Short communication

Wet electrolytic oxidation of cationic red X-GRL

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Abstract

Wet electrolytic oxidation (WEO) under mild condition, a relatively less reported process which coupled the advantages of both wet air oxidation (WAO) and electrochemical oxidation (EO) was investigated for the removal of one azo dye, cationic red X-GRL, in a 2 L autoclave reactor. It was found that this novel process showed synergistic effect for TOC removal compared with that by the individual WAO and EO, and presented much higher dye removal efficiency. At similar conditions of temperature of 100–180 °C, $P_{N_2} = 0.50$ MPa and $P_{O_2} = 0.14$ MPa, a little introduction of current density of 2 mA cm^{-2} led to the apparent reaction constants for WEO two times larger than those of WAO. Possible mechanism for the synergistic effect was discussed based on the analysis of free-radical generation and intermediates detected by GC/MS.
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Keywords: Wet electrolytic oxidation; Wet air oxidation; Electrochemical oxidation; Cationic red X-GRL; Synergistic effect

1. Introduction

Effluents from textile dyeing industry cause severe environmental problems due to their strong color, high total organic carbon (TOC) and low biodegradability [1,2], therefore, these wastewaters must be efficiently treated to meet related standards before being discharged to the environment.

Wet air oxidation (WAO) is an effective way to deal with high-concentrated dyeing wastewater [3–5]. However, the application of traditional WAO is still limited mainly because of the requirements of high temperature, high oxygen pressure and long operation time, which result in high treatment cost. Catalytic wet air oxidation (CWAO) has been attempted to alleviate the treatment conditions especially on temperature and total pressure [6,7], but CWAO is still far from solution due to second pollution and the decrease of treatment efficiency.

Compared with CWAO, electrochemical oxidation (EO) is a clean catalytic technology using electrons as catalysts. Researches for dyeing wastewater treatment by EO under classical conditions (e.g., room temperature and atmospheric pressure) were extensively investigated [8,9] while no satisfactory results were achieved on that of high-concentrated. Therefore,

sound processes efficient for high-concentrated dyeing wastewater treatment without second pollution are urgently required to solve this environmental problem.

Wet electrolytic oxidation (WEO) is a novel process, which integrated WAO and EO, performing WAO in the presence of current. The current can activate the dissolved oxygen and catalyze the oxidation of organics, besides, the radicals triggered by electrochemical reactions catalyze WAO and accelerate the WAO chain reactions, so that WEO integrates advantages of both WAO and EO at proper operation conditions and thus promotes organics degradation. Serikawa et al. [10] found this process prominently effective for acetic acid wastewater under the conditions of temperature at 250 °C and pressure at 7 MPa. But that condition is still quite rigorous for the application in industry due to the high treatment cost and rigorous equipment requirements. If this process could be extended under much more mild conditions and relatively good results could be achieved, then it would be much more promising for environmental remediation.

The present work is an original attempt for high-concentrated dyeing wastewater treatment using WEO process under relatively mild conditions (temperature not more than 180 °C and total pressure less than 0.8 MPa). Cationic red X-GRL was chosen as the model pollutant because it is widely used in textile, plastic and varnish industries; furthermore, it is hardly biodegradable by the conventional biological process [2].

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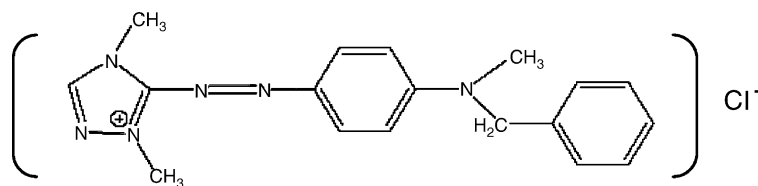
Scheme 1. Structural formula of cationic red X-GRL.

