

Article

Ti/RuO₂-IrO₂-SnO₂ Anode for Electrochemical Degradation of Pollutants in Pharmaceutical Wastewater: Optimization and Degradation Performances

Guozhen Zhang ^{1,2}, Xingxing Huang ^{1,2}, Jinye Ma ^{1,2}, Fuping Wu ^{1,2} and Tianhong Zhou ^{1,2,*}

¹ Key Laboratory of Yellow River Water Environment in Gansu Province, Lanzhou Jiaotong University, Lanzhou 730070, China; guozhenzhang126@126.com (G.Z.); qianmoxingxing@163.com (X.H.); 18143774108@163.com (J.M.); wfp123@mail.lzjtu.cn (F.W.)

² School of Environmental and Municipal Engineering, Lanzhou Jiaotong University, Lanzhou 730070, China

* Correspondence: zhoutianhong@mail.lzjtu.cn

Abstract: Electrochemical oxidation technology is an effective technique to treat high-concentration wastewater, which can directly oxidize refractory pollutants into simple inorganic compounds such as H₂O and CO₂. In this work, two-dimensionally stable anodes, Ti/RuO₂-IrO₂-SnO₂, have been developed in order to degrade organic pollutants from pharmaceutical wastewater. Characterization by scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDS), and X-ray diffraction (XRD) showed that the oxide coating was successfully fabricated on the Ti plate surface. Electrocatalytic oxidation conditions of high concentration pharmaceutical wastewater was discussed and optimized, and the best results showed that the COD removal rate was 95.92% with the energy consumption was 58.09 kW·h/kgCOD under the electrode distance of 3 cm, current density of 8 mA/cm², initial pH of 2, and air flow of 18 L/min.

Keywords: electrocatalytic oxidation; pharmaceutical wastewater; Ti/RuO₂-IrO₂-SnO₂ anode; COD removal; energy consumption; electrochemistry



Citation: Zhang, G.; Huang, X.; Ma, J.; Wu, F.; Zhou, T. Ti/RuO₂-IrO₂-SnO₂ Anode for Electrochemical Degradation of Pollutants in Pharmaceutical Wastewater: Optimization and Degradation Performances. *Sustainability* **2021**, *13*, 126. <https://dx.doi.org/10.3390/su13010126>

Received: 17 November 2020

Accepted: 21 December 2020

Published: 24 December 2020

Publisher's Note: MDPI stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.



Copyright: © 2020 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

1. Introduction

In the past several decades, pharmaceutical industry has played an important role in social development, but it also produces a lot of environmental pollution. The pharmaceutical industry wastewater is highly complex and contains a large number of toxic and poorly biodegradable compounds. Due to the unique properties of the pharmaceutical industry, it is recognized as one of the difficult high-concentration organic wastewater [1,2]. Traditional treatment methods (such as adsorption, cohesion, filtration, ion exchange, etc.) are not enough to completely purify the mineralized pharmaceutical wastewater, and the post-treatment procedures are too complicated, which limits the application in actual engineering [3,4]. In recent years, many researchers have devoted themselves to the development of advanced oxidation methods to treat wastewater, mainly including chemical oxidation, Fenton oxidation, wet air oxidation, supercritical water oxidation, photochemical oxidation and electrochemical oxidation [5–9]. Among many advanced oxidation methods, electrocatalytic oxidation technology, as the green chemical technology, can degrade complex organic pollutants in wastewater into non-toxic small molecular organic compounds or carbon dioxide and water through mineralization of various organic pollutants [10–15]. A large number of studies have shown that electrocatalytic oxidation technology is one of the effective methods for the treatment of high concentration pharmaceutical wastewater, but the technology is still in the initial stage [16].

In the electrocatalytic oxidation technology, the electrode is the key factor to complete the electrochemical reaction and improve the current efficiency. Different electrode materials can change the electrochemical reaction rate by orders of magnitude. Therefore,

choosing the appropriate electrode material is an effective way to improve the efficiency of the electrochemical reaction. Since the development of the dimensionally stable anodes (DSA) electrode in the 1960s, it has good stability and catalytic activity and quickly gained popularity and has been widely used. The DSA electrode is a kind of metal oxide (such as Ti/SnO₂) coating electrode with excellent electrocatalytic activity. This electrode has the advantages of high oxygen evolution potential, low cost, and easy operation, but also has low stability and short life.

Nowadays, to prolong the electrode life, researchers usually doped noble metal oxides (such as RuO₂ and IrO₂) with strong corrosion resistance and high stability into the titanium substrate anode coating [17,18]. For instance, Jiang et al. used a nanocrystal Ti/IrO₂ coating electrode to degrade TNT red water, the results show that the COD removal rate was 68.5% after 30 h [19]. Zhang et al. utilized the Ti/SnO₂-RuO₂ composite electrode to degrade industrial gallic acid effluent, and the COD removal rate was 76.0% after 6 h [20]. Pathiraja et al. developed the Ti/IrO₂ and Ti/IrO₂-SnO₂ electrodes to degrade chlorpyrifos. The chemical oxygen demand (COD) results revealed that the as-prepared Ti/IrO₂-SnO₂ electrode has 78.2% COD removal efficiency in comparison to 65.1% of COD removal efficiency obtained with Ti/IrO₂ electrode after the electrolysis time of 6 h. Additionally, the instantaneous current efficiency value is always high in Ti/IrO₂-SnO₂ electrode during the period of reaction under similar conditions than the Ti/IrO₂ electrode [21]. Obviously, the doping of noble metal oxides is beneficial to improve the electrochemical performance and the stability and the electrode life.

Hence, in this work, we used the ternary oxide composite Ti/RuO₂-IrO₂-SnO₂ as the anode for electrocatalytic oxidation of pharmaceutical wastewater for the first time. The effects of electrode distance, current density, initial pH, and air-flow on the electrocatalytic degradation performance of organic from pharmaceutical wastewater were systematically investigated. The optimal reaction conditions were determined and the energy consumption of the reaction was investigated. In addition, the SEM, XRD, and EDS techniques are employed to analyze the surface morphology, structure, and composition of Ti/RuO₂-IrO₂-SnO₂ anode before and after the electrocatalytic reaction.

