Rapid decolorization of azo dyes in aqueous solution by an ultrasound-assisted electrocatalytic oxidation process

Zhihui Ai [a,b,*], Jinpo Li [a], Lizhi Zhang [a], Shuncheng Lee [b]

[a] Key Laboratory of Pesticide and Chemical Biology of Ministry of Education, College of Chemistry, Central China Normal University, Wuhan 430079, People's Republic of China
[b] Department of Civil and Structural Engineering, Research Center for Environmental Technology and Management, The Hong Kong Polytechnic University, Hong Kong, People's Republic of China

A B S T R A C T

In this study, we developed a novel ultrasound-assisted electrocatalytic oxidation (US–EO) process to decolorize azo dyes in aqueous solution. Rhodamine B was decolorized completely within several minutes in this developed US–EO system. Oxidation parameters such as applied potentials, power of the ultrasound, initial pH of the solution, and initial concentration of RhB were systematically studied and optimized. An obvious synergistic effect was found in decolorization of RhB by the US–EO process when comparing with either ultrasound (US) process or electrocatalytic oxidation (EO) one. Additionally, the decolorization of other azo dyes, such as methylene blue, reactive brilliant red X-3B, and methyl orange, were also effective in the US–EO system. The results indicated that US–EO system was effective for the decolorization of azo dyes, suggesting its great potential in dyeing wastewater treatment.

© 2009 Elsevier B.V. All rights reserved.

1. Introduction

Textile dyes and other industrial dyestuffs constitute one of the largest groups of organic compounds that represent an increasing environmental danger. Because of the large content of aromatics in dye molecules and the stability of modern dyes, conventional biological treatment methods are ineffective for their decolorization and degradation in some cases. Therefore, it is urgent to seek for some novel technologies to decolorize or degrade these organic dyes pollutants.

Physicochemical methods based on the production and use of hydroxyl radical, called advanced oxidation processes (AOPs) (e.g., $H_2O_2 + UV$, $UV + O_3$, $H_2O_2 + O_3$, TiO_2 photocatalysis, Fenton oxidation, electrocatalytic oxidation), are attractive for wastewater treatments [1–9]. Among all the AOPs technologies, the electrocatalytic oxidation (EO) is one of the mostly widely used methods to remove both organic and inorganic impurities from wastewater. With strong oxidative ability, the EO process does not form the second pollution during the treatment process. However, there are still some problems involved in the EO process. For instance, the rate of degradation did not satisfy the need of industry, the electric current was not used completely and some co-reactions of the decomposed water were occurred. Therefore, many researchers are attempting to improve the current efficiency of the EO methods for the treatment of wastewater by integrating EO with other advanced oxidation processes [3,10–13]. For example, electro-Fenton, photoelectrocatalytic oxidation and photoelectron-Fenton have been developed to treat wastewater recently.

At present, environmental sonochemistry is a rapidly growing AOP for degradation of organic compounds. Ultrasonic chemical methods have shown effective for the treatment of a variety of chemical contaminants in aqueous solutions [14–19]. Different from other AOPs such as Fenton and photocatalysis technologies, ultrasound (US) oxidation does not require the addition of any chemicals and can be used for the treatment of turbid solutions. The chemical effects of US irradiation arise from high temperature (up to 5000 °C) and pressure (hundreds of bars), which are attained when the adiabatic compressed bubbles are violently collapsed [22]. Under these extreme conditions, the radical species, such as hydroxyl radicals and hydrogen atoms, are produced via the pyrolysis of water in the collapsing cavitation bubbles and can either react with organic compounds or recombine with other radical species [23]. The oxidation pathways include the direct thermal reaction in the vicinity of the cavitation bubbles and the free radical oxidation. Additionally, US irradiation can eliminate the impurity layer at the catalyst surface and increase of its active surface by pitting in heterogeneous processes. Furthermore, US irradiation can decrease the transit time of intermediates and products through the boundary layer at the solid–liquid interface, increasing the reaction rates for mass transfer limited reactions [20,21].