2. Experimental

2.1. Chemicals

The structure of the cationic red X-GRL dye was shown in Scheme 1. The dye was purified by extraction with methanol at 50 °C to reach the purity not less than 99.5% based on an industrial cationic red X-GRL (Jin jiang chemical dyestuff Co. Ltd., China) [11]. The synthetic wastewater is prepared by the purified dye and an inert electrolyte sodium sulfate ($3\,g\,L^{-1}$), which is used to form the required conductance. For the convenience of pressure comparison, the pressure of the oxygen and nitrogen at different temperature in Figs. 2–4 was that converted into 298 K by the ideal gas law.

2.2. Equipments and procedures

The WEO experiments were carried out in a 2 L stainless autoclave equipped with a cooling coil and a magnetic stirring system, as shown in Fig. 1. It was modified based on the commercial products of WAO system (CJ-2, Weihai New Era Chem. Ind. Mac. Co., China) by introducing the electrodes wires into the reactor and a hollow Teflon tube vessel adhibiting closely to the inner wall of the reactor. The reactor kept the final volume at 2 L after the modification. The anode fixed in the centre of the reactor, was a novel β-PbO$_2$ electrode (Φ 45 mm × 200 mm) modified with fluorine resin on ceramic media, which showed perfect stability and efficiency for organic wastewater treatment in our previous work [12]. The cathode was stainless steel net

(grid 1 mm × 1 mm), which was attached to the inert Teflon wall of the reactor and concentric with the anode. Before the WEO experiments began, dye wastewater (1.3 L) was fed in through sample inlet pipe and nitrogen (0.5 MPa) was supplied for 5 min to purge the air in the reactor. After that, the nitrogen supply valve was closed with the pressure in the reactor at 0.5 MPa and the reactor was then heated isolatedly until it reached the required temperature. Then, the calculated pure oxygen was fed in and the dc supply was switched on. This point was defined as 'zero time' in all experiments. Liquid samples were taken through sampling pipe at time intervals. In WAO experiments the dc supply was switched off and in EO experiments the nitrogen instead of oxygen was fed in at the zero time.

2.3. Analysis

Dye concentration was measured at 530 nm by UV–vis Spectrophotometer (Techcomp 8500, China). The samples and initial solutions were analyzed for total organic carbon (TOC) by TOC analyzer (Appollo 9000, Teledyne Tekmar Dohrmann, USA). The conductance of the solution was measured by a conductance meter (DDS-11 A, Shanghai Precision & Scientific Instrument Co. Ltd., China). The intermediates during the dye degradation of WAO and WEO were detected by GC–MS (Trace 2000, ThermoQuest Co., USA). The column was HP-5 (30 m × 0.32 mm × 0.25 μm). Oven method: initial temperature was 50 °C, rate was 15.0 °C/min; final and maximum temperatures were 240 and 350 °C, respectively.
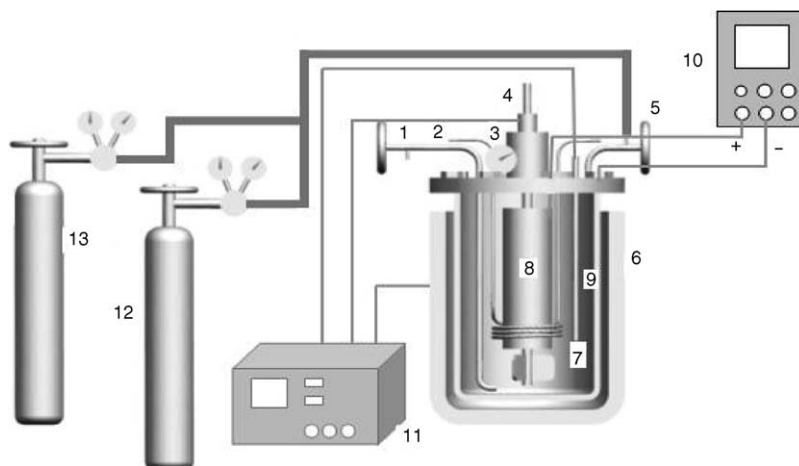

