Short Communication

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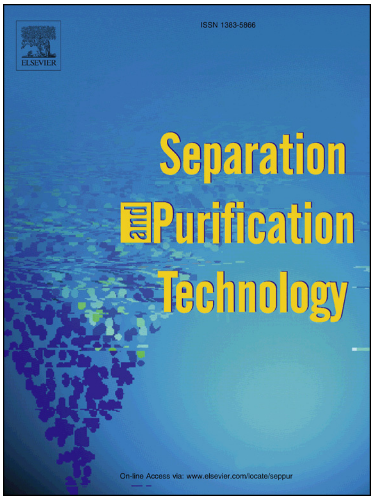

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Combined electro-catazone/electro-peroxone process for rapid and effective Rhodamine B degradation

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Abstract

An integral electro-catazone and electro-peroxone (E-cataperoxone) process was developed for quick and effective oxidation of Rhodamine B (RhB) as the model refractory organic pollutant in this study. A mesoflower-structured TiO_2-coated porous Titanium gas diffuser (MFT-PTGD) acted as both the anode and the O_3 gas diffuser, while carbon polytetrafluoroethylene was used as the cathode. During O_3/O_2 mixture flowing through the MFT-PTGD, O_3 was electrochemically catalyzed simultaneously by the TiO_2 mesoflower at the anode (via an electro-catazone reaction) and the *in situ* generated H_2O_2 at the cathode (via an electro-peroxone reaction) to achieve a high yield of ·OH. The individual processes show integral effects and significantly enhances the RhB degradation rate and efficacy. Additionally, owing to the unique three-dimensional porous structure and flow-through configuration of the MFT-PTGD anode, the O_3 flow-through mode is superior to O_3 flow-by mode for the E-cataperoxone oxidation of RhB. These results suggest that the E-cataperoxone process is an effective and promising means of degrading refractory organic pollutants in wastewater.

Keywords: Electro-cataperoxone, Electro-catazone, Electro-peroxone, Refractory organic pollutant, Hydroxyl radical (·OH)

1. Introduction

Electro-peroxone (E-peroxone) treatment [1-3], a new electrochemically driven process combining conventional electrolysis with ozonation processes, has attracted great attentions in recent years. In E-peroxone treatment, an O_3/O_2 mixture is sparged into a reactor, which is typically equipped with a Pt anode and a carbon polytetrafluoroethylene (carbon-PTFE) cathode [4, 5]. The cathode functions as an electrocatalyst for the *in situ* electrochemical reduction of O_2 to H_2O_2 (Eq. (1)) [6]. The *in situ* generated H_2O_2 then reacts with the sparged O_3 to yield aqueous ·OH (Eq. (2)) [7, 8], which is a much stronger oxidant than O_3 or H_2O_2 and can effectively oxidize organic pollutants to CO_2 and H_2O without any secondary pollution. Therefore, E-peroxone treatment has been considered an effective and environmentally friendly oxidation technology for wastewater purification.

In E-peroxone treatment, ·OH is primarily generated by the cathode-induced reaction (Eqs. (1) and (2)) [7, 8], while the traditionally used Pt anode barely contributes to the ·OH yield attributing to its poor ability in ·OH generation.

$$O_2 + 2H^+ + 2e \rightarrow {}_2H \qquad (1)$$

$$H_2O_2 + 2O_3 \rightarrow 2\bullet OH + 3O_2 \qquad (2)$$

To increase the contribution of the anode, researchers have replaced the Pt anode with a boron-doped diamond (BDD) anode [9], which is effective in producing ·OH from water discharge (Eq. (3)) [10] during E-peroxone treatment.

$$BDD + {}_2H \rightarrow O \quad B[\bullet DD] + O^+H + {}^- \qquad (3)$$

Unfortunately, the total organic carbon (TOC) removal attained using the BDD anode is the same as those using other anodes (i.e., Ti/RuO_2-IrO_2, Pt) [9], indicating that this type of anode does not improve the efficacy of E-peroxone treatment. Specifically, the BDD anode does not improve treatment performance because the ·OH produced in the vicinity of the BDD anode tends to adsorb on the anode surface rather than diffusing into the bulk solution to oxidize organic pollutants. Moreover, the anodes previously used in E-peroxone and other combined electrolysis-ozonation processes have low catalytic activities for converting O_3 to ·OH, termed heterogeneous catalytic ozonation (catazone) [11]. Finally, the anodes are generally planar in shape, consequently causing the relatively larger diffusion length (tens of μm) for O_3 traveling from the bulk solution to the anode surface [12] and leading to insufficient utilization of the sparged O_3 and low ·OH production.

