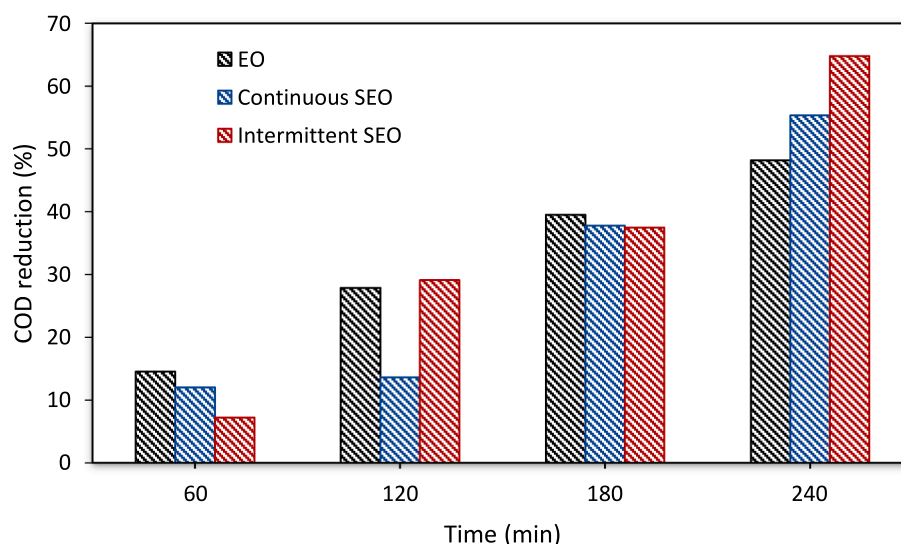


Fig. 9. Effect of ultrasound modes on the COD removal of POME (operating conditions: 0.2 A, 500 mL, solution pH at 8.5, electrode distance at 2 cm).

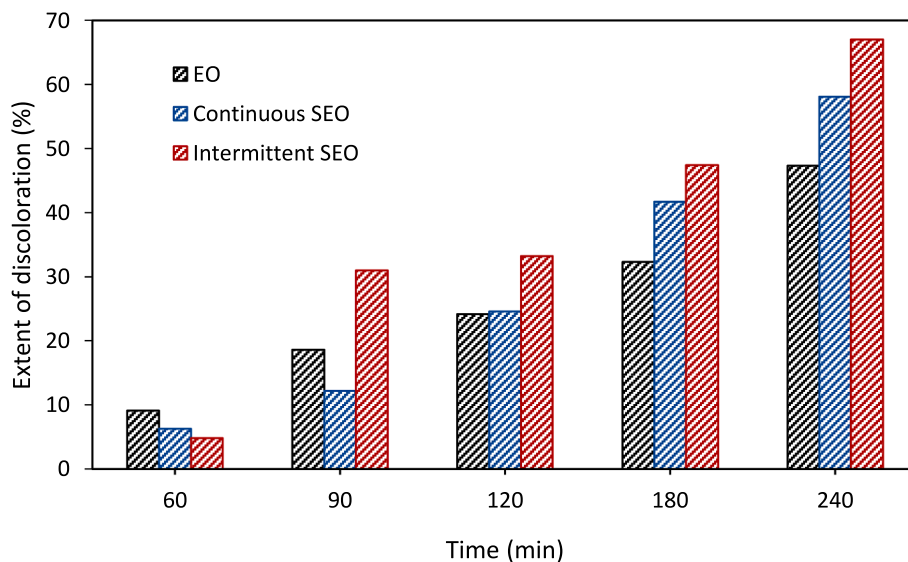


Fig. 10. Effect of ultrasound modes on the discoloration of POME (operating conditions: 0.2 A, 500 mL, solution pH at 8.5, electrode distance at 2 cm).