2. Materials and Methods

2.1. Reagent and Materials

All chemicals were purchased commercially and can be used without further purification. Iridium hexahydrate (H₂IrCl₆·6H₂O, AR), Hydrochloric acid (HCl, AR), Sodium hydroxide (NaOH, AR), Oxalic acid (C₂H₂O₄, AR) were purchased from Tianjin Damao Chemical Co., Ltd. (Tianjin, China). Tin (IV) chloride (SnCl₄·5H₂O, AR) was purchased from Shanghai Zhongqin Chemical Reagent Co., Ltd. (Shanghai, China). Ruthenium (III) chloride (RuCl₃·xH₂O, AR), Citric acid (C₆H₈O₇, AR), Ethylene glycol ((CH₂OH)₂, AR) were purchased from Tianjin Yongda Chemical Reagent Co., Ltd. (Tianjin, China). Deionized water with a specific resistance of 18.2 MΩ·cm was obtained by reverse osmosis, by ion-exchange and filtration. Ti plate was obtained from Baoji Changli Special Metal Co., Ltd. (Baoji, China). The pharmaceutical wastewater is taken from the Chinese medicine extraction workshop of Gansu Lanyao Pharmaceutical Co., Ltd. (Lanzhou, China), the composition of pharmaceutical wastewater is shown in Table 1.

Table 1. The composition of pharmaceutical wastewater.

	Compound	Molecular Formula	Concentration	Unit
1	Tetrahydrofuran	C ₄ H ₈ O	303.438	mg/L
2	ethyl acetate	C ₄ H ₈ O ₂	4179.921	mg/L
3	ethanol	C ₂ H ₆ O	18,016.768	mg/L

2.2. Characterization

The surface morphology of the electrodes was observed by SEM (ULTRA plus, Carl Zeiss AG, Jena, German) and quantitative analyze trace element on the electrode surface

by EDS (ULTRA plus, Carl Zeiss AG, Jena, German). Under 30 kw, 60 kV and 60 mA Cu K α ($\lambda = 1.5406 \text{ \AA}$), the phase formation on the electrode was investigated via powder X-ray diffraction (XRD) technology on X'pert pro X-Ray Diffractometer. Diffraction patterns in the 20 to 80° regions were recorded at a rate of 5°/min. Track box furnace (KSL1400X, Kejing, Hefei, China) was used for the sintering of anodic oxide coating. Reactor power supply was provided by DC stabilized power supply (APS3005S-3D, Gratten, Nanjing, China). The pH of raw water was measured by PHS-3C pH meter (Yoke Instrument, Shanghai, China). The content of COD in water samples before and after reaction was measured by UV-vis spectrophotometer (UV-2800, UNICO, Shanghai, China).

2.3. Preparation of the Ti/RuO₂-IrO₂-SnO₂ Electrode

The Ti/RuO₂-IrO₂-SnO₂ electrode was prepared by a simple thermal decomposition method according to the previous literatures [22,23]. Typically, Ti plates with dimensions of 250 × 250 × 2 mm were used as the substrates. The Ti plates was etched in 20% boiling oxalic acid for 2 h, washed with deionized water and stored in ethanol solution. This pre-treatment served to remove the surface oxide layer and improve the coating adhesion of Ti plates. Ruthenium chloride, chloroiridic acid, and tin tetrachloride were used as the precursor materials. Using the Pechini method, the polymeric precursor solution was prepared by mixing citric acid (CA) and ethylene glycol (EG) at 60–70 °C. A certain molar ratio of Ru-Ir-Sn precursor was added to the polymer solution, and it was kept at 60–70 °C for 30 min to dissolve. The obtained precursor solution was evenly coated on both sides of the Ti substrate with a brush, dried at 80 °C for 8 min and then sintered in track box furnace at 300 °C for 10 min. The above steps were repeated until the precursor solution was used up. Finally, the sample was put into track box furnace and annealed at 550 °C for 1 h [24].

2.4. Experimental Device

The experimental reactor consisted of a power supply, Ti/RuO₂-IrO₂-SnO₂ anode, Ti cathode, aerator, and an electrocatalytic cell as shown in Figure 1. The electrocatalytic oxidation cell is made of quartz glass with a size of 250 × 160 × 280 mm. The built-in anode is a self-made Ti/RuO₂-IrO₂-SnO₂ electrode plate. The cathode is a Ti plate purchased from Baoji Changli Special Metal Co., Ltd. The electrodes were connected to power supply to install the reactor. The reactor is an improved parallel structure reactor with a shared-anode and double electrolytic cells, that is, it is composed of one anode plate and two cathode plates. The effective area of the anode plate immersed in solution is 250 × 250 × 2 mm. This device can double the treatment capacity of organic pollutants without increasing the area of the electrolytic cell, and effectively improve the utilization efficiency of the anode plate.

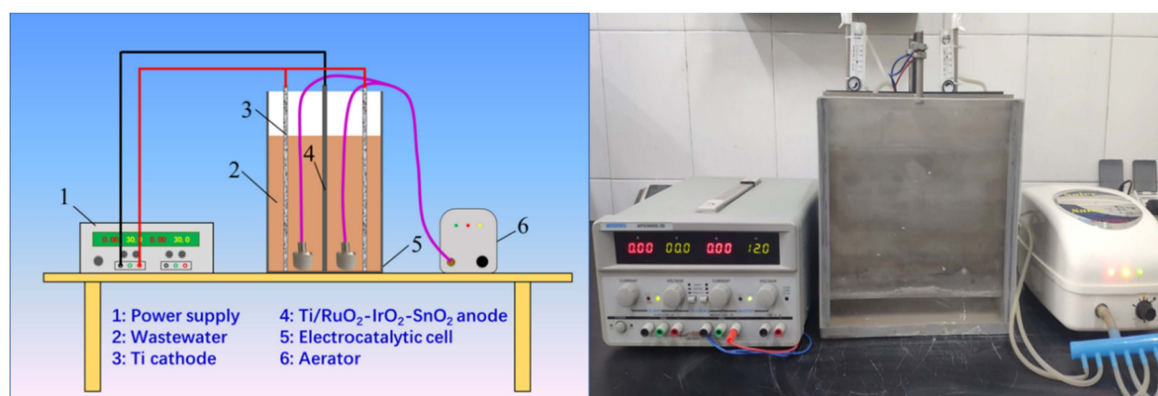


Figure 1. Experimental device.

2.5. Experimental Procedure and Analytical Methods

The COD value in the system was determined by the fast confined catalytic digestion-spectrophotomete. The detection limit of this method for COD is 50~1000 mg/L [25]. The water samples in this experiment were measured after dilution. Generally, experiments were proceeding three times in parallel for each process, and the final data was taking the average values.

The electrocatalytic performance of the reactor was evaluated according to the COD removal rate and energy consumption. Determination of COD using fast closed digestion method. The COD removal rate and energy consumption were calculated using the following formula [26]:

$$\text{COD removal rate (\%)} = (\text{COD}_0 - \text{COD}_1) / \text{COD}_0 \cdot 100 \quad (1)$$

$$\text{Energy consumption (EC)} = U \cdot I \cdot T / (\text{COD}_0 - \text{COD}_1) / V \quad (2)$$

where COD_0 is the COD value of raw pharmaceutical wastewater, mg/L; COD_1 is the COD value of the treated pharmaceutical wastewater, mg/L; U is the reaction voltage, V; I is the reaction current, A; T is the reaction time, h; V is the volume of pharmaceutical wastewater, L.

