

Article

Preparation of Ti_4O_7 Reactive Electrochemical Membrane for Electrochemical Oxidation of Coking Wastewater

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Abstract: The effluent of coking wastewater comprises hundreds of refractory organics and is characterized by high toxicity and non-biodegradation. Electrochemical advanced oxidation processes (EAOPs) have been widely applied in the field of water purification. In this study, a Ti_4O_7 reactive electrochemical membrane (REM) was prepared using the plasma spraying method for the electro-oxidation of coking wastewater. The composition and surface morphology of the Ti_4O_7 REM were characterized via X-ray diffraction (XRD) and scanning electron microscopy (SEM), respectively. The computational fluid dynamics (CFD) simulation was used to compare the mass transfer performance of the Ti_4O_7 REM in traditional batch (TB) mode and flow-through (FT) mode. In the FT mode, the effects of current density and anode–cathode distance on the treatment efficiency were investigated, and the electrocatalytic performance of the anode on coking wastewater was analyzed. The results showed that the COD removal efficiency reached 76.2% with an energy consumption of 110.5 kWh kg^{−1} COD under the optimal condition. In addition, cathodic polarization provides an effective technique for maintaining the long-term activity of the Ti_4O_7 REM. The three-dimensional fluorescence results and UV-vis spectrum showed that the aromatic compounds could be effectively degraded using the Ti_4O_7 REM. The Ti_4O_7 REM demonstrated excellent performance of electrochemical oxidation and satisfactory stability, which had a strong potential for application in the field of practical wastewater and engineering practices that respond to the concept of sustainable development.

Keywords: Ti_4O_7 reactive electrochemical membrane; electrochemical oxidation; coking wastewater; mass transfer



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1. Introduction

Coking wastewater, generated from the process of coking and gas production, is a typical industrial wastewater with high toxicity and poor biodegradability, which contains a series of organic pollutants, including phenols, polycyclic aromatic hydrocarbons, chlorinated organic compounds, and heterocyclic compounds [1], causing great harm to the ecological environment. In order to deal with this problem, biological treatment has been applied to sewage treatment in recent years [2,3]. However, phenolic compounds in coking wastewater have a strong inhibitory effect on microorganisms [4], so there are still some deficiencies in degrading wastewater, like the effluent quality of coking wastewater, especially the chemical oxygen demand (COD) not meeting the disposal standards after biotreatment. Therefore, its tailwater requires more advanced treatment, such as adsorption, membrane separation, and chemical oxidation process for the removal of these refractory organics [5,6]. Nevertheless, these technologies also encounter many problems in degrading pollutants, such as being inefficient in mineralizing contaminants, secondary pollution, high costs, etc.

In recent years, electrochemical advanced oxidation processes (EAOPs) have successfully attracted significant interest, owing to their strong oxidation ability, mild operating

conditions, and environmental friendliness [7–9]. The performance of electrochemical oxidation is dependent on anode materials, which can greatly affect the formation of reactive species on the anode surface. Boron-doped diamonds (BDD) anode is considered to be the most promising electrode due to its extremely wide potential window and superior chemical stability. However, the high fabrication cost of BDD anode limits its large-scale application in wastewater treatment. RuO₂- and IrO₂- anodes are economically feasible, but are prone to relatively lower mineralization efficiencies [10]. Although PbO₂- and SnO₂- anodes exhibit high efficiency, they suffer from low durability and high toxicity [11]. Rare earth element has been named as a potential improvement in the electrochemical application [12]. For instance, rare earth element Yb-doped Ti/RuO₂-SnO₂ electrode can enhance the electrocatalytic activity [13]. However, the economic feasibility has become one of the most important factors that limit its large-scale application [14]. Therefore, it is important to develop an ideal electrode material that has high conductivity, chemical stability, and a relatively low production cost. Recently, Magnéli-phase Ti₄O₇ has received widespread attention as a non-active anode material to replace BDD electrode for water purification. Zaky and Chaplin have expanded the application of commercial Ti₄O₇ electrode (Ebonex) for the electrochemical oxidation of p-substituted phenolic compounds [15]. However, Ebonex electrodes often contain a range of Magnéli phases ($n = 4$ to 10), which can affect electrode conductivity [16]. Recently, various studies have been conducted to prepare Ti₄O₇ electrodes for the oxidation of recalcitrant compounds. For instance, Pralay Gayen et al. have developed Ti₄O₇ electrode using pulsed electrodeposition for the removal of atrazine and clothianidin [17]. Lin et al. fabricated Ti₄O₇ electrode by Ce³⁺ doping for the efficient electro-oxidation of perfluorooctanesulfonate (PFOS) [8]. However, there are some limitations in these approaches, especially the potential danger of hydrogen reduction and expensive synthesis route. Moreover, most of these studies focused on the use of Ti₄O₇ electrodes to degrade the model organic compounds in aqueous phase, but few studies investigated their applications on real wastewater treatment.

