Electrochemical degradation of tetracycline by γ-Al$_2$O$_3$–Bi–(Sn/Sb) three-dimensional particle electrode

Wenquan Sun[a,b,*], Biao Ma[a], Yongjun Sun[a,b,*], Huaili Zheng[c], Genchao Ma[a]

[a]College of Urban Construction, Nanjing Tech University, Nanjing, 211800, China, email: coneflower@163.com (W. Sun), 489439901@qq.com (B. Ma), sunyongjun008@163.com (Y. Sun), 939324613@qq.com (G. Ma)
[b]Jiangsu Key Laboratory of Industrial Water-Conservation & Emission Reduction, College of Environment, Nanjing Tech University, Nanjing, 211800, China
[c]Key laboratory of the Three Gorges Reservoir Region's Eco-Environment, State Ministry of Education, Chongqing University, Chongqing, 400045, China, email: zhl@cqu.edu.cn (H. Zheng)

ABSTRACT

In this work, the degradation of tetracycline (TC) in wastewater was investigated using the γ-Al$_2$O$_3$–Bi–(Sn/Sb) particle electrodes. Parameters affecting the degradation efficiency and energy consumption of the γ-Al$_2$O$_3$–Bi–(Sn/Sb) particle electrodes, such as electrical conductivity, initial pH, air flow, current intensity, plate distance, filling ratio, and initial wastewater concentration, were systematically investigated. Results showed that the optimal conditions were 4000 mS·cm^{-1} conductivity, pH 6, 15 mL·min^{-1} air flow, 0.1 A current intensity, 4 cm plate distance, 0.05 g·mL^{-1} filling ratio, and 100 mg·L^{-1} wastewater concentration. More than 90% and 70% of TC and total organic carbon were degraded, respectively, under the optimal conditions. In addition, the γ-Al$_2$O$_3$–Bi–(Sn/Sb) particle electrodes had good stability and reproducibility.

Keywords: Particle electrode; Three-dimensional electrode reactor; Electrochemical oxidation; Advanced treatment; Tetracycline

1. Introduction

In recent years, studies have shown that high residues and various kinds of antibiotics are present in Chinese rivers and have even reached levels provided by international standards [1–2]. Moreover, tetracycline (TC) antibiotics are widely used in therapy, poultry, and aquaculture breeding [3]. Animals absorb 10–30% of the TC antibiotics and the remainder goes into the water. These TC antibiotic residues affect entire ecosystems, especially the circulatory system, thereby affecting the food chain [4]. TC antibiotics persist in the environment and negatively affect aquatic ecosystems. Bacteria in the water became drug resistant and affect aquatic life [5]. Moreover, studies showed that TC has exceeded the standard level for tap water in Guangzhou and Macao (77.5% and 100%, respectively) [6]. TC is a potential threat to human health simultaneously through drinking water and the food chain [7–8]. Therefore, new and effective methods have to be developed to degrade TC in water.

Developments in TC wastewater treatment have gained attention worldwide. Nowadays, advanced oxidation technology is considered as an effective method to deal with TC antibiotic materials [9]. Advanced oxidation technology uses redox reactions through the active substances of hydroxyl radicals [10–11]. Usually, advanced oxidation treatment techniques for removing TC include photocatalytic degradation [12], electrochemical oxidation [13], Fenton reaction [14], and ozonation [15]. Compared with the traditional adsorption and biological treatment methods, advanced oxidation technology is adapted for TC water quality characteristics. It has a fast oxidation rate and good treatment effects. During advanced oxidation, sludge and secondary pollutants are not produced [16].

As a novel advanced oxidation technology, the three-dimensional electrode method has attracted

*Corresponding author.

increasing attention in successfully degrading organic pollutants, especially in treating antibiotics in wastewater [17]. Compared with the traditional two-dimensional cell electrode technology, three-dimensional electrodes are loaded with activated carbon or metal particles between the two-dimensional plate [18]. Three-dimensional electrode technology increases the electrolytic cell surface because it charges the particle electrode surface through an applied voltage [19]. The three-dimensional electrodes provide rapid mass transfer and reaction speed with small particle spacing. Moreover, it improves current and time–space efficiency [20]. Furthermore, additional chemicals and secondary pollutants are not produced by this method. Therefore, further research of new three-dimensional particle electrodes is needed for TC wastewater treatment [21].

In this paper, γ-Al$_2$O$_3$–Bi–(Sn/Sb) particle electrodes were prepared using the impregnation method. Key parameters that influence electrode efficiency for removing TC wastewater were investigated to optimize electrical conductivity, initial pH, air flow, current intensity, plate distance, filling ratio, and initial wastewater concentration. Moreover, the stability and reproducibility of γ-Al$_2$O$_3$–Bi–(Sn/Sb) particle electrodes were investigated.

2. Materials and methods

2.1. Materials

Bi(NO$_3$)$_3$·5H$_2$O, SnCl$_4$·5H$_2$O, and SbCl$_3$ were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). γ-Al$_2$O$_3$ electrodes were provided by Nanjing Chemical Reagent Co., Ltd. (Nanjing, China). TCs were obtained from Aladdin Industrial Co., Ltd. (Shanghai, China). All aqueous and standard solutions were prepared with deionized water. All other reagents were of analytical grade and purchased from Nanjing Shengjianquan Chemical Glassware Instrument Co., Ltd. The TC wastewater was composed of TC and deionized water at a concentration of 100 mg·L^{-1}. It was stored in a brown bottle and preserved at 4°C for later use. Na$_2$SO$_4$ was used to increase the wastewater conductivity. The three-dimensional particle electrodes were prepared in the lab according to our previous work [22].

