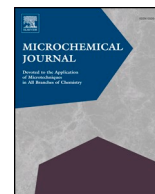




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Efficient sonoelectrochemical decomposition of chlorpyrifos in aqueous solution



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ABSTRACT

In this study, we selected the stainless-steel mesh as the electrode material, supplemented with conventional power ultrasound in the electrochemical degradation of the chlorpyrifos effluent. The effect of different operating conditions, such as voltage, initial electrolyte concentration, temperature and ultrasonic power were investigated with synthetic effluent to gain the most efficient degradation rate. The best reaction parameters were: voltage of 20 V, electrolyte concentration of 2 mg L⁻¹, ultrasonic power of 200 W, as well as 20 °C, which led to 93.3% and 72.8% of degradation in US-EC and EC system. Applying higher concentrations of electrolyte (sodium sulfate) and higher voltages, the chlorpyrifos solution can be more efficiently degraded with a high synergy of 37%. The degradation of chlorpyrifos followed pseudo-first-order kinetics.

1. Introduction

With the rapid development of industry, population growth and long-term drought, water shortages had become a global issue, and various water pollutions are undoubtedly worsened [1]. Pollution may occur anywhere in the water system, especially organic contaminants [2,3,4,5]. When pesticides were unreasonably or excessively used, they can cause pollution of soil, groundwater, and rivers. Chlorpyrifos (o, o-diethyl-o-(3,5,6-trichloro-2-pyridinyl)phosphorothioate) was one of the top five commercial insecticides and is an organophosphorus pesticides widely used in agriculture now. Chlorpyrifos (CPS) (Fig. 1) had many unique advantages because it can effectively kill plant food pests by damaging the audit system. It can stay in the soil for 2–4 months and can only be degraded by microorganisms [6]. Although this organophosphate insecticide had obvious advantages, the residual pesticide also caused serious pollution.

Advanced Oxidation Processes (AOPs) as an alternative method to treat CPS wastewater, had attracted more and more attention. So far, various processes had been proposed for the treatment of CPS wastewater, containing the photocatalytic degradation [7,8,9,10,11,12], biodegradation [13] and bio-adsorption [14,15,16,17,18]. Similarly, they all used the hydroxyl radicals generated in the system as reactants. Sonoelectrochemical (US-EC) was a completely novel field by combining ultrasonic

[19] irradiation in electrochemical (EC) processes to change the reaction [20], which had broad research prospects and development potential. At present, there were little studies on the wastewater of CPS. Compared with other advanced oxidation processes, the US-EC process had some unique advantages, e.g. (1) Mild reaction conditions, (2) Excellent mass transfer, (3) Wide range of treated wastewater concentrations, (4) Electricity was the sole reactant and no additional chemicals are required, and it was a safe and efficient treatment technology [21]. The irradiation of ultrasound can effectively destroy refractory organic contaminants [22].

The US-EC studies had been extensively involved in wastewater treatment, nevertheless, these studies mainly used novel electrodes such as boron-doped diamond (BDD), dimension stable anode (DSA), etc. which can constitute more active oxygen release capability and/or higher reaction sites, in favor of the EC oxidation for pollutant decontaminations. In other fields, developing a new and efficient material had always been a scientific problem [23,24,25,26,27]. For example, the development of these electrodes was a huge challenge, including: synthetic process, price, Electrode life, etc., it needed to be further optimized and studied [28]. Therefore, the use of common and simple electrodes to study the US-EC treatment of wastewater was very meaningful, applying cheap and easily available materials or waste materials as raw materials was consistent with the policy of sustainable development [29,30,31,32].

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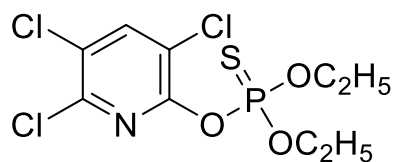


Fig. 1. Chemical structure of CPS.