In addition to anode material, the mass transfer efficiency has also been recognized to exert a significant influence on the electrochemical oxidation performance. Traditional EAOPs reactors utilize parallel plate electrodes, where water is forced through a narrow flow channel in the range of millimeter to centimeter [7]. This typical operation is defined as flow-by mode, in which a stagnant boundary layer (~100 µm) is formed near the surface of the electrode [18]. However, simulated data suggest that the reaction between hydroxyl radical (•OH) formed via water oxidation and organic contaminants only occurs in a narrow zone, within 1 µm around the anode surface [19]. Therefore, the conventional reactors operated in flow-by mode often face the problem of poor mass transfer due to the thick diffusion layer, which results in the low current efficiency and high energy consumption. In order to minimize diffusional limitations and enhance mass transfer, research has focused on the use of a reactive electrochemical membrane (REM) to develop electrochemical filter systems, by combining membrane filtration technology with the EAOP [16,20]. As a result of electrochemical filter systems, a carbon nanotube (CNT) reactors showed a two- to six-fold increase in the observed rate constant (k_{obs}) values compared to their traditional systems [21]. However, CNTs are not active for •OH production, and membranes with nanopores can be easily contaminated. Consequently, it is critical to seek micropore electrode materials with high electrochemical activity for water treatment.

Thus, in this study, we used a Ti₄O₇ REM with the micropore structure developed by the method of plasma spraying for the electrochemical oxidation of coking wastewater. X-ray diffraction (XRD), scanning electron microscopy (SEM), and energy-dispersive X-ray spectroscopy (EDS) were employed to analyze the composition and surface morphology. The chronoamperometry (CA) result and computational fluid dynamics (CFD) simulation were employed to assess the mass transfer performance of the Ti₄O₇ REM in the two typical systems, flow-through (FT) mode and traditional batch (TB) mode. The effects of operating parameters, including the applied current density and anode–cathode distance, on the performance of the reactive electrochemical were evaluated, and energy consumption was

also investigated. To obtain long-term stability, cathodic polarization was carried out. Furthermore, this study also evaluated the three-dimensional fluorescence and UV-vis results before and after the treatment of the electrochemical oxidation of coking wastewater. The Ti_4O_7 REM exhibited a satisfactory performance and provided a reference for the advanced treatment of coking wastewater.

2. Materials and Methods

2.1. Materials

The commercial Ti_4O_7 powders (purity 95.0%, 50 nm) were purchased from Yongxin Huiyou New Material and Technologies Co., Ltd., Huizhou, China. Porous titanium plates (50 mm $\times$ 50 mm $\times$ 1.0 mm, 5 μm filtration accuracy) were provided by Baoji Yinggao Metal Materials Industry Co., Ltd., Baoji, China. The chemicals were used as received without further purification. Sodium hydroxide (NaOH), oxalic acid (OA), dichromate, and other chemicals were of analytical grade and purchased from Beijing Lanyi Chemical Reagent Co., Ltd., Beijing, China.

2.2. Experimental Procedure

Coking wastewater was collected from a coking plant from Shanxi Province of China, which was the effluent treated by an anaerobic–anoxic–oxic (AAO) system, with the characteristics of 9.00 ± 0.05 pH value, 250 ± 20 mg/L COD concentration, 90 ± 10 mg/L TOC concentration, and 10 ± 2 mg/L $\text{NH}_3\text{--N}$ concentration.

2.3. Synthesis of Ti_4O_7 REM

The Ti_4O_7 REM was developed via the method of plasma spraying. Before preparation, the porous Ti plate was submerged in NaOH solution (5%, m/m) at 90 °C for 1 h and then etched in boiling OA solution (10%, m/m) for 2 h to obtain a uniform roughness surface. After that, the Ti_4O_7 powders were sprayed onto the pretreated Ti plate to prepare the Ti_4O_7 REM with the method of plasma spraying.

2.4. Reactor Configuration

The electrochemical oxidation experiments were conducted in FT mode or TB mode with the Ti_4O_7 REM (50 mm $\times$ 50 mm $\times$ 1 mm) serving as the anode, and the penetrating Ti plate serving as the cathode (Figures S1 and S2). In each treatment, the electrolytic reactor contained 400 mL wastewater and 0.1 M Na_2SO_4 to support the electrolyte with a constant current density for 3 h treatment. In FT mode, the wastewater was continuously recirculated through the Ti_4O_7 REM using a peristaltic pump (YZ1515X, SHENCHEN, Baoding, China), in which the solution first flowed through the anode followed by the cathode. In TB mode, the anode and cathode were placed in a cell and stirred continuously at a rate of 800 $\text{r}\cdot\text{min}^{-1}$. The pH value was not adjusted for all experiments, and all experiments were performed in 3 replicates at a constant temperature (25 ± 1 °C).

