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Decolorization of CI Reactive Black 8 by electrochemical process with/without ultrasonic irradiation

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ABSTRACT

The decolorization of CI Reactive Black 8 by anodic oxidation with Ti/RuO_2-IrO_2 anode and stainless steel cathode was carried out in an electrochemical cell with or without ultrasonic irradiation. The effect of current density, initial pH value, initial dye concentration and electrolyte concentration on the decolorization rate of CI Reactive Black 8 in both two processes was investigated. The results showed that the decolorization followed pseudo-first-order kinetics. The decolorization rate increased with increasing the current density, but decreased with increasing the initial dye concentration and electrolyte concentration. The acidic condition favored CI Reactive Black 8 decolorization. The presence of ultrasonic irradiation could enhance electrochemical oxidation (EC) of CI Reactive Black 8, and the enhancement effect tended to increase with increasing the initial dye concentration, pH value, and electrolyte concentration, but decrease with increasing the current density. In the presence of ultrasonic irradiation, a 32.4% COD removal efficiency was achieved after 90 min EC when initial concentration was 100 mg l^{-1}, current density was 31.7 mA cm^{-2}, initial pH value was 5.4, the electrolyte concentration was 0.1 mol l^{-1} and the acoustic power was 100 W l^{-1}. The specific oxygen uptake rate (SOUR) tests showed that SOUR decreased during the first 15 min, but it increased with reaction time afterwards.

Keywords: Sonoelectrochemistry; Anodic oxidation; Ti/RuO_2–IrO_2 anode; CI Reactive Black 8; Decolorization; COD

1. Introduction

The presence of dyes in wastewater and nature environment is a serious worldwide problem. They not only give an undesirable color to the natural water, but also contaminate the water due to their inherent toxicity, mutagenicity and carcinogenicity. Azo dyes account for about 70% of all textile dyestuffs, which are characterized by the presence of azo groups consisting of two nitrogen atoms [1–3]. They are commonly used in many industries such as textile, paper printing, food, leather, pharmaceutical, and cosmetic [4–7].

As dye wastewater may significantly affect aquatic life and public health, a variety of treatment methods have been employed to control dye contaminated wastewater [8]. However, biodegradation is not an effective solution due to the azo dyes' feature of stability against microbial attack. Adsorption method just transfers the contaminant from wastewater to the solid phase and further treatment is required [9]. Among various treatment methods, electrochemical oxidation (EC) is considered

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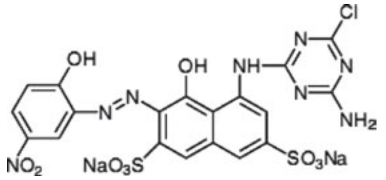
as an environment-friendly technology [10–12]. Dye can be oxidized by the hydroxyl radical formed at the surface of a high oxygen overvoltage anode from oxidation of water [13,14]. However, a long reaction time or high current density is usually needed to achieve satisfactory degradation efficiency by EC alone. The combination of EC with other technologies has great degradation ability, fast reaction rate and high efficiency, which has become one of the most promising technologies and active research aspects in these years [15].

Recently, there have been increasing reports on the use of ultrasonic irradiation (US) for wastewater treatment. The mechanisms of ultrasound to destroy organic pollutants include pyrolytic fragmentation within the bubble, supercritical phase reactions in the interfacial region with radial gradient in temperature and local radical density, and radical reactions in the bulk solution at ambient temperature [16]. But the single US is difficult to meet the requirement for wastewater treatment in some cases. Hence, the combination of ultrasound with other technologies has been one of active research fields in recent years [17–24]. Many researchers found that there was an obvious enhancement on the degradation of pollutants when US was coupled with the electrochemical process (US/EC) [25–30]. Furthermore, biological treatment is usually employed in sequence with chemical oxidation to reduce the operating costs. Therefore, the biodegradability assessment of the effluent from chemical oxidation has been paid more attention in recent years [31]. To our knowledge, there are few investigations on the variation of biodegradability during the combined US/EC process. The specific oxygen uptake rate (SOUR), which is prompt response of activated sludge, is thought to be a more realistic index than the other traditional biodegradability index [32]. In this study, CI Reactive Black 8 was chosen as the target compound due to its low price and wide usage in the textile industries. The decolorization of CI Reactive Black 8 by anodic oxidation with Ti/RuO_2-IrO_2 electrode was carried out in an electrochemical cell with or without ultrasonic irradiation. The effect of operative conditions such as current density, initial pH value, initial dye concentration and electrolyte concentration on the decolorization of CI Reactive Black 8 by the electrochemical process with/without US was investigated. The biodegradability assessment during the treatment was also investigated using SOUR test.