2.2. Apparatus and procedure

The treatment of TC wastewater was performed in a three-dimensional electrode reactor (as shown in Fig. 1) made from organic glass. The effective volume of the reactor was 500 mL, with length 80 mm × width 80 mm × height 100 mm. Card slots were set every 1 cm on the reactor wall to change the spacing of the plate in the experiment. Compressed air was sparged into the reactor through a microporous plate attached to the lower part of the tank. The particle electrodes were packed between the anode (titanium) and cathode (graphite) in the three-dimensional electrode reactor. The effective surface area of the anode and cathode was 8 cm × 10 cm. The thicknesses of the anode and cathode material were 2 mm and 1 cm, respectively. To eliminate the impact of filler particle electrode adsorption TC, we used adsorption saturation filling particles in the process of electrolysis experiment. 500 mL wastewater with predetermined conductivity and pH was fed into the three-dimensional electrode reactor. The plate electrode was connected to the power supply and the air pump was opened. The wastewater was electrolyzed for 180 min, samples were withdrawn, and voltage current was recorded every 30 min for analysis. Subsequently, the concentrations of TC and total organic carbon (TOC) were determined. The experiment results were the average value of three repeated tests and the error was less than 5%.
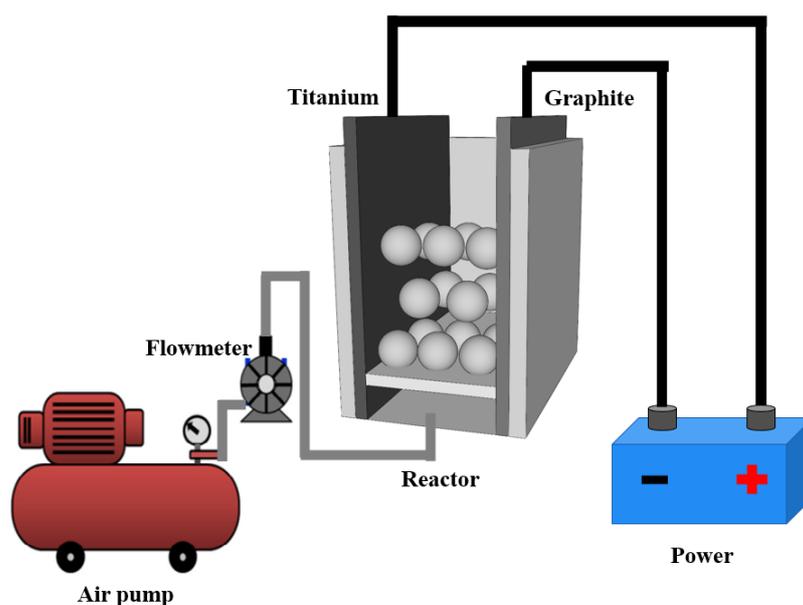
Fig. 1. Dimensional electrode reactor.

2.3. Analytical methods

The concentration of TC in the solution was analyzed using high-performance liquid chromatography (HPLC; KNAUER, Germany). Column: Eurospher 100-5C18, 4.6 mm × 250 mm; the mobile phase was a mixture of 0.01 M oxalic acid in HPLC-grade-water-acetonitrile-methanol (70:20:10 V/V); flow rate: 1 mL·min⁻¹; detector: UV at 360 nm; and sample size: 20 μL. The retention time for TC was 5.97 min [23]. The TC removal rate was determined using the following equation:

$$\text{TC removal rate (\%)} = (C_0 - C_t)/C_0 \times 100\% \tag{1}$$

where C_0 and C_t are the concentrations of TC before and after the reaction, respectively.

The removal rate of TOC was measured using a TOC analyzer (Shimadzu, TOC-VCSH, Japan) to evaluate the degree of pollution in wastewater. All the experimental data are expressed in terms of arithmetic averages of at least three replicates. The TOC removal rate was determined using the following equation:

$$\text{TOC removal rate (\%)} = (C_0 - C_t)/C_0 \times 100\% \tag{2}$$

where C_0 and C_t are the concentrations of TOC before and after the reaction, respectively.

The following equation calculated and expressed the energy consumption (E) [24].

$$E = \frac{UIt}{(COD_0 - COD_t)V_L} \tag{3}$$

where, COD_0 and COD_t are the initial and final concentration of COD (mg O_2·L⁻¹), U is the cell potential (V), I is the current (A), and V_L is the volume of electrolyte solution (L).

3. Results and discussion

3.1. Effect of electrical conductivity on the degradation of TC

The electrical conductivity reflected the size of the population of conductive particles in the solution, which highly affects the electrochemical degradation of organic matter. In this research, to investigate the degradation of TC wastewater under different conductivities, Na_2SO_4 was used to adjust the electrical conductivity of the solution. As shown in Fig. 2, the voltage and conductivity changed linearly.