2.5. Analytical Techniques

The crystalline phases of this Ti_4O_7 REM were analyzed using X-ray diffraction (XRD, Rigaku, Tokyo, Japan) with Cu K α radiation at 40 kV/40 mA. The surface morphologies and elemental analyses were explored using scanning electron microscopy (SEM, ZEISS, Oberkochen, Germany) coupled with energy-dispersive X-ray spectroscopy (EDX, Oxford, London, UK).

Total organic carbon (TOC) was determined using a TOC analyzer (TOC-L, Shimadzu, Kyoto, Japan), and the chemical oxygen demand (COD) was measured via the titrimetric technique with dichromate as the oxidant. COD conversion was calculated according to the following Equation (1):

$$\text{COD conversion}(\%) = \left(1 - \frac{\text{COD}_t}{\text{COD}_0}\right) \times 100 \quad (1)$$

where COD_0 is the initial COD concentration (mg L^{-1}), and COD_t is the final COD concentration (mg L^{-1}).

In the electrolysis process, the energy consumption (EC) was calculated by the results of the COD test and Equation (2) [13]:

$$EC = \frac{1000UIt}{\Delta COD V} \quad (2)$$

where V (L) is the volume of the coking wastewater, ΔCOD (mg/L) is the dynamic change in the COD concentration, U (V) is the applied voltage, I (A) is the current, and t (h) is the electrolysis time.

The current efficiency (CE) was calculated as follows [13]:

$$CE = FV \frac{\Delta COD}{8It} \quad (3)$$

where ΔCOD (mg/L) is the dynamic change in the COD concentration, F is $96,485 \text{ C mol}^{-1}$, V is the solution volume (L), and the oxygen equivalent mass is $8 \text{ (g eq}^{-1}\text{)}$.

The mass transfer behavior was evaluated via CA analysis using electrochemical workstation (Metrohm, Basel, Switzerland) and CFD simulation. The CA experiment was conducted in 1 mM oxalic acid solution with 10 mM Na_2SO_4 electrolyte.

Numerical simulations using Fluent@ software (2022R1) were performed to study the liquid flow in the electrochemical reactor, including turbulent flow, velocity contour, and vector contour. We used the computer of DELL (G15), whose CPU was intel core (i7-101325) and GPU was RTX3060. The steady state calculation of the simulation showed that the iteration steps were achieved at 452 steps and 420 steps in the FT operation and TB operation, respectively. The effects of turbulence characteristics were simulated by the standard $k-\epsilon$ model. The inlet flow at the top of the FT reactor was set to 400 mL/min , and the bottom outlet was set to the pressure outlet boundary condition. The stirring rate of the TB system was set to 800 r/min . The conditions of no slip and no permeable wall were set for both reaction systems. The turbulence model was calculated according to the following Equation (4):

$$Re = \frac{\rho \cdot v \cdot d}{\mu} \quad (4)$$

where ρ is the liquid density, $\text{Kg} \cdot \text{m}^{-3}$; v is the fluid velocity, m s^{-1} ; d is the length of the geometric feature of the fluid flow region, m; and μ is hybrid hydrodynamic viscosity coefficient, $\text{N} \cdot \text{s} \cdot \text{m}^{-1}$. The UV-vis spectra of the samples were recorded from 180 to 500 nm using an ultraviolet spectrophotometer (Yuanxi, Shanghai, China). The three-dimensional fluorescence spectrum was measured using a fluorescence spectrophotometer (Hitachi, Tokyo, Japan). The excitation–emission matrix (EEM) spectra of fluorescence were obtained by acquiring emission spectra between 250 and 550 nm at increments of 5 nm, with excitation wavelengths of 200–450 nm at increments of 5 nm. The excitation and emission slit widths were set to 10 nm, while the scanning speed was 3000 nm min^{-1} .

3. Results

3.1. Characterization of the Ti_4O_7 REM

The XRD pattern, SEM image, and EDX spectra of the Ti_4O_7 REM are presented in Figures 1 and 2. The characteristic peaks at 20.8° , 26.4° , and other peaks matched well with the Ti_4O_7 standard data (JCPDS Card 183 No. 50-0787) [22], indicating that a high-purity Ti_4O_7 REM was obtained (Figure 1). The surface morphology of the Ti_4O_7 REM is shown in Figure 2a. As presented, the Ti_4O_7 powders were uniformly sprayed on the porous Ti plate, which formed a rough and homogenous distribution. Such a rough structure could provide abundant active sites for $\bullet\text{OH}$ generation on the anode surface [23], and the homogenous coating layer may prevent the dissolution of the coating from corrosive fluid and thus strengthen the stability of the electrode [24,25]. As displayed in the inset,

the surficial pore sizes ranged between approximately 1.6 and 8.5 μm . The elements distribution was investigated using EDX mapping analysis under SEM observation. The EDX spectrum (Figure 2b) demonstrates that titanium oxides were the only composition of the prepared Ti_4O_7 REM. The ratio of titanium to oxygen atoms on the Ti_4O_7 REM surface was 36.23%:63.77%, close to 4:7, confirming the formation of a Ti_4O_7 coating layer on the substrate. The porous structure of the REM is determined by mercury porosimetry, and the results are presented in Figure S3. The porosimetry results measured a Ti_4O_7 REM porosity of $42.18 \pm 2.3\%$, specific surface area of $0.890 \pm 0.2 \text{ m}^2 \text{ g}^{-1}$, and median pore diameter of $1.21 \pm 0.02 \mu\text{m}$ (based on pore volume data).