Recently, a novel anodic-induced electrocatalytic ozonation process called electro-catazone (E-catazone) was developed by combining heterogeneous catalytic ozonation and electrolysis [13]. In this process, a self-prepared mesoflower-structured TiO_2-coated porous titanium gas diffuser (MFT-PTGD) multifunctional anode serves as the anode, O_2/O_3 gas diffuser and highly efficient catalyst (in the case of the TiO_2 mesoflowers) for the catazone reaction. When the current is applied to the MFT-PTGD under O_3 flow, the positive holes on the surface of the TiO_2 mesoflowers are electro-generated at anodic potentials (Eq. (4)). These holes can then absorb sparged O_3 (Eq. (5)) and catalyze it to ·OH (Eq. (6)) both in the vicinity of the anode and in the bulk solution.

$$\mathrm{TiO_2}\left[h^{+}e^{-}\right]\xrightarrow{-e^{-}}\mathrm{TiO_2}\left[\ \right]^{+} \qquad (4)$$

$$\mathrm{TiO_2}\left[\ \right]^{+}+\mathrm{O_3}\rightarrow\mathrm{TiO_2}\left[\mathrm{O_3}\right]^{+}\rightarrow\mathrm{TiO_2}\left[\mathrm{O}\right]^{+}+\mathrm{O_2} \qquad (5)$$

$$\mathrm{TiO_2}\left[\mathrm{O}\right]^{+}+\mathrm{H_2O}\rightarrow\mathrm{TiO_2}\left[\bullet\mathrm{OH}\right]^{+}+\ \bullet\mathrm{OH(aq)} \qquad (6)$$

Besides multi-catalytic capabilities on MFT-PTGD, TiO_2 mesoflowers also provides unique three-dimensional porous structure, the novel morphology for MFT-PTGD [14], and thus achieve a short diffusion length of less than 1 μm and a great enhancement of O_3 mass transfer to the porous interfaces of the anode [13]. Thus, the E-catazone process provides a higher catalytic activity (i.e., higher ·OH production) and organic degradation rate than that in the processes of its individual component, namely, electrolysis, ozonation and catazone. Nevertheless, unlike the carbon-PTFE cathode used in the E-peroxone reaction, the Pt cathode used in the E-catazone reaction does not participate in the degradation of organic materials because of its poor ability to form H_2O_2 and thus ·OH via subsequent peroxone reactions. It is therefore very essential to enhance cathodic oxidation ability of E-catazone process.

To achieve the oxidation of organics mediated simultaneously by both anodic- and cathodic-produced aqueous ·OH, a new process combining E-catazone and E-peroxone, called E-cataperoxone, is proposed in this study. Here, a self-prepared MFT-PTGD serves as an anode and gas diffuser, while carbon-PTFE serves as the cathode. First, O_3 is sparged through the MFT-PTGD, where participating in the E-catazone reaction to form ·OH. Next, the sparged O_3 mixes with O_2 in the bulk solution and undergoes E-peroxone treatment to produce ·OH. In this way, E-cataperoxone achieves the integration of E-catazone and E-peroxone processes for better performance in organic pollution degradation. Such an integral E-catazone/E-peroxone system has not been reported to date. To test this hypothesis, E-cataperoxone was used to degrade Rhodamine B (RhB), which is often used as a model compound for refractory organic pollutants in wastewater. E-cataperoxone performance was compared with that in the processes of its individual component, and the effect of the O_3 flow mode used in E-cataperoxone treatment was evaluated.

2. Materials and Methods

2.1 Materials

A porous titanium gas diffuser (purity 99%, 20 mm length, 20 mm diameter, average pore size of 51 μm) was purchased from Yinggao Metal Materials Co., Ltd. (Baoji, China). Analytical grade ethanol, hydrofluoric acid (40 wt%), hydrochloric acid (37 wt%), sodium hydroxide, and Rhodamine B were obtained from Sinopharm (Shanghai, China).