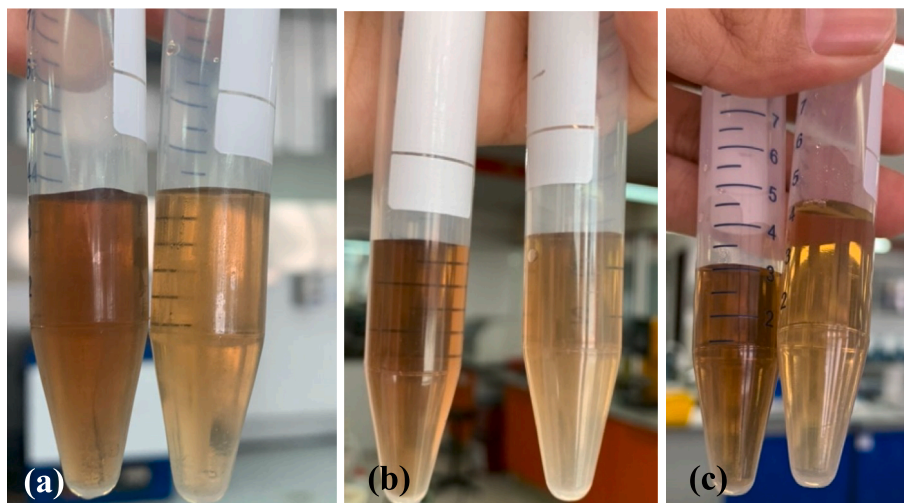


Fig. 11. Physical observation of POME: pristine POME solution, (a) POME solution after 4 h EO treatment, (b) POME solution after continuous ultrasound SEO treatment for 4 h, (c) POME solution after intermittent ultrasound SEO treatment for 4 h.

Table 3
Energy consumption of POME degradation operated under different modes.

Process	Energy consumption for EO (kWh/kg COD removed)
EO	32.82
Continuous SEO	25.91
Intermittent SEO	30.78

COD reduction [45]. Hence, this implies further in-depth study on the costing aspect of AOPs for POME treatment should be looked into by researchers. Nonetheless, the potential of SEO in wastewater treatment should not be judged solely based on such estimation performed on a single process. Instead, the impacts and benefits of SEO on other treatment processes should also be evaluated and included in the consideration.

Despite the fact that the final COD of POME was in the range of 200–300 mg/L (decreased from the original range of 600–700 mg/L), which is still too high to be discharged to the environment, the successful degradation of organic compounds in POME indicates the potential of SEO for POME treatment, either as a tertiary treatment or

incorporated as pre-treatment or post-treatment for other advanced processes such as membrane filtration and adsorption [46,47]. Indeed, the integration of AOPs with other treatment processes has not been widely reported yet, but integrating photocatalysis with membrane filtration was found to enhance the overall decolorization of POME from 60 to 70% to greater than 99% [48]. The proposed integration was developed based on the fact that AOPs could not degrade all pollutants. At the same time, the presence of photocatalysis as a pre-treatment process prior to membrane filtration alleviated the fouling severity as compared to membrane performance without pre-treatment. The observation emphasizes the potential synergism between AOPs with other treatment processes that addresses the shortcomings of each individual process. Hence, not only are further experiments required to optimize the operating conditions of SEO in treating POME to fully explore the potential of such processes in treating POME, but also SEO's integration with other treatment processes to achieve better overall synergistic performance should be investigated.