3. Results and Discussion

3.1. Characterization of the Electrodes

The stability and lifetime of the electrode is a significant factor affecting the capability of the electrocatalytic oxidation reactor. The configuration of surface and constituent elements of electrodes are often served as precise and straightforward indicators for evaluating electrode stability [27]. As shown in Figure 2, the surface morphology of electrode was studied by SEM and EDS. In Figure 2a, the surface of the titanium electrode is generally flat with a few small particles. In Figure 2b, the anode ($\text{Ti}/\text{RuO}_2\text{-IrO}_2\text{-SnO}_2$) was inerratic with many cracks that is representative “cracked clay” characteristic of electrodes produced by thermal decomposition, which may be caused by the high-temperature calcination of the precursor coating of the metal oxide formed on the surface of the Ti plates. The calcination of the electrode surface not only facilitates the formation of oxide coatings, but also increases the electrochemically active surface area [28].

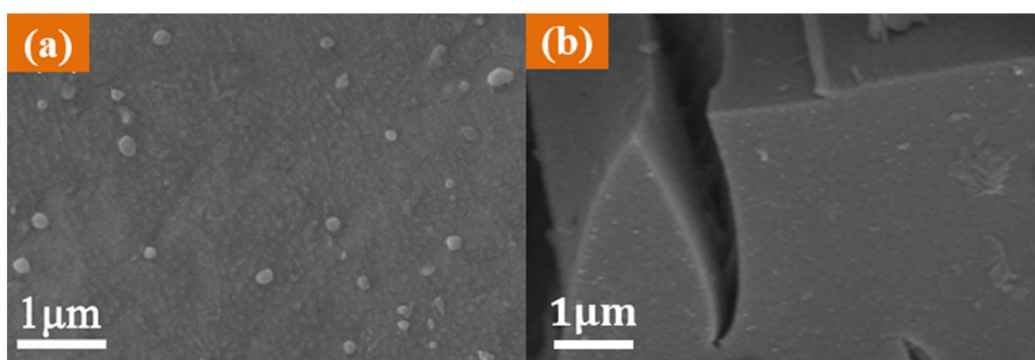


Figure 2. SEM images of (a) Ti and (b) $\text{Ti}/\text{RuO}_2\text{-IrO}_2\text{-SnO}_2$ electrode.

The EDS spectrum of the coating on the $\text{RuO}_2\text{-IrO}_2\text{-SnO}_2$ anode showed that Sn, Ru, Ir, Ti, C and O were on the electrode surface (as shown in Figure 3). This indicated that RuO_2 , IrO_2 , and SnO_2 were successfully coated on the Ti plates. The C signal comes from the presence of adventitious carbon on the electrode surface. The observed titanium signal may be due to the inability of the oxide coating to completely cover the surface of the titanium substrate. In addition, we obtain the percentage of element content on the electrode surface through EDS analysis (as shown in Table 2). The weight percentages of Ti, Ru, Ir and Sn are 27.37, 8.71, 4.56 and 7.47%, respectively. After calculation, it is found that there are 17.16%

of RuO_2 , 0.33% of IrO_2 , and 14.19% SnO_2 on the surface of the Ti plate, respectively. The high concentration of ruthenium oxide is located in the electrode, which not only provides more active sites for electrocatalytic oxidation, but also enhances the stability and life of the electrode.

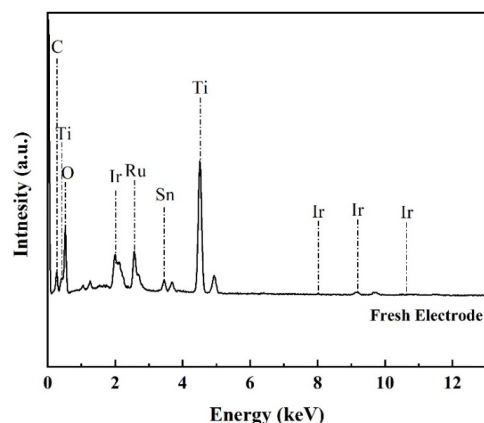


Figure 3. EDS spectra of $\text{Ti/RuO}_2\text{-IrO}_2\text{-SnO}_2$ electrode.

Table 2. Element content of $\text{Ti/RuO}_2\text{-IrO}_2\text{-SnO}_2$ electrode.

Element	C	O	Ti	Ru	Ir	Sn
wt%	9.86	42.03	27.37	8.71	4.56	7.47

Furthermore, the crystal structure and chemical composition of the electrode was also evaluated by the XRD technique, and given in Figure 4. Obviously, the identified phases were RuO_2 (JCPDS: 40-1290), IrO_2 (JCPDS: 15-0870), SnO_2 (JCPDS: 70-4177), Ti (JCPDS: 44-1288) and TiO_2 (JCPDS: 01-1292, 04-0477). Except for the above diffraction peaks, there are no other obvious diffraction peaks in the XRD pattern. For $\text{Ti/RuO}_2\text{-IrO}_2\text{-SnO}_2$ electrode plate, the diffraction angle 2θ is 28.009° , 35.050° , 54.245° , 66.989° corresponding to the (110), (101), (211), (112) crystal planes of RuO_2 , the diffraction angle 2θ is 34.714° , 40.062° , 50.024° corresponding to the (101), (200), (211) crystal planes of IrO_2 , the diffraction angle 2θ is 26.601° , 37.974° , 54.790° corresponding to the (110), (200), (220) crystal planes of SnO_2 . The Ti diffraction angle 2θ is 38.481° , 55.541° , corresponding to crystal planes (110) and (200), the rutile diffraction angle 2θ is 27.506° , 76.082° , corresponding to crystal planes (110) and (202), the anatase diffraction angle 2θ is 68.594° , 70.357° , corresponding to crystal planes (116) and (220). This indicates that there are thin layers of RuO_2 , IrO_2 , SnO_2 and TiO_2 on the electrode.

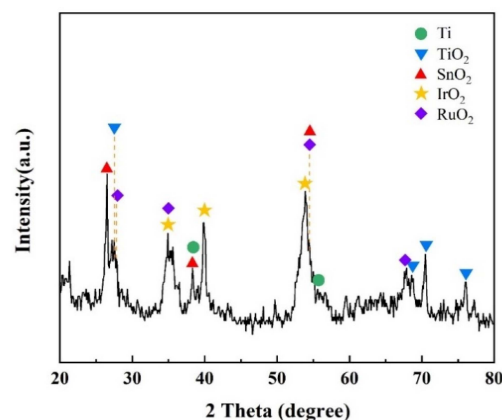


Figure 4. XRD patterns of $\text{Ti/RuO}_2\text{-IrO}_2\text{-SnO}_2$ electrode.