2.2 Preparation of the mesoflower-structured TiO_2-coated porous titanium diffuser anode and carbon-PTFE cathode

The MFT-PTGD anode was prepared via a series of procedures including degreasing, etching, and hydrothermal treatment with annealing, as described in our previous study [13, 14]. The carbon-PTFE electrode was prepared with Vulcan XC-72 carbon powder (Cabot Corp., USA), PTFE dispersion, and anhydrous ethanol [6].

2.3 E-catazone, E-peroxone, and E-cataperoxone treatment of RhB

Treatments were conducted in a glass column reactor containing 300 mL RhB solution with the initial chemical oxygen demand (COD) of 1100 mg/L. Since most of the industrial dye wastewaters with RhB are acidic and pH ranging from 3.0 to 4.0 is the optimal condition commonly used in E-peroxone [3] and other advance oxidation processes (AOP) like electro-Fenton [6], the initial pH of the system was set as 3.5. In all the tests, an O_3 generator (Tonglin Technology Co., China) was used to pass O_3/O_2 mixture through the reactor at a constant flow rate of 0.4 L/min and an O_3 dosage of 9.0 mg/L, while a DC power supply (PS-305DM, Longwei Electric Co., Ltd, Dongguan, China) was used to provide a constant current of 235 mA. In the E-catazone process, MFT-PTGD functioned as the anode and gas diffuser, while a 0.1 cm^2 Pt plate was used as the cathode. In the E-peroxone process, the Pt plate was used as the anode and a 25 cm^2 carbon-PTFE slab as the cathode. Here, a pure PTGD, without catalyst coating, served as the gas diffuser and was placed near the anode and cathode. In the E-cataperoxone process, O_3 was flowed through the MFT-PTGD diffuser anode, with carbon-PTFE as the cathode (Figure 1). The effect on COD removal of the O_3 sparging mode (flow-through or flow-by) in the E-cataperoxone process was also investigated via a comparison flow-by test in which O_3 was flowed by the MFT-PTGD anode via a PTGD diffuser**.**

2.4 Analytical methods

The O_3 concentration in the ozone generator influent was measured via potassium iodide absorption followed by sodium thiosulfate titration [15]. During RhB degradation, the samples of the reaction mixture were collected at various reaction times (up to 2 h) for analysis. COD was measured colorimetrically using a DR/5000 spectrophotometer (Hach Co., Loveland, CO, USA). Ultraviolet–visible (UV–vis) absorption spectra were recorded using a SPECORD 200 spectrophotometer after diluting the samples forty-fold. The ·OH concentration was analyzed using the *N,N*-dimethyl-p-nitrosoaniline (RNO) trapping method [13]. The formation of ·OH radical intermediates in various oxidation processes was monitored by bleaching the RNO solution. To detect ·OH radicals, 0.1 mol/L phosphate buffer solution (PBS, pH 3.5) was used as the electrolyte. The 1 mL samples collected in different processes after 2 h reaction were immediately added to a 4 mL scavenger solution containing PBS and RNO, and were mixed well. Subsequently, the RNO absorbance at 350 nm was measured and used to calculate the RNO absorbance decrement efficiency, which represents the ·OH concentration, using $[(R_0 - R_t)/ R_0] \times 100\%$. Here, R_0 and R_t represent the RNO absorbance at reaction time $t = 0$ min and $t = 2$ h, respectively.

3. Results and Discussion

3.1 Integral effect of E-catazone and E-peroxone process for RhB degradation

In the E-cataperoxone process integrating E-catazone and E-peroxone, a COD removal efficiency reached 94.2% after 2 h reaction (Figure 2(a)), indicating that RhB was effectively oxidized to CO_2 and H_2O. In contrast, the E-peroxone and E-catazone treatments only achieved 74.2% and 79.4% COD removal, respectively. These results indicated that E-cataperoxone achieved a strong integral effect between E-catazone and E-peroxone for RhB oxidation. Figure 2(b) also shows that the COD degradation curves fit well with the pseudo-first-order kinetic model. Moreover, the calculated rate constant (k) for E-cataperoxone (1.70 h^{-1}) is 2.00 and 2.77 times higher than those for E-catazone (0.55 h^{-1}) and E-peroxone (0.45 h^{-1}), respectively, suggesting a faster oxidation of RhB in E-cataperoxone. In addition to COD removal, the UV–vis spectra of the RhB solution in the different processes (Figure 3) illustrated that the spectrum for the raw RhB solution exhibits peaks at 553 nm, 370–296 nm and 258 nm, attributed to azo compounds, anthraquinone groups [16] and aromatic compounds [16], respectively. After only 15 min reaction in E-cataperoxone, these peaks significantly declined and almost disappeared, demonstrating that the color was completely removed and the corresponding compounds were effectively decomposed. In comparison, after 15 min of E-catazone treatment, the peak at 553 nm disappeared, but not the peak at 258 nm (Figure 3 (inset)). The results indicated that although the complete decoloration was achieved, the intermediate compounds (e.g., aromatic compounds) were not fully degraded. Meanwhile, in the case of E-peroxone, none of the peaks disappeared after 15 min, suggesting incomplete decoloration and degradation of RhB.