Conclusion and future perspectives

This study showed that the EO and SEO processes could be used to degrade CR dye and organic compounds in aerobically treated POME to a satisfactorily degree. Particularly, SEO process operated with intermittent US recorded the highest degradation efficiency, with 95% removal of CR and 65% COD reduction from POME. To be precise, the intermittent SEO was able to achieve about 10% higher extent of degradation compared to continuous SEO for both CR and POME. This performance enhancement in the SEO process is held to be due to the increase in mass transport between pollutants and hydroxyl radicals as well as electrode cleaning in the presence of US. In terms of energy consumption, SEO consumed less than 50% of the energy used for EO process (556.96 kWh/kg dye) to degrade CR dye. Surprisingly, such significant energy savings were not observed for POME treatment. The energy consumed for continuous and intermittent SEO degradation of POME was only slightly lower than that for the EO process (26–31 kWh/kg COD as compared to 33 kWh/kg COD). This reflects that the complex constituents of real wastewater might influence the performance of SEO and the degradation performance of a synthetic pollutant solution does not necessarily reflect the same achievement that could be obtained for real wastewater. Nonetheless, it implies that further experiments are required to explore the removal efficiency and energy consumed by the process on the treatment of real, complex effluents to obtain a more conclusive insight into its performance as an individual process or part of an integrated treatment system.

To date, many thrilling hybrid technology for the degradation of organic compound have been introduced, which portrays high potential but currently limited to lab scale application. So, for this hybrid SEO process to achieve a successful scaled-up arrangement and industrial commercialisation, several operational and design configuration need to be extensively researched.

- Energy consumption: Continuous and pulsed mode sonication should be wisely optimised for application in larger reactor and much longer electrolysis duration, knowing that it is not necessary to have constant sonication to achieve high degradation efficiency. Also, the exploration of smart strategies interlinking both sonication mode and ultrasound frequency is important to develop a reactor that is economically viable especially its energetic cost. In addition, for a scaled-up reactor, common design favouring continuous flow of effluent instead of having static solution as per laboratory scale. Hence, it is worth to have more investigation on the relationship between fluid flow rate and the suitable ultrasound intensity to meet optimised operational condition.
- Pollutant mineralisation efficacy: The generation of powerful radical species responsible in degradation of organic pollutant is influenced by the aspects mentioned in the above, as well as the stability of electrodes used in the reactor. In order to improve the electrode stability in acoustic condition, longevity and enhancing degradation performance, studies on synthesis of electrode materials is highly required. Besides that, positioning of both electrodes and transducers are deemed to be significant especially for large-scale application. Having sufficient acoustic field covering the reactor space and making sure electrode located in the strategic point in the field are among the aspects that could easily be overlooked but hold huge influence in the pollutant mineralisation efficacy.

In conclusion, extensive researches in many sonication aspects are still required as there are not much studies have been reported on this hybrid technology. With vast optimisation studies on this hybrid SEO process, it could well develop into a cost-effective, highly efficient treatment process on an industrial scale.

CRedit authorship contribution statement

Siti Zulaikha Kalet: Investigation, Data curation, Writing – original draft. **Saiyidah Anisah Ismail:** Methodology, Validation, Writing – review & editing, Visualization. **Wei Lun Ang:** Conceptualization, Methodology, Resources, Writing – review & editing, Supervision, Project administration, Funding acquisition. **Mark D. Symes:** Writing – review & editing.

Declaration of Competing Interest

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

Data availability

Data will be made available on request.

Acknowledgement

The authors would like to thank the Universiti Kebangsaan Malaysia for funding this work through the research grant DPK-2021-014. This collaboration leading to this work was supported by the Royal Academy of Engineering under the Frontiers of Development scheme (FoE2122-10-6). MDS thanks the Royal Society for a University Research Fellowship (UF150104).