Fig. 3 shows the effect of electrical conductivity on the degradation of TC wastewater. With less than 4000 ms·cm⁻¹ conductivity, the degradation efficiency of TC wastewater increased as the conductivity gradually increased. The maximum degradation efficiency of TC wastewater was at 4000 ms·cm⁻¹, thus the degradation efficiency of TC wastewater reduced with a continuous increase in conductivity. This finding may be explained by following reason: with the increase of the conductivity, the bypass current of the three-dimensional electrode system increased, thereby reducing the reaction current and current efficiency. Therefore, the main electrode and particle electrodes were contaminated, which reduced the TC degradation efficiency [25].
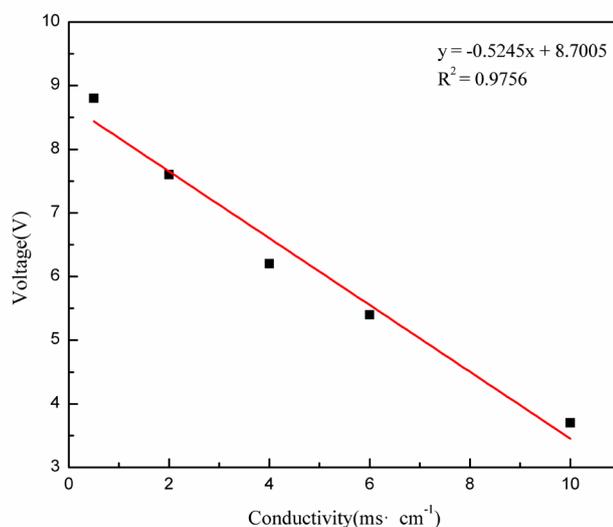
Fig. 2. Effect of electrical conductivity on cell voltage (cell current I = 0.1 A).
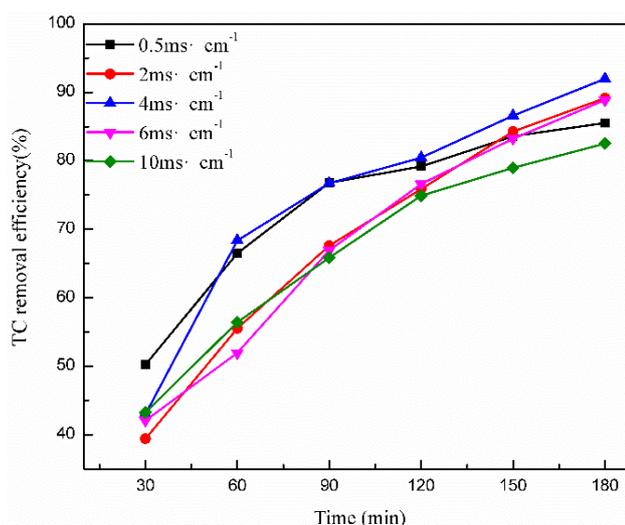
Fig. 3. Effects of electrical conductivity on TC removal efficiency. (pH 6, 15 mL·min⁻¹ air flow, 0.1 A current intensity, 4 cm plate distance, 0.05 g·mL⁻¹ filling ratio).

As shown in Fig. 4, the increase of the electrical conductivity decreased the energy consumption in the reaction. When the electrical conductivity was 500 ms·cm⁻¹, the degradation of 1 kg TC required 142 kwh of energy. However, the degradation of 1 kg TC required only 42kwh of energy when the conductivity reached 4000 ms·cm⁻¹. The energy consumption was reduced by 3.5 times. The increase in electrical conductivity reduced the reaction voltage and output power of the power supply under a constant current. Therefore, the energy consumption of the reaction was greatly reduced [26]. Thus, the electrical conductivity of 4000 ms·cm⁻¹ was selected as the optimal conductivity.
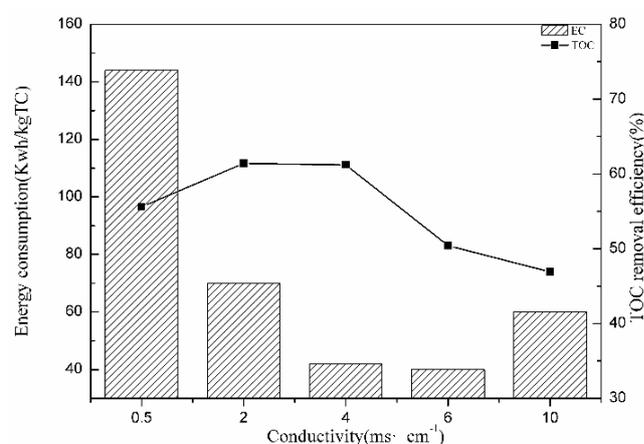
Fig. 4. Effect of electrical conductivity on power consumption and TOC. (pH 6, 15 mL·min^{-1} air flow, 0.1 A current intensity, 4 cm plate distance, 0.05 g·mL^{-1} filling ratio).
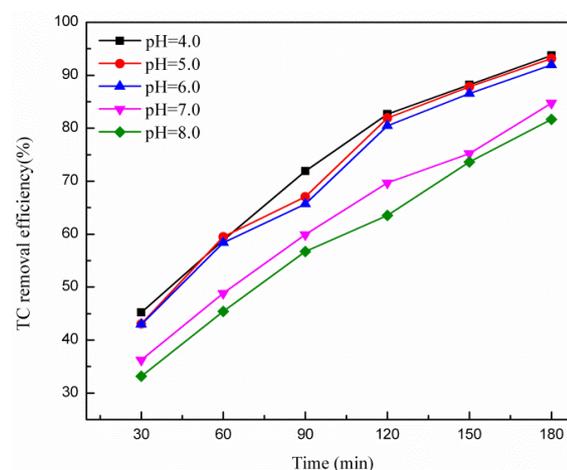
3.2. Effect of initial pH on the degradation of TC