3.2. Performance of Electrocatalytic Reactor

3.2.1. Effect of Electrode Distance

For the electrocatalytic oxidation, it was of interest to investigate the effect of electrode distance. At a current density of 1 mA/cm^2 , air flow of 12 L/min , pH of 7, as shown in Figure 5, When the electrode distance increased from 3 to 5 cm, the COD removal rate dropped by 10.2%. The experimental results indicated that the electrocatalytic performance with a plate spacing of 3 cm higher than a plate spacing of 5 cm. The reason was that when the distance between the plates is 5 cm, the distance between the two plates is too large, and the ion transmission distance between the two plates becomes longer, which increases the mass transfer resistance and weakens the mass transfer effect, thereby resulting in reduced electrochemical reaction efficiency [29,30]. Enhancing the electrode distance requires increasing the battery voltage output to maintain a constant current density. Under high voltage, not only energy consumption increase, but side reactions such as the release of hydrogen and oxygen will occur on the surface of the anode and cathode, which will reduce the efficiency of organic degradation [31,32].

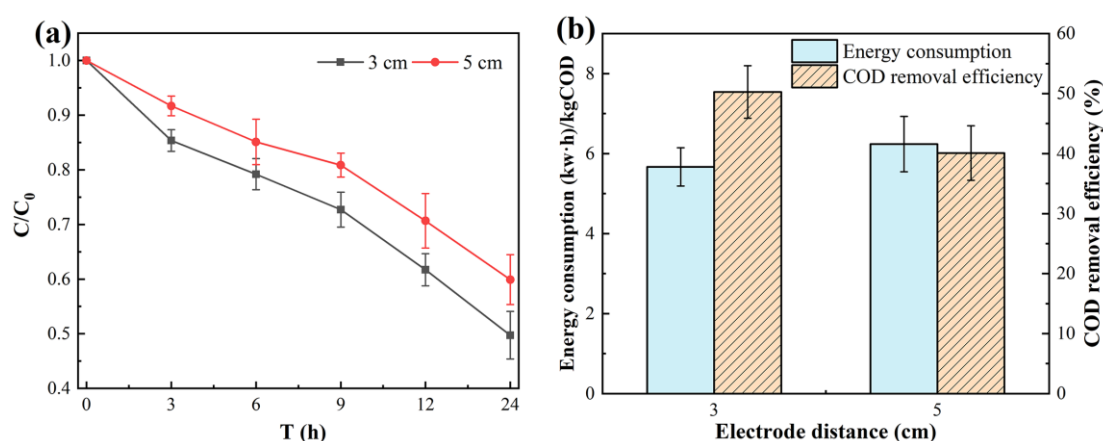


Figure 5. (a) Effect of electrode distance and (b) energy consumption at the current density of 1 mA/cm^2 , air flow of 12 L/min , pH of 7.

In addition, Sun et al. found that the electrocatalytic oxidation performance is significantly reduced, the operating cost is increased with the distance between the anode and cathode decreases (especially less than 3 cm). It may be because the distance between the two electrodes is small, which makes it difficult for the solution between the plates to exchange with the solution outside the plates, which leads to polarization of wastewater concentration. This situation will affect the mass transfer efficiency, resulting in a decrease in the degradation rate [33]. At the same time, when the distance between the electrodes is very close, the surface of the electrode cannot be supplemented with oxygen, resulting in a reduction in the generation efficiency of OH and the degradation efficiency of pollutants. Therefore, the optimal electrode distance is 3 cm.

3.2.2. Effect of Current Density

Current density affects electrocatalytic performance by affecting electron transfer in oxidation reactions, and proper current density is critical for electrocatalytic removal of COD in wastewater. In Figure 6a, the degradation rate of COD increases obviously when the current density gradually increases in the range of $1\text{--}8 \text{ mA/cm}^2$. When the current density was 8 mA/cm^2 , the COD removal rate was 90.52%, with the energy consumption of $81.71(\text{kW}\cdot\text{h})/\text{kg COD}$. As the current density reached 10 mA/cm^2 , the COD removal rate was 90.48%.

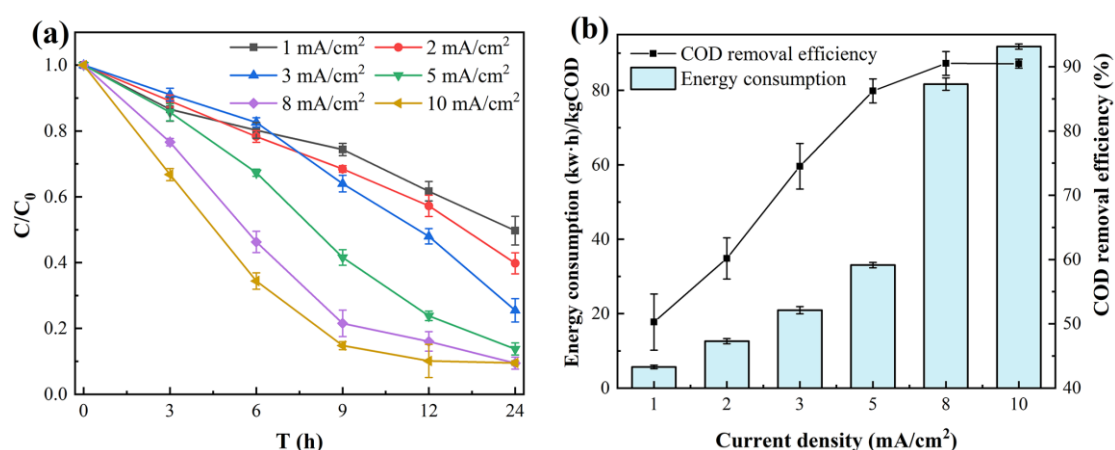


Figure 6. (a) Effect of current density and (b) energy consumption at the electrode distance of 3 cm, air flow of 12 L/min, pH of 7.

The current density has a significant impact on the COD removal effect of the electrocatalytic system, and directly affects the current transmission rate and treatment effect in the electrochemical reaction process. As shown in Figure 6b, in the process of enhancing the current density from 1 to 8 mA/cm², the degradation efficiency showed the simultaneously increasing trend. With the increase in current density, the rate and intensity of charge transfer also increase, thereby promoting the formation of active intermediates and increasing the degradation efficiency of pollutant in wastewater [34,35]. It may be that the side reactions also occur on the electrode surface under too high current density, and the concentration of the active group decreases, thereby reducing the efficiency of reaction electrolysis and increasing energy consumption. At the same time, the tank voltage is too high, the bypass current and short-circuit current increase significantly, the temperature of the wastewater rises, and part of the electrical energy is converted into heat. Therefore, the best current density is 8 mA/cm².

3.2.3. Effect of Air Flow

In general, the degradation efficiency of organic pollutants is affected by the reactive oxygen radicals in the catalytic oxidation reaction system, and the formation of reactive oxygen radicals (e.g., superoxide radical, hydroxyl radical) is related to the oxygen of reaction system, as shown in the Equations (3) and (4) [36,37].