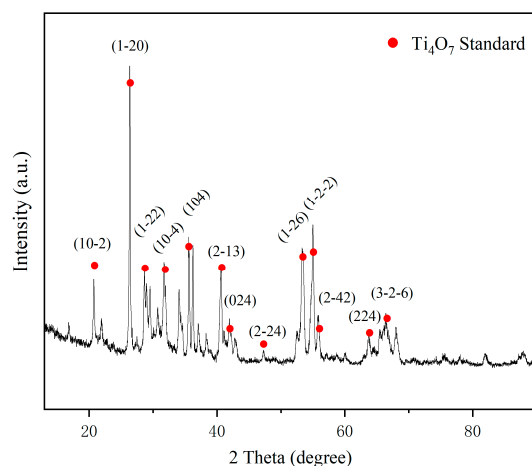


Figure 1. XRD pattern of the Ti_4O_7 REM.

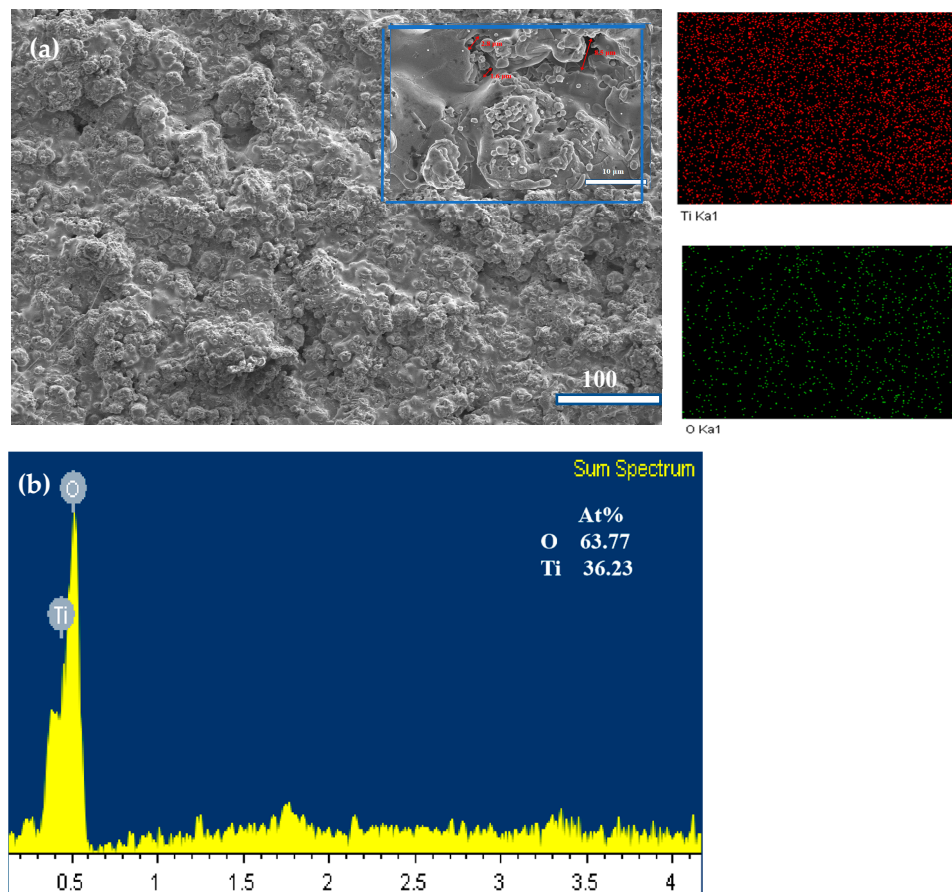


Figure 2. (a) SEM image and (b) EDX surface scan result of the Ti_4O_7 REM.

3.2. Mass Transfer Performance

Electrochemical oxidation performance is dependent on the reaction kinetics and the transport of organic compounds to the electrode surface. Since the actual electron transfer step is extremely fast ($\sim 10^{-16}$ s) [18], the measured rate constant is limited by the mass transfer process. Here, the mass transfer performance in two operations was investigated. A CA measurement was performed to evaluate the mass transfer performance of the Ti_4O_7 REM in the TB system and FT system. As can be seen from Figure 3, the Ti_4O_7 REM in the TB system and FT system decreased rapidly after 6 s and then maintained a stable value of 2 mA/cm^2 and 8 mA/cm^2 , respectively, indicating that the mass transfer of the Ti_4O_7 REM in the FT system was significantly higher than that in the TB system. This may be due to the fact that the oxalic acid molecule inevitably slipped away with the continuous stirred solution and bypassed the electrode surface in the TB system [26]. When the reactor operated in the FT system, the oxalic acid molecule would be forced across the porous structure by the enhanced convection, thus facilitating the mass transfer of organics to the electrode surface [27].