Furthermore, the great majority of reactions volume was relatively small ($V \leq 250$ mL), with a lower concentration of solution ($C_0 < 450$ mg L⁻¹) [33], electrode was complicated and expensive to produced [34], which would limit further applications. Mechanical effects were usually closely associated with low-frequency ultrasound. In this case, cavitation can easily occur, so that the electrode surface can be effectively cleaned, but less hydroxyl radicals are produced [35]. Though the high frequency of ultrasound can produce more ·OH [36], taking into account the economic and cavitation at low frequencies, this article discussed the use of low-cost electrode materials (stainless steel) at low frequency ultrasound (40 kHz) to treat larger volumes (400 mL) of wastewater at higher concentrations. This study was intended to explore a process of US-EC degrading CPS wastewater: (a) discuss the synergistic effect of the US-EC system on the CPS degradation, (b) investigate the effects of important parameters on the CPS degradation, (c) propose the reaction mechanism, the detection of hydroxyl radicals and the promotional role of US.

2. Experimental

2.1. Materials and experimental setup

We chose CPS (> 99.9%) as a model pollutant which obtained from Shanghai Aladdin Biochemical Technology Co., Ltd. Ethyl acetate (> 99%, Sinopharm Chemical Reagent Co., Ltd.), CPS (> 40%, Shandong Province Joint Pesticide Industry Co., Ltd.) and sodium sulfate (> 99%, Sinopharm Chemical Reagent Co., Ltd.) were used as received without further purification. Distilled water was used to prepare the solution.

A schematic diagram of the applied device for the US-EC process is shown in Fig. 2. Ultrasound was generated by an ultrasonic power generator (Ningbo New Chi Biotechnology Co., Ltd.). The ultrasonic waves were introduced into the reaction solution by an ultrasound transducer (Ningbo New Chi Biotechnology Co., Ltd.), which was fixed at the bottom of a double-walled cylindrical glass reactor and which operated in continuous mode at 40 kHz. The EC system was composed of a Universal-Power Supply with AV (alternating current) and DC (direct current) powers (Long Wei Instruments (HK) Co., Ltd.).

Two stainless-steel electrodes were used in the investigation. The anode was stainless-steel and then made into a cylindrical mesh (diameter: 20 mm, height: 8 mm, surface area: 3140 mm², immersion depth 5 mm) and the cathode was of the same electrode material and shape

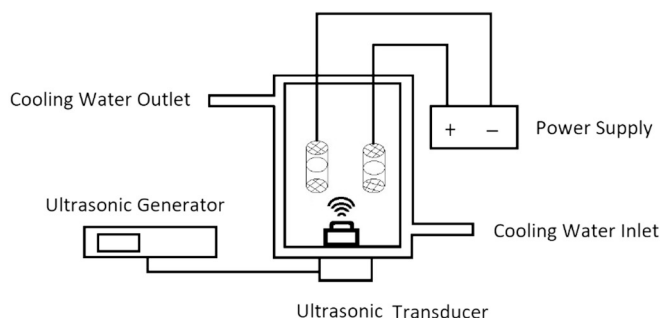


Fig. 2. Schematic diagram of experimental set-up. SS: stainless-steel.

with a distance of 40 mm between the electrodes. The ultrasonic transducer can provide the highest acoustic energy and can achieve high-quality transmission in the middle of the reactor [37].

2.2. A typical treatment

The CPS solution was set to a certain concentration, 400 mL was poured into the reactor (in Fig. 2), additional electrolyte (Na₂SO₄) was added, and then stirred for 10 min. During the experiment, setting the desired voltage and ultrasonic power through the control panel. Keep the temperature constant by circulating the condenser. The reaction time was 1 h, 2 mL samples were taken from the reactor at intervals of 10 min, centrifuged successively, liquid-liquid extraction, filtration, nitrogen blowing, and dilution steps were used to purify the samples and analyzed by UV-Vis. The results given here are the means of two or more parallel experiments.

2.3. Analysis

2.3.1. Analysis of CPS measurements

The residual concentration of CPS in the reaction solution was monitored by absorbance measurement (previously measured absorbance peak) using an UV-vis spectrophotometer (UV-3600 Shimadzu). The CPS solution with different standard concentrations was determined and its maximum absorption wavelength at 250–300 nm was determined (Fig. 3a). The standard curve was drawn with good linearity in the range of 0.5–100 mg L⁻¹, $R^2 = 0.99914$. The concentration of CPS produced in the system is proportional to the absorbance. The absorbance values of the samples at different stages were measured, the residual CPS concentration was calculated using the calibration curve, and the degradation rate was calculated (Fig. 3).