Obviously, a systematic investigation of the oxygen (or air) concentration in the reaction system is of great significance for improving the performance of electrocatalytic oxidation. Figure 7 shows the law of COD removal efficiency and energy consumption in wastewater when the air flow rate is increased from 6 L/min to 30 L/min. With the increase in air flow rate, the removal rate of COD in wastewater is increasing because the concentration of H₂O₂ produced by the system increases. The increase in air velocity increases the dissolved oxygen in the water, increases the cathode efficiency, and produces more H₂O₂, which promotes an increase in the removal rate of wastewater COD. When the rate reaches 18 L/min, the best COD removal rate is 94.06%, and the energy consumption is 74.63 (kW·h)/kgCOD. When the air velocity is higher than 18 L/min, the wastewater COD removal rate does not increase significantly with the increase in the air velocity, indicating that when the air velocity is higher than 18 L/min, the wastewater COD removal rate is mainly controlled by the electrochemical kinetics that produces H₂O₂. In addition, increasing the oxygen/air concentration in the catalytic reaction system promotes the formation of active oxygen species, thereby improving the removal efficiency of COD [38].

Excessively increasing the air flow makes it difficult for the organic pollutants in the wastewater to be effectively adsorbed on the electrode surface and react with active oxygen species, which causes the COD removal rate to gradually decrease [39,40]. The results further imply that the electrocatalytic degradation rate is the largest when the aeration amount is 18 L/min.

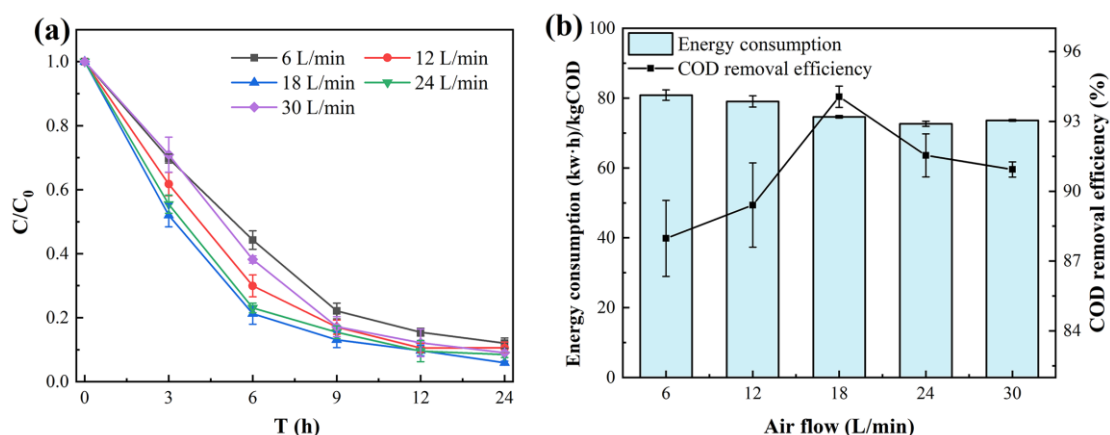


Figure 7. (a) Effect of air flow and (b) energy consumption at the electrode distance of 3 cm, current density of $8 \text{ mA}/\text{cm}^2$, pH of 7.

3.2.4. Effect of Initial pH

The initial pH value in the electrocatalytic reaction determines the reaction process and the direction of the chemical reaction, and the rate of hydrogen peroxide or hydroxyl radical at the cathode is affected by the initial pH (as shown in Figure 8). At electrode distance of 3 cm, the current density of $8 \text{ mA}/\text{cm}^2$, air flow of 18 L/min, the COD removal rate increased with the decreasing pH as shown in Figure 8. The removal rate of COD was 91.45% at pH 7, and the energy consumption was $53.93(\text{kw}\cdot\text{h})/\text{kgCOD}$. In this process, hydroxyl radicals play an important role in the removal of hard-degradable pollutants [41]. Under the dual action of the electric field and the DSA electrode, a large amount of $\cdot\text{OH}$ is generated in the reactor [42,43]. Compared with pH 7, the COD removal rate was 95.92% and the energy consumption was to $58.09(\text{kw}\cdot\text{h})/\text{kgCOD}$ at pH 2. It may be because H_2O_2 is more easily produced in the reaction system at the lower pH ($\text{O}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2\text{O}_2$), thereby further increasing the degradation efficiency [44].

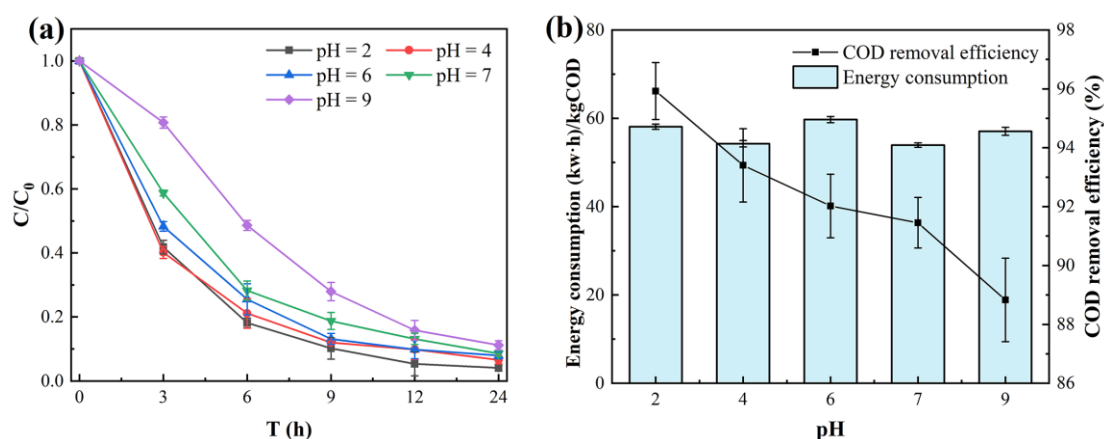


Figure 8. (a) Effect of initial pH and (b) energy consumption at the electrode distance of 3 cm, current density of $8 \text{ mA}/\text{cm}^2$, air flow of 18 L/min.

3.3. Characterization of the Electrode after Reaction

To further demonstrate the Ti/RuO₂-IrO₂-SnO₂ electrode has excellent electrocatalytic ability and stability, we checked the surface morphology of the Ti/RuO₂-IrO₂-SnO₂ electrode after long-term operation by SEM and EDS technology, and the results are given in Figures 9 and 10. On the whole, the surface of the anode and cathode electrodes has undergone significant changes for a long time. For the cathode (Figure 9a), the smoothness of the surface of the Ti plate is reduced, and the surface has a coral-like structure. This may be due to the accumulation of organic molecules during the reaction. For the anode (Figure 9b), the surface smoothness of the Ti/RuO₂-IrO₂-SnO₂ electrode also decreases, and a large number of granular structures are accumulated on the surface and cracks, with a particle diameter of about 300 nm. This may be due to the adsorption of a large amount of particulate organic on the surface of the oxide coating of the anode during the long-term reaction.