References

- [1] J. Wang, S. Wang, Toxicity changes of wastewater during various advanced oxidation processes treatment: An overview, *J. Clean. Prod.* 315 (2021), 128202, <https://doi.org/10.1016/j.jclepro.2021.128202>.
- [2] R.Y. Krishnan, S. Manikandan, R. Subbaiya, M. Biruntha, M. Govarthanan, N. Karmegam, Removal of emerging micropollutants originating from pharmaceuticals and personal care products (PPCPs) in water and wastewater by advanced oxidation processes: A review, *Environ. Technol. Innov.* 23 (2021), 101757, <https://doi.org/10.1016/j.eti.2021.101757>.
- [3] M. Ilyas, W. Ahmad, H. Khan, S. Yousaf, M. Yasir, A. Khan, Environmental and health impacts of industrial wastewater effluents in Pakistan: a review, *Rev. Environ. Health.* 34 (2019) 171–186, <https://doi.org/10.1515/reveh-2018-0078>.
- [4] R. Ji, J. Chen, T. Liu, X. Zhou, Y. Zhang, Critical review of perovskites-based advanced oxidation processes for wastewater treatment: Operational parameters, reaction mechanisms, and prospects, *Chinese Chem. Lett.* 33 (2022) 643–652, <https://doi.org/10.1016/j.ccl.2021.07.043>.
- [5] P. Gautam, S. Kumar, S. Lokhandwala, Advanced oxidation processes for treatment of leachate from hazardous waste landfill: A critical review, *J. Clean. Prod.* 237 (2019), 117639, <https://doi.org/10.1016/j.jclepro.2019.117639>.
- [6] J.J. Rueda-Marquez, I. Levchuk, P. Fernández Ibañez, M. Sillanpää, A critical review on application of photocatalysis for toxicity reduction of real wastewaters, *J. Clean. Prod.* 258 (2020) 120694, [10.1016/j.jclepro.2020.120694](https://doi.org/10.1016/j.jclepro.2020.120694).
- [7] D.O. Carpenter, Health effects of persistent organic pollutants: the challenge for the Pacific Basin and for the world 26 (2011) 61–69, <https://doi.org/10.1515/reveh.2011.009>.
- [8] W.H. Glaze, J.-W. Kang, D.H. Chapin, The Chemistry of Water Treatment Processes Involving Ozone, Hydrogen Peroxide and Ultraviolet Radiation, *Ozone Sci. Eng.* 9 (1987) 335–352, <https://doi.org/10.1080/01919518708552148>.
- [9] B. Thokchom, A.B. Pandit, P. Qiu, B. Park, J. Choi, J. Khim, A review on sono-electrochemical technology as an upcoming alternative for pollutant degradation, *Ultrason. Sonochem.* 27 (2015) 210–234, <https://doi.org/10.1016/j.ultsonch.2015.05.015>.
- [10] Y. He, H. Lin, Z. Guo, W. Zhang, H. Li, W. Huang, Recent developments and advances in boron-doped diamond electrodes for electrochemical oxidation of organic pollutants, *Sep. Purif. Technol.* 212 (2019) 802–821, <https://doi.org/10.1016/j.seppur.2018.11.056>.
- [11] S. Ben Kacem, S.C. Elaoud, A.M. Asensio, M. Panizza, D. Clematis, Electrochemical and sono-electrochemical degradation of Allura Red and Erythrosine B dyes with Ti-PbO₂ anode, *J. Electroanal. Chem.* 889 (2021), 115212, <https://doi.org/10.1016/j.jelechem.2021.115212>.
- [12] F.C. Moreira, R.A.R. Boaventura, E. Brillas, V.J.P. Vilar, Electrochemical advanced oxidation processes: A review on their application to synthetic and real wastewaters, *Appl. Catal. B Environ.* 202 (2017) 217–261, <https://doi.org/10.1016/j.apcatb.2016.08.037>.
- [13] J.S. Foord, K.B. Holt, R.G. Compton, F. Marken, D.-H. Kim, Mechanistic aspects of the sono-electrochemical degradation of the reactive dye Procion Blue at boron-doped diamond electrodes, *Diam. Relat. Mater.* 10 (2001) 662–666, [https://doi.org/10.1016/S0925-9635\(00\)00561-6](https://doi.org/10.1016/S0925-9635(00)00561-6).