The initial pH has a significant role in the three-dimensional electrode system. It directly affects the over potential of the electrodes in the solution and the activity of hydroxyl radicals in electrochemical processes. Initial pH levels of 4–8 were investigated to determine their effect on the particle electrodes for TC degradation.

As shown in Fig. 5, the removal efficiency of TC wastewater increased with the decrease in initial pH. The TC degradation efficiency was as high as 93.7% when the initial pH was 4. However, results showed that the TC degradation efficiency exceeded 90% under acidic conditions. The TC degradation efficiency fell to 80% when the initial pH exceeded 6. A large number of H^{+} in the solution was consumed to generate ·OH under acidic conditions, thereby decreasing the H$_2$ evolution side reactions. Therefore, the TC degradation efficiency was high under acidic conditions. Moreover, the side reaction of H$_2$ evolution reduces the TC degradation efficiency under alkaline conditions [27,28].

Fig. 6 shows the energy consumption and the removal rate of TOC in different initial pH levels of the TC wastewater. The energy consumption of the reaction under acidic conditions was obviously lower than that under alkaline conditions. However, the removal rate of TOC was higher under alkaline conditions.

Overall, the best conditions for TC degradation were obtained at pH 6 with relatively low energy consumption and improved removal rate of TOC. Therefore, pH 6 was considered the optimal pH in the subsequent experiments.

3.3. Effect of air flow on the degradation of TC

As shown in Fig. 7, the TC degradation efficiency was only 80% with 2.5 mL·min^{-1} air flow under an electrolysis time of 180 min. When the air flow rate was 40 mL·min^{-1}, the TC degradation efficiency exceeded 95%. This phenomenon showed that the air flow of the three-dimensional electrode system significantly affected the TC degradation. However, the significant change was the TC degradation efficiency in

Fig. 5. Effects of pH value on TC removal efficiency. (4000 mS·cm^{-1} conductivity, 15 mL·min^{-1} air flow, 0.1 A current intensity, 4 cm plate distance, 0.05 g·mL^{-1} filling ratio).
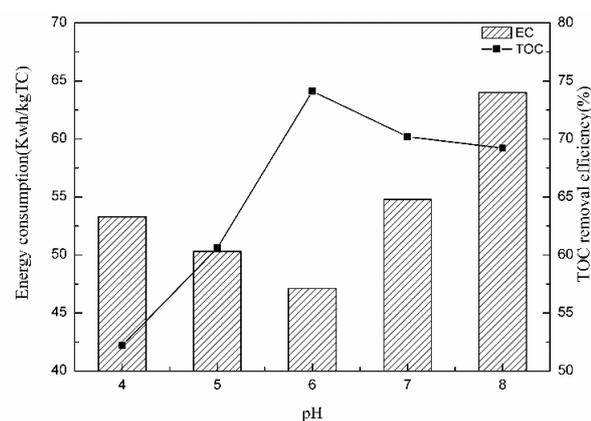
Fig. 6. Effect of pH value on power consumption and TOC. (4000 mS·cm^{-1} conductivity, 15 mL·min^{-1} air flow, 0.1 A current intensity, 4 cm plate distance, 0.05 g·mL^{-1} filling ratio).
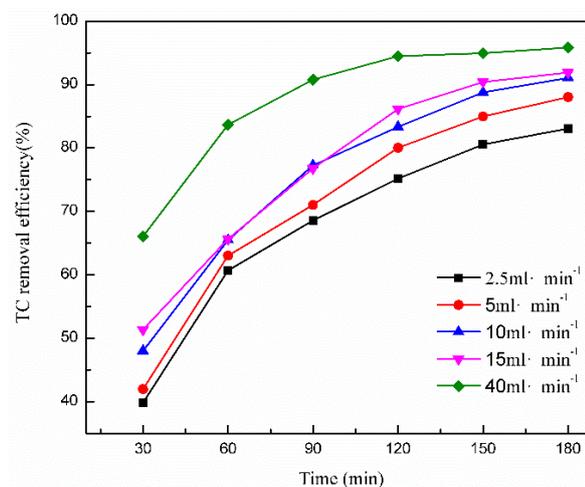
Fig. 7. Effects of air flow on TC removal efficiency. (4000 mS·cm^{-1} conductivity, pH 6, 0.1 A current intensity, 4 cm plate distance, 0.05 g·mL^{-1} filling ratio).

the middle response time when the air flow was 15 and 40 mL·min⁻¹.