2.3.2. Detection of hydroxyl radicals

A new method to detect the hydroxyl radical generated by US-EC reaction was proposed. With the crystal violet as the reagent, the crystal violet solution faded after reacting with the hydroxyl radical, and the change of the absorbance value was measured by Vis spectrophotometer (Shanghai spectral instruments Co., Ltd.). The amount of hydroxyl radical produced was measured.

The crystal violet solution is scanned at full wavelength in the 300–800 nm by Visible spectrophotometer, determine the maximum absorption wavelength of crystal violet solution at 580 nm (Fig. 3b).

2.4. Evaluation

2.4.1. Degradation degree

The CPS is identified by the maximum absorption wavelength of the UV-vis absorption spectrum, the concentration of CPS was quantified by the conversion of absorbance. The degradation rate (D%) was calculated with the formula shown in Eq. (1).

$$D\% = \frac{C_0 - C_t}{C_0} \times 100\% \quad (1)$$

C_0 is the initial concentration of CPS and C_t is the concentration of CPS after a period of reaction.

2.4.2. Synergistic effect

Synergy effects are evaluated by calculating a synergy index, the synergies of the US-EC system can be calculated from the degradation rate constants of the combined system and its individual systems according to the following formula [38]:

$$S = \left(\frac{k_{EC/US}}{k_{US} + k_{EC}} - 1 \right) \times 100\% \quad (2)$$

where $k_{EC/US}$, k_{EC} and k_{US} are the rate constants of the US-EC, US and EC system, respectively.

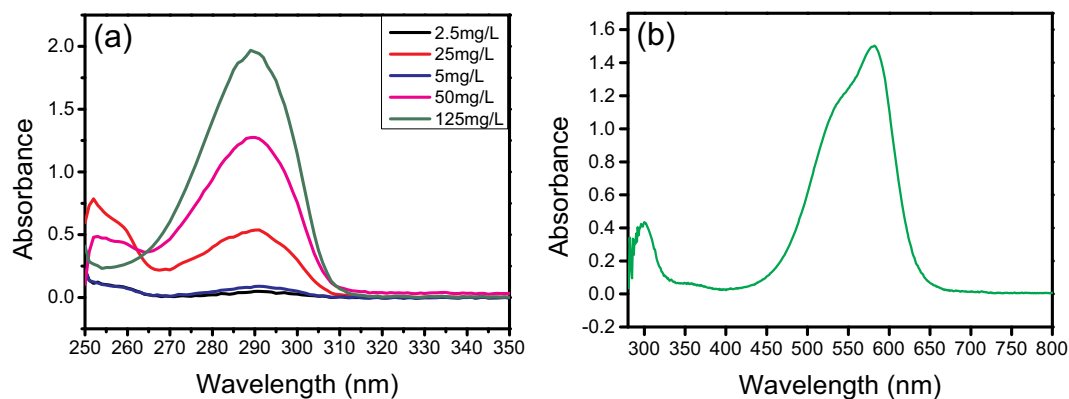


Fig. 3. UV-Vis spectra of (a) CPS and (b) crystal violet solution. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

A synergy index value > 1 indicates that the combined process exceeds the sum of the individual processes, otherwise a synergy index < 1 means that the combined system produces a negative effect.

3. Results and discussion

3.1. Comparative degradation of CPS in different systems

A series of comparative experiments were conducted using 2 g L^{-1} Na_2SO_4 as the electrolyte. As shown in Fig. 4, a single ultrasound system resulted in a relatively low rate of degradation of CPS within 60 min reaction time. Meanwhile, the EC system achieved CPS removal efficiency of 72.8%, while the US-EC system could significantly improve the efficiency to 93.3%. From Table 1, we compared some several varieties between three systems.

In addition, during the EC process, the current during the reaction ranged from 0.45 to 0.37 A. The combined system processed current increased from 0.45 to 0.65 A compared to the single EC system. When the current increases, the mass transfer in the reaction is also improved [39]. During the EC reaction, a yellow passivation layer and many bubbles were found on the anode surface, which reduced the mass transfer and hindered the reaction. However, this phenomenon has not been observed in the US-EC system. The mechanical effect of cavitation caused by ultrasound cleans the electrode surface and prevents the formation of such a passivation layer, increasing mass transfer and electrode activation [40]. This effect ensures that the reaction can work under a stable current. The experimental results show that US-EC wastewater treatment using this experimental device is effective.

