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Oxygen as a promoter for efficient degradation of organic pollutants by high-temperature and high-pressure electrochemistry†

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The introduction of oxygen in electrochemical oxidation at relatively high temperature and pressure as a promoter resulting in synergetic effects, greatly improves the mineralization of high-concentrated organic pollutants.

Recently, considerable attention has been focused on organic pollutants degradation by advanced electrochemical oxidation processes due to their easy operation and environmental compatibility.[1–3] Normally, these processes are operated at ambient temperatures and pressures, where powerful hydroxyl radicals are supposed to be generated on non-active electrodes.[4–6] To improve treatment efficiency, various electrodes[1–8] and electrochemical processes[7–11] have been developed; however, they are not satisfactory for the abatement of high-concentrated organic pollutants.[7] Our findings suggested that the incorporation of relatively cheap oxygen as a promoter in electrochemical oxidation at high temperature and pressure would lead to a very high current efficiency and a great improvement on mineralization for highly concentrated organic pollutants.

In a typical degradation procedure, it was operated in a cylindrical reactor (Fig. S1†), a 2 L stainless autoclave equipped with a cooling coil, a magnetic stirring system and temperature controller. The anode, a novel β-PbO_2 electrode (Φ = 45 × 200 mm) modified with fluorine resin, which had been proven efficient for organic pollutant degradation based on hydroxyl radical oxidation mechanism and shown a long service life,[6] was located in the centre of the reactor. The cathode was a stainless steel net (grid 1 × 1 mm) which was attached to the inert wall of the reactor and concentric with the anode. In the present work, an azo dye of cationic red (X-GRL, the structure is shown in Fig. S2†) and *p*-nitrophenol (PNP) were used as model pollutants because they are biorefractory and widely presented in various types of wastewater which could not be effectively treated by traditional technologies including biological oxidation. The synthetic wastewater was prepared by the model pollutant with a desired concentration and an inert electrolyte sodium sulfate (3 g L^{-1}) which was used to form the required conductance, and then it was adjusted to pH 5 before treatment. After the introduction of wastewater (1.5 L) and the start of the stirring and controller system (300 rpm), nitrogen (0.5 MPa) was supplied for 5 min to purge the air in the reactor and pre-heated separately until it reached the required temperature. Then the pure oxygen was fed in until reached the desired pressure, the experiments started, maintaining current constantly at the 0.5 A with only minor adjustments of the applied voltage (4.8 V). During treatment, samples were taken through the sampling pipe at time intervals.

As can be seen in Fig. 1, high temperature promotes X-GRL degradation in the presence of oxygen. At 25 °C the X-GRL removal was less than 30% even after treatment for 90 min and hereafter changed little, indicating the generation rate of hydroxyl radical by electrochemical oxidation under ambient conditions was very limited. Nevertheless, at 160 °C, it could be completely removed within 30 min. Similar trends were observed for COD removal, which increased from 8% at 25 °C to 42% at 160 °C after treatment for 90 min.

To further explore the role of oxygen on COD removal, several control experiments were carried out in different processes: electrochemical oxidation at high temperature and pressure (P1), electrochemical oxidation at ambient conditions (P2) and oxygen oxidation at the same temperature and pressure with that of P1 (P3). Fig. 2 shows the role of oxygen on COD removal in the three processes after treatment for 120 min. In P3, *i.e.*, wet oxidation, where free radicals are formed by the support of oxygen under high temperature, and thus lead to the degradation of organic compounds (RH).[12,13]

$$RH + O_2 \rightarrow HO_2^{\bullet} + R^{\bullet} \quad (1)$$

$$H_2O + O_2 \rightarrow HO_2^{\bullet} + {}^{\bullet}OH \quad (2)$$

$${}^{\bullet}OH + RH \rightarrow R^{\bullet} + H_2O \quad (3)$$

$$R^{\bullet} + O_2 \rightarrow ROO^{\bullet} \quad (4)$$

$$ROO^{\bullet} + RH \rightarrow ROOH + R^{\bullet} \quad (5)$$

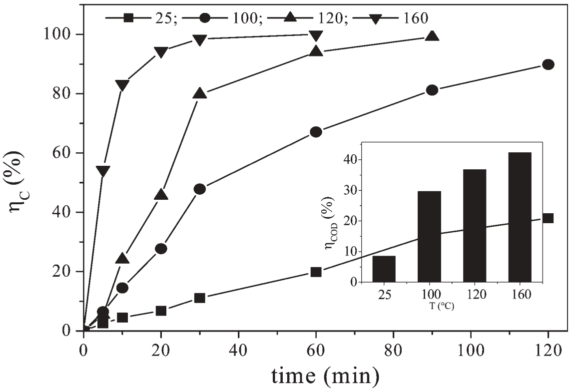

Fig. 1 Effect of temperature on X-GRL degradation: X-GRL = 500 mg L^{-1}, O_2 = 0.5 MPa, current = 0.5 A.