2. Materials and methods

The commercial dye CI Reactive Black 8 was purchased from Wenzhou Rosi Dyestuff Co. Ltd. (China) and used without further purification. The structure and relevant data of CI Reactive Black 8 are shown in Table 1. Sodium hydroxide (CP Grade, 95%) was obtained from Tianjin No. 3 Chemicals Reagent Factory (China). Sulphuric acid (AR Grade, 95–98%) was obtained from Wuhan Yatai Chemicals Reagent Co. Ltd. (China). All solutions were prepared with distilled water.

Table 1
Chemical structure and relevant data for CI Reactive Black 8

Name	CI Reactive Black 8 (K-BR)
Color index (C.I.)	18207
Formula	$C_{19}H_{11}ClN_8Na_2O_{10}S_2$
Structure	
FW (g mol^{-1})	656.5
λ_{max} (nm)	587

The experimental setup was similar to our previous study [33]. Batch experiments were performed in a rectangular electrolytic reactor (plexy glass) containing 200 ml solution. Electrolyses were conducted under constant current conditions using a direct current (DC) power supply (Model WYK-305) from Yangzhou Jintong Source Co. Ltd. (China). One 5 cm × 11.9 cm plate anode (Ti/RuO_2–IrO_2) and one plate cathode (stainless steel) of the same dimension were arranged parallel to each other at a distance of 3.8 cm. The working surface area of the electrode was 31.5 cm^2. A magnetic stirrer (Model 78-1, Hangzhou Instrument Motors Factory, China) provided the mixing of the solution in the reactor. Stock solution of CI Reactive Black 8 was freshly prepared in distilled water before each run. Sulphuric acid or sodium hydroxide was used to adjust the pH of the dye solution. The stock solution was fed into the plexy glass reactor. In the meantime, sonication was performed using a KS-250 ultrasonic generator (250 W, 20 kHz, Ninbo Kesheng Instrument Co., China) equipped with a titanium probe transducer during US/EC processing. The tip of the probe (1 cm in diameter) was placed in the center between the two electrodes and dipped in the solution from the top of the reactor (2 cm into the liquid layer). The sonication was administered in a pulse mode of 2.5 s on and 2.1 s off. The acoustic power was determined calorimetrically and fixed at P = 100 W l^{-1} [34]. The reactor was immersed into a water bath to keep the temperature around 20°C. At pre-selected time intervals, samples were withdrawn from the electrolytic cell and measured by Shimadzu UV-1700 spectrophotometer (Shimadzu Co., Japan) at the dye's maximum absorption wavelength of 587 nm.

To conduct the SOUR test, 145 ml activated sludge was aerated 5 min and mixed with 5 ml treated wastewater, and the dissolved oxygen (DO) concentration of the mixed solution was measured by Orion-model-810 oxygen meter. Oxygen uptake rate (OUR) was measured through the slope of the DO concentration versus time:

$$\mathrm{OUR} = \Delta\mathrm{DO}/\Delta t \tag{1}$$

SOUR was determined by dividing OUR to the mixed liquor volatile suspended solids (MLSS) concentration:

$$\mathrm{SOUR} = \mathrm{OUR}/\mathrm{MLSS} \tag{2}$$

where the MLSS were measured by filtration and evaporation the solution at 105°C for 2 h. Then the I_{SOUR} was calculated by the following equations:

$$I_{\mathrm{SOUR}} = \frac{\mathrm{SOUR_t}}{\mathrm{SOUR_b}} \tag{3}$$

where $\mathrm{SOUR_t}$ is the SOUR of the mixed liquor in the presence of CI Reactive Black 8 solution at different time intervals and $\mathrm{SOUR_b}$ is the SOUR of the sample containing only distilled water [32,35].