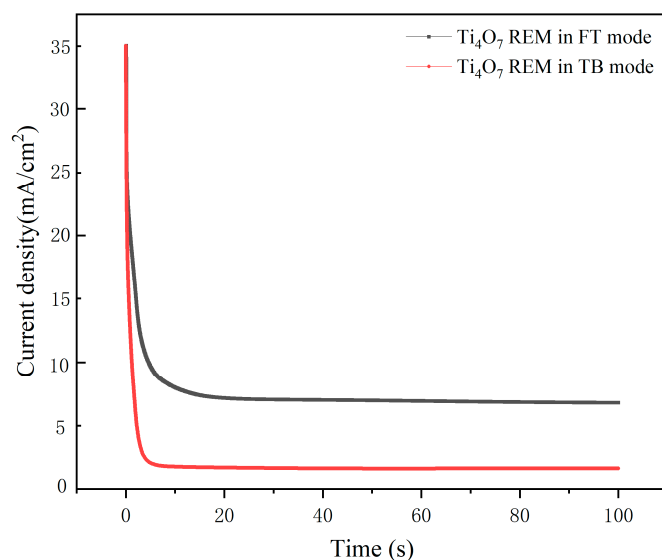


Figure 3. CA analysis of Ti_4O_7 REM compared between FT mode and TB mode.

To intuitively compare the mass transfer performance of the Ti_4O_7 REM in two systems, CFD simulation was performed (Figure 4). Two important parameters, including turbulence intensity and velocity distribution, which control the thickness of the diffusion layer, were investigated. As presented, the high flow velocity in the TB system only existed close to the stirring area, and the flow velocity around the electrode was very low and chaotic, which resulted in heterogeneous velocity distribution and the formation of turbulent flow. Compared with the TB system, the FT operation showed a more uniform velocity distribution across the electrode interface, and thus could not form large-scale turbulence in the reactor. Moreover, the flow velocity across the electrode surface in the FT system was obviously higher than that of the TB system, which could meet the requirement of water flux. Therefore, it can be proved that the FT operation was more conducive to enhance the mass transfer performance compared with the TB mode based on the CFD simulation, which was consistent with the CA experiment. Consequently, subsequent electrochemical oxidation experiments were carried out in the FT system.

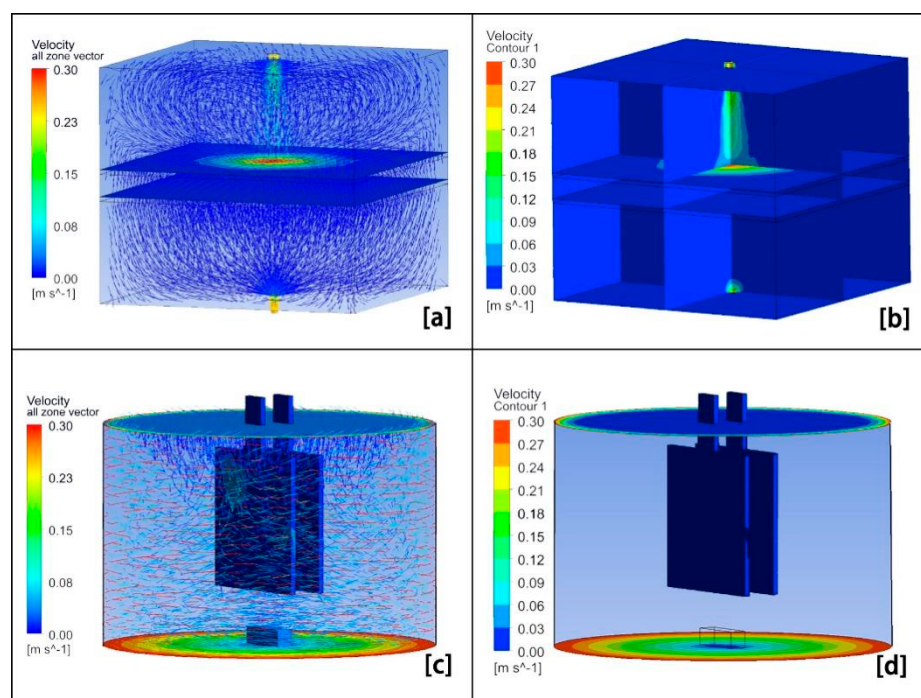


Figure 4. The velocity distribution (a) and turbulence intensity (b) of Ti_4O_7 REM in FT mode; the velocity distribution (c) and turbulence intensity (d) of Ti_4O_7 REM in TB mode.

