Recent developments and advances in Ti/TiO$_2$-NTs/PbO$_2$ electrodes: A general Review of their controllable preparation and application in wastewater treatment

FuQiang Wei, Chao Hu, Bo Wang, JiaQi Ju, HeYing Chen, Ying Wang
College of Ocean Science and Engineering, Shanghai Maritime University, Shanghai 201306, China.

ABSTRACT

Ti/TiO$_2$-NTs(nanotubes)/PbO$_2$ is a new composite electrode material, which has been considered as an optimal electrode material for electrochemical oxidation of organic contaminants in the aquatic environment due to its good physical and chemical properties, such as good electrocatalytic activity, high oxygen evolution potential, corrosion resistance, good stability, environmental friendliness and simple preparation. The fundamental research and practical application of Ti/TiO$_2$-NTs(nanotubes)/PbO$_2$ electrodes in the mineralization of organic pollutants have been well developed up to now. So this paper mainly reviews the preparation methods of Ti/TiO$_2$-NTs/PbO$_2$ electrodes and the structural characterization methods of electrode materials first. And then, the basic principle of electrocatalytic oxidation will be introduced in detail and the application of this electrodes in water treatment is going to be summarized systematically. Further, we also proposed the existing problems in recent research and the potential development direction of electrocatalytic water treatment technology in the future, which could provide reference for the follow-up research.

Key words: PbO$_2$; Ti/TiO$_2$-NTs electrodes; Electrochemical oxidation; Wastewater treatment
1. Introduction

With the rapid development of modern economy and society, and the rise of petrochemical industry and pharmaceutical industry, refractory substances in industrial wastewater are increasing day by day. A large number of chemical substances are used and discharged into the natural environment\(^1\). The organic wastewater produced by people in daily life is also excessively discharged into the natural water body, resulting in the eutrophication of water body and other hazards. For these wastewater, although the traditional treatment methods have certain treatment effect, but for printing and dyeing, leather, paper and other wastewater containing high concentration, high toxicity and strong stability of organic pollutants, the limitations of these methods will be highlighted\(^2\). In addition, the traditional treatment method will produce a large number of harmful sludge, easy to cause secondary pollution. Therefore, it is difficult for traditional water treatment methods to meet the requirements of environmental protection\(^3\). In recent years, electrocatalytic technology has attracted the continuous attention of scholars at home and abroad for its effective treatment of refractory organic wastewater. Electrocatalysis technology can be carried out under normal temperature and pressure, and can easily control the reaction direction and rate effectively by changing the electric field at the solid-liquid interface\(^4\). The core of electrocatalysis technology lies in electrode materials. In electrocatalytic technology, the main reaction of pollutant degradation occurs in the anode region, which directly affects the degradation efficiency and mineralization degree of organic pollutants\(^5\). Currently, a wide variety of electrodes are applied in electrocatalytic oxidation technology, such as titanium electrode, graphite electrode, platinum electrode, RuO\(_2\) electrode, glassy carbon electrode, PbO\(_2\) electrode and BDD electrode, etc.\(^6\). As a typical representative of electrode materials, Ti matrix metal oxide electrode has been widely used in electrocatalytic water treatment due to its excellent characteristics. At present, there are many literatures on Ti matrix metal oxide electrode at home and abroad, among which PbO\(_2\) has been paid more attention and applied in the field of electrocatalytic water treatment due to its high oxygen evolution potential, strong oxidation capacity, good corrosion resistance and relatively low price, etc.\(^7\)-\(^9\). However, practical application shows that PbO\(_2\) electrode still has some problems: the coating adhesion is low, easy to fall off, the service life is unstable in the electrolysis process, and the catalytic performance of the electrode material is lower than that of Sb-SnO\(_2\) and BDD electrode, etc.\(^10\)-\(^15\) Therefore, finding anode materials with good stability and high catalytic performance is the key to popularize electrochemical water treatment\(^10\)-\(^15\). How to prepare TiO\(_2\) modified nanometer electrode materials with excellent properties has become one of the active topics in the current material research, so it is of great scientific significance to conduct technical modification of titanium matrix to further improve the stability and catalysis of such electrodes\(^16\). A new composite material Ti/TiO\(_2\)-NTs /PbO\(_2\) was prepared by relevant researchers. This material formed a highly ordered layer of titanium dioxide nanotubes (TiO\(_2\)-NTs) with large specific surface area on the surface of titanium matrix, which enabled PbO\(_2\) to be well supported on the titanium matrix, improved its electrocatalytic capacity and greatly improved the degradation rate of organic matters. Based on the latest research work at home and abroad and the latest research progress, the author will elaborate on the preparation method of Ti/ TiO\(_2\)-NTs /PbO\(_2\) electrodes and the structural characterization methods of electrode materials. At the same time, the basic principle of electrocatalytic oxidation is introduced in detail and the application of this electrode in water treatment is summarized systematically.