The superior performance of E-cataperoxone is due to its higher ·OH yield in bulk solution. As shown in Figure 4, the RNO decrement efficiency is higher in E-cataperoxone treatment than those in the processes of individual components (E-peroxone and E-catazone), indicating higher ·OH production. It is worth noting that a significantly positive correlation was observed between the COD removal and hydroxyl radical (Figure 2 and Figure 4), showing the obvious integral effect in the E-cataperoxone process. These results indicated that the combination of E-catazone and E-peroxone can effectively enhance anodic and cathodic oxidation ability via the simultaneous generation of ·OH at both MFT-PTGD anode and carbon-PTFE cathode. In details, during O_3/O_2 mixture flowing through the MFT-PTGD anode, O_3 was electrochemically catalyzed by the TiO_2 mesoflower via an E-catazone reaction (Eq. (4–6)) [13]. The subsequent E-peroxone reaction (Eqs. (1) and (2)) achieved O_3 reacting with *in situ* electro-generated H_2O_2 at the carbon-PTFE cathode [2, 7, 8]. Both anodic E-catazone and cathodic E-peroxone reactions are effective in producing •OH, consequently leading to the high •OH yield (Figure 4) and the enhancement of RhB oxidation (Figure 2). Moreover, another advantage of E-cataperoxone process is the simplified oxidation system compared to conventional ozonation/electrolysis processes. Since MFT-PTGD anode used in E-cataperoxone system is multifunctional, simultaneously acting as the anode, O_2/O_3 gas diffuser and O_3 catalyst, only MFT-PTGD and cathode are placed in the E-cataperoxone reactor without using additional gas diffusers.

3.2 Effect of O_3 flow mode on RhB degradation

The superior performance of E-cataperoxone is also explained by its excellent mass transfer property, as demonstrated by the difference between the COD removal, reaction kinetics, and RNO decrement efficiency achieved in flow-through mode vs. flow-by mode. Interestingly, when E-cataperoxone was operated in flow-by mode, which is typically used in E-peroxone and other reported electrolysis-ozone processes, dramatic decreases were observed in both COD removal (from 94.0% in flow-through mode to 84.0% at 1.5 h; Figure 2a) and k (from 1.70 h^{-1} to 1.13 h^{-1}; Figure 2b). This reduced performance under flow-by mode is attributed to the difference in mass transfer of reactants. In flow-through mode, sparging O_3 through the MFT-PTGD anode triggers the forced convection of O_3 through the highly porous structure of MFT-PTGD [13], enhancing mass transfer of the reactants (O_3 and RhB) to the catalysts (i.e., TiO_2-mesoflowers) on the MFT-PTGD surface, especially the inner pore surface. In contrast, in flow-by mode, the inner pore surface is barely accessible to the reactants, and mass transfer to the rest of the surface is less effective. Thus, flow-through significantly facilitates the O_3-RhB solution-TiO_2 three-phase reaction (i.e., E-catazone), increasing the ·OH yield. This effect is demonstrated by the greater RNO decrement efficiency obtained in flow-through mode compared to flow-by mode (Figure 4).

4. Conclusions

The proposed E-cataperoxone process successfully integrates E-catazone and E-peroxone processes to enhance the ·OH-mediated oxidation of RhB pollutants. By utilizing an MFT-PTGD anode and carbon-PTFE cathode, O_3 can be electrochemically catalyzed simultaneously by TiO_2 mesoflowers at the anode and *in situ* generated H_2O_2 at the cathode to achieve a high yield of ·OH. Such integral effect significantly enhances the rate and efficiency of COD removal. Thus, E-cataperoxone provides a significantly higher oxidation ability than the processes of its individual component and is promising for the treatment of refractory organic pollutants.