- [14] E. Bringas, J. Saiz, I. Ortiz, Kinetics of ultrasound-enhanced electrochemical oxidation of diuron on boron-doped diamond electrodes, *Chem. Eng. J.* 172 (2011) 1016–1022, <https://doi.org/10.1016/j.cej.2011.07.016>.
- [15] W.L. Ang, P.J. McHugh, M.D. Symes, Sonoelectrochemical processes for the degradation of persistent organic pollutants, *Chem. Eng. J.* 444 (2022), 136573, <https://doi.org/10.1016/j.cej.2022.136573>.
- [16] R. Patidar, V.C. Srivastava, Ultrasound-assisted electrochemical treatment of cosmetic industry wastewater: Mechanistic and detoxification analysis, *J. Hazard. Mater.* 422 (2022), <https://doi.org/10.1016/j.jhazmat.2021.126842>.
- [17] H. Li, X. Fang, X.L. Luo, R. Feng, Ultrasound inhibit the electrolysis reaction of water, *J. Xiamen Univ. Nat. Sci.* 32 (1993).
- [18] M. Siddique, R. Farooq, Z.M. Khan, Z. Khan, S.F. Shaikat, Enhanced decomposition of reactive blue 19 dye in ultrasound assisted electrochemical reactor, *Ultrason. Sonochem.* 18 (2011) 190–196, <https://doi.org/10.1016/j.ultsonch.2010.05.004>.
- [19] A. Somayajula, P. Asaithambi, M. Suresh, M. Matheswaran, Sonoelectrochemical oxidation for decolorization of Reactive Red 195, *Ultrason. Sonochem.* 19 (2012) 803–811, <https://doi.org/10.1016/j.ultsonch.2011.12.019>.
- [20] M. Shestakova, M. Vinatoru, T.J. Mason, E. Iakovleva, M. Sillanpää, Sonoelectrochemical degradation of formic acid using Ti/Ta₂O₅-SnO₂ electrodes, *J. Mol. Liq.* 223 (2016) 388–394, <https://doi.org/10.1016/j.molliq.2016.08.054>.
- [21] F. Xie, Y. Xu, K. Xia, C. Jia, P. Zhang, Alternate pulses of ultrasound and electricity enhanced electrochemical process for p-nitrophenol degradation, *Ultrason. Sonochem.* 28 (2016) 199–206, <https://doi.org/10.1016/j.ultsonch.2015.07.011>.
- [22] A. Nouri, E. Mahmoudi, W.L. Ang, G. Panomsuwan, O. Jongprateep, Sugar molasses as a sustainable precursor for the synthesis of graphene sand composite adsorbent for tetracycline and methylene blue removal, *Environ. Sci. Pollut. Res.* (2022), <https://doi.org/10.1007/s11356-022-21996-z>.
- [23] S. Ghorai, A.K. Sarkar, A.B. Panda, S. Pal, Effective removal of Congo red dye from aqueous solution using modified xanthan gum/silica hybrid nanocomposite as adsorbent, *Bioresour. Technol.* 144 (2013) 485–491, <https://doi.org/10.1016/j.biortech.2013.06.108>.
- [24] F.A. Ujang, N.A. Osman, J. Idris, M.I.E. Halmi, M.A. Hassan, A.M. Roslan, Start-up treatment of palm oil mill effluent (POME) final discharge using Napier Grass in wetland system, *IOP Conf. Ser. Mater. Sci. Eng.* 368 (2018), <https://doi.org/10.1088/1757-899X/368/1/012008>.
- [25] B.K. Korbahiti, Kezban Meltem Turan, Evaluation of Energy Consumption in Electrochemical Oxidation of Acid Violet 7 Textile Dye using Pt/Ir Electrodes, *J. Turkish Chem. Soc. Sect. A Chem.* 3 (2017) 75–92, 10.18596/jotcsa.31804.