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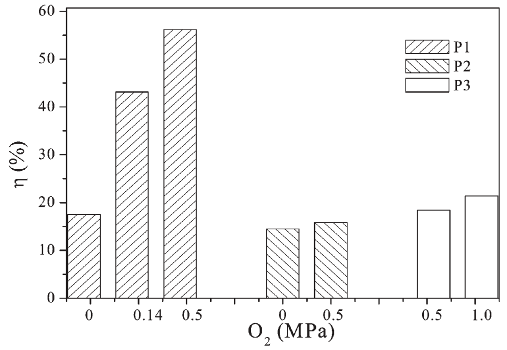

Fig. 2 Role of oxygen on COD removal in three processes.

Due to the relatively mild hydrothermal conditions (temperature 160 °C, oxygen pressure 0.5 MPa), the reactions are too restricted in initiation stage to form sufficient free radicals,[14] which lead to the insignificant enhancement in P3. In P2, though hydrogen peroxide generation by oxygen electrochemical reduction in the same electrochemical system was proved previously[3] and detected in this work (Table 1), the effect of oxygen was not obvious because of the lower oxidation potential of hydrogen peroxide compared with that of hydroxyl radical. Hydrogen peroxide can be generated by two-electron reduction of oxygen at the cathode,

$$O_2 + 2\,H^+ + 2\,e^- \rightarrow H_2O_2 \qquad (6)$$

However in P1 a significant enhancement of oxygen on COD removal was observed. Furthermore, the COD removal in the presence of oxygen in P1 (56.2%) was found much higher than the sum of that in the absence of oxygen in P1 (17.5%) and that in P3 (18.4%), indicating the existence of a synergetic effect. This fact suggested that the presence of oxygen at hydrothermal conditions would bring about other benefits on pollutant degradation besides the promotion of hydrogen peroxide formation and wet oxidation, which led to the electrochemical and wet oxidation benefiting each other. On the one hand, the generated hydrogen peroxide was much higher than that in the other two processes, though the detected concentration was rather low due to the rapid decomposition under high temperature.[15] The higher presence of hydrogen peroxide in P1 would result in the generation of hydroxyl radicals due to the thermal decomposition by scission of the oxygen–oxygen bond,[16]

$$H_2O_2 \rightarrow 2\,{}^{\bullet}OH \qquad (7)$$

In this way, wet oxidation was promoted to wet peroxide oxidation which was verified to be more efficient for the shortening of initiation stage by high concentration of radicals and thus accelerated the degradation as shown in eqn (3). Furthermore, it was found that even at an elevated temperature of 200 °C, the COD removal by wet oxidation was about 35% after 120 min treatment, which was much less than that by P1 at 160 °C (56.2%). This fact justified the use of electrochemistry to convert pollutants by wet oxidation.

Table 1 Hydrogen peroxide (mg L^{-1}) formation in the three processes

Process	60 min	120 min
P1	0.72	3.32
P2	0.22	0.64
P3	0.37	0.51

[a] *Conditions*: P1: T = 160 °C, O_2 = 0.5 MPa, I = 0.5 A; P2: T = 25 °C, O_2 0.5 MPa, I = 0.5 A; P3: T = 160 °C, O_2 = 0.5 MPa, I = 0 A.

On the other hand, the electrochemical oxidation also benefited from the presence of oxygen at hydrothermal conditions. In the electrochemical oxidation at ambient conditions, with the increase of the initial dye concentration, much more pollutant molecules would be adsorbed on the surface of the electrode, which would reduce the water absorbed on the surface and thus reduced the generation of hydroxyl radicals, resulting in the electrode fouling.[17] Therefore both color and COD removal decreased dramatically with the increase of the initial X-GRL concentration in P2 (ESI, Table S1†). However, in P1 it showed a good and stable performance for the dye and COD removal in a wider initial dye concentration ranges from 500 to 2000 mg L^{-1}, where the dye removal changed little and the COD removal decreased slightly from 43.2 to 36.4%. This effect should be contributed by a lot of free radicals brought about by the wet oxidation, which reduced the dye concentration on the electrode surface and thus alleviated the electrode fouling. Therefore the integration of oxygen under hydrothermal conditions acts as a promoter which overcomes the disadvantages of wet oxidation and electrochemical oxidation at ambient conditions, and hence provides an alternative for high concentration organic pollutant degradation.