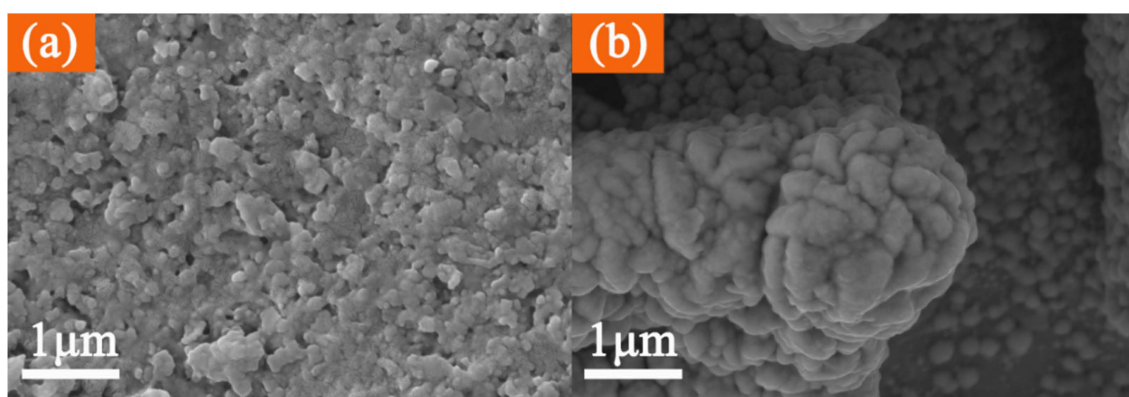


Figure 9. SEM images of (a) Ti plate and (b) Ti/RuO₂-IrO₂-SnO₂ electrode after reaction.

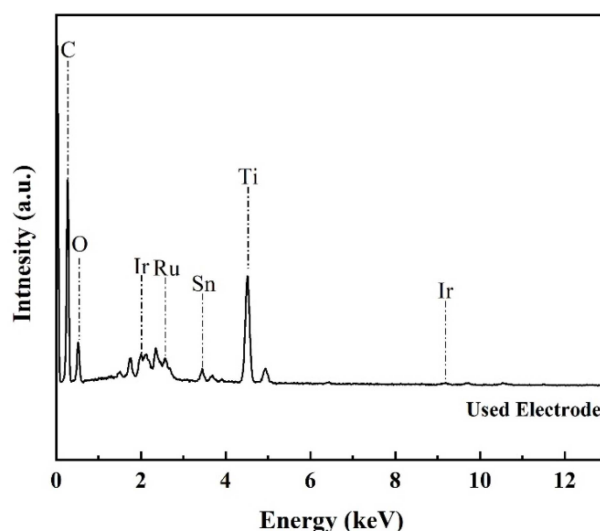


Figure 10. EDS of Ti/RuO₂-IrO₂-SnO₂ electrode after reaction.

To verify this, we conducted EDS analysis for the anode material Ti/RuO₂-IrO₂-SnO₂, and the results are shown in Figure 10. Obviously, Ti, Sn, Ru, Ir and other metal elements still exist on the electrode surface. In addition, compared with fresh electrodes (see Figure 3), the content of C element on the electrode surface greatly increases after a long time of reaction, which is caused by the adsorption of a large number of organic pollutants in the wastewater on the electrode surface. In addition, according to the results of the weight percentage of each element (as shown in Table 3), the carbon content has

increased from 9.86 to 54.85%, which further proves that our inference is reasonable. The above results further suggested that the Ti/RuO₂-IrO₂-SnO₂ electrode exhibited excellent activity and stability for the electrocatalytic oxidation of pharmaceutical wastewater during the long-term reaction.

Table 3. Element content of Ti/RuO₂-IrO₂-SnO₂ electrode after reaction.

Element	C	O	Ti	Ru	Ir	Sn
wt%	54.85	22.65	15.52	1.63	2.75	2.60

4. Conclusions

In summary, we use a simple thermal decomposition method to prepare an oxide coating (RuO₂-IrO₂-SnO₂) on the Ti substrate as an anode material for the electrocatalytic oxidation of pollutants in pharmaceutical wastewater. Experimental results show that the ternary oxide composite coating electrode has an excellent performance in the electrocatalytic oxidation of pharmaceutical wastewater. COD removal efficiency and energy consumption were used as evaluation indexes, and various parameters (such as electrode distance, current density, air flow, and pH) were optimized. The optimal reaction conditions are that the electrode distance is 3 cm, the current density is 8 mA/cm², the air flow rate is 18 L/min, and the pH is 2. Under these conditions for 24 h of operation, the COD removal rate was 95.92%, and the energy consumption was 58.09 kW·h/kgCOD. No other pollutants are generated during the reaction, the pollutant concentration of the effluent is greatly reduced, and there is no secondary pollution. It is an environment-friendly, efficient and stable method for the degradation of organic pollutants in various industrial wastewaters.

But compared with the traditional water treatment technology, the operating cost of the electrocatalytic oxidation method has a certain increase, but with the development of new electrocatalytic materials, the production cost will be greatly reduced. The TiO₂ used in this article also reduces the cost of the electrode plate to a certain extent. This work helps to understand the good oxidative degradation performance of the electrocatalytic oxidation system on high-concentration wastewater, the feasibility of the electrocatalytic oxidation method used in actual industrial wastewater treatment is explored, which provides certain technical support for the practical application of this technology.

Author Contributions: Conceptualization, G.Z.; formal analysis, X.H.; data curation, X.H. and J.M.; writing—original draft preparation, X.H.; writing—review and editing, T.Z.; funding acquisition, F.W. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the National Natural Science Foundation of China, grant number No. 51768031, National Key Research and Development Project, grant number (2019YFD1100103), Tianyou innovation team of Lanzhou Jiaotong University, grant number (TY202005) and the Youth Science Foundation of Lanzhou Jiaotong University, grant number (No. 2019012).

Informed Consent Statement: Informed consent was obtained from all subjects involved in the study.

Data Availability Statement: The data presented in this study are available in [supplementary material].

Acknowledgments: This research was supported by the financial contribution from Key laboratory of Yellow River Water Environment in Gansu Province and School of Environmental and Municipal Engineering of Lanzhou Jiaotong University. This work was supported by the National Natural Science Foundation of China (No. 51768031), National Key Research and Development Project(2019YFD1100103), Tianyou innovation team of Lanzhou Jiaotong University (TY202005), the Youth Science Foundation of Lanzhou Jiaotong University (No. 2019012).