Compared with EO process or the US process alone, the combination of US and EO is very attractive to improve their own efficiencies because of the enhanced hydroxyl radical production and mass transfer. In the US irradiation degradation experiment, the chemical reaction associated with acoustic cavitations occurred. The actual yields of formation of OH radicals, under low frequency sonolysis (20–50 kHz), have been reported [24,25], however, the yield of OH and H radicals produced under low frequency sonolysis is probably quite low and not enough to fully account for the degradation process. At the same time, US irradiation may enhance the mass transfer and decomposition of H_2O_2 generated by EO process in aqueous solution due to higher diffusion coefficients [19]. In this study, we developed a novel US–EO system and found its rapid and effective oxidation ability on the decolorization of organic azo dyestuffs in aqueous solution. The developed US–EO system is promising for dyeing wastewater treatment.
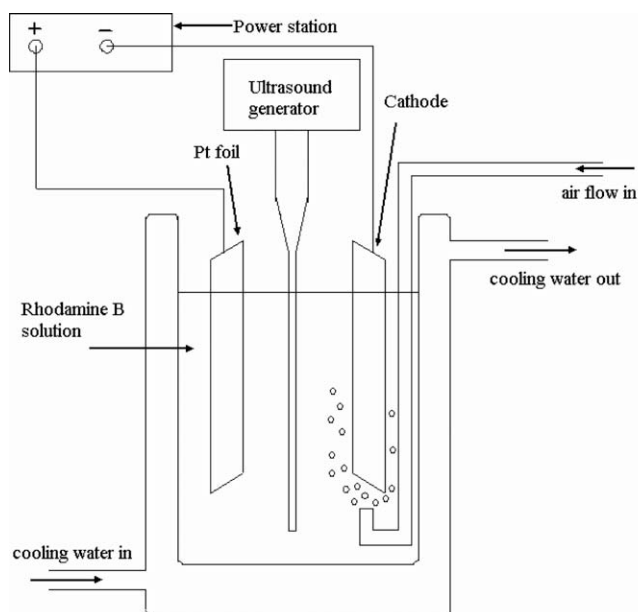
2. Experimental

2.1. Chemicals and reagents

Sodium sulfate anhydrous, sulfuric acid, sodium hydroxide and other chemicals were of analytical grade and purchased from Shanghai Chemical Reagents Company, China. Azo dyes were of commercially available analytical grade without any purification. Doubly distilled water was used in all experiments. Active carbon fiber (ACF) and titanium mesh were purchased from Southern Chemicals Import and Export Corporation in China.

2.2. Decolorization experiments

A schematic illustration of the reactor is shown in Scheme 1. Decolorization experiments were performed with 100 mL of dyes solutions in a cylindrical water-jacketed glass reactor (200 mL). US irradiation process was performed with a KS-250 ultrasonic generator (the frequency of ultrasound was 22 kHz, KQ-100, Kunshan Instrument Co., China) equipped with a titanium probe transducer. The tip of the probe was 1 cm in diameter and was placed 2 cm into the liquid phase. The sonication was administered in

Scheme 1. Schematic representation of an experimental setup for ultrasonic-assisted electrochemical oxidation.

pulses with a 50% duty cycle. The reactor was immersed into a water bath to keep the temperature be constant at around 25 °C. EO process was preformed by using a potentiostat (CHI-660B, Shanghai, China).The anode was a Pt sheet (purity: 99.99%) of 2.0 cm^2 in area obtained from Beijing Academy of Steel Service (China). The ACF electrode was used as the working cathode (3.0 cm^2 in area). A predetermined amount of Na_2SO_4 aqueous solution was used as the electrolyte to increase the conductivity. The initial pH of the dye solution was about 6 without adjustion. In some cases, the initial pH value of RhB solution was adjusted by the addition of 0.10 M H_2SO_4 or 0.10 M NaOH, respectively. A 5 L min^{-1} of fresh air was fed to the solution. Before decolorization, the system was kept in the dark for 30 min to establish the adsorption/desorption equilibrium between the solution and the electrode. US–EO processes were carried out by combination of both US and EO systems. The decolorization experiments of methylene blue, reactive brilliant red X-3B and methyl orange were similar to that of RhB.

2.3. Analysis

The UV–vis spectrum was used to estimate the decolorization of azo dyes. The adsorption of dyes solutions were measured using a U-3310 UV–vis spectrometer (HITACHI). The maximum absorbances of dyes solution below the concentration of 20 mg/L obey Lambert–Beers's law. The standard calibration curves of the dyes solutions were used to estimate the percentage of decolorization. The percentage of decolorization was calculated according to Eq. (1).

$$Decolorization\ [\%] = (1 - C/C_0) \times 100 \qquad (1)$$

where C_0 is the initial concentration of the dye; C is the concentration of the dye after the US, EO or US–EO treatment.