As shown in Fig. 8, the energy consumption of the electrochemical catalytic reaction decreased as air flow increased. Air flow basically has the following functions: (1) it provides a stirring effect that enhances the efficiency of mass transfer and eliminates concentration polarization [29]; (2) under acidic conditions, the oxygen in the air can react with H^+ to form H_2O_2 at the cathode reaction and then generate ·OH to degrade TC [30]; and (3) oxygen can inhibit the oxygen evolution reaction at the anode and improve current efficiency [31]. The change in energy consumption during TC degradation is minimal when the air flow rates were 15 and 40 mL min⁻¹, and the energy consumptions were 51.5 and 51.2 kWh, respectively. Considering that aeration lasted for 2 h in the experiment, increasing the oxygen could increase the power consumption of the air pump. Therefore, the optimal air flow rate was 15 mL·min⁻¹.

3.4. Effect of current intensity on the degradation of TC

As shown in Fig. 9, the removal rate of TC increased with increasing current intensity. The TC removal rate was approximately 85% at 0.5 A after 20 min in the three-dimensional electrode system, which was superior to current intensities of 0.01, 0.05, and 0.1 A. However, numerous bubbles in the reaction tank were present due to the increased current voltage, thereby leading to hydrogen and oxygen evolution reactions at the cathode and anode. Thus,water electrolysis occurred [32]. Moreover, high current strength increased the bypass and short-circuit currents, and reaction current decreased with the current efficiency in the three-dimensional electrode system [33,34]. This phenomenon decreased the degradation reaction during electro-catalysis.

As shown in Fig. 10, the energy consumption increased at a current intensity of 0.5 A.The energy consumption was 27.1 kWh·kg·TC⁻¹, and the TOC degradation rate was 58.7% when the current intensity was 0.01 A. However, the energy consumption increased to 138.8 kWh·kg·TC⁻¹ when the current intensity increased to 0.5 A. The TC and TOC degradation rates were 99.9% and 90.9%, respectively. However, energy consumption increased more than 5 times, because the low utilization ratio of electric power led to an increasing energy consumption under the high current intensity.

Results showed that the TC degradation rate and the energy consumption were 91.9% and 47.2 kWh·kg·TC⁻¹, respectively, at a current intensity of 0.1 A. Under this condition, a high removal rate of TC under low energy consumption and low side effects were observed. Therefore, the optimal intensity adopted in the tests was 0.1 A.

3.5. Effect of plate distance on the degradation of TC

As shown in Fig. 11, the maximum TC degradation efficiency of 91.4% was obtained at 3 cm plate distance. The decline in TC removal efficiency was not obvious when the plate spacing was reduced. The TC and TOC degradation rates declined sharply and the energy consumption increased when the plate spacing was increased. The convection and diffusion of mass transfer distance were
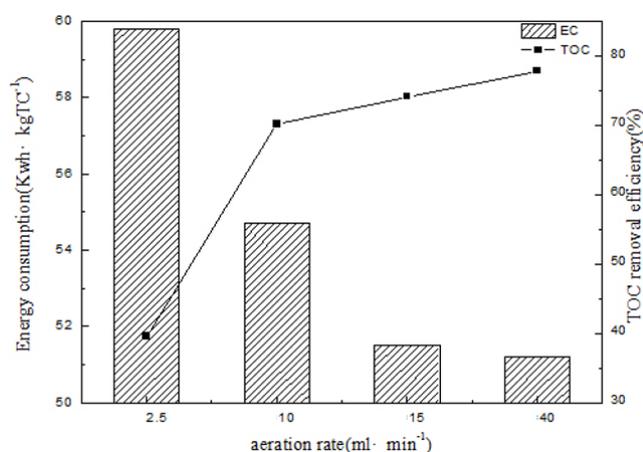
Fig. 8. Effect of air flow value on power consumption and TOC. (4000 mS·cm⁻¹ conductivity, pH 6, 0.1 A current intensity, 4 cm plate distance, 0.05 g·mL⁻¹ filling ratio).
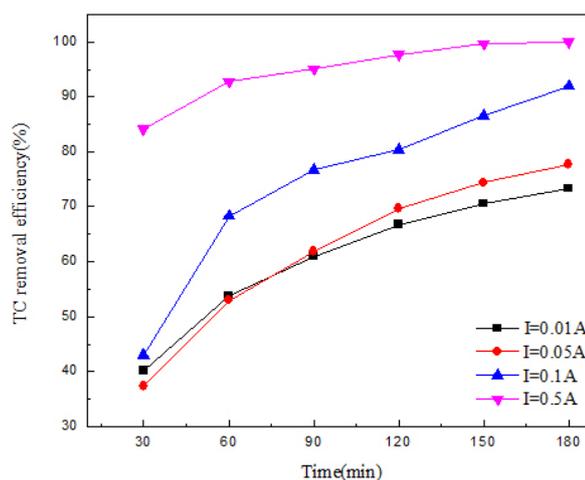
Fig. 9. Effects of current intensity on TC removal efficiency. (4000 mS·cm⁻¹ conductivity, pH 6, 15 mL·min⁻¹ air flow, 4 cm plate distance, 0.05 g·mL⁻¹ filling ratio).
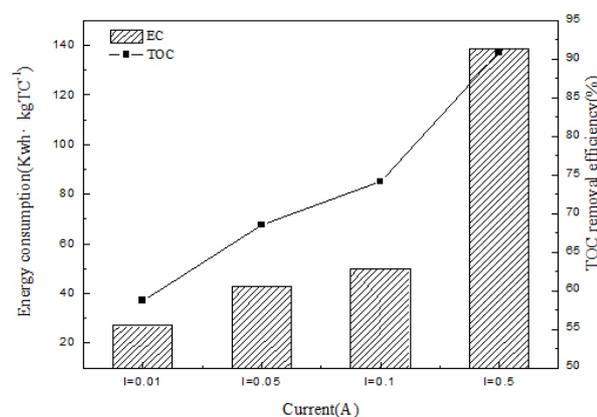
Fig. 10. Effect of current intensity on power consumption and TOC. (4000 mS·cm⁻¹ conductivity, pH 6, 15 mL·min⁻¹ air flow, 4 cm plate distance, 0.05 g·mL⁻¹ filling ratio).
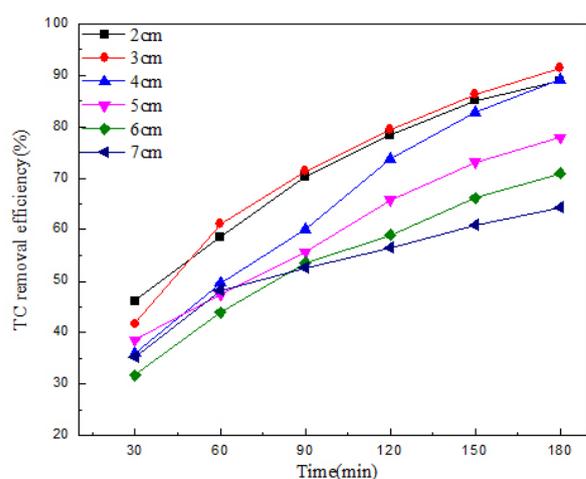
Fig. 11. Effects of plate distance on TC removal efficiency. (4000 mS·cm⁻¹ conductivity, pH 6, 15 mL·min⁻¹ air flow, 0.1 A current intensity, 0.05 g·mL⁻¹ filling ratio).