3. Results and discussion

3.1. Effect of initial dye concentration on the decolorization of CI Reactive Black 8

The decolorization of CI Reactive Black 8 by the electrochemical process with and without US at different initial dye concentrations was investigated when current density (j) was 31.7 mA cm^{-2}, initial pH value was 5.4, the electrolyte concentration was 0.1 mol l^{-1} and the acoustic power was 100 W l^{-1}. The initial dye concentrations investigated in this study were 50, 100 and 200 mg l^{-1}, respectively. As can be seen in Fig. 1, the removal of CI Reactive Black 8 follows apparent pseudo-first-order kinetics according to the following rate equation:

$$A = A_0 \exp(-kt) \tag{4}$$

where A_0 and A is the absorbance of CI Reactive Black 8 concentration at time 0 and t min, respectively, and k is the pseudo-first-order rate constant. Table 2 shows all the pseudo-first-order rate constants in the EC and US/EC process. As shown in Table 2, the decolorization rate decreased with increase in the initial concentration. The rate constants calculated are 0.0098, 0.0085 and 0.0081 min^{-1} in the EC process and 0.0113, 0.0103, and 0.0101 min^{-1} in the US/EC process for 50, 100 and 200 mg l^{-1} of initial concentration, respectively. The effect of initial concentration on the decolorization rate was not pronounced in both the process, while the total amount of removed CI Reactive Black 8 was increasing with increased in the initial concentration. Specifically, the total amount of removed CI Reactive Black 8 after 90 min reaction was 30.5, 56, and 104 mg l^{-1} in the EC process and 33, 63 and 122 mg l^{-1} in the US/EC process for 50, 100 and 200 mg l^{-1}, respectively. It indicated that more CI Reactive Black 8 was degraded with the higher initial dye concentration in both processes. The similar result was reported by Ai et al. when the azo dyes were decolorized by ultrasound-assisted electrocatalytic oxidation process [25].

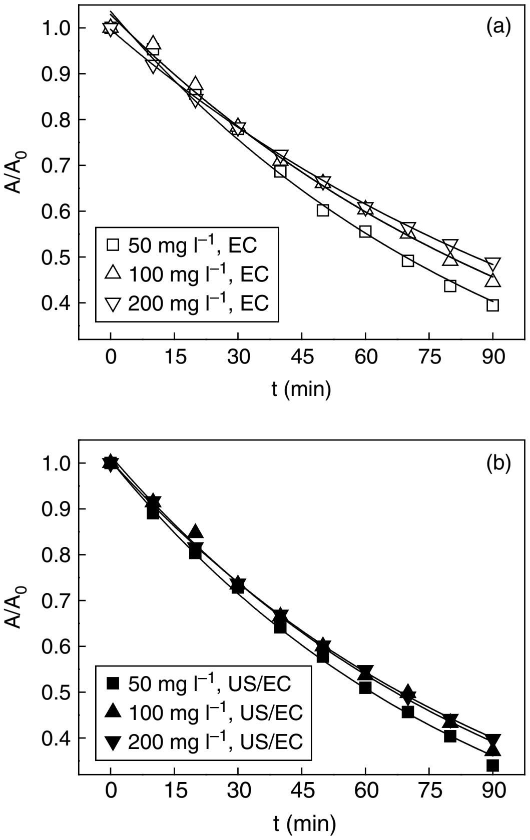


Fig. 1. Effect of initial dye concentration of CI Reactive Black 8 in (a) electrochemical process and (b) electrochemical with ultrasonic irradiation process (pH$_0$ 5.4, j = 31.7 mA cm^{-2}, [Na$_2$SO$_4$] = 0.1 mol l^{-1} and P = 100 W l^{-1}).

When CI Reactive Black 8 was treated by US alone, negligible color removal was achieved (data not shown). It indicated US alone could not decolorize CI Reactive Black 8 due to its hydrophilic characteristics. Accordingly, the enhancement factor (f) was defined as the ratio of the rate constant of US/EC to that of EC:

$$f = \frac{k_{\mathrm{US/EC}}}{k_{\mathrm{EC}}} \tag{5}$$

Table 2
The pseudo-first-order rate constants in the electrochemical process with/without ultrasonic irradiation