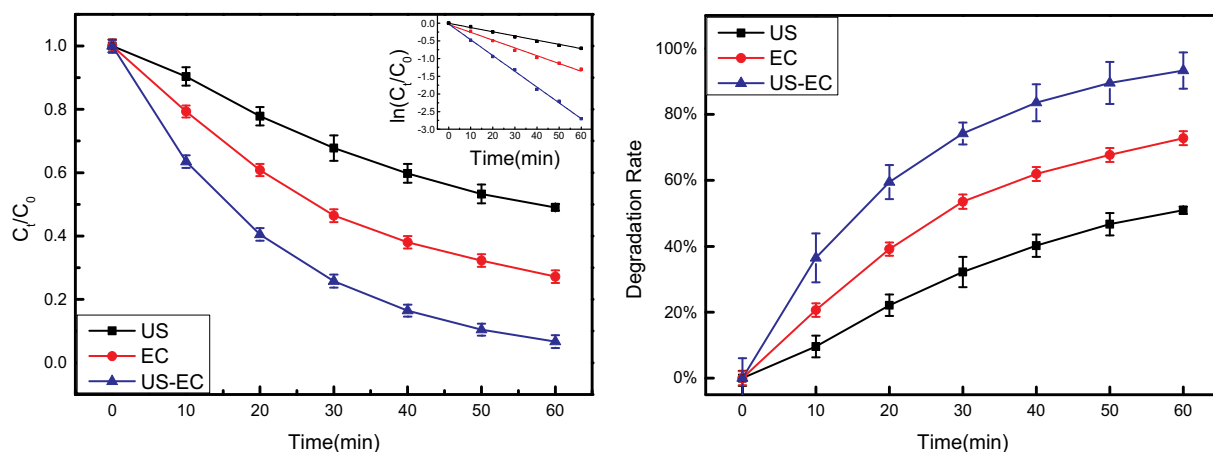


Fig. 4. Degradation curve of CPS in the US-EC, EC, US systems. Initial conditions were: 800 mg L^{-1} CPS, 20 V electrical voltage, temperature $(20 \pm 2) ^\circ\text{C}$, 2 g L^{-1} Na_2SO_4 electrolyte, ultrasound power 200 W.

Table 1

Some differences between the three systems.

System	Current change (A)	Degradation rate (%)	Rate constant
US-EC	0.45–0.65	93.3	4.465×10^{-2}
EC	0.45–0.37	72.8	2.201×10^{-2}
US	0	50.94	1.235×10^{-2}

3.2. Factors affecting the degradation of CPS in the US-EC system

3.2.1. Electrolyte

In addition, the degradation of CPS by three common electrolytes (Na_2SO_4 , NaNO_3 , and NaCl) in the US-EC system was discussed (Fig. 5). When sodium nitrate was selected as the electrolyte, CPS was degraded by 94.4% after 1 h, and the degradation rate was the highest.

Usually, a certain amount of salt can be added to the aqueous solution to enhance ultrasonic oxidation [41]. Wall et al. [42] observed that sodium sulfate and sodium chloride can increase the SL intensity, which is an important factor to measure the collapse strength and free radicals in the ultrasonic process. Sodium chloride can increase SL intensity faster than sodium sulfate in the abstract, it is easy to form organochlorine compounds in the EC process which could be consumed in the process by absorbing the EC energy [43], leading to the decrease of degradation rate. $> 90\%$ removal efficiency of CPS was achieved in the cases of Na_2SO_4 and NaNO_3 after 1 h, but it was relatively low in the case of NaCl . In addition, when the sodium sulfate is added into solution, the pH of solution is neutral, which is favorable for protecting the electrode from corrosion. Taking into consideration the stability,