Fig. 1. WEO system: (1) sample inlet and sampling; (2) cooling water inlet; (3) pressure gauge; (4) stirring system; (5) gas outlet; (6) electric heating jacket; (7) temperature sensor; (8) anode; (9) cathode; (10) dc supply; (11) reactor controller; (12) oxygen; (13) nitrogen.
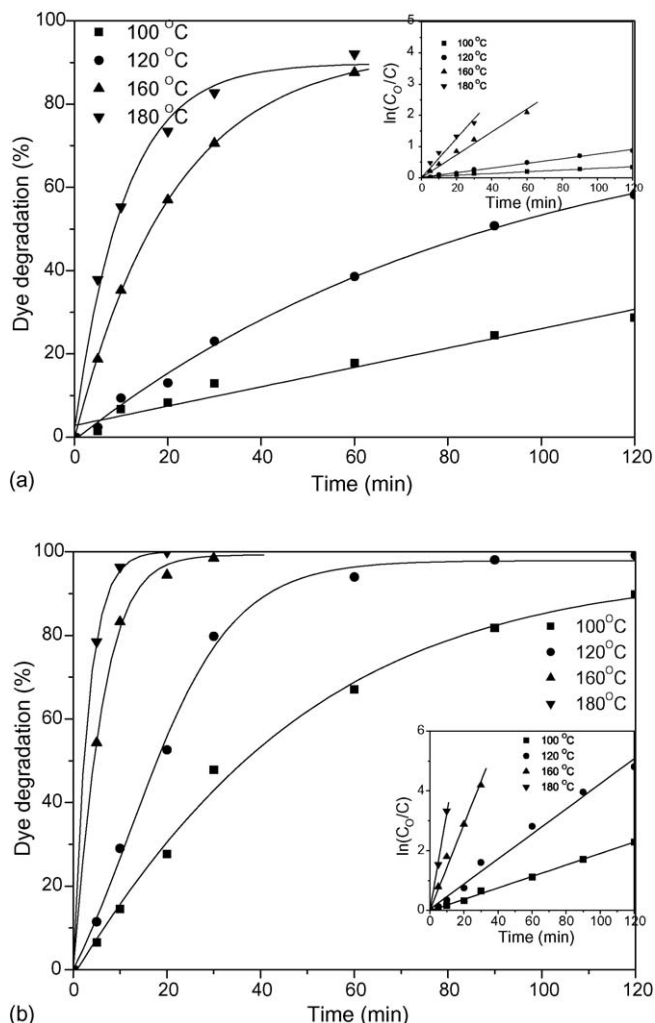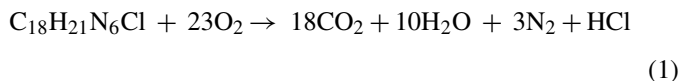
Fig. 2. Effect of temperature on dye degradation by (a) WAO and (b) WEO. Operational condition: (a) $C_{dye} = 500\,mg\,L^{-1}$, $P_{O_2} = 0.14\,MPa$, $P_{N_2} = 0.50\,MPa$, Na_2SO_4 $3\,g\,L^{-1}$; (b) $C_{dye} = 500\,mg\,L^{-1}$, $P_{O_2} = 0.14\,MPa$, $P_{N_2} = 0.50\,MPa$, $I = 0.5\,A$, Na_2SO_4 $3\,g\,L^{-1}$.