No.	C_0 (mg l^{-1})	pH$_0$	j (mA cm^{-2})	Na$_2$SO$_4$ (mol l^{-1})	EC		US/EC		f
					k (min^{-1})	R^2	k (min^{-1})	R^2	
1	50	5.4	31.7	0.1	0.0098 ± 0.0006	0.9862	0.0113 ± 0.0003	0.9978	1.15
2	100	5.4	31.7	0.1	0.0085 ± 0.0005	0.9886	0.0103 ± 0.0004	0.9950	1.21
3	200	5.4	31.7	0.1	0.0081 ± 0.0001	0.9994	0.0101 ± 0.0001	0.9994	1.25
4	100	5.4	15.9	0.1	0.0056 ± 0.0002	0.9954	0.0072 ± 0.0001	0.9996	1.28
5	100	5.4	47.6	0.1	0.0123 ± 0.0006	0.9886	0.0133 ± 0.0003	0.9982	1.08
6	100	3.2	31.7	0.1	0.0123 ± 0.0004	0.9962	0.0140 ± 0.0004	0.9974	1.14
7	100	8.1	31.7	0.1	0.0091 ± 0.0002	0.9982	0.0124 ± 0.0002	0.9992	1.36
8	100	5.4	31.7	0.05	0.0127 ± 0.0002	0.9988	0.0131 ± 0.0004	0.9974	1.02

where k_{EC} denotes the pseudo-first-order rate constants in the electrochemical process and $k_{US/EC}$ denotes the pseudo-first-order rate constants in the electrochemical process combined with ultrasonic irradiation. As shown in Table 2, the f values were all larger than 1. This indicated that the decolorizaiton rate of the electrochemical process could be enhanced by the ultrasonic irradiation. This was due to the fact that ultrasound irradiation increases the turbulence of the solution and enhances the mass transfer of CI Reactive Black 8 [20]. The ultrasound irradiation also could decompose of the CI Reactive Black 8 aggregate in the solution and make it in a monomolecular state [21]. And the cavitation phenomenon of ultrasound might lead to the production of more hydroxyl radicals in the solution. Therefore, the ultrasound plays an important role in the improvement of decolorization rate in the combined US/EC process. The f values were 1.15, 1.21, and 1.25 for 50, 100 and 200 mg l^{-1} of initial dye concentration, respectively. The lower initial dye concentration would result in the lower f value. With the decrease of the initial dye concentration, the intermediate products would become dominant. In consequence, the side reactions between hydroxyl radicals and the intermediate products would be significant. Therefore, the enhancement of US on the electrochemical process was less pronounced with the decreasing initial dye concentration.

3.2. Effect of current density on the decolorization of CI Reactive Black 8

The effect of current density on the decolorization of CI Reactive Black 8 by the electrochemical process with and without US at different current densities was investigated when CI Reactive Black 8 concentration was 100 mg l^{-1}, initial pH value was 5.4, the electrolyte concentration was 0.1 mol l^{-1} and the acoustic power was 100 W l^{-1}. The current densities investigated in this study were 15.9, 31.7 and 47.6 mA cm^{-2}, respectively. As shown in Fig. 2, the decolorization rate increased when the current density rose from 15.9 to 47.6 mA cm^{-2} in both processes. The rate constants calculated were 0.0056, 0.0085 and 0.0123 min^{-1} in the EC process and 0.0072, 0.0103, and 0.0133 min^{-1} in the US/EC process for 15.9, 31.7 and 47.6 mA cm^{-2} of current density, respectively. It was found

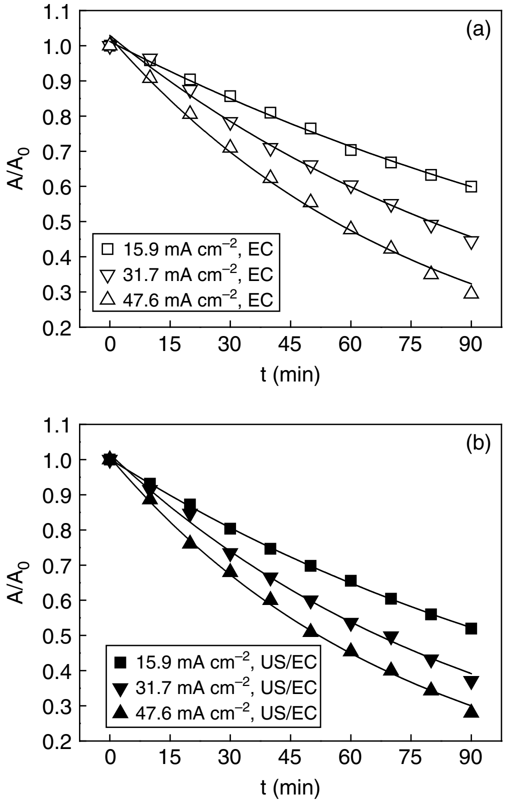


Fig. 2. Effect of current density of CI Reactive Black 8 in (a) electrochemical process and (b) electrochemical with ultrasonic irradiation process (C_0 = 100 mg l^{-1}, pH$_0$ 5.4, [Na$_2$SO$_4$] = 0.1 mol l^{-1} and P = 100 W l^{-1}).