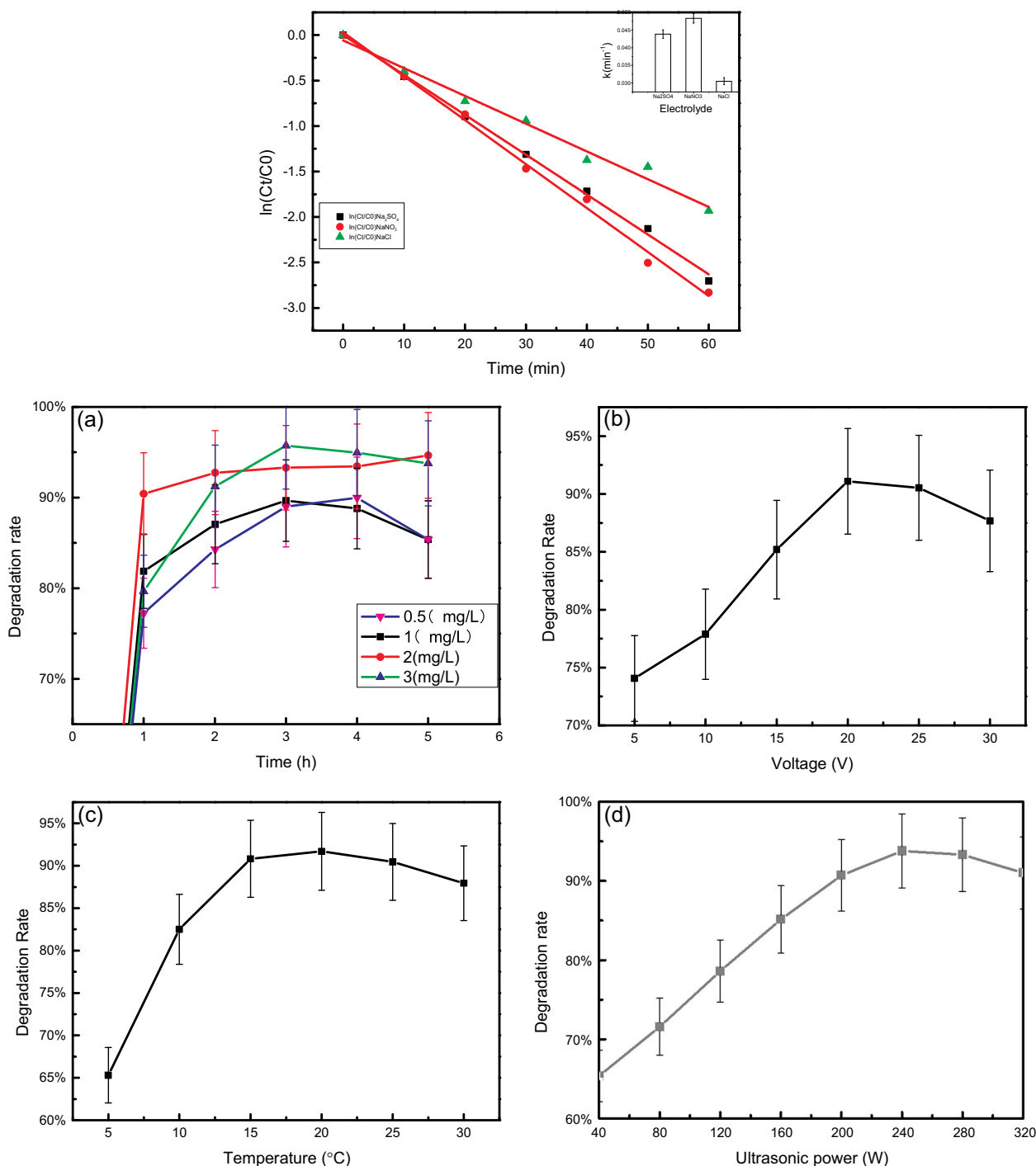


Fig. 5. (1) Degradation of CPS in the US-EC system with three different electrolytes; (2) Effects of (a) electrolyte (Na_2SO_4) concentration, (b) different voltage, (c) solution temperature, and (d) ultrasonic power on the CPS degradation in the US-EC system. Except the investigated factor, other conditions were: voltage 20 V, electrolyte (Na_2SO_4) concentration 2 mg L^{-1} , ultrasonic power 200 W, temperature $20 \text{ }^\circ\text{C}$.

harmlessness, and economy, sodium sulfate was chosen as the electrolyte in the experiment.

3.2.2. Initial electrolyte concentration

As shown in Fig. 5a, increasing the concentration of Na_2SO_4 electrolyte could lead to a gradual enhance in the degradation efficiency of CPS in the range of $0.5\text{--}3 \text{ g L}^{-1}$, but result in marginal improvements of CPS in the range of $0.5\text{--}3 \text{ g L}^{-1}$. It was received that higher concentrations of electrolytes would be benefit for US-EC processes [44], owing to the improved EC efficiency and US cavitation effect [23]. The addition of inorganic salts can not only drive the organic pollutants toward the bubble-bulk interface

with the increased aqueous ionic strength, but also favor the increase of the collapsing cavitation bubbles by changing the vapor pressure and surface tension [45]. However, more concentrated electrolyte would be disadvantageous for decomposition of target organic pollutants result from the more intensive aqueous interactions [46]. Therefore, in the US-EC system, the concentration of sodium sulfate electrolyte was properly determined to be 2 g L^{-1} .