Conflicts of Interest: The authors declare no conflict of interest.

Abbreviations

DSA	Dimensionally Stable Anodes
COD	Chemical Oxygen Demand
EC	Energy Consumption

References

- Lucas, D.; Barcelo, D.; Rodriguezmozaz, S. Removal of pharmaceuticals from wastewater by fungal treatment and reduction of hazard quotients. *Sci. Total Environ.* **2016**, *571*, 909–915. [\[CrossRef\]](#) [\[PubMed\]](#)
- Zhao, F.; Ju, F.; Huang, K.; Mao, Y.; Zhang, X.X.; Ren, H.; Zhang, T. Comprehensive insights into the key components of bacterial assemblages in pharmaceutical wastewater treatment plants. *Sci. Total Environ.* **2019**, *651*, 2148–2215. [\[CrossRef\]](#) [\[PubMed\]](#)
- Zhang, J.F.; Chang, V.W.C.; Giannis, A.; Wang, J.Y. Removal of cytostatic drugs from aquatic environment: A review. *Sci. Total Environ.* **2013**, *445*, 281–298. [\[CrossRef\]](#) [\[PubMed\]](#)
- Wang, X.H.; Lin, A.Y.C. Is the phototransformation of pharmaceuticals a natural purification process that decreases ecological and human health risks? *Environ. Pollut.* **2014**, *186*, 203–215. [\[CrossRef\]](#) [\[PubMed\]](#)
- Sarkar, S.; Bhattacharjee, C.; Sarkar, S. Studies on the performance of annular photo reactor (APR) for pharmaceutical wastewater treatment. *J. Water Process Eng.* **2017**, *19*, 26–34. [\[CrossRef\]](#)
- Mirzaei, A.; Chen, Z.; Haghighat, F.; Yerushalmi, L. Removal of pharmaceuticals from water by homo/heterogenous Fenton-type processes—A review. *Chemosphere* **2017**, *174*, 665–688. [\[CrossRef\]](#)
- Zhan, J.; Li, Z.; Yu, G.; Pan, X.; Wang, J.; Zhu, W.; Han, X.; Wang, Y. Enhanced treatment of pharmaceutical wastewater by combining three-dimensional electrochemical process with ozonation to in situ regenerate granular activated carbon particle electrodes. *Sep. Purif. Technol.* **2019**, *208*, 12–18. [\[CrossRef\]](#)
- Li, L.; Jiang, L.; Yang, L.; Li, J.; Lu, N.; Qu, J. Optimization of Degradation Kinetics towards O-CP in H₃PW₁₂O₄₀/TiO₂ Photoelectrocatalytic System. *Sustainability* **2019**, *11*, 3551. [\[CrossRef\]](#)
- Chinh, V.D.; Broggi, A.; Di Palma, L.; Scarsella, M.; Speranza, G.; Vilardi, G.; Thang, P.N. XPS spectra analysis of Ti²⁺, Ti³⁺ ions and dye photodegradation evaluation of titania-silica mixed oxide nanoparticles. *J. Electron. Mater.* **2018**, *47*, 2215–2224. [\[CrossRef\]](#)
- Meiramkulova, K.; Jakupova, Z.; Orynbekov, D.; Tashenov, E.; Kydyrbekova, A.; Mkilima, T.; Inglezakis, V.J. Evaluation of electrochemical methods for poultry slaughterhouse wastewater treatment. *Sustainability* **2020**, *12*, 5110. [\[CrossRef\]](#)
- An, H.; Zhu, B.; Li, J.; Zhou, J.; Wang, S.; Zhang, S.; Wu, S.; Huang, W. Synthesis and characterization of thermally stable nanotubular TiO₂ and its photocatalytic activity. *J. Phys. Chem. C* **2008**, *112*, 18772–18775. [\[CrossRef\]](#)
- Sohn, Y.S.; Smith, Y.R.; Misra, M.; Subramanian, V. Electrochemically assisted photocatalytic degradation of methyl orange using anodized titanium dioxide nanotubes. *Appl. Catal. B Environ.* **2008**, *84*, 372–378. [\[CrossRef\]](#)
- Kai, H.; Ishibashi, Y.; Mori, T.; Ishibashi, H.; Kawaguchi, I.; Ohwaki, H.; Takemasa, T.; Arizono, K. Decolorization and Estrogenic Activity of Colored Livestock Wastewater after Electrolysis Treatment. *J. Mater. Cycles Waste Manag.* **2010**, *12*, 128–135. [\[CrossRef\]](#)
- Liu, J.; Huang, L.; Li, S.; Feng, Y. Deep treatment efficiency of electrochemical catalytic oxidation for secondary effluent pharmaceutical. *Chin. J. Environ. Eng.* **2016**, *10*, 6269–6274.
- Fang, C.; Megharaj, M.; Naidu, R. Electrochemical advanced oxidation processes (EAOP) to degrade per- and polyfluoroalkyl substances (PFASs). *J. Adv. Oxid. Technol.* **2017**, *20*. [\[CrossRef\]](#)
- Yan, H.; Bai, Z.; Chao, S.; Cui, Q.; Niu, L.; Yang, L.; Qiao, J.; Jiang, K. Effects of additives on palladium nanocrystals supported on multiwalled carbon nanotubes and their electrocatalytic properties toward formic acid oxidation. *Ionics* **2014**, *20*, 259–268. [\[CrossRef\]](#)
- Guerrini, E.; Colombo, A.; Trasatti, S. Surface modification of RuO₂ electrodes by laser irradiation and ion implantation: Evidence of electrocatalytic effects. *J. Chem. Sci.* **2009**, *121*, 639. [\[CrossRef\]](#)
- Nandi, S.; Nair, A.S.; Pathak, B. First principles investigation on the applicability of ruthenium as a potential ORR catalyst. *J. Chem. Sci.* **2020**, *132*, 132. [\[CrossRef\]](#)
- Jiang, N.; Wang, Y.; Zhao, Q.; Ye, Z. Application of Ti/IrO₂ electrode in the electrochemical oxidation of the TNT red water. *Environ. Pollut.* **2020**, *259*, 113801. [\[CrossRef\]](#)
- Zhang, Y.; He, P.; Jia, L.; Zhang, T.; Liu, H.; Wang, S.; Zhou, S. Dimensionally stable Ti/SnO₂-RuO₂ composite electrode based highly efficient electrocatalytic degradation of industrial gallic acid effluent. *Chemosphere* **2019**, *224*, 707–715. [\[CrossRef\]](#)
- Pathiraja, G.C.; Jayatilaka, P.B.; Weerakkody, C.; Karunarathne, P.; Nanayakkara, N. Comparison study of dimensionally stable anodes for degradation of chlorpyrifos in water. *Curr. Sci.* **2014**, *107*, 219–226.
- Aguilar, Z.G.; Coreño, O.; Salazar, M.; Sirés, I.; Brillas, E.; Nava, J.L. Ti | Ir-Sn-Sb oxide anode: Service life and role of the acid sites content during water oxidation to hydroxyl radicals. *J. Electroanal. Chem.* **2018**, *820*, 82–88. [\[CrossRef\]](#)
- Zhang, Y.B.; Ma, Q.Q.; Feng, K.K.; Guo, J.; Wei, X.L.; Shao, Y.Q.; Zhuang, J.H.; Lin, T.S. Effects of microstructure and electrochemical properties of Ti/IrO₂-SnO₂-Ta₂O₅ as anodes on binder-free asymmetric supercapacitors with Ti/RuO₂-NiO as cathodes. *Ceram. Int.* **2020**, *46*, 17640–17650. [\[CrossRef\]](#)
- Xin, Y.L.; Xu, L.K.; Wang, J.; Li, X. Effect of sintering temperature on microstructure and electrocatalytic properties of Ti/IrO₂-Ta₂O₅ Anodes by pechini method. *Rare Met. Mater. Eng.* **2010**, *39*, 1903–1907.