that the current density had a significant influence on the decolorization rate. During anodic oxidation, CI Reactive Black 8 was destroyed by the hydroxyl radicals electro-generated at the surface of a high oxygen overvoltage anode:

$$H_2O \rightarrow H^+ + {}^{\bullet}OH + e^- \qquad (6)$$

The higher production of hydroxyl radicals from water oxidation would be expected at a higher current density [36,37], which would result in a higher decolorization rate [38,39].

Compared with the electrochemical process alone, the decolorization of CI Reactive Black 8 was enhanced by the electrochemical with US process. The *f* values were 1.28, 1.21, and 1.08 for 15.9, 31.7 and 47.6 mA cm^{-2} of current density, respectively. It decreased with increasing the current density because hydroxyl radicals produced by EC increased strongly compared with those formed by US.

3.3. Effect of initial pH on the decolorization of CI Reactive Black 8

In this study, the initial pH values investigated for the electrochemical processes with and without US were 3.2, 5.4 and 8.1. The initial dye concentration was 100 mg l^{-1}, the current density was 31.7 mA cm^{-2}, the electrolyte concentration was 0.1 mol l^{-1} and the acoustic power was 100 W l^{-1}. As shown in Fig. 3, in the electrochemical process the decolorization rate decreased with the increase in the initial pH value by 5.4. Afterwards, the decolorization rate increased. Similar result was observed in the coupled US/EC process. The rate constants calculated were 0.0123, 0.0085 and 0.0091 min^{-1} in the EC process and 0.0143, 0.0104, and 0.0123 min^{-1} in the US/EC process for 3.2, 5.4 and 8.1 of initial pH value, respectively. The results demonstrated that the initial pH value at 3.2 and 8.1 favored CI Reactive Black 8 decolorization in this study. The optimal initial pH value was 3.2 in the both processes. This may be due to the fact that the decreasing initial pH value increases the oxygen over potential. The oxygen evolution reaction is inhibited in acidic condition [40]. On the other hand, the OH$^-$ anions would change into hydroxyl radicals by losing electrons on the anode surface in alkaline condition [14,41]:

$$OH^- \rightarrow {}^{\bullet}OH + e^- \qquad (7)$$

The increased production of hydroxyl radicals would subsequently enhance the decolorization rate [6].

As a result, both acidic and weak base conditions favored CI Reactive Black 8 decolorization in electrochemical process and the combined electrochemical and ultrasonic process. The *f* values were 1.14, 1.21, and 1.36 for 3.2, 5.4 and 8.1 of initial pH value, respectively, indicating the enhancement effect tended to increase with increased in the initial pH value.

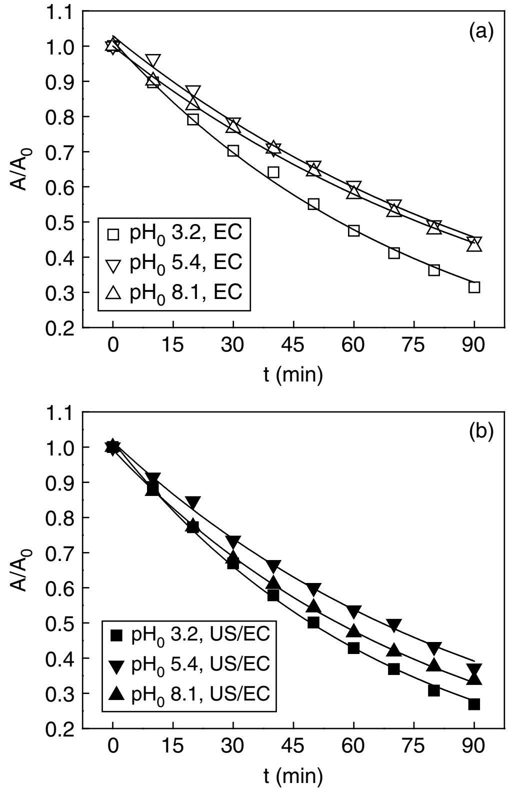


Fig. 3. Effect of initial pH value of CI Reactive Black 8 in (a) electrochemical process and (b) electrochemical with ultrasonic irradiation process (C_0=100 mg l^{-1}, j = 31.7 mA cm^{-2}, [Na$_2$SO$_4$] = 0.1 mol l^{-1} and P = 100 W l^{-1}).