Acknowledgements

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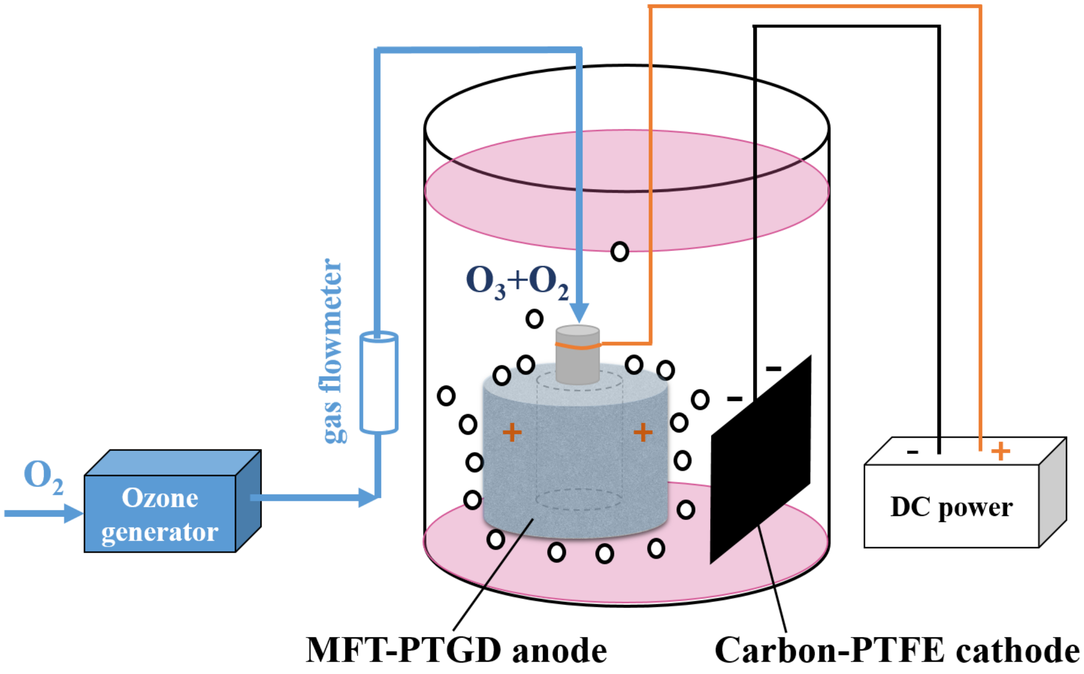
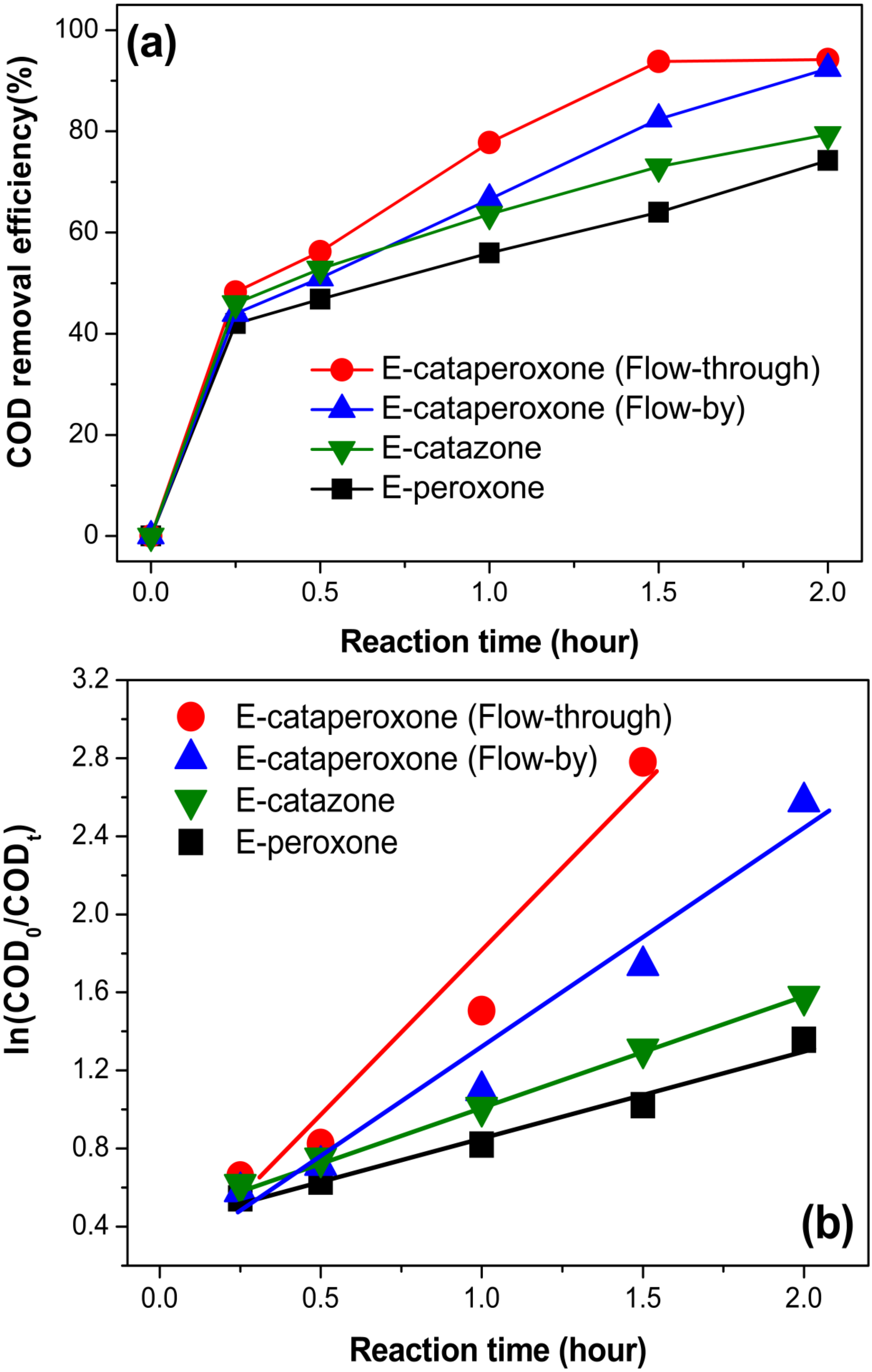
Figure 1. Schematic of the reactor used for E-cataperoxone process

