



Detection of hydroxyl radicals in sonoelectrochemical system

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ABSTRACT

We established an efficient method to trap the hydroxyl radicals ($\cdot\text{OH}$) derived from the sonoelectrochemical system, the model compound crystal violet was used as a scavenger. Parameters affecting the trapping reaction, such as reaction time, electrolyte, applied voltage, power, and solution pH, were investigated. The dynamics model was used to analyze the reaction kinetics and the origin of $\cdot\text{OH}$.

The detection method is stable and accurate, comparing with the single electrochemical and ultrasonic systems, more $\cdot\text{OH}$ could be trapped in the sonoelectrochemical system; the higher the concentration of the scavenger, the more $\cdot\text{OH}$ is captured; the $\cdot\text{OH}$ is promoted to generate in the alkaline conditions; appropriate electrolyte concentration and voltage will enhance the $\cdot\text{OH}$ yields by increasing the current efficiency; inhibitors can significantly reduce the yields of $\cdot\text{OH}$, inorganic inhibitors have better removal effect than organic inhibitors on the $\cdot\text{OH}$; the enhancement of power is beneficial to the generation of cavitation effect increasing free radical production, it is not conducive to generate $\cdot\text{OH}$ when the power is strengthened to a certain degree; the $\cdot\text{OH}$ may be produced by the decomposition of water molecules and the oxidation of OH^- in the system; the process follows first-order reaction kinetics with good linearity.

1. Introduction

For the increasingly serious pollution of biodegradable organic wastewater, the traditional water treatment methods often can't achieve satisfactory effect [1]. Advanced oxidation processes (AOPs) have been widely applied as alternative methods for the treatment of aqueous effluent and have remarkable results, such as photocatalytic process [2,3], many documents have reported that a series of prominent achievements be gained in this field, nevertheless, it has always been an enormous challenge to synthesize efficient and stable photocatalyst [4,5]. Sonoelectrochemical (US-EC) technology which electrochemical (EC) oxidation combined with ultrasound, is a novel idea for disposing the wastewater [6,7], which has favorable features such as mild operational condition, efficient functioning at room temperature and no additional requirement of chemicals. Although sonoelectrochemical technology had made many achievements in the treatment of wastewater, the mechanism of reaction is too complicated to be explored so far.

The great majority of studies indicated that hydroxyl radicals ($\cdot\text{OH}$) were generated numerously during advanced oxidation processes [8,9], and just the $\cdot\text{OH}$, which had strong oxidation ability, enables organic contaminants to be degraded [10,11], but the $\cdot\text{OH}$ is extremely short-

lived [12] and is difficult to be captured. The oxidation mechanism is still in the speculative phase and lacks valid experimental data, which has hindered the generation of $\cdot\text{OH}$ and the optimization of reaction conditions, the accurate characterization of the concentration of $\cdot\text{OH}$ has an irreplaceable guiding significance for the treatment of biodegradable organic wastewater. As far as we are concerned, no relative literatures had been published about detecting the $\cdot\text{OH}$ in US-EC systems. It is very necessary to establish a reliable and stable detection method of $\cdot\text{OH}$ in the US-EC oxidation system.

In recent years, different methods had been gradually applied and utilized to detect the $\cdot\text{OH}$ in the various systems, so that we have more choices. Owing to many interference factors, accuracy has always been a major challenge in various detection methods. We can indirectly quantify the $\cdot\text{OH}$ in the system through the change of concentration when the $\cdot\text{OH}$ reacts with scavengers, so selecting the scavenger is particularly important. Dye reagents can be oxidized by the $\cdot\text{OH}$ to produce fading reactions, which indirectly measure the concentration of $\cdot\text{OH}$, such as crystal violet.

In the experiment, crystal violet was selected as the capture on account of the stable structure [13–15], and the absorbance of the capture was detected by the spectrophotometry, thus indirectly indicating the $\cdot\text{OH}$ generated in the system. The effect of different reaction factors on

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the formation of $\cdot\text{OH}$ in the oxidation reaction was conducted, which can be used as the evaluation criterion for the optimization of the reaction conditions; the origin of the $\cdot\text{OH}$ was discussed; finally, the reaction kinetics analysis was carried out.

2. Experimental

2.1. Materials

The chemical reagents of all experiments were analytical reagent grades, and all solutions were prepared from distilled water without further purification. Crystal violet and sodium carbonate were supplied by Shanghai Qiang shun Chemical Reagent Co., Ltd., China. Sodium sulfate, *tert*-butanol, absolute ethanol, anhydrous methanol, sodium hydrogen carbonate, sulfuric acid, and sodium hydroxide were purchased from National Chemicals Co., Ltd., China.

Potassium hydrogen phthalate, mixed phosphoric acid Salt are two pH buffering reagents provided by Shanghai Lichen Instrument Technology Co., Ltd., China. The crystal violet was dissolved by a small amount of absolute alcohol and was prepared by distilled water, then sodium sulfate was added into the solution, magnetically stirring for half an hour. The pH of the solution was adjusted by NaOH and H_2SO_4 .