3.4. Effect of electrolyte concentration on the decolorization of CI Reactive Black 8

The decolorization of CI Reactive Black 8 at different electrolyte concentration by the electrochemical process with and without US at different electrolyte concentration were investigated when CI Reactive Black 8 concentration was 100 mg l^{-1}, current density was 31.7 mA cm^{-2}, initial pH value was 5.4 and the acoustic power was 100 W l^{-1}. The electrolyte concentrations investigated in this study were 0.05 and 0.1 mg l^{-1}, respectively. As shown in Fig. 4, the decolorization rate was more rapid when the electrolyte concentration was 0.05 mg l^{-1}. The rate constants were 0.0127 and 0.0085 min^{-1} in the EC process and 0.0131 and 0.0103 min^{-1} in the US/EC process for 0.05 and 0.1 mg l^{-1} of electrolyte concentration, respectively. With increase in the sulfate concentration, the hydroxyl radicals would be quenched by the sulfate ion as the following equation:

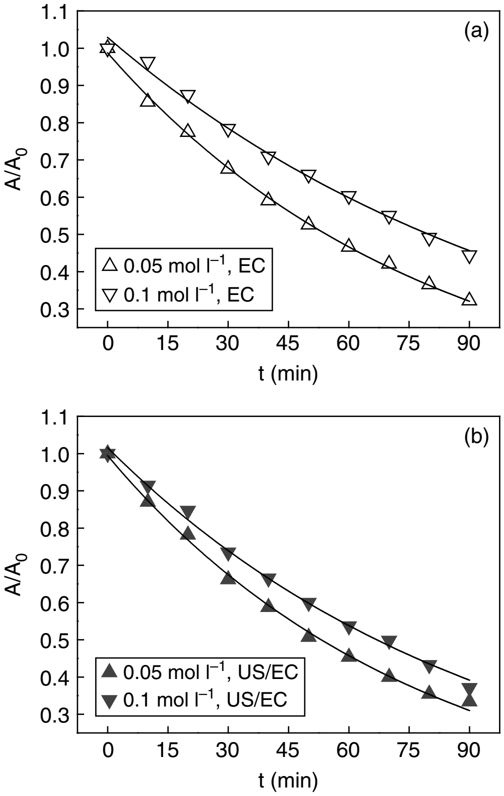


Fig. 4. Effect of electrolyte concentration of CI Reactive Black 8 in (a) electrochemical process and (b) electrochemical with ultrasonic irradiation process (C_0 = 100 mg l^{-1}, pH$_0$ 5.4, j = 31.7 mA cm^{-2} and P = 100 W l^{-1}).

$$^{\bullet}OH + SO_4^{2-} \rightarrow OH^- + SO_4^- \qquad (8)$$

The possible consumption of the generated hydroxyl radical by high SO_4^{2-} concentration would decrease the degradation efficiency [42,43].

Therefore, the decolorization efficiency was increased with decrease in the electrolyte concentration. The f values were 1.02, 1.21 for 0.05 and 0.1 mg l^{-1} of electrolyte concentration, respectively, which indicated the enhancement effect was more significant when the electrolyte concentration was higher.

3.5. UV-vis spectra change in the electrochemical process with ultrasonic irradiation

To clarify the changes in molecular and structural characteristics of CI Reactive Black 8 as a result of the coupled US/EC process, representative UV–visible (vis) spectra changes in the dye solution as a function of reaction time were observed and the corresponding spectra are shown in Fig. 5. From these spectra, the absorption spectrum of CI Reactive Black 8 in water exhibits two bands with the main band located at 580 nm in the visible region and another band in the UV region located at 330 nm. For CI Reactive Black 8, the adsorption peaks at wavelength 330 nm and 580 nm are attributed to aromatic structures and extended chromophore, comprising both aromatic rings, connected through the azo bond, respectively [16,44]. Following the combined US/EC process almost total suppression of the absorbance signals was observed. The disappearance of the both absorbance bands was due to the fragmentation of the azo group and the aromatic rings over time.