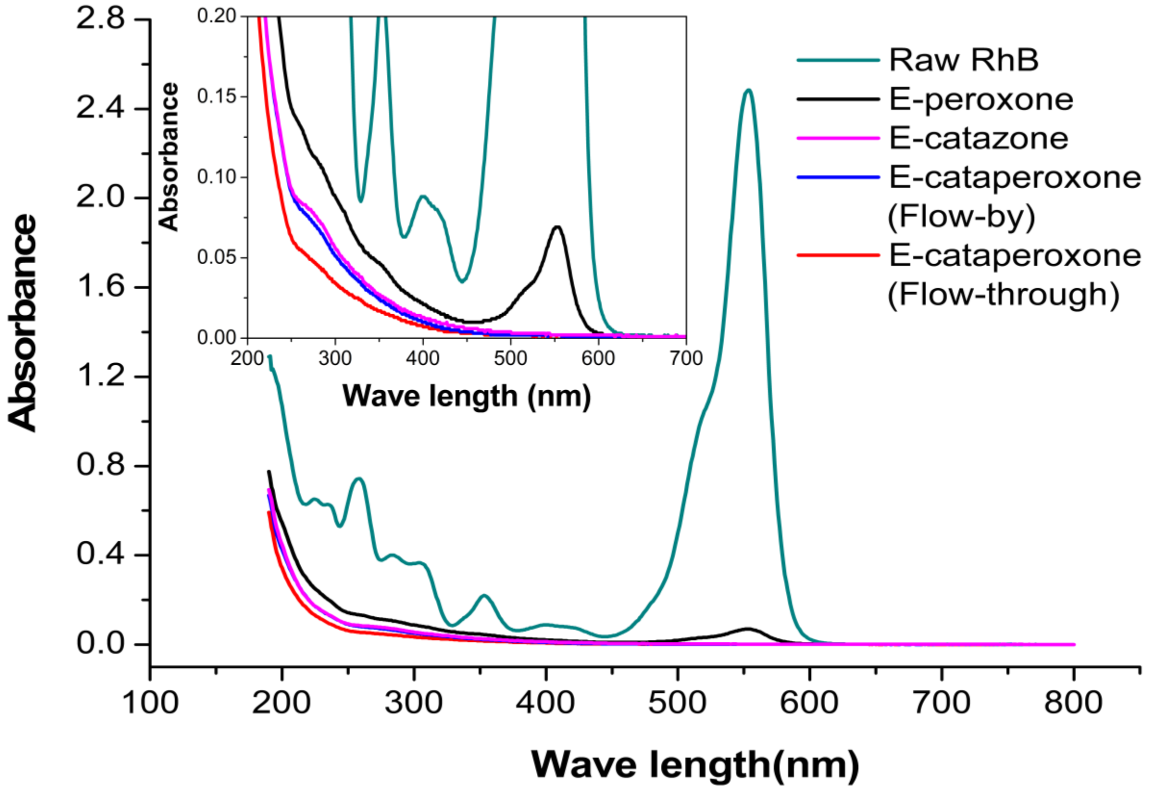
Figure 2. COD removal efficiency (a) and pseudo-first order curves (b) for E-cataperoxone (flow-through), E-cataperoxone (flow-by), E-catazone and E-peroxone process.