2.2. Apparatus

The SEM images were taken using a SUPRA-55 field emission scanning electron microscope (Carl Zeiss AG, Germany). The UV–Vis full-band scanning spectrum of crystal violet was obtained using a UV-3600 spectrophotometer (Shimadzu Corporation, Japan). The XRF spectra were taken by an X-Ray Fluorescence Spectrometer (Bruker). The reaction applied an ultrasonic generator, which was manufactured by PHS-25 PH Meter (Shanghai instrument electric science instrument). A schematic diagram of the applied device for the US-EC process is shown in Fig. 2a. The ultrasonic generator was manufactured by Ningbo New Chi Biotechnology Co., Ltd. Ultrasonic waves were introduced into the reaction solution through an ultrasonic transducer which produced by Ningbo New Chi Biotechnology Co., Ltd. and fixed at the bottom of the double-walled cylindrical glass reactor, operating in a continuous mode of 40 kHz.

2.3. Procedures

2.3.1. The UV–Vis spectra of scavenger

Distilled water was selected as a reference to perform a full-band scan of $0.1 \text{ mmol}\cdot\text{L}^{-1}$ crystal violet in the range of 250–800 nm using an UV–Vis spectrophotometer, which can determine the maximum absorption wavelength of the scavenger at 580 nm from Fig. 1.

2.3.2. The production of $\cdot\text{OH}$

The US-EC process was described in Fig. 2a, using crystal violet (initial concentration of $0.2 \text{ mmol}\cdot\text{L}^{-1}$) as model capture and $0.02 \text{ mol}\cdot\text{L}^{-1}$ Na_2SO_4 as supporting electrolyte in the experiment.

The stainless-steel (SS) was selected as electrode owing to possess some outstanding properties, such as high surface area (to supply more sites for reactions and enhance electrode kinetics), good electrical conductivity (to promote the electron transfer), high stability and low cost, as shown in Fig. 2b. The anode was made into a cylindrical mesh that the increase of the surface area can enhance oxygen contact with electrode (diameter: 20 mm, height: 8 mm, surface area: 3140 mm^2 , immersion depth 5 mm), and the cathode had the same electrode material and shape at a distance of 40 mm between the electrodes. Ultrasonic transducers provide the highest level of sound energy and deliver high quality transmissions in the middle of the reactor, the experimental setup as shown in Fig. 2a.

The surface topography and element composition of the SS electrode were observed using field emission scanning electron microscopy

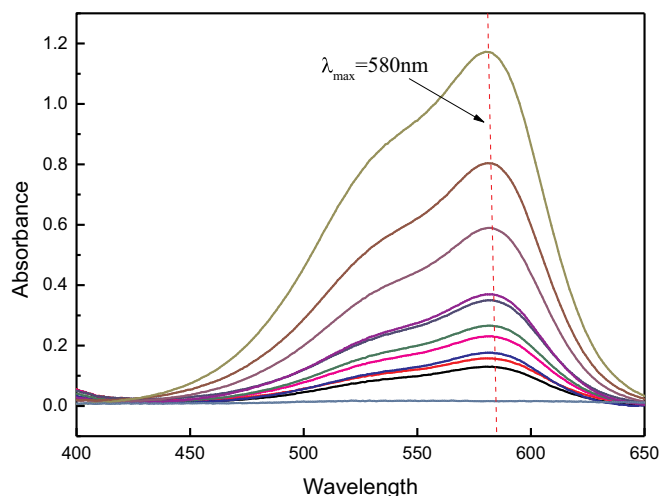


Fig. 1. The UV–Vis spectra of crystal violet at different concentrations.

(FE-SEM) and X-ray energy dispersive spectroscopy (EDS), as shown in Fig. 2b. Observing the FE-SEM image of the commercially available SS electrode, the texture of the SS electrode was quite tight and uniform. This type of electrode possessed highly reactive and stable characteristics based on the EDS analyses of all electrodes. Fig. 2c displays the main components of the SS electrode are Fe, Ni and Mn, and the Fe peak is sharp.

2.3.3. The detection of $\cdot\text{OH}$

In order to ensure the strongest response signal of the capture, the maximum absorption wavelength is set at the detection wavelength. At specified time intervals, 1 ml samples were taken from the reactor and diluted with distilled water to 5 ml. The concentration of the capture was calculated from the absorbance decay at the maximum dye wavelength $\lambda_{\text{max}} = 580 \text{ nm}$ and translated into the concentration of $\cdot\text{OH}$. The results shown in this paper are average of three parallel experiments.

2.3.4. The quantification of scavenger

In this study, a linear regression was performed on the concentration of the reference material and the standard working curves of the crystal violet were obtained: $y = 29.01433 - 0.04129x$ ($R = 0.99907$), the crystal violet material showed a good linear relationship within a certain range, as shown in Table 1 and Fig. 3.

2.3.5. Evaluation of test method

In this paper, the amount of $\cdot\text{OH}$ produced in the solution after the oxidation reaction was measured. The measurement and calculation results were shown in Table 2, the $\cdot\text{OH}$ generated in the Sonoelectrochemistry where the crystal violet was selected as a scavenger was determined by spectrophotometry, the method had good precision.

2.3.6. Calculation of inhibition rate

$$\varnothing\% = \frac{C_{\text{blank}} - C_{\text{inhibition}}}{C_{\text{blank}}} \times 100\% \quad (2-1)$$

Among them, $\varnothing\%$ is the inhibition rate of $\cdot\text{OH}$ radical, %; C_{blank} is the concentration of $\cdot\text{OH}$ captured when no inhibitor is added, $\mu\text{mol}\cdot\text{L}^{-1}$; $C_{\text{inhibition}}$ is the concentration of $\cdot\text{OH}$ detected after adding inhibitor, $\mu\text{mol}\cdot\text{L}^{-1}$.

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