- [26] S.A. Ismail, W.L. Ang, A.W. Mohammad, Electro-Fenton technology for wastewater treatment: A bibliometric analysis of current research trends, future perspectives and energy consumption analysis, *J. Water Process Eng.* 40 (2021), 101952, <https://doi.org/10.1016/j.jwpe.2021.101952>.
- [27] M. Lounis, M.E. Samar, O. Hamdaoui, Sono-electrochemical degradation of Orange G in pure water, natural water, and seawater: effect of operating parameters, *Desalin. Water Treat.* 57 (2016) 22533–22542, <https://doi.org/10.1080/19443994.2015.1129513>.
- [28] C. Yin, T. Ye, Y. Yu, W. Li, Q. Ren, Detection of hydroxyl radicals in sonoelectrochemical system, *Microchem. J.* 144 (2019) 369–376, <https://doi.org/10.1016/j.microc.2018.09.025>.
- [29] R. Patidar, V.C. Srivastava, Mechanistic insight into ultrasound-induced enhancement of electrochemical oxidation of ofloxacin: Multi-response optimization and cost analysis, *Chemosphere* 257 (2020), <https://doi.org/10.1016/j.chemosphere.2020.127121>.
- [30] G. Donoso, J.R. Dominguez, T. González, S. Correia, E.M. Cuerda-Correa, Electrochemical and sonochemical advanced oxidation processes applied to tartrazine removal. Influence of operational conditions and aqueous matrix, *Environ. Res.* 202 (2021), 10.1016/j.envres.2021.111517.
- [31] M. Dietrich, M. Franke, M. Stelter, P. Braeutigam, Degradation of endocrine disruptor bisphenol A by ultrasound-assisted electrochemical oxidation in water, *Ultrason. Sonochem.* 39 (2017) 741–749, <https://doi.org/10.1016/j.ultsonch.2017.05.038>.
- [32] Q. Ren, C. Yin, Z. Chen, M. Cheng, Y. Ren, X. Xie, Y. Li, X. Zhao, L. Xu, H. Yang, W. Li, Efficient sonoelectrochemical decomposition of chlorpyrifos in aqueous solution, *Microchem. J.* 145 (2019) 146–153, <https://doi.org/10.1016/j.microc.2018.10.032>.
- [33] K. Kim, E. Cho, B. Thokchom, M. Cui, M. Jang, J. Kim, Synergistic sonoelectrochemical removal of substituted phenols: Implications of ultrasonic parameters and physicochemical properties, *Ultrason. Sonochem.* 24 (2015) 172–177, <https://doi.org/10.1016/j.ultsonch.2014.11.004>.
- [34] M.A. Radi, N. Nasirizadeh, M. Rohani-Moghadam, M. Dehghani, The comparison of sonochemistry, electrochemistry and sonoelectrochemistry techniques on decolorization of C.I Reactive Blue 49, *Ultrason. Sonochem.* 27 (2015) 609–615.
- [35] D.M. Deojay, J.Z. Sostaric, L.K. Weavers, Exploring the effects of pulsed ultrasound at 205 and 616kHz on the sonochemical degradation of octylbenzene sulfonate, *Ultrason. Sonochem.* 18 (2011) 801–809, <https://doi.org/10.1016/j.ultsonch.2010.10.005>.
- [36] R. Xiao, D. Diaz-Rivera, Z. He, L.K. Weavers, Using pulsed wave ultrasound to evaluate the suitability of hydroxyl radical scavengers in sonochemical systems, *Ultrason. Sonochem.* 20 (2013) 990–996, <https://doi.org/10.1016/j.ultsonch.2012.11.012>.
- [37] K. Xia, F. Xie, Y. Ma, Degradation of nitrobenzene in aqueous solution by dual-pulse ultrasound enhanced electrochemical process, *Ultrason. Sonochem.* 21 (2014) 549–553, <https://doi.org/10.1016/j.ultsonch.2013.09.010>.