Fig. 12. Effect of plate distance on power consumption and TOC. (4000 mS·cm⁻¹ conductivity, pH 6, 15 mL·min⁻¹ air flow, 0.1 A current intensity, 0.05 g·mL⁻¹ filling ratio).

reduced as the plate spacing was reduced. Increasing the mass transfer improved the speed and efficiency of the electrochemical reaction. Moreover, the removal rate of organic matter was improved. However, the stability of the operation was affected when the substrate spacing was too small, which was disadvantageous to the reaction [35]. Therefore, 4 cm was selected as the optimal plate distance (Fig. 12).

3.6. Effect of particle electrode filling ratio on the degradation of TC

As shown in Fig. 13, the removal rate of TC increased as the particle electrode filling ratio increased from less than 0.05 g·mL⁻¹. The high particle electrode filling ratio increased the more active substance and improved the efficiency of the TC degradation. The maximum TC degradation efficiency was 98% when particle electrode filling ratio was 0.05 g·mL⁻¹. The removal rate of TC decreased when the increase in particle electrode filling ratio exceeded 0.05 g·mL⁻¹. The high particle electrode filling ratio increased the chance of contact. In this condition,the short circuit and bypass currents reduced the current reaction efficiency, thereby reducing the TC degradation efficiency [31,36].

As shown in Fig. 14, the energy consumption with a degrading unit mass was 47.8 kWh·kg TC⁻¹ when the particle electrode filling ratio was 0.05 g·mL⁻¹. Moreover, the TOC degradation efficiency increased to 74.1%. Therefore, the optimal particle electrode filling ratio was 0.05 g·mL⁻¹.