In each validation test, two points were selected as the research objects. In the FT reactor, the points of the central positions of the anode surface and the cathode surface were selected. And in the TB reactor, the mid-point between cathode and anode and the central position of the anode surface was selected. The simulated and experimental values of the two reactors under different boundary conditions were compared. As shown in Figure S7, the standard deviation between the simulated value and the experimental value was less than 5%, and thus the accuracy of the model was verified.

3.3. Effect of Current Density

Figure 5 shows the effect of current density on the COD removal efficiency of coking wastewater via electrochemical oxidation using the Ti_4O_7 REM. As presented, the COD removal rates showed accelerative trends with the applied current density. The COD removal efficiencies were 60.0%, 66.7%, 75.0%, and 77.6% for the applied current densities of 5, 10, 15, and 20 mA/cm^2 , respectively. However, when the current density was over 15 mA/cm^2 , the COD removal could not be improved significantly by further increasing the current density. This is due to the fact that the mass transfer of organic compounds to the anode surface was limited by the side reaction at higher current densities [28]. As a result, the optimal current density for the electrochemical oxidation of coking wastewater was determined to be at 15 mA/cm^2 .

3.4. Effect of Anode–Cathode Distance

Figure 6 reveals the effect of anode–cathode distance (5 mm, 10 mm, 15 mm, and 20 mm) on the COD removal efficiency. As shown in Figure 6, the COD removal efficiencies were 72.3%, 75.4%, 68.4%, and 65.6% for distances of 5, 10, 15, and 20 mm, respectively. When the anode–cathode distance was smaller than 10 mm, the COD removal efficiency decreased. However, when the distance was greater than 10 mm, the COD removal decreased with the increase in the anode–cathode distance. This may be attributed to the longer diffusion distance which resulted from the larger anode–cathode. However, a very small anode–cathode distance was prone to short circuiting and generated a short-circuit current [29].

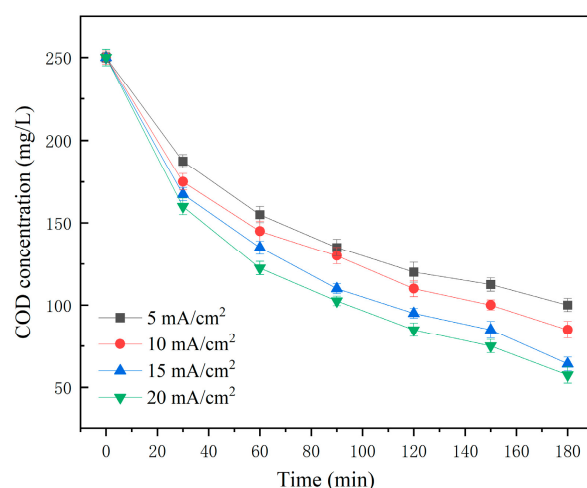


Figure 5. The effect of current density on COD removal.

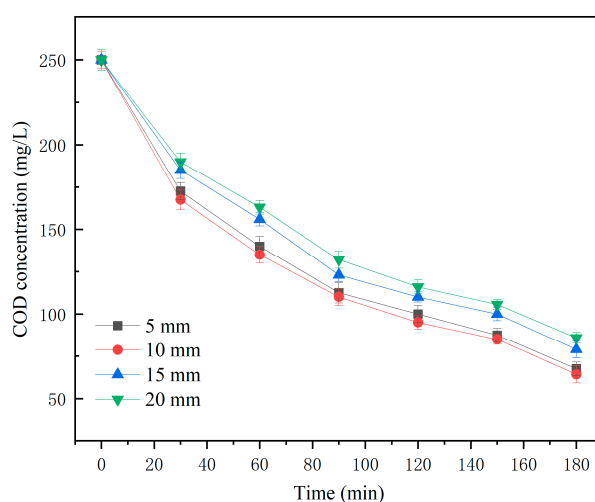


Figure 6. The effect of anode–cathode distance on COD removal.

3.5. Energy Consumption

The energy consumption and current efficiency of the Ti_4O_7 REM in coking wastewater were investigated under an optimal current density of 15 mA/cm^2 and anode–cathode distance of 10 mm. Figure S8 shows the energy consumption and current efficiency as a function of electrolysis times during the electrochemical oxidation process. The energy consumption curve shows a trend of decreasing followed by increasing, while the current efficiency curve indicates an opposite trend of increasing first and then decreasing. At the beginning, the concentration of $\bullet\text{OH}$ generated at the anode surface was too low, so that the organic compounds could not be fully degraded, resulting in high electrode energy consumption. As the electrolysis proceeded, more $\bullet\text{OH}$ was produced, and more pollutants were degraded accordingly, resulting in the improved current efficiency and declined energy consumption of the Ti_4O_7 REM. However, after a period of treatment, the polarization of organic contaminants around the electrode was significant. Moreover, the side reaction and mass transfer limitation made the pollutant degradation weaker, which contributed to the reduced current efficiency and far more energy consumption. After 3 h of electrolysis, the energy consumption for COD removal via Ti_4O_7 anode oxidation would be $110.5 \text{ kWh kg}^{-1}\text{COD}$, which was much higher than that of $\text{Ti/SnO}_2\text{-Sb}$ anode [29], and comparable to that of BDD anode [3,30].