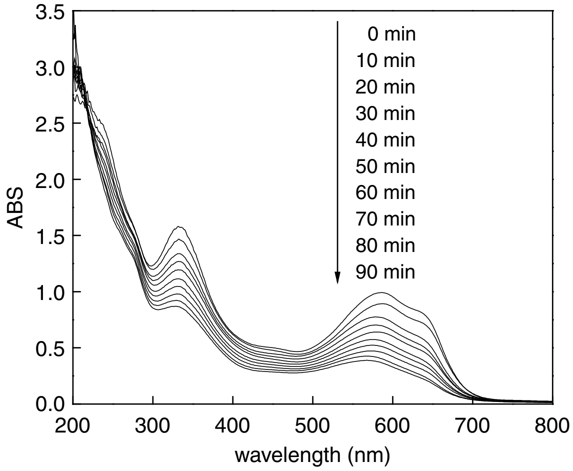


Fig. 5. UV-vis spectral changes with reaction time (C_0 = 100 mg l^{-1}, j = 31.7 mA cm^{-2}, pH$_0$ 5.4, [Na_2SO_4] = 0.1 mol l^{-1} and P = 100 W l^{-1}).

3.6. Changes of COD and biodegradability with reaction time

The change of COD removal efficiency and the biodegradability was investigated with CI Reactive Black 8 concentration 100 mg l^{-1}, current density 31.7 mA cm^{-2}, initial pH value 5.4, the electrolyte concentration 0.1 mol l^{-1} and the acoustic power 100 W l^{-1}. As can be seen in Fig. 6, the COD removal efficiency was 32.4% compared with 62.9% of CI Reactive Black 8 removal efficiency. This was due to the fact that the intermediates were less reactive towards oxidation by hydroxyl radicals than CI Reactive Black 8. Monitoring the biodegradation-associated SOUR could determine the short-term toxicity of effluent [31,32,35]. The I_{SOUR} decreased at the beginning of the reaction. After 15 min, a positive correlation between oxygen consumption rate and reaction time was evident from Fig. 6, the I_{SOUR} increased from 1.003 to 1.112 from 15 to 90 min. The reason might be that the toxic intermediates were produced during the first 15 min, and further treatment could convert these intermediates to less toxic products.

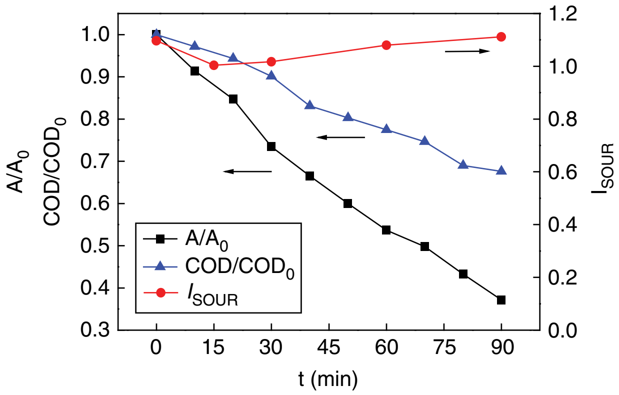


Fig. 6. The relationship between decolorization efficiency and oxygen consumption rate (C_0 = 100 mg l^{-1}, j = 31.7 mA cm^{-2}, pH$_0$ 5.4, [Na$_2$SO$_4$] = 0.1 mol l^{-1} and P = 100 W l^{-1}).

4. Conclusions

Both EC process and the combined US/EC process can remove CI Reactive Black 8 effectively. The enhancement effect was achieved in the coupled US/EC process, and the maximum enhancement effect could achieve 36%. The decolorization of CI Reactive Black 8 followed apparent pseudo-first-order kinetics. The decolorization rate increased with increasing the current density, but decreased with increasing the initial concentration and electrolyte concentration. Both acidic and weak alkaline conditions favored CI Reactive Black 8 decolorization. The f value tended to increase with increasing the initial dye concentration, pH value and electrolyte concentration. The enhancement of US on the electrochemical process was more significant when the current density was lower. The COD removal efficiency was 32.4% compared with 62.9% of CI Reactive Black 8 removal efficiency after 90 min reaction when initial concentration was 100 mg l^{-1}, current density was 31.7 mA cm^{-2}, initial pH value was 5.4, the electrolyte concentration was 0.1 mol l^{-1} and the acoustic power was 100 W l^{-1}. The I_{SOUR} decreased at the beginning of the process, and then increased with the reaction time.

Acknowledgements

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