3.7. Effect of initial concentration on the degradation of TC

As shown in Fig. 15, the degradation of TC continuously decreased as the initial concentration increased. When the initial concentration reached 50 or 100 mg·L⁻¹, the removal rate of TC exceeded 90%. When the initial concentration reached 300 mg·L⁻¹, the rate was only 67.4%. Because the degradation of TC produced more intermediate with increasing initial concentration of TC in the process of electrical catalytic degradation. The competition between
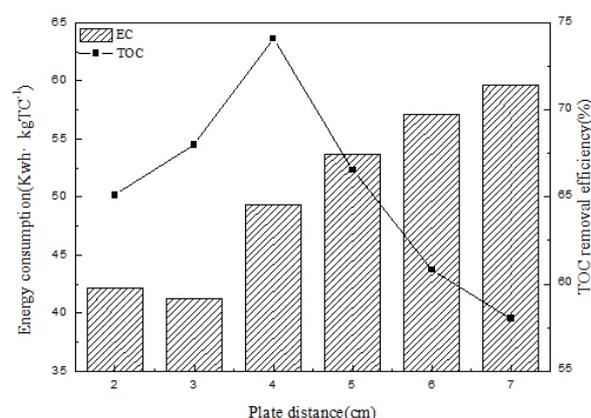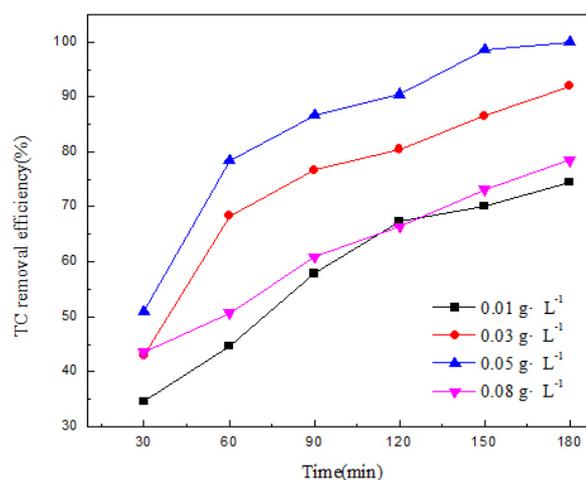
Fig. 13. Effects of particle electrode filling ratio on TC removal efficiency. (4000 mS·cm⁻¹ conductivity, pH 6, 15 mL·min⁻¹ air flow, 0.1 A current intensity, 4 cm plate distance).
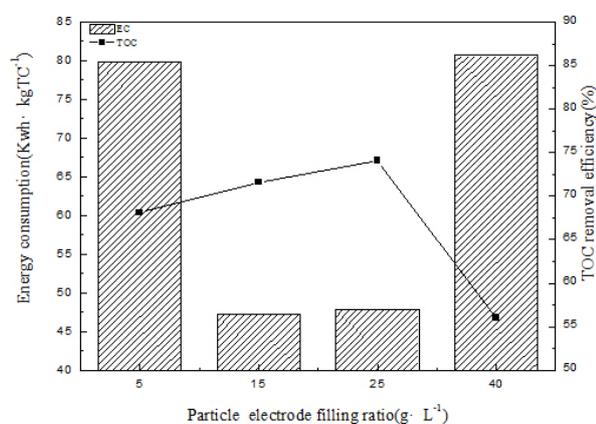
Fig. 14. Effect of particle electrode filling ratio on power consumption and TOC. (4000 mS·cm⁻¹ conductivity, pH 6, 15 mL·min⁻¹ air flow, 0.1 A current intensity, 4 cm plate distance).
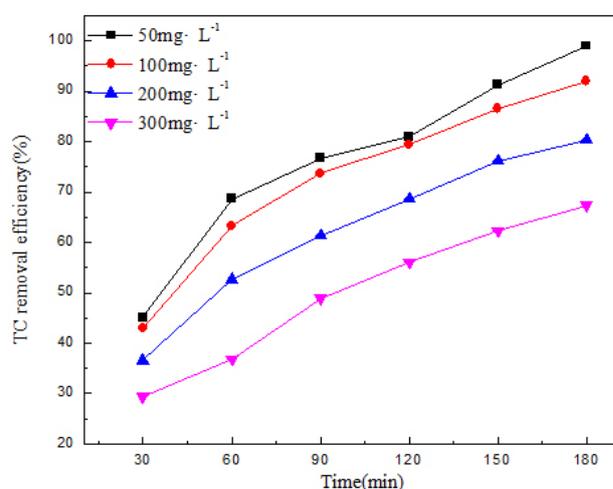
Fig. 15. Effects of initial concentration on TC removal rate. (4000 mS·cm⁻¹ conductivity, pH 6, 15 mL·min⁻¹ air flow, 0.1 A current intensity, 4 cm plate distance, 0.05 g·mL⁻¹ filling ratio).

intermediate and TC molecules led to inefficient TC degradation [37]. When the initial TC concentration increased from 50 mg·L⁻¹ to 300 mg·L⁻¹, the number of hydroxyl radicals showed a declining trend because the catalytic particle electrode point was dominated by organic matter [38].

However, Energy consumption was significantly reduced as initial TC concentrations increased. As shown in Fig. 16, when the initial TC concentrations reached 50 and 300 mg·L⁻¹, the EC of TC were 99.8 and 16.5 kWh·kg TC⁻¹, respectively. The EC was reduced by more than 80%. Therefore, wastewater with high TC concentrations exhibited low power consumption and the optimal TC concentration was 100 mg·L⁻¹.

3.8. Stability of γ-Al₂O₃–Bi–(Sn/Sb) particle electrode

The stability of γ-Al₂O₃–Bi–(Sn/Sb) particle electrode was studied through its repeated use. Moreover, the degradation efficiency of TC using γ-Al₂O₃–Bi–(Sn/Sb) was measured to evaluate the stability of the electrode with an electrolysis time of 180 min in three-dimensional systems.