- [38] R.H. De Lima Leite, P. Cognet, A.M. Wilhelm, H. Delmas, Anodic oxidation of 2,4-dihydroxybenzoic acid for wastewater treatment, *J. Appl. Electrochem.* 33 (2003) 693–701, 10.1023/A:1025056001368.
- [39] Y.Z. Ren, Z.L. Wu, M. Franke, P. Braeutigam, B. Ondruschka, D.J. Comeskey, P. M. King, Sonoelectrochemical degradation of phenol in aqueous solutions, *Ultrason. Sonochem.* 20 (2013) 715–721, <https://doi.org/10.1016/j.ultsonch.2012.09.004>.
- [40] J. Theerthagiri, J. Madhavan, S.J. Lee, M.Y. Choi, M. Ashokkumar, B.G. Pollet, Sonoelectrochemistry for energy and environmental applications, *Ultrason. Sonochem.* 63 (2020), 104960, <https://doi.org/10.1016/j.ultsonch.2020.104960>.
- [41] P. Ritesh, V.C. Srivastava, Understanding of ultrasound enhanced electrochemical oxidation of persistent organic pollutants, *J. Water Process Eng.* 37 (2020), <https://doi.org/10.1016/j.jwpe.2020.101378>.
- [42] K. Fedorov, K. Dinesh, X. Sun, R. Darvishi Cheshmeh Soltani, Z. Wang, S. Sonawane, G. Boczkaj, Synergistic effects of hybrid advanced oxidation processes (AOPs) based on hydrodynamic cavitation phenomenon – A review, *Chem. Eng. J.* 432 (2022) 134191, 10.1016/j.cej.2021.134191.
- [43] S. Sani, A.F. Dashti, R. Adnan, Applications of Fenton oxidation processes for decontamination of palm oil mill effluent: A review, *Arab. J. Chem.* 13 (2020) 7302–7323, <https://doi.org/10.1016/j.arabjc.2020.08.009>.
- [44] Y.W. Cheng, C.C. Chong, M.K. Lam, M. Ayoub, C.K. Cheng, J.W. Lim, S. Yusup, Y. Tang, J. Bai, Holistic process evaluation of non-conventional palm oil mill effluent (POME) treatment technologies: A conceptual and comparative review, *J. Hazard. Mater.* 409 (2021), 124964, <https://doi.org/10.1016/j.jhazmat.2020.124964>.
- [45] M.H. Alhaji, K. Sanaullah, S.F. Salleh, R. Bains, S.F. Lim, A.R.H. Rigit, K.A.M. Said, A. Khan, Photo-oxidation of pre-treated palm oil mill Effluent using cylindrical column immobilized photoreactor, *Process Saf. Environ. Prot.* 117 (2018) 180–189, <https://doi.org/10.1016/j.psep.2018.04.012>.
- [46] Z.N. Hayawin, Z.B. Syirat, M.F. Ibrahim, J.N. Faizah, A.A. Astimar, A. W. Noorshamsiana, M. Ropandi, A.W. Nursulihatimarsyila, S. Abd-Aziz, Pollutants removal from palm oil mill effluent (POME) final discharge using oil palm kernel shell activated carbon in the up-flow continuous adsorption system, *Int. J. Environ. Sci. Technol.* (2022), <https://doi.org/10.1007/s13762-022-04268-8>.
- [47] W. Lun Ang, T. Balakrishnan, T. Veeraiya, M.H. Mohammad Elham, M.S.F. Adlee, T. Fujioka, Performance Evaluation of Tubular Ceramic Membrane for Palm Oil Mill Effluent Treatment, *J. Kejuruter.* 32 (3) (2020) 513–521.
- [48] D.A.B. Sidik, N.H.H. Hairom, M.K. Ahmad, R.H. Madon, A.W. Mohammad, Performance of membrane photocatalytic reactor incorporated with ZnO-Cymbopogon citratus in treating palm oil mill secondary effluent, *Process Saf. Environ. Prot.* 143 (2020) 273–284, <https://doi.org/10.1016/j.psep.2020.06.038>.