3. Results and discussion

3.1. Comparison of US, EO and US–EO process on the decolorization of RhB

The RhB decolorization was used to investigate the oxidative efficiencies of the US, EO and US–EO processes. Fig. 1 shows the change of the concentrations of RhB solution as a function of reaction time in these three processes. It was found that RhB could not be decolorized in US process. However, the decolorization of RhB was obvious in EO and US–EO processes. Interestingly, 91.4% of RhB could be degraded within 6 min in the US–EO process, which was much higher than that of US (0.4%) or EO (24.5%) process. This reveals that the decolorization of RhB is greatly accelerated by the integration of US and EO and there is an obvious synergetic effect between the US and EO processes. As mentioned before, ultrasound irradiation has both chemical and physical effects on heterogeneous processes. The chemical effects of US irradiation are due to its acoustic cavitation, where the high temperatures and pressures can be reached inside the cavitation bubbles, leading to the thermal decomposition of water molecules into ·OH an H· [19–21]. In this case, only US irradiation could not decolorize RhB (Fig. 1), indicating that the chemical reaction associated with US irradiation not be the key point for the decolorization of RhB, because the yield of OH and H radicals produced under low frequency sonolysis is probably quite low [19]. Therefore, the physical effects of cavitation induced by sonication play an important role for the enhancement of decolorization efficiency by US–EO process.

The physical effects of US improve the decolorization rate by enhancing the electrocatalytic oxidation and the production of free radicals, resulting in the generation of additional hydroxyl radical
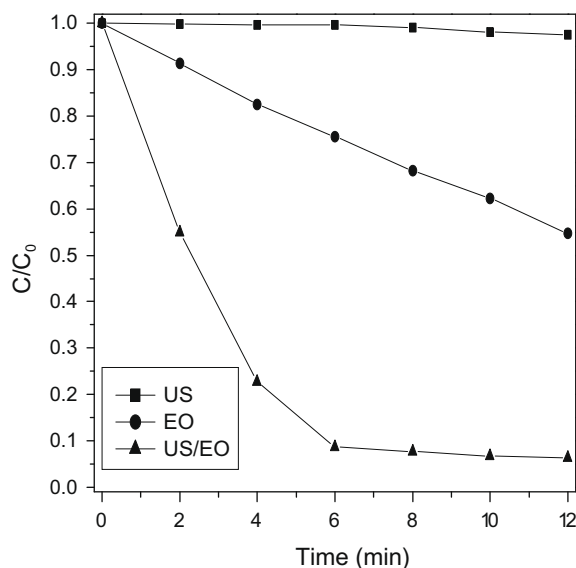
Fig. 1. Comparison of US, EO and US–EO processes for decolorization of RhB. The initial concentration of RhB was 5 mg/L; pH 6.5; the applied potential was 4.0 V; the US power output was 400 W; the reaction temperature was 25 °C.

Fig. 2. The effect of the applied potentials on the decolorization of RhB in US–EO process. The initial concentration of RhB was 5 mg/L; pH 6.5; the US power output was 400 W; the reaction temperature was 25 °C.

to react with the substrate [20]. Additionally, US irradiation can eliminate the impurity layer at the surface of electrode and increase of its activity, as well as increase the reaction rates for mass transfer. Most likely, US could on one hand enhance the mass transfer of RhB and enable most RhB to enter into the ACF and react on the electrode interface. On the other hand, aeration of air might increase the turbulence of the aqueous solution, which would increase the migration of some related substances from the collapsing cavities into the bulk of the solution and the H_2O_2 was generated in the ACF cathode by the reduction of air. The combining technique of electrogenerated H_2O_2 and US can enhance the decolorization of RhB.

3.2. Effect of the applied potentials on the US–EO decolorization of RhB in US–EO process

The applied potentials can affect the current input at the constant surface area of the electrode. In order to understand the effect of the applied potential on the US–EO decolorization of RhB, experiments were performed at the different applied potentials of 1.2, 2.0, 4.0, 6.0, and 8.0 V, respectively (Fig. 2). It was found that the applied potentials had a significant influence on the decolorization of RhB. The decolorization was significant while the applied potentials equal to or higher than 4.0 V, and there was no remarkable decolorization when applied potential was lower than 2.0 V. The higher potential resulted in a better decolorization. However, too higher applied potential would consume too much electrical energy. We chose the applied potential of 4.0 V for the following decolorization experiments. The phenomenon of an optimum power in a sonochemical reaction has been observed by other researchers [19,20]. As the acoustic power is increased, the numbers of bubbles generated in the liquid medium are increased, which could result in higher decolorization efficiency.