2. Preparation and properties of Ti/TiO\(_2\)-NTs /PbO\(_2\)

Preparation of Ti/ TiO\(_2\)-NTs /PbO\(_2\) electrode this paper mainly introduces the step-by-step prep-
aration process, namely the preparation of TiO$_2$-NTs intermediate layer and the preparation of Ti/ TiO$_2$-NTs /PbO$_2$ surface layer.

2.1 Preparation of TiO$_2$-NTs intermediate layer

TiO$_2$ nanomaterials, as a new type of inorganic semiconductor material, have good electronic conductivity\[^{17-19}\], especially tubular nano titanium dioxide, which has attracted more and more attention due to its controllable size and highly ordered characteristics. At present, the preparation methods of TiO$_2$ nanotubes mainly include template synthesis, anodic oxidation and hydrothermal synthesis\[^{20}\].

2.1.1 Hydrothermal synthesis

Since Kasuga et al.\[^{21}\] introduced the hydrothermal synthesis to prepare TiO$_2$ nanotubes, this method has been widely used. The preparation of TiO$_2$ nanotubes by this method is based on the principle that TiO$_2$ powder is used as titanium source in a high-pressure reaction kettle to conduct chemical reaction with concentrated alkali solution. Meanwhile, it is kept stirring at high temperature and taken out at room temperature after natural cooling. After pickling, washing and drying, TiO$_2$ nanotubes are obtained\[^{22}\]. Obviously, when TiO$_2$ nanotube array is prepared by hydrothermal synthesis, reaction time and temperature have very important influences on the morphology, structure and performance of nanotube array\[^{23}\].

Liu et al.\[^{24}\] prepared TiO$_2$ nanoarray on FTO substrate by simple hydrothermal synthesis. The results showed that with the increase of hydrothermal reaction temperature between 150-\(^{\circ}\)C and 180\(^{\circ}\)C, the radial growth of nanotubes accelerated, and the surface density and voids of the whole array of nanotubes decreased. With the increase of hydrothermal reaction time, the nanotubes grow along the axial direction and the radial width is basically unchanged. Deng et al.\[^{25}\] synthesized anatase TiO$_2$ nano powder by hydrothermal synthesis with TiCl$_4$ as titanium source and NH$_3$·H$_2$O as pH value regulator. Zhang\[^{26}\] successfully prepared TiO$_2$ nanotubes with exposed \{001\} crystal surface by hydrothermal synthesis using tetrabutyl titanate, KF, concentrated sulfuric acid and anhydrous ethanol as raw materials. Lv et al.\[^{27}\] took TiCl$_4$ as the titanium source, extended the reaction time to 30h, and prepared highly oriented ultra-long diamond TiO$_2$ nanotube array by one-step hydrothermal synthesis, with a film thickness of up to 30 microns. As the preparation time of the traditional hydrothermal synthesis varies from a few hours to more than a few days after heating by oven, the application of this method in photoelectric catalysis is limited\[^{28}\]. In order to shorten the reaction time, Yang et al.\[^{29}\] adopted microwave-assisted hydrothermal synthesis, which can speed up the heating rate in the crystallization process and provide higher reaction kinetics, and accelerate the formation of nanotubes, reducing the reaction time to 1-2h.

2.1.2 Template synthesis

The template synthesis method firstly prepares the template whose structure characteristics and size meet the requirements of TiO$_2$ nanotube formation, and then deposits TiO$_2$ onto the template. Finally, according to the properties of the template, the template is removed by calcining, acid or alkali dissolution, etc. to form the nanotube array. At present, the templates used to prepare TiO$_2$ nanotube array by template synthesis mainly include polymer templates, porous anodic alumina templates\[^{30}\], metal templates, etc. Porous alumina templates have been widely used in the market due to their good properties such as uniform and neat distribution of deposition holes on the surface and electrochemical regulation of hole diameter and film thickness. Hoyer\[^{31}\] deposited amorphous TiO$_2$ on a single crystal anodized alumina (AAO) template under nitrogen protection and applied voltage of 400mV, removed the template and dehydrated at high temperature to obtain anatase TiO$_2$ nanotube. Zhang\[^{32}\] used AAO template to prepare large area of homogeneous and orderly TiO$_2$ nanotubes by direct current deposition method, and controlled reaction conditions, it was found that the array morphology and structure of the prepared nanotubes annealed at different temperatures all changed. Therefore, the temperature has a great influ-
ence on the formation of TiO$_2$ nanotubes. Nguyen et al.[33] used P123 as a soft template to form a water-based self-packaging system and prepared a series of anatase and diamond dual-crystal TiO$_2$ with a high specific surface area, providing a new basis for preparing mesoporous TiO$