Such a promotion was also observed on PNP degradation both on COD (the straight lines) and DOC removal (the dashed lines), as shown in Fig. 3. The DOC removal by P1 could reach around 60% within 120 min, while in P2 and P3 it was no more than 10 and 3%. A similar phenomenon was observed for COD removal. Moreover, in P2, the average current efficiency (ACE)[18] was found to present initially a high value near 100%, but decreased dramatically to below 30% in 120 min, which was similar with the observation under ambient conditions.[6] However, in P1, the ACE remained more than 100% and it even increased with the treatment time, demonstrating a higher efficiency. To further determine the promotion quantitatively, the synergetic factor (f) for DOC and COD removal was introduced by the following equation,

$$f = \eta_{P1}/(\eta_{P2} + \eta_{P3}) \qquad (8)$$

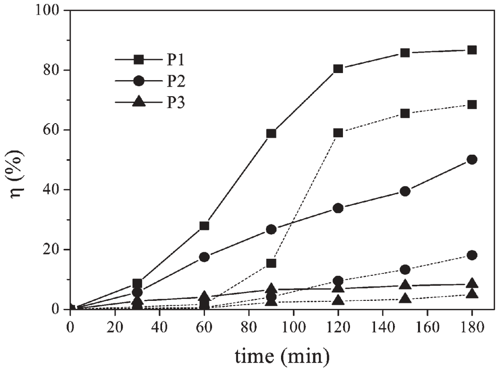

Fig. 3 Synergetic effects for PNP degradation.

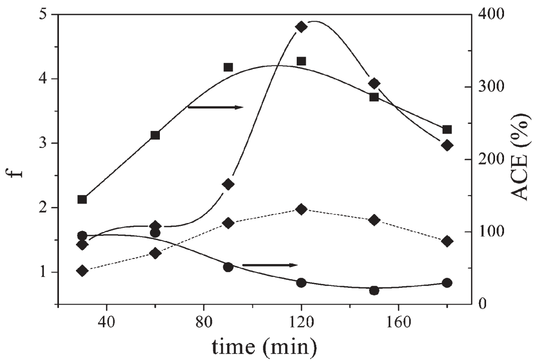

Fig. 4 Synergetic factors and ACE.

where, η_{P1}, η_{P2}, η_{P3} are the COD removal for P1, P2 and P3 at given time t, respectively. Thus the synergetic factor calculated for DOC and COD removal could reach as high as 4.81 and 1.98, respectively. Further such a synergetic effect was established at temperatures in the range 100–160 °C, where the synergetic factors for COD removal were in the range 1.54–1.98 (ESI, Fig. S3†). During all the treatment time, the synergetic factors for the DOC were observed to be much larger than that of the COD, indicating that P1 was advantageous not only for the degradation but also mineralization of organic pollutants (Fig. 4).

This assumption was confirmed by the identification of degradation products. In P1, intermediates such as hydroquinone, *p*-nitrocatechol, benzoquinone and carboxylic acids (*e.g.* fumaric acid and oxalic acid) were identified, and after treatment for 3 h, the main residual products were carboxylic acids. However, in P2 after treatment the same time, the main intermediates were hydroxylated benzene compounds, principally hydroquinone and benzoquinone, and no carboxylic acids were detected. Such a trend of intermediates in the two processes not only evidenced the existence of hydroxyl radicals due to the hydroxylation products, but also confirmed the deeper mineralization by P1 accounting for the difference of intermediate types and contents.

A similar conclusion could be drawn for X-GRL degradation (ESI, Fig. S4 and Table S2†). In P2, the degradation intermediates are mainly benzenamine, *N*-phenylmethylene after azo bond cleavage, and a small amount of *N*-methylaniline and benzaldehyde. However, in P1, besides the above three intermediates, other deep degradation products such as benzoic acid and hydroquinone are detected. According to the proposed degradation pathway (ESI, Fig. S5†), P1 degraded X-GRL much more thoroughly than P2.

In addition, preliminary investigation showed that the anode showed good stability for organic pollutant degradation for one month under 180 °C, though the electrode life required detailed monitoring at high temperature and pressure.

In summary, the introduction of oxygen in electrochemical oxidation at high temperature and pressure, leads to the promotion of wet peroxide oxidation and the reduction of electrode fouling, which shows synergetic effects for efficient organic pollutant degradation. The oxygen, acting as a promoter, leads to the process achieving good performance in relatively mild conditions and wider initial concentration ranges. Therefore, this method would not only offer a promising alternative for highly concentrated organic pollutant treatment, but also might open up a new research area for non-classical electrochemistry at high temperature and pressure which needs detailed investigation to gain insights into many aspects including the thermodynamics, kinetics and physico-chemical characteristics.

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18 The average current efficiency (ACE) was calculated by the following:

$$\mathrm{ACE} = \frac{(\mathrm{COD}_0 - \mathrm{COD}_\mathrm{t})FV}{8It} \times 100\%$$

where, COD_0, COD_t are the chemical oxygen demand at initial time and the given time t (g O_2 L^{-1}), respectively, I is the current (A), F is the Faraday constant (96487 C mol^{-1}), t is the treatment time (s), and V is the volume of the solution (L).