3.2.3. Voltage

The current has a significant impact on the US-EC system, it is effective to provide higher current for the system by increasing the input

voltage. Under the same experimental conditions, different voltages were applied to the experiment. The results are shown in Fig. 5b. At a voltage of 10 V, 78% of the CPS was degraded within 1 h. When the voltage was increased to 20 V and 30 V, the degradation rate of CPS was 93% and 88% respectively. The voltage increases from 10 V to 30 V, and at the same time current increases from 0.19 to 0.75 A. From 10 V to 20 V, the degradation rate increased significantly, indicating that higher voltage will benefit the US-EC system, but when the voltage is further increased to 30 V, the degradation rate decreases slightly. This may be the reason that the supply current causes an oxygen evolution reaction near the anode and leads to competition with direct anodic degradation of CPS. In addition, the application of higher current densities is not cost-effective [47]. Amorim et al. observed similar current effects [48] in their survey.

3.2.4. Temperature

Temperature has a significant effect on mass transfer coefficients and kinetic parameters [49]. With the use of ultrasound, the temperature of the solution will also increase, so it is necessary to study the effect of CPS degradation in this system at different temperatures. The degradation at a temperature in the range of 5–30 °C is as shown in Fig. 5c. A difference of about 28% between the lowest and highest reaction temperatures was observed. When the temperature is raised, the time is reduced that for degrading the organic substances in the solution. This may be due to the formation of $S_2O_8^{2-}$ [50] which can oxidize organics, and the degradation rates will increase with increasing temperature. These results are consistent with the results of other authors.

Taking into account the operating conditions, degradation efficiency, and lost energy, the reaction temperature was set on 20 °C. In a relatively small temperature range, the heat and diffusion properties of CPS are not clearly reflected by the degree of degradation [51]. Therefore, in order to study the influence of temperature in the reaction, more experimental exploration and detailed analysis are needed in a wider temperature range.

3.2.5. Ultrasonic power

The study explored the degradation of CPS at different ultrasonic powers in the US-EC system. The results obtained are shown in Fig. 5d. At a single ultrasound power of 200 W, only 50.94% of CPS degraded after 60 min of sonication alone. Regardless of the ultrasonic power used, no > 60% of the CPS was degraded by sonication after 30 min. However, after 60 mins of EC treatment, the removal rate reached 72.8%. When ultrasound was combined with electron beams in the US-EC progress, significant degradation of CPS was observed. From Fig. 5d, it can be seen that when the ultrasonic power increases from 40 W to 200 W, the degradation rate in the system is obviously improved. When the ultrasonic power output exceeds 200 W, the degradation of CPS is gradually reduced.

In general, as the ultrasonic power increases, acoustic bubbles generate more, resulting in higher temperature and pressure in the cavitation location. The prolonged growth and collapse of these bubbles will also result in the removal and recombination of free radicals on the electrodes, thereby reducing the transfer of reactive species such as hydroxyl radicals into the solution and enhancing the elimination of solutes adsorbed at the bubble-water interface. As the cavitation effect gradually strengthens, the probability of recombination of hydroxyl radicals increases and the amount used for degradation decreases.

3.3. Degradation kinetics

The rate constant and the calculated synergy index *S* are plotted in Fig. 4 and Table 1. For a single system, the rate constants are $1.235 \times 10^{-2} \text{ min}^{-1}$ (US) and 2.201×10^{-2} (EC), respectively. The

rate constant increases to $4.465 \times 10^{-2} \text{ min}^{-1}$ in the combined system, which means that rate constant is higher than the sum of the rate constants of the individual systems, the interaction between the US and the EC system is beneficial. From Eq. (2), the synergistic effect of US-EC combination is 37%, which demonstrates a slightly positive synergy for the combined system, indicating that the US-EC system could degrade CPS faster than the corresponding EC system.