The amount of stoichiometric oxygen was calculated by the dye scheme and the oxidation products were thought to be CO_2 and H_2O. The equation can be described as follows:

$$C_{18}H_{21}N_6Cl + 23O_2 \rightarrow 18CO_2 + 10H_2O + 3N_2 + HCl \tag{1}$$

3. Results and discussions

3.1. Improvement of WEO

Temperature was confirmed to be the most important parameter in the WAO system for dye degradation. Fig. 2(a) shows the effect of temperature from 100 to 180 °C for dye degradation in the WAO system. It indicated that the efficiency increased with longer treatment time and higher temperature. However, it slowed down obviously after being treated 60 min. For example, after treatment of 30 min, the efficiency was 17.8% at 100 °C, 38.6% at 120 °C, 87.6% at 160 °C, and 92.1% at 180 °C. Simi-

Table 1
Apparent reaction constants for dye degradation by WAO and WEO

$T\,(°C)$	WAO		WEO		K_2/K_1
	$K_1\,(10^{-3}\,s^{-1})$	R^2	$K_2\,(10^{-3}\,s^{-1})$	R^2	
100	0.133	0.982	0.326	0.995	2.45
120	0.222	0.995	0.645	0.985	2.90
160	0.720	0.998	2.761	0.998	3.83
180	1.347	0.990	5.171	0.999	3.84

lar tendency was observed under the WEO system, as shown in Fig. 2(b).

Obviously, the degradation of dye by WEO was greatly enhanced from that of WAO. To better disclose the promotion kinetically, the degradation of dye in WAO and WEO were tried by the apparent first order reaction, as shown in Fig. 2.

Table 1 shows the kinetic data, which indicates that the dye degradations in the two processes fit the apparent first order reaction well. Also, the rate of K_2/K_1 increased greatly at a higher temperature, though after 160 °C the increasing rate slowed down. The apparent reaction constants of WEO were 2.45–3.84 times than those of WAO. This showed that an introduction of low current density of $2\,mA\,cm^{-2}$ into the WAO system would catalyze the oxidation and enhance the dye degradation significantly. These results supported the superiority of WEO process than that of WAO at a higher temperature. Therefore, WEO would be potentially much more cost-effective than WAO for dyeing wastewater treatment.

Another fact could be noted that in the WAO system dye degradation under low temperature (e. g., 100 °C) would almost be terminated after treated 120 min, which indicated that the oxidation capacity would be too limited to further proceed the degradation. However, in the WEO system, this tendency was considerably improved. At the same temperature of 100 °C in WEO, the removal efficiency kept on increasing as the time went on. This comparison revealed that WEO not only improved dye degradation but also might promote mineralization, which could be indicated by TOC in the following section.

3.2. Synergistic effect

Based on the above results, WEO was an excellent technology for dyeing wastewater treatment. To study into this technology, we further compared cationic red X-GRL mineralization by EO, WAO and WEO.

Carbon balance was very important to demonstrate the degree of dye eliminated by oxidation. We did many control experiments to indicate that the decrease of liquid samples TOC can disclose the oxidation well. The effect of adsorption in the electrodes or in reactor walls was studied, and the absorbance and TOC of the solution was observed hardly varied (<1.0%) after it was carried out for 120 min at room temperature. Based on the adsorption theory, desorption is much easier at a higher temperature, so it is reasonable to ignore the effect of the adsorption in the electrodes and in reactor walls under the high temperature conditions of WAO and WEO. As for evaporation, the TOC value of liquid phase samples at the operation temperature
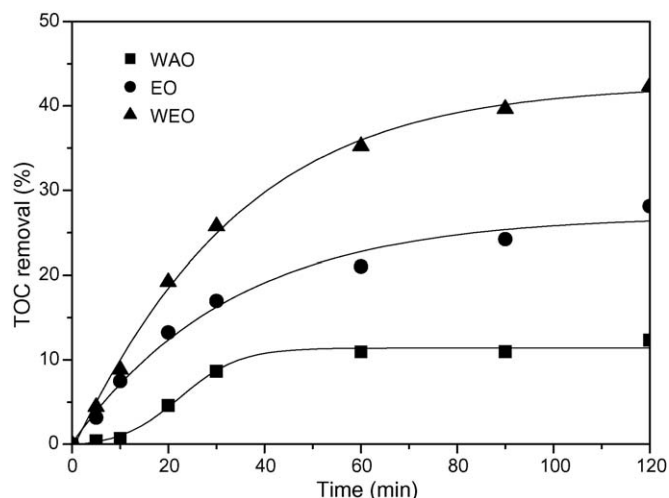
Fig. 3. TOC removal by WEO, EO and WAO. Operational conditions: $T = 120\,^{\circ}C$, $C_{dye} = 500\,mg\,L^{-1}$, $P_{N_2} = 0.50\,MPa$, Na_2SO_4 $3\,g\,L^{-1}$. WEO ($P_{O_2} = 0.14\,MPa$, $I = 0.5\,A$), EO ($I = 0.5\,A$), WAO ($P_{O_2} = 0.14\,MPa$).