3.3. Effect of power outputs of ultrasound on the decolorization of RhB in US–EO process

In the US process, the high applied electric powder of US setup is favorable for rapid and complete mineralization of organic compounds [18]. We compared the decolorization of RhB in US–EO
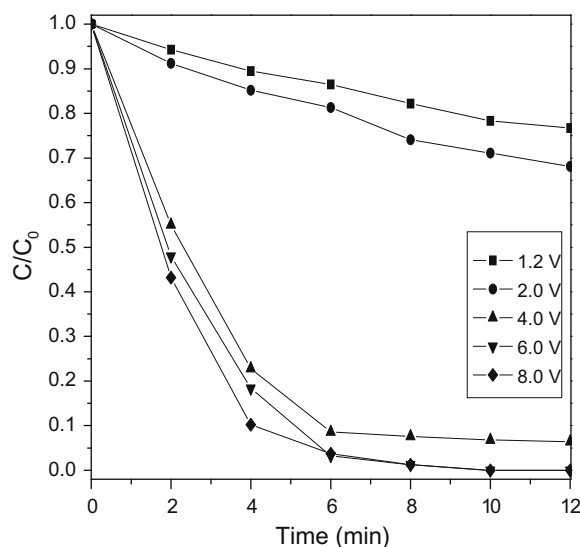
process at different ultrasound power outputs of 100, 200, 400, 600 and 800 W, respectively (Fig. 3). The decolorization of RhB increases with increasing the power output from 100 to 400 W, and then decreases when the power outputs are higher than 400 W. Therefore, there is an optimal ultrasound power output of 400 W for the decolorization in US–EO process. The existence of this optimal ultrasound power output may be explained in terms of cavitational activity. Higher levels of acoustic power increase the number of cavitational events and the free radicals to enhance decolorization consequently [26]. For a cavitation bubble, the maximum bubble size is dependent on the density of the liquid, the applied frequency, the hydrostatic pressure and the acoustic pressure as Eq. (2).

$$R_{max} = \frac{4}{3\omega_a}(P_A - P_h)\left(\frac{2}{\rho P_A}\right)\left[1 + \frac{2}{3P_h}(P_A - P_h)\right]^{1/3} \qquad (2)$$

where ω_a is the applied acoustic frequency and P_h is the external (hydrostatic) pressure, which is 1 atm under our experimental conditions, and ρ is the density of the medium. In addition, the bubble collapse time is τ, R_m is proportional to the maximum bubble size (Eq. (3)).

$$\tau = 0.915R_m(\rho/P_m)^{1/2}(1 + P_{vg}/P_m) \qquad (3)$$

where P_m is the pressure in liquid (i.e., $P_m = P_h + P_a$) and P_{vg} is the vapor pressure in the bubble. Therefore, at high acoustic intensity (i.e., large P_A values) the cavitation bubbles are able to grow larger in size during a rare faction cycle so that insufficient time is available for complete collapse during a single compression cycle. As the above equations predict and the experimental results show, there is an optimum power density which can be applied during sonochemical irradiation in order to obtain maximum reaction rates [18].

Under the present experimental conditions, the decolorization of RhB decreased when increasing the ultrasound power output higher than 400 W. Generally, the production of the acoustic bubbles increases with the increasing the power output of US, leading to higher localized temperatures and pressures at the cavitation sites. However, the delayed growth and long collapse duration of these bubbles will also allow radical scavenging and recombina-
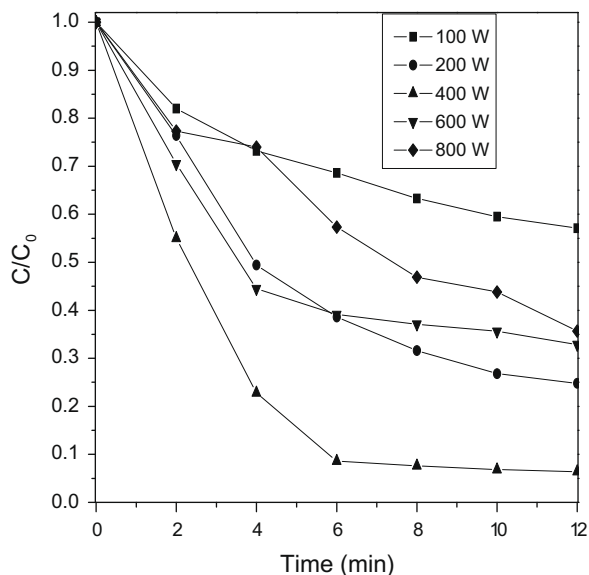
Fig. 3. The effect of US power outputs on the decolorization of RhB in US–EO process. The initial concentration of RhB was 5 mg/L; pH 6.5; the applied potential was 4.0 V; the reaction temperature was 25 °C.