3.6. Electrode Stability and Cathodic Polarization

Previous studies had reported that the activity degradation of Magnéli Ti_4O_7 with long-term application was observed due to the formation of a passivation layer on the electrode surface [31]. Bejan et al. found that anode activity improved when the anode was polarized previously by the cathode during the electrochemical oxidation of p-nitrosodimethylaniline [32]. In this experiment, COD degradation using Ti_4O_7 REMs under cathodic polarization and non-polarization was compared. As shown in Figure 7, the effect of cathodic polarization could be observed when the anode was cathodically polarized for 2 h before each test cycle. Although the Ti_4O_7 REM without cathodic polarization exhibited satisfactory stability, the effect of cathodic polarization resulted in better long-term electrode performance.

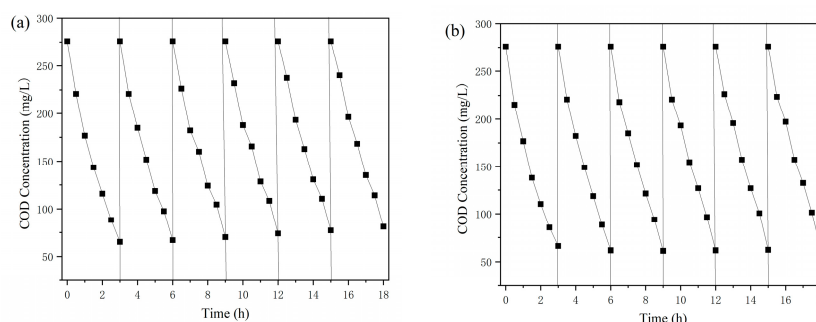


Figure 7. (a) COD degradation for 6 consecutive experiments without cathodic polarization; (b) COD degradation for 6 experiments with cathodic polarization using Ti_4O_7 REM.

The COD removal efficiencies are listed in Table 1. For the Ti_4O_7 REM without cathodic polarization, the COD removal gradually declined from 76.2% to 73.1%. Interestingly, an improvement in anodic reactivity was found in the second cycle with the effect of cathodic polarization, in which the COD removal increased from 76.3% to 77.6%. Although the anodic activity still slightly degraded gradually with the increase in cycling times, the rate of decline was much lower than that without cathode polarization. The results indicated that cathodic polarization could slow down the formation of the surface passivation layer, and thus improve the electrode activity.

Table 1. Comparison of COD removal among cycling experiments with and without cathodic polarization.

Condition	Cycle						
	COD Removal (%)	1	2	3	4	5	6
Without cathodic polarization		76.2	75.8	74.9	73.6	73.4	73.0
With cathodic polarization		76.3	77.6	77.8	77.4	77.1	76.7

3.7. Treatment of Real Wastewater

Figure 8 presents the three-dimensional fluorescence spectra of the coking wastewater before and after treatment. As shown in Figure 8a, the most intense fluorescence center of the coking wastewater was positioned at $\text{Ex}/\text{Em} = 310/400$. Table S1 shows the excitation and emission wavelengths of the peaks of different fluorescent substances [29]. Therefore, the compounds in the coking wastewater were mainly humic acids, which was consistent with the previous study [29]. The fluorescence intensity of the coking wastewater after treatment was greatly reduced (Figure 8b), suggesting that the electrochemical oxidation has a favorable catalytic effect on soluble contaminants in the coking wastewater.

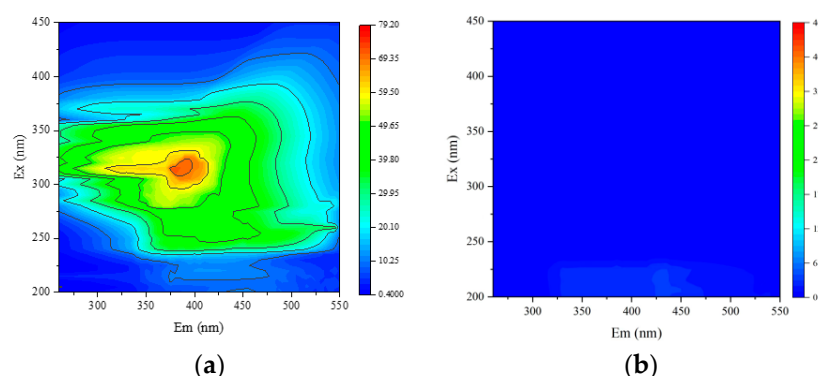


Figure 8. Three-dimensional fluorescence spectra before (a) and after (b) electrolysis.