The data for CPS degradation were analyzed using pseudo-first-order kinetics, according to Eq. (3):

$$\ln C = \ln C_0 - kt \quad (3)$$

where, *C* and *C*₀ are measured and initial concentrations of the pesticide, respectively, (mg L^{-1}), *k* (min^{-1}) is the reaction rate constant, and *t* (min) is the degradation time.

The pseudo-first-order kinetic could be applied for the degradation of CPS in both US-EC system and EC system, with the related degradation rate constant (*S*_{CPS}) of 4.465×10^{-2} and 2.201×10^{-2} respectively.

The synergy of the US-EC system can be explained by the fact that ultrasonic radiation produces both chemical and physical effects in heterogeneous processes. The air bubbles generated by acoustic cavitation undergo growth and collapse stages, and then produce high temperature and pressure, decomposing the water molecules into $\cdot\text{OH}$ and $\cdot\text{H}$ [52], as shown in Eq. (6), and chemical reactions are closely related to cavitation. With ultrasound alone, the degradation efficiency is very low because the yield of hydroxyl radicals generated by low-frequency ultrasound is very low [35]. In addition to the ultrasonic cavitation effect, the main improvement is the electrode surface material updates, especially low-frequency ultrasound [53], cavitation microfluidization makes strong stirring effect on the solution by ultrasonic cavitation, thereby increasing the mass transfer rate of the electrode surface. Therefore, the combination of ultrasound and electrocatalysis has a significant synergistic effect on the formation of $\cdot\text{OH}$.

3.4. Reaction mechanism in the US-EC system and the promotional role of US

The $\cdot\text{OH}$ can be highly active and selectively react with many kinds of organic compounds, It has the following characteristics: (1) Oxidation ability, is a very strong oxidant, (2) $\cdot\text{OH}$ is very lively, Most of the organic reaction rate constant of 10^6 – $10^{10} \text{ mol}^{-1}\cdot\text{L}\cdot\text{s}^{-1}$ [54], (3) low selectivity, and unrelated to the concentration of reactants, (4) short life span, there is a certain difference in different environmental media, generally $< 10^{-4} \text{ s}$, only 10^{-9} s in liquid [55], (5) high processing efficiency, does not produce secondary pollution.

The generation of $\cdot\text{OH}$ is the commonness and key of the wastewater treatment technology of the US-EC system. Therefore, the study of $\cdot\text{OH}$ is of great significance for environmental EC research. The $\cdot\text{OH}$ is easy to attack high electron density points, and crystal violet with high electron density S=P group electrophilic addition reaction, lead to fade the crystal purple. By measuring the change of crystal violet absorbance value, the $\cdot\text{OH}$ can be indirectly measured.

The author has initially detected and compared the generation of $\cdot\text{OH}$ in the EC and US-EC system. The relationship between hydroxyl radical generation of the EC system and the US-EC system is shown in Fig. 6. Under both systems, $\cdot\text{OH}$ shows an increasing trend over time. Between 0 and 20 min, the amounts of $\cdot\text{OH}$ generated by the two systems are almost the same, but after 20 min, the amount of $\cdot\text{OH}$ production gradually increased compared with the EC system. As shown in Eqs. (6) and (7), this phenomenon may be attributed to the supporting role of ultrasound in the US-EC system.

It is established that the direct oxidation and indirect oxidation procedures are commonly contained in EC oxidation processes [56]. Combining with the discussion above, a reaction mechanism in the US-

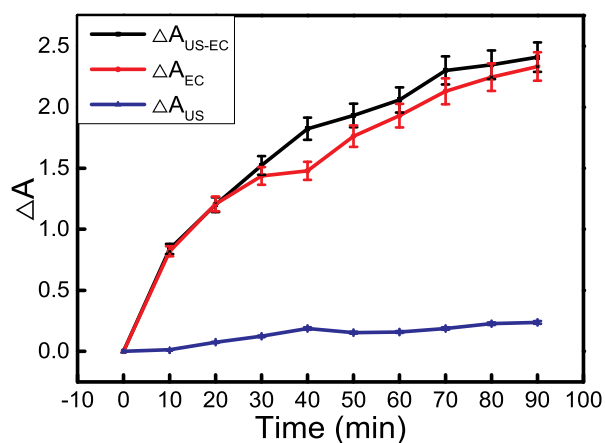


Fig. 6. The production of hydroxyl radical.