25. National Environmental Protection Agency. *Water and Waste Water Monitoring and Analysis Method*, 4th ed.; China Environmental Press: Beijing, China, 2002.
26. Sun, W.; Ma, B.; Sun, Y.; Zheng, H.; Ma, G. Electrochemical degradation of tetracycline by γ - Al_2O_3 -Bi-(Sn/Sb) three-dimensional particle electrode. *Desalin. Water Treat.* **2017**, *98*, 152–160. [[CrossRef](#)]
27. Mukimin, A.; Vistanty, H.; Zen, N.; Purwanto, A.; Wicaksono, K.A. Performance of bioequalization-electrocatalytic integrated method for pollutants removal of hand-drawn batik wastewater. *J. Water Process Eng.* **2018**, *21*, 77–83. [[CrossRef](#)]
28. Wang, H.; Wang, J.; Bo, G.; Wu, S.; Luo, L. Degradation of pollutants in polluted river water using Ti/IrO₂-Ta₂O₅ coating electrode and evaluation of electrode characteristics. *J. Clean. Prod.* **2020**, *273*, 123019. [[CrossRef](#)]
29. Lv, G.; Wu, D.; Fu, R. Performance of carbon aerogels particle electrodes for the aqueous phase electro-catalytic oxidation of simulated phenol wastewaters. *J. Hazard. Mater.* **2009**, *165*, 961–966. [[CrossRef](#)]
30. Tijani, J.O.; Fatoba, O.O.; Madzivire, G.; Petrik, L.F. A review of combined advanced oxidation technologies for the removal of organic pollutants from water. *Water Air Soil Pollut.* **2014**, *225*, 2102. [[CrossRef](#)]
31. Zhang, C.; Jiang, Y.; Li, Y.; Hu, Z.; Zhou, L.; Zhou, M. Three-dimensional electrochemical process for wastewater treatment: A general review. *Chem. Eng. J.* **2013**, *228*, 455–467. [[CrossRef](#)]
32. Raschitor, A.; Llanos, J.; Canizares, P.; Rodrigo, M.A. (Novel integrated electrodialysis/electro-oxidation process for the efficient degradation of 2, 4-dichlorophenoxyacetic acid. *Chemosphere* **2017**, *182*, 85–89. [[CrossRef](#)] [[PubMed](#)]
33. Sun, Y.; Zhu, S.; Sun, W.; Zheng, H. Degradation of high-chemical oxygen demand concentration pesticide wastewater by 3D electrocatalytic oxidation. *J. Environ. Chem. Eng.* **2019**, *7*, 103276. [[CrossRef](#)]
34. Ventura, A.; Jacquet, G.; Bermond, A.; Camel, V. Electrochemical generation of the Fenton's reagent: Application to atrazine degradation. *Water Res.* **2002**, *36*, 3517–3522. [[CrossRef](#)]
35. Pangarkar, B.L.; Deshmukh, S.K.; Thorat, P.V. Multi-effect air gap membrane distillation process for pesticide wastewater treatment. *Membr. Water Treat.* **2017**, *8*, 529–541.
36. Weisz, A.D.; Rodenas, L.G.; Morando, P.J.; Regazzoni, A.E.; Blesa, M.A. FTIR study of the adsorption of single pollutants and mixtures of pollutants onto titanium dioxide in water: Oxalic and salicylic acids. *Catal. Today* **2002**, *76*, 103–112. [[CrossRef](#)]
37. Bi, Q. Investigation on Preparation and Properties of Electrode Materials for Electrochemical Oxidation of Organic Wastewater. Ph.D. Thesis, Xi'an University of Architecture and Technology, Xi'an, China, 2014.
38. Wu, X.; Yang, X.; Wu, D.; Fu, R. Feasibility study of using carbon aerogel as particle electrodes for decoloration of RBRX dye solution in a three-dimensional electrode reactor. *Chem. Eng. J.* **2008**, *138*, 47–54. [[CrossRef](#)]
39. Xiong, Y.; He, C.; Karlsson, H.T.; Zhu, X. Performance of three-phase three-dimensional electrode reactor for the reduction of COD in simulated wastewater-containing phenol. *Chemosphere* **2003**, *50*, 131–136. [[CrossRef](#)]
40. Yan, L.; Ma, H.; Wang, B.; Wang, Y.; Chen, Y. Electrochemical treatment of petroleum refinery wastewater with three-dimensional multi-phase electrode. *Desalination* **2011**, *276*, 397–402. [[CrossRef](#)]
41. Horáková, M.; Klementová, Š.; Kříž, P.; Balakrishna, S.K.; Špatenka, P.; Golovko, O.; Hájková, P.; Exnar, P. The synergistic effect of advanced oxidation processes to eliminate resistant chemical compounds. *Surf. Coat. Technol.* **2014**, *241*, 154–158. [[CrossRef](#)]
42. Feng, Y.J.; Li, X.Y. Electro-catalytic oxidation of phenol on several metal-oxide electrodes in aqueous solution. *Water Res.* **2003**, *37*, 2399–2407. [[CrossRef](#)]
43. García-Mancha, N.; Monsalvo, V.M.; Puyol, D.; Rodriguez, J.J.; Mohedano, A.F. Enhanced anaerobic degradability of highly polluted pesticides-bearing wastewater under thermophilic conditions. *J. Hazard. Mater.* **2017**, *339*, 320–329. [[CrossRef](#)] [[PubMed](#)]
44. Vuorilehto, K.; Tamminen, A. Application of a solid ion-exchange electrolyte in three-dimensional electrodes. *J. Appl. Electrochem.* **1997**, *27*, 749–755. [[CrossRef](#)]