Fig. 4. The effect of pH on the decolorization of RhB in US–EO process. The initial concentration of RhB was 5 mg/L; the applied potential was 4.0 V; the US power output was 400 W; the reaction temperature was 25 °C.

tion reactions on the surface of electrode, thus inhibiting mass transfer of hydroxyl radical or other reactive species into solution, as well as enhancing decolorization of solutes adsorbed on the bubble–water interface. However, the number of reactive species in the solution may reduce because although cavitation is more violent, there are more cavitational events increasing the opportunities for these species to be recombined.

3.4. Effect of the Initial pH on the decolorization of RhB in US–EO process

The decolorization of RhB by US–EO process was studied under different initial pH values. The relationship between the decolorization and the initial pH values is shown in Fig. 4. It was found that the decolorization of RhB in US–EO process changed with increasing pH values from 3.0 to 11.0, and there is an optimum neutral condition in the decolorization process. Either the acid or the alkali condition is adverse to the decolorization of RhB. This phenomenon can be explained by the electrogenerated H_2O_2 and equilibrium adsorption of the RhB on the ACF. In general, in acid condition, the RhB can not easily be adsorbed on the surface of ACF electrode below pH 5.0, which is not propitious to the decolorization of RhB. And the produce of hydroxyl radical is difficult in basic medium, which results in the decrease of the decolorization ratio especially in the strong alkaline. So the optimum pH of the solution was the neutral condition.

3.5. Effect of the initial concentrations on the decolorization of RhB in US–EO process

The decolorization of RhB was investigated with changing the initial concentrations in US–EO process (5, 10, 20, 30, 50 mg L^{-1}). As shown in Fig. 5, the initial concentrations of RhB do not have significant effect on the decolorization in the US–EO process. It is observed that increasing concentration of the RhB does not affect the ability of US–EO oxidation significantly as the decolorization rates are almost constant. However, it is reported that the decolorization efficiencies in both electrochemical process and ultrasonic treatment are strongly dependent on the initial concentrations [27–30]. In the US–EO process, increasing the concentrations of
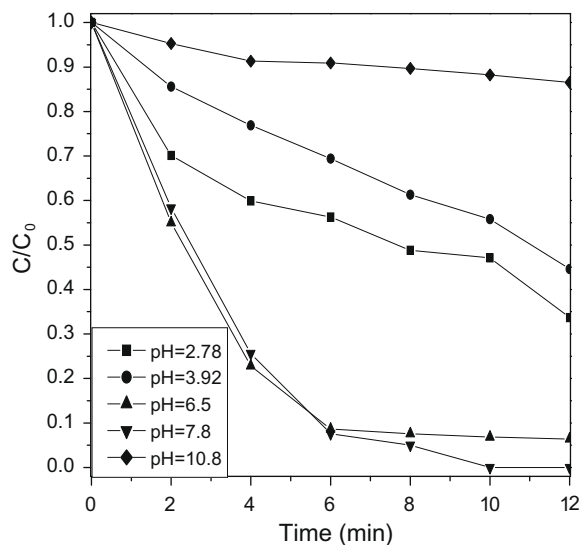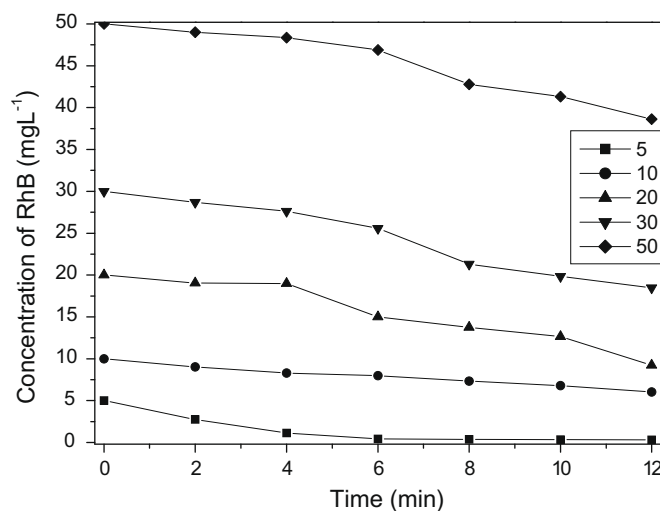

Fig. 5. The effect of initial concentrations of RhB on the decolorization in US–EO process. pH 6.5; the applied potential was 4.0 V; the US power output was 400 W; the reaction temperature was 25 °C.

RhB did not affect the decolorization efficiency, indicating that the synergetic effect exists in the US–EO process.