EC system as well as the promotional role of US could be proposed as illustrated in Fig. 7. The $\cdot\text{OH}$ is electrocatalytically generated on the electrode, through oxidatively decomposing water or directly oxidizing hydroxyl ions [57] under the action of an electric field (Eqs. (4) and

(5)).



4. Conclusion

In this study, we established an US-EC system using common stainless-steel electrodes to improve effectively the degradation of CPS, a residual pesticide. The synergistic factor was 37% in the combined reaction system, which is more attractive than sonication and EC single-system treatment synergy. The results showed that the process of ultrasonic EC treatment of CPS pesticides followed pseudo-first-order reaction.

The initial concentration of CPS was 900 mg L^{-1} , which was degraded > 90% after 1 h. The system was found to work effectively in the temperature range of 15–35 °C and sonication showed good

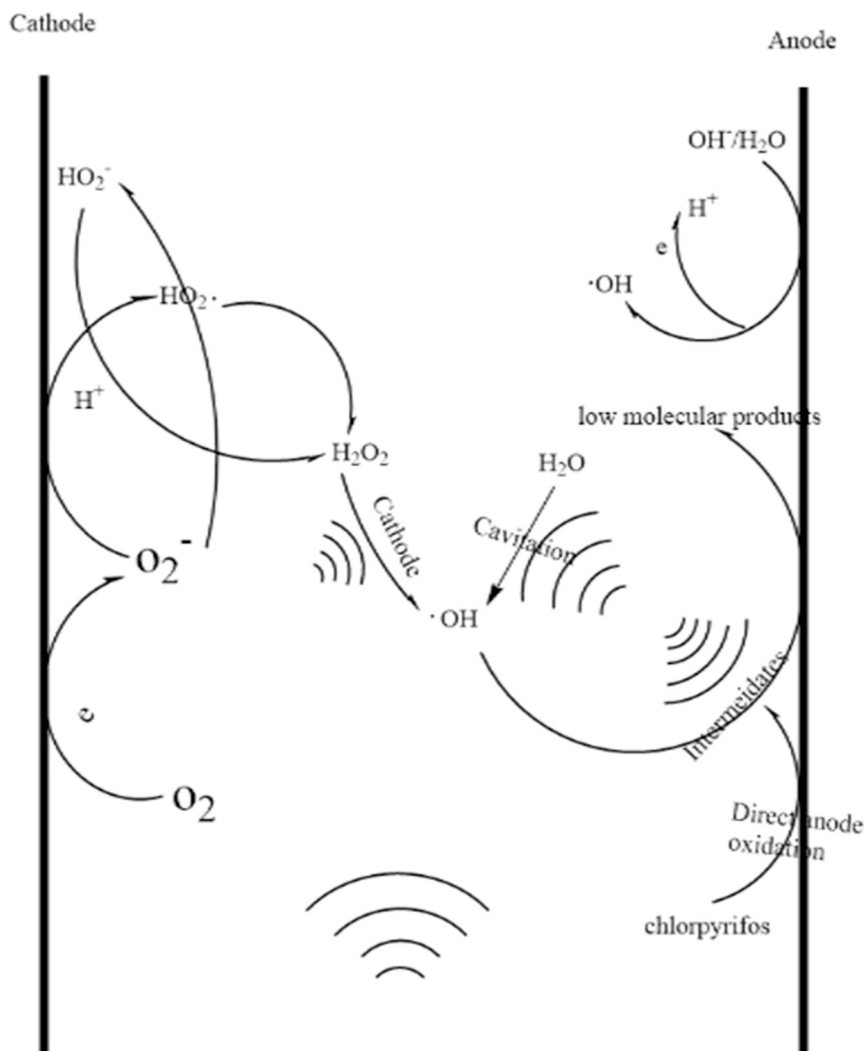


Fig. 7. The proposed reaction mechanism in the US-EC system.

processing performance at a voltage of 20 V and a Na_2SO_4 concentration of 2 g L^{-1} at an ultrasonic power of 200 W. The results of this study show that ultrasonic is an effective method to improve the common electrooxidation process in aqueous solution of refractory organic pollutants. The US-EC system has the advantages of simple setting, cheap electrode material and high energy utilization efficiency, and has great potential for large-scale and industrial application in the treatment of wastewater with high pollutant concentration. However, its application in complex wastewater needs further study.

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