As shown in Fig. 17, the TC degradation rate still reached 83.7% using the γ-Al₂O₃–Bi–(Sn/Sb) particle electrode, which was used for four times. The TC degradation rate was reduced by 8.3% after using the electrode for the first time. Thus, the three-dimensional degradation system showed good stability. The TC degradation rate decreased to 45% after reusing the electrode for 20 times,which was close to the degradation efficiency of two-dimensional systems. The reduction in electric catalytic activity was because of the following: (1) with repetition, the particle electrode frequently crashed and rubbed in the system. This phenomenon led to the loss of the active components, there by decreasing the TC degradation rate [39]. (2) With repetition, intermediate and carbon molecules constantly accumulated in the surface area of the particle electrode, there by hindering the contact between TC and active components.
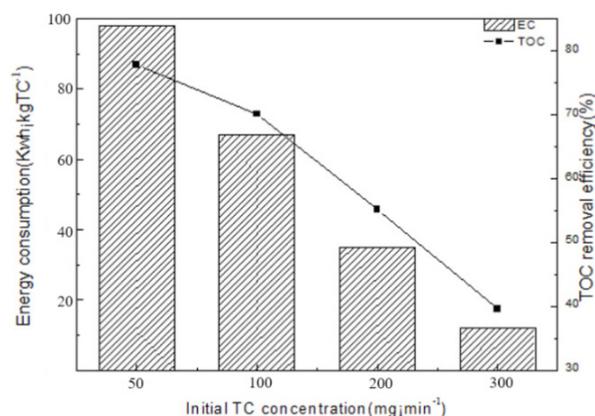
Fig. 16. Effect of initial TC concentration on power consumption and TOC. (4000 mS·cm⁻¹ conductivity, pH 6, 15 mL·min⁻¹ air flow, 0.1 A current intensity, 4 cm plate distance, 0.05 g·mL⁻¹ filling ratio).
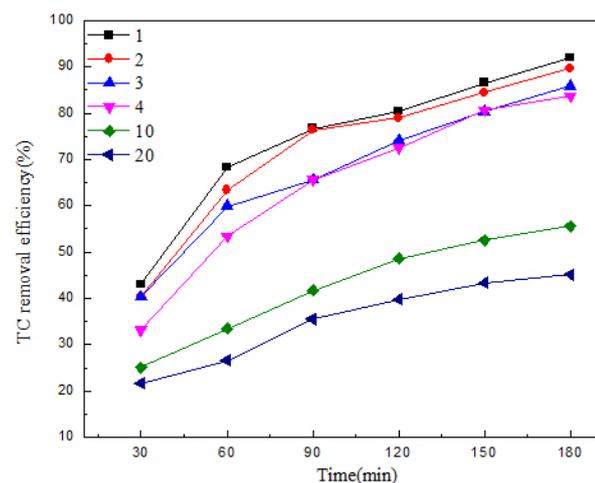
Fig. 17. Effects of repeated times on TC removal. (4000 mS·cm⁻¹ conductivity, pH 6, 15 mL·min⁻¹ air flow, 0.1 A current intensity, 4 cm plate distance, 0.05 g·mL⁻¹ filling ratio).

3.9. Reproducibility of γ-Al₂O₃–Bi–(Sn/Sb) particle electrode

Results showed that the degradation rate of TC and the intensity of the particle electrode were reduced after constant repetition. The experiment used the γ-Al₂O₃–Bi–(Sn/Sb) particle electrode to evaluate its reproducibility. The particle electrode was repeatedly washed with distilled water and dried in the oven at 50°C. Subsequently, the particle electrode was roasted in a muffle furnace at 500°C for 180 min. The purpose was to remove the carbon and organic materials on the surface of the particle electrode. Moreover, the regenerated γ-Al₂O₃–Bi–(Sn/Sb) particle electrode was used to degrade TC in the experiment.

As shown in Fig. 18, the TC degradation efficiency reached 70.8% after 2 h using the regenerated γ-Al₂O₃–Bi–(Sn/Sb) particle electrode. The TC degradation efficiency of the regenerated electrode increased by 15.1% compared with the three-dimensional particle electrode after 10 times of use, because the loss of the active component, carbon, and organic materials on the surface of the particle electrode led
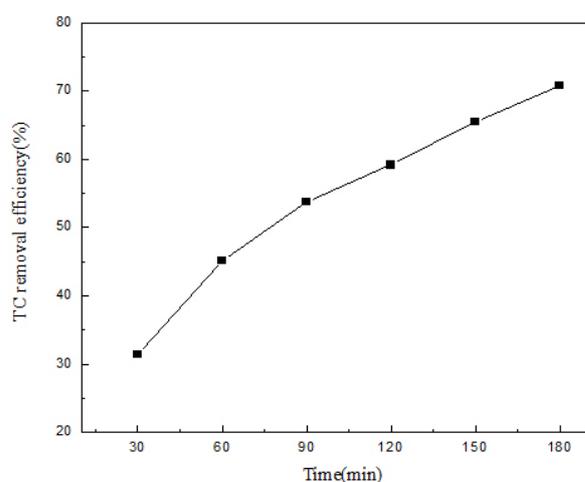
Fig. 18. Effect of particle electrode regeneration on TC removal rate. (4000 mS·cm^{-1} conductivity, pH 6, 15 mL·min^{-1} air flow, 0.1 A current intensity, 4 cm plate distance, 0.05 g·mL^{-1} filling ratio)

to decreased TC degradation efficiency [40]. Thus, results showed that the particle electrode has good reproducibility.

4. Conclusions

As shown in this study, Results showed that the optimal conditions are 4000 mS·cm^{-1} conductivity, pH 6, 15 mL·min^{-1} air flow, 0.1 A current intensity, 4 cm plate distance, 0.05 g·mL^{-1} filling ratio, and 100 mg·L^{-1} wastewater concentration. Under the optimal conditions, TC and TOC degradation rates were 91.95% and 74.1%, respectively. The degradation of TC was synergistically affected by the direct oxidation and indirect oxidation of intermediate molecules. Results showed that the loaded γ-Al$_2$O$_3$–Bi–(Sn/Sb) particle electrode has good stability and reproducibility after repeated use.

Acknowledgements

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