UV-vis spectroscopy has been widely used to characterize the properties of organic matter in coking wastewater through the identification of peaks and UV parameters. In this work, UV-vis spectra in the wavelength range of 180–500 nm were conducted before and after electrochemical oxidation for 3 h using the Ti_4O_7 REM. As shown in Figure 9, strong absorption peaks at 200–250 nm were found, indicating that single-ring aromatic compounds such as phenol and aniline were present in coking wastewater [33]. Furthermore, the adsorption band in the range of 300–370 nm was formed by polycyclic aromatic hydrocarbons and heterocyclic organic compounds, which suggested that the coking wastewater probably comprises aromatic compounds and heterocyclic substances [29,34]. The peak intensity decreased significantly as the degradation time increased, indicating that organic compounds, including single-ring aromatic compounds, polycyclic aromatic hydrocarbons, and heterocyclic organic compounds, could be degraded during the electrochemical oxidation process.

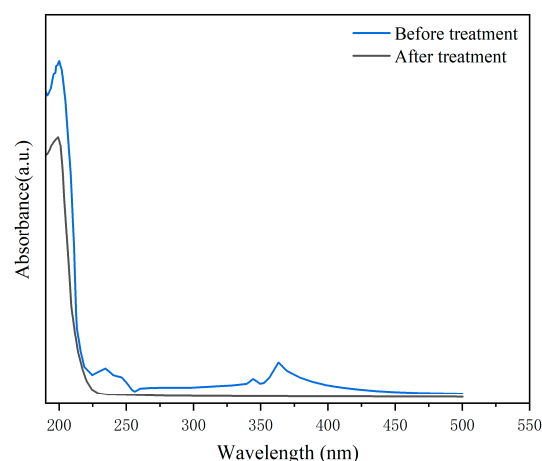


Figure 9. UV-vis spectra of different electrolysis time.

4. Discussion

He et al. [29] reported that the $\text{Ti}/\text{SnO}_2\text{-Sb}$ electrode was utilized for the treatment of coking wastewater. The COD removal efficiency reached 83.05% with an energy consumption of $396.56 \text{ kWh (kg COD)}^{-1}$ under the optimal conditions (current density of 25 mA m^{-2} , Na_2SO_4 concentration of 35 mM, and plate spacing of 10 mm). Obviously, the energy consumption of the $\text{Ti}/\text{SnO}_2\text{-Sb}$ electrode was much higher than that of the Ti_4O_7 REM in our work. It was noted that the initial COD concentration dealt with in the study of He et al. [29] was $230 \pm 20 \text{ mg/L}$, which was similar to that in our study ($250 \pm 20 \text{ mg/L}$), showing major similarity. Wang et al. [3] used the BDD anode to treat coking wastewater with an orthogonal experiment, indicating that the current was the main influencing factor, and the energy consumption for COD removal would be

88.1 kW h kg⁻¹ COD. Less energy consumption might be related to the short electrolysis time and lower initial COD concentration (220 mg/L). These results showed that the Ti₄O₇ REM developed using a plasma spraying method has an advantage of an economical saving in the treatment of coking wastewater.

Chaplin et al. [15] proved that Ebonex electrode exhibited a promising mass transfer performance due to its advection-enhanced mass transfer rate, which was 10-fold higher than those obtained in traditional flow-by mode. Lin et al. [35] estimated the mass transfer rate of porous Ti₄O₇ anode in a batch reactor using the limiting current method. In this work, the mass transfer performance of the Ti₄O₇ REM in two operations was compared using CFD simulation for the first time, suggesting that the FT operation was more conducive to enhance mass transfer due to its uniform flow rate.

5. Conclusions

The Ti₄O₇ REM was successfully prepared using plasma spraying technology, which could effectively be used for the treatment of coking wastewater. The following results were obtained:

1. The surface of the prepared Ti₄O₇ REM was proven to be highly pure and uniform by the characterization of XRD and SEM.
2. CFD simulation was employed to compare the mass transfer performance of the Ti₄O₇ REM in TB mode and FT mode, indicating that the FT operation was more conducive to enhance mass transfer, which correlated well with the CA result.
3. In the FT mode, the effect of current density and anode–cathode distance on the COD removal efficiency was investigated. The results showed that the COD removal efficiencies increased with the applied current density and decreased with the increase in the anode–cathode distance. The COD removal efficiency of the Ti₄O₇ REM could reach 76.2% with an energy consumption of 110.5 kWh kg⁻¹ COD under the optimal condition.
4. The Ti₄O₇ REM exhibited satisfactory stability during cycling experiments. However, the effect of cathodic polarization could result in better long-term electrode performance.
5. According to the three-dimensional fluorescence analysis, the characteristic peak of humic acid in the coking wastewater disappeared, which suggested that the Ti₄O₇ REM had excellent catalytic properties for dissolved organic matters. Based on the UV–vis analysis, the aromatic compounds and heterocyclic organic compounds were significantly degraded.

Thus, the Ti₄O₇ REM electrochemical oxidation process has been proven to be economically favorable and technologically feasible for application in treating coking wastewater. This study provided an insight into a “green” and ecological approach to wastewater treatment.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/su152115488/s1>.

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