3.6. Effect of the electrolyte concentration on the decolorization of RhB in US–EO system

In general, increasing the concentration of electrolyte may result an increasing of decolorization in the EO process, because the addition of electrolyte sodium sulfate could improve the electrical conductivity of the wastewater to a suitable level [19]. Fig. 6 presents the effect of the dosage of Na_2SO_4 on the decolorization of RhB in the electrolyte aqueous solution. As the Na_2SO_4 dosage decreases, the conductivity decreases with an increase in electrical resistance and the consumption of electricity energy. It is observed in Fig. 6 that more than 60% decolorization occurs less than 12 min, and the decolorization reached 100% after at 12 min with the addition of 21.3 g/L of Na_2SO_4. The great ionic strength will generally
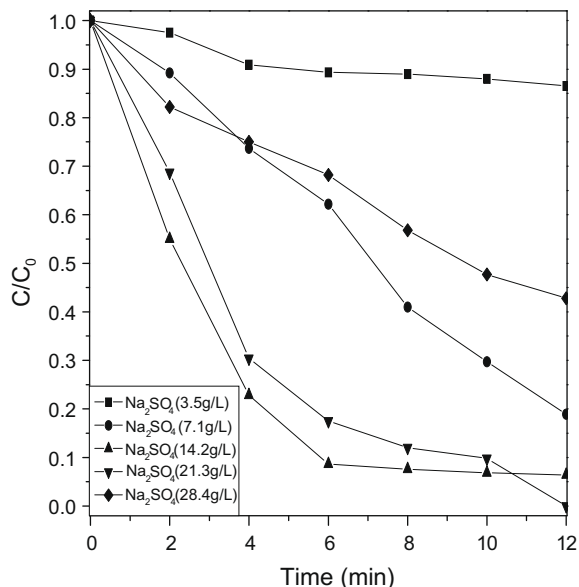
Fig. 6. The effect of the electrolyte concentrations on the decolorization of RhB in US–EO process. The initial concentration of RhB was 5 mg/L; pH 6.5; the applied potential was 4.0 V; the US power output was 400 W; the reaction temperature was 25 °C.

cause an increase in current density at the same cell voltage or a decrease in the cell voltage with an increase in the cell solution conductivity at a constant current density. However, the higher dosage (more than 21.3 g/L) also induces over consumption of electricity energy and causes some problem in the next step of reducing salt.

3.7. The variation of UV–vis spectra during the decolorization of RhB in US–EO process

The variation of adsorption spectra of RhB during the US–EO process is shown in Fig. 7. The adsorption spectrum of RhB solution was characterized by its maximum adsorption at 555 nm in the
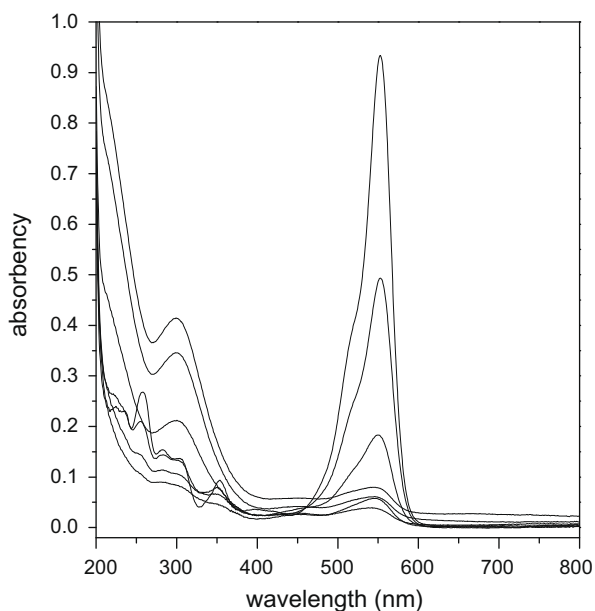

Fig. 7. The variation of UV–vis spectra during the decolorization of RhB in US–EO process. The initial concentration of RhB was 5 mg/L; pH 6.5; the applied potential was 4.0 V; the US power output was 400 W; the reaction temperature was 25 °C.
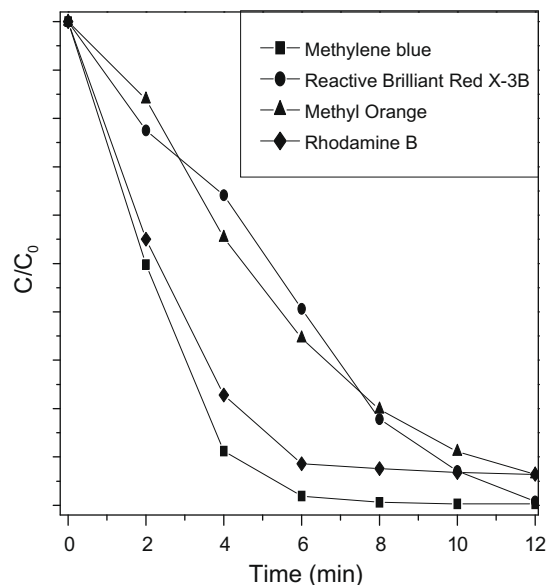