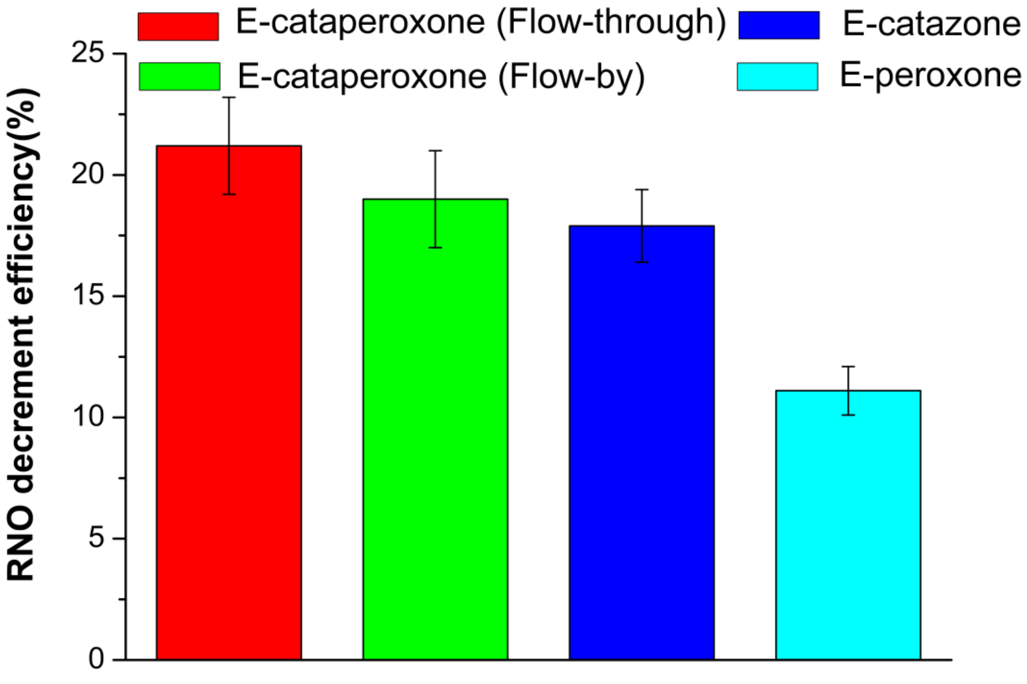
Figure 3. UV–vis spectra of RhB solution after 15 min of different oxidation treatment