differed less than 3.0% with those of sharply cooled to room temperature before taken out of the reactor, which meant the evaporation could be neglectable to the total TOC removal due to the relatively low temperature ($120\,^{\circ}C$) and concentration. Furthermore, the pressure of the gas phase in the reactor was more than 0.5 MPa, so we did not take account into the evaporation of the intermediates, either. Therefore, we think it is properly to use the liquid phase TOC removal to represent the mineralization of the dyeing wastewater and disclose the mineralization comparison of WEO, EO and WAO.

Fig. 3 shows the TOC removal by WAO, EO and WEO under similar conditions. It was observed that the dye mineralization by WEO system was much better than that of both WAO and EO. TOC removal by WEO could reach around 40% within 120 min, while in WAO system it was only 10%. Further calculation indicated the TOC removal by WEO was better than the sum of that of WAO and EO, which meant that there existed synergistic effect in WEO system. If we define the synergistic effect factor f as Eq. (2),

$$f(\%) = \frac{\eta_{WEO} - (\eta_{WAO} + \eta_{EO})}{\eta_{WAO} + \eta_{EO}} \times 100 \qquad (2)$$

where, η is the TOC removal in every process, i.e., WAO, EO or WEO. The synergistic effect factor during the induction time (at 5 min) was 23.5%, and it varied around 10% with the reaction proceeding.
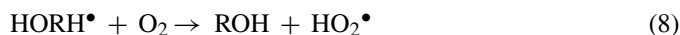
3.3. Possible degradation mechanism

Generally, organics degradation by WAO was recognized as a free-radical mechanism [13], and in our research it included three phases. The first phase was an induction phase, where organics removal was very slow due to low concentration of free radicals [14]. When the solution had sufficient free radicals, it came the exponential phase, thereafter it released the speed and the removal increased only a little, nearly stationary phase. Therefore, an introduction of free radicals would shorten induc-

tion phase and promote degradation. As proved in previous work, organics degradation by EO on the novel β-PbO_2 anode was a free-radical mechanism where hydroxyl radical ($^{\bullet}OH$) formed on the anode [15]. The oxidation mechanism of the β-PbO_2 anode in organic wastewater could be described as follows:

$$PbO_2(h^+) + H_2O_{ads} \rightarrow PbO_2(^{\bullet}OH)_{ads} + H^+ \qquad (3)$$
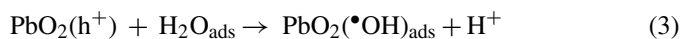
where $PbO_2(h^+)$, H_2O_{ads} are the active sites of the anode, the molecular water adsorbed in the surface of the anode, respectively.

In fact, hydroxyl radical was an extremely potent oxidant, which was able to oxidize organic compounds and generate other free radicals in the presence of organic compounds (RH). The following reaction could take place by the addition of molecular oxygen and thus [16]:

$$^{\bullet}OH + RH \rightarrow R^{\bullet} + H_2O \qquad (4)$$

$$R^{\bullet} + O_2 \rightarrow ROO^{\bullet} \qquad (5)$$

$$ROO^{\bullet} + RH \rightarrow ROOH + R^{\bullet} \qquad (6)$$

$$^{\bullet}OH + RH \rightarrow HORH^{\bullet} \qquad (7)$$

$$HORH^{\bullet} + O_2 \rightarrow ROH + HO_2^{\bullet} \qquad (8)$$

These reactions generated organic radicals and other free radicals, which in turn initiated chain reactions of dye degradation with the help of dissolved oxygen. Thus in the WEO system, the reaction intermediates helped to form more of the free radicals which increased to accelerate the speed of the reaction. Also, the effective use of the dissolved oxygen generated on the anode might be one factor promoted the degradation. As shown in Fig. 4, the addition of oxygen promoted the oxidation of pollutants and achieved an obviously better minimization while it was similar when the oxygen excessed the calculated stoichiometric pressure by Eq. (1) (0.14 MPa). When the oxygen excess, though higher dissolved oxygen at a higher pressure in
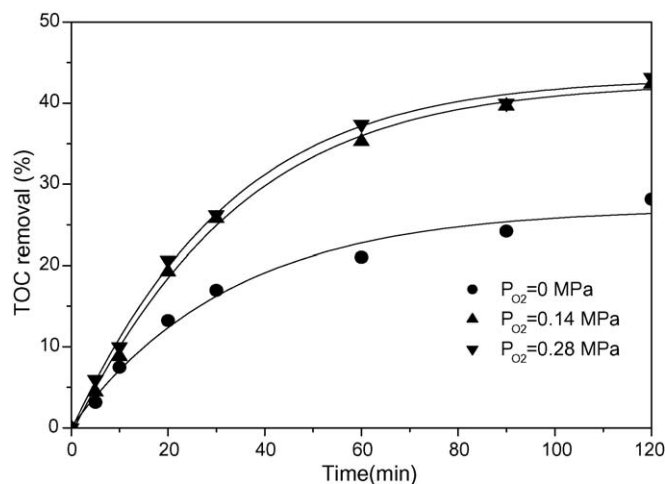

Fig. 4. Effect of oxygen amount on dye TOC removal by WEO. Operational conditions: $T = 120\,^{\circ}C$, $C_{dye} = 500\,mg\,L^{-1}$, $I = 0.5\,A$, $P_{N_2} = 0.50\,MPa$, Na_2SO_4 $3\,g\,L^{-1}$.

liquid solution by the Henry's law, the activated dissolved oxygen by the current increased little and this might be the reason for WEO to hardly removal further TOC. Similar conclusion was drawn by the study of linear alkylbenzene sulfonate degraded by WAO [17]. The degradation intermediates in the three process of EO, WAO and WEO were detected by GC–MS, and the products such as benzaldehyde (C_7H_7O), benzoic acid ($C_7H_6O_2$) 2,4-dimethyl-2,4-dihydro-[1,2,4] triazol-3-one ($C_4H_7N_3O$) and p-benzoquinone ($C_6H_4O_2$) were detected. The products were similar in the above three process, however, much more benzoic acid was detected in WEO, which showed the oxidation of organics in WEO was more thoroughly than those of WAO and EO. Further investigation on active species determination and the variation of the intermediates would be help to probe dye degradation mechanism of the WEO process and the synergetic effect.

4. Conclusions

WEO, a new promising process, which used current to catalyze the oxidation of pollutants by oxygen, was studied for cationic red X-GRL treatment under moderate conditions. Under relatively mild conditions (120–180 °C, $P_{N_2} = 0.50$ MPa, $P_{O_2} = 0.14$ MPa), the concentration of cationic red X-GRL could be removed completely after 120 min in WEO, which was much better than that of WAO. As for WAO and WEO, the reactions were found to proceed according to first order exponential decay and the apparent reaction constants of WEO were two (2.45–3.84) times more than those of WAO. Meanwhile, there existed the synergistic effect in WEO system at 120 °C in dye TOC removal. The synergistic efficiency at 5 min was 23.5%, after the induction time, the efficiency varied near 10% with the reaction proceeding. Based on the analysis of free-radical mechanism and the intermediates detected by GC–MS, the mechanisms for current catalyzing oxygen oxidation of pollutants and the synergistic effect of WEO were discussed.

Acknowledgements

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