Fig. 8. The decolorization of different dyes solutions in US–EO process. The initial concentrations of dyes were 5 mg/L; pH 6.5; the applied potential was 4.0 V; the US power output was 400 W; the reaction temperature was 25 °C.

visible region, which was attributed to the chromophore-containing azo linkage (conjugated xanthene ring) of the dye molecules. It was found the adsorption peak at 555 nm diminished with increasing US–EO reaction time, indicating that the rapid decolorization of RhB was attributed to the decomposition of the conjugated xanthene ring in RhB. This is reasonable because the N=N bond of the azo dye is a most active site for attack by ·OH radicals. Accordingly, the solution changed from rose color to colorless in the degrading process.

3.8. Decolorization of other azo dyes in the US–EO process

In order to evaluate the oxidative efficiency of this developed US–EO process, some other dyes pollutants, such as methylene blue, reactive brilliant red X-3B, methyl orange were also compared. As expected, the decolorization of dyes pollutants is relatively rapid in the US–EO process. As showed in Fig. 8, all of the dyes were degraded completely in less than 10 min, suggesting the high efficiency and non-selectivity of this US–EO system.

4. Conclusions

In summary, we developed a novel ultrasound-assisted electrochemical (US–EO) system for effective decolorization of azo dyes in aqueous solution. There was an obvious synergistic effect in the US–EO process when comparing with either ultrasound (US) process or electrocatalytic oxidation (EO) process. The rapid and effective decolorization of dye pollutants in US–EO system suggested its great potential in dyeing wastewater treatment.

Acknowledgements

References

[1] C. Canton, S. Esplugas, J. Casado, Mineralization of phenol inaqueous solution by ozonation using iron or copper salts, light, Appl. Catal. B 43 (2003) 139–149.

[2] U. Bali, E.C. Catalkaya, F. Sengul, Photochemical degradation, mineralization of phenol: a comparative study, J. Environ. Sci. Heal. A 38 (2003) 2259–2275.

[3] J.P. Li, X. Zhang, Z.H. Ai, F.L. Jia, L.Z. Zhang, J. Lin, Efficient visible light degradation of rhodamine B by a photo-electrochemical process based on a Bi_2WO_6 nanoplate film electrode, J. Phys. Chem. C 111 (2007) 6832–6836.

[4] T.G. Garoma, Degradation of tert-butyl alcohol in dilute aqueous solution by an O_3/UV process, Environ. Sci. Technol. 38 (2004) 5246–5252.

[5] Y.M. Cho, W.Y. Choi, C.H. Lee, T.W. Hyeon, H.I. Lee, Visible light-induced degradation of carbon tetrachloride on dye-sensitized TiO_2, Environ. Sci. Technol. 35 (2001) 966–970.

[6] Y.S. Cao, L. Yi, L. Huang, Y. Hou, Y.T. Lu, Mechanism and pathways of chlorfenapyr photocatalytic degradation in aqueous suspension of TiO_2, Environ. Sci. Technol. 40 (2006) 3373–3377.

[7] F.J. Rivas, J. Frades, M.A. Alonso, C. Montoya, J.M. Monteagudo, Fenton's oxidation of food processing wastewater components. Kinetic modeling of protocatechuic acid degradation, J. Agr. Food Chem. 53 (2005) 10097–10104.

[8] K.D. Lin, D.X. Yuan, M. Chen, Y.Z. Deng, Kinetics, products of photo-Fenton degradation of triazophos, J. Agr. Food Chem. 52 (2004) 7614–7620.

[9] H. Liu, C. Wang, X.Z. Li, X.L. Xuan, C.C. Jiang, H.N. Cui, A novel electro-Fenton process for water treatment: reaction-controlled pH adjustment and performance assessment, Environ. Sci. Technol. 41 (2007) 2937–2943.

[10] M.H. Zhou, Q.Z. Dai, L.C. Lei, C.A. Ma, D.H. Wang, Long life modified lead dioxide anode for organic wastewater treatment: electrochemical characteristics and degradation mechanism, Environ. Sci. Technol. 39 (2005) 363–370.