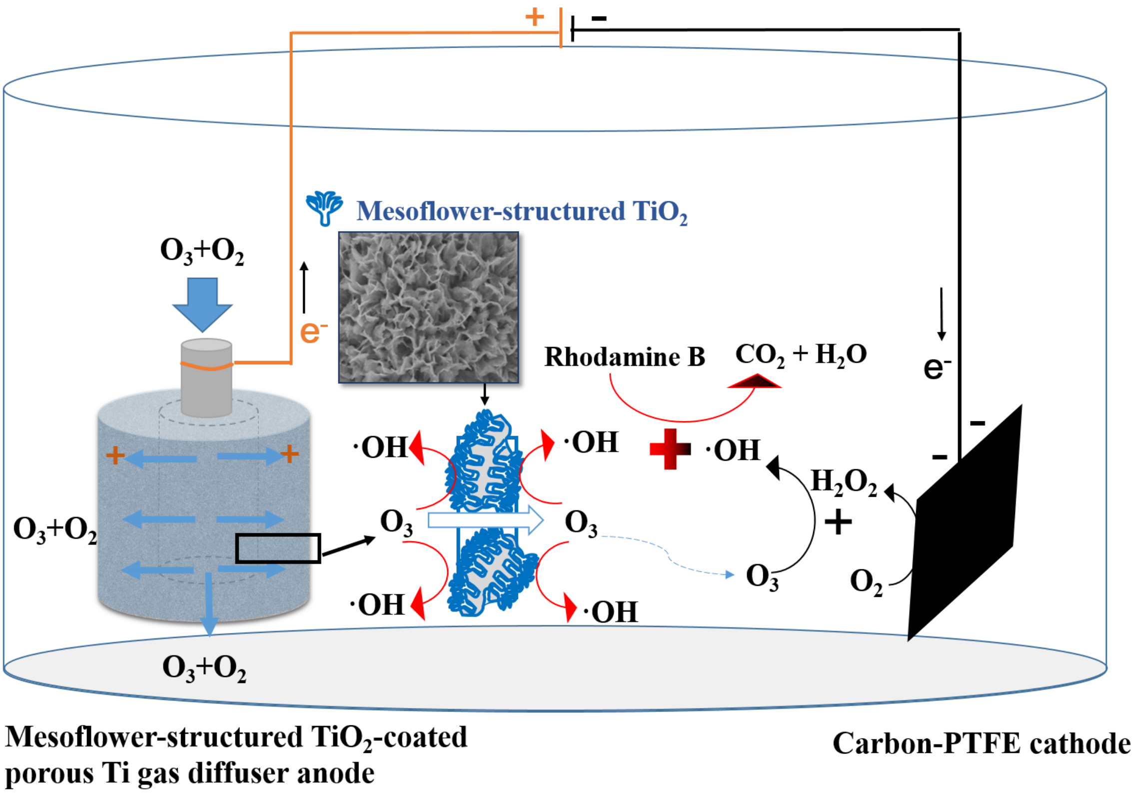
Figure 4. RNO decrement efficiency in different processes after 2 h of reaction


O$_2$
Ozone generator
gas flowmeter
O$_3$+O$_2$
+
+
-
-
-
+
DC power
MFT-PTGD anode
Carbon-PTFE cathode


(a)
COD removal efficiency(%)
0
20
40
60
80
100
0.0
0.5
1.0
1.5
2.0
Reaction time (hour)
E-cataperoxone (Flow-through)
E-cataperoxone (Flow-by)
E-catazone
E-peroxone
(b)
ln(COD0/CODt)
0.4
0.8
1.2
1.6
2.0
2.4
2.8
3.2
0.0
0.5
1.0
1.5
2.0
Reaction time (hour)
E-cataperoxone (Flow-through)
E-cataperoxone (Flow-by)
E-catazone
E-peroxone


Absorbance
2.8
2.4
2.0
1.6
1.2
0.8
0.4
0.0
100
200
300
400
500
600
700
800
Wave length(nm)
Absorbance
0.20
0.15
0.10
0.05
0.00
200
300
400
500
600
700
Wave length (nm)
Raw RhB
E-peroxone
E-catazone
E-cataperoxone (Flow-by)
E-cataperoxone (Flow-through)


E-cataperoxone (Flow-through)
E-catazone
E-cataperoxone (Flow-by)
E-peroxone
RNO decrement efficiency(%)
25
20
15
10
5
0


+
-
Mesoflower-structured TiO_2
O_3+O_2
e^-
e^-
Rhodamine B
$CO_2 + H_2O$
·OH
·OH
·OH
H_2O_2
O_3
O_3
O_3+O_2
O_3
O_2
·OH
·OH
-
-
O_3+O_2
Mesoflower-structured TiO_2-coated porous Ti gas diffuser anode
Carbon-PTFE cathode

Highlights:

- An E-cataperoxone process was developed for Rhodamine B oxidation
- A mesoflower-like TiO_2-coated porous Ti gas diffuser acted as anode and O_3 diffuser
- Carbon polytetrafluoroethylene was used as the cathode
- Simultaneous oxidation of organics by both anodic- and cathodic-produced aqueous •OH
- Excellent organics degradation performance by synergetic E-catazone and E-peroxone processes