[11] B. Boye, M.M. Dieng, E. Brillas, Degradation of herbicide 4-chlorophenoxyacetic acid by advanced electrochemical oxidation methods, Environ. Sci. Technol. 36 (2002) 3030–3035.

[12] J. Casado, J. Fornaguera, M.I. Galán, Mineralization of aromatics in water by sunlight-assisted electro-Fenton technology in a pilot reactor, Environ. Sci. Technol. 39 (2005) 1843–1847.

[13] X.Z. Li, H.S. Liu, Development of an $E-H_2O_2$/TiO_2 photoelectrocatalytic oxidation system for water and wastewater treatment, Environ. Sci. Technol. 39 (2005) 4614–4620.

[14] L. Weavers, N. Malmstadt, M. Hoffmann, Kinetics and mechanism of pentachlorophenol degradation by sonication, ozonation, and sonolytic ozonation, Environ. Sci. Technol. 34 (2000) 1280–1285.

[15] J. Joseph, H. Destaillats, H. Hung, M. Hoffmann, The sonochemical degradation of azobenzene, related azo dyes: rate enhancements via Fenton's reactions, J. Phys. Chem. A 104 (2000) 301–307.

[16] J. Kang, M. Hoffmann, Kinetics and mechanism of the sonolytic destruction of methyl tert-butyl ether by ultrasonic irradiation in the presence of ozone, Environ. Sci. Technol. 34 (1998) 3194–3199.

[17] H. Destaillats, H. Hung, M. Hoffmann, Degradation of alkylphenol ethoxylate surfactants in water with ultraonic irradiation, Environ. Sci. Technol. 34 (2000) 311–317.

[18] J.W. Kang, H.M. Hung, A. Lin, M.R. Hoffmann, Sonolytic destruction of methyl tert-butyl ether by ultrasonic irradiation: the role of O_3, H_2O_2, frequency, and power density, Environ. Sci. Technol. 33 (1999) 3199–3205.

[19] Y. Nagata, M. Nakagawa, H. Okuno, Y. Mizukoshi, B. Yim, Y. Maeda, Sonochemical degradation of chlorophenols in water, Ultrason. Sonochem. 7 (2000) 115–120.

[20] Y. Yasman, V. Bulatov, V.V. Gridin, S. Agur, N. Galil, R. Armon, I. Schechter, A new sono-electrochemical method for enhanced detoxification of hydrophilic chloroorganic pollutants in water, Ultrason. Sonochem. 11 (2004) 365–372.

[21] Y. Yasman, V. Bulatov, I. Rabin, M. Binetti, I. Schechter, Enhanced electro-catalytic degradation of chloroorganic compounds in the presence of ultrasound, Ultrason. Sonochem. 13 (2006) 271–277.

[22] K.S. Suslick, Advances in sonochemistry, Science 247 (1990) 1439–1444.

[23] J. Peller, O. Wiest, P.V. Kamat, Sonolysis of 2,4-dichlorophenoxyacetic acid in aqueous solutions. Evidence for OH-radical-mediated degradation, J. Phys. Chem. A 105 (2001) 3176–3181.

[24] K. Makino, M.M. Mossoba, P. Riesz, Chemical effects of ultrasound on aqueous solutions. Evidence for ·OH and ·H by spin trapping, J. Am. Chem. Soc. 104 (1982) 3537–3539.

[25] K. Makino, M.M. Mossoba, P. Riesz, Chemical effects of ultrasound on aqueous solutions. Formation of hydroxyl radicals, hydrogen atoms, J. Phys. Chem. 87 (1983) 1369–1377.

[26] E.M.D. Psillakis, N. Kalogerakis, Monitoring the sonochemical degradation of phthalate esters in water using solid-phase microextraction, Chemosphere 54 (2004) 849–857.

[27] D. Rajkumar, K. Palanivelu, Electrochemical degradation of cresols for wastewater treatment, Ind. Eng. Chem. Res. 42 (2003) 1833–1839.

[28] P. Marco, C. Giacomo, Electrochemical degradation of methyl red using BDD and PbO_2 anodes, Ind. Eng. Chem. Res. 47 (2008) 6816–6820.

[29] S. Raghua, L.C. Woo, S. Chellammal, S. Palanichamy, C.A. Basha, Evaluation of electrochemical oxidation techniques for degradation of dye effluents—a comparative approach, Journal of Hazardous Materials, in press.

[30] R.A. Torres, W. Torres, P. Peringer, C. Pulgarin, Electrochemical degradation of p-substituted phenols of industrial interest on Pt electrodes. Attempt of a structure – reactivity relationship assessment, Chemosphere 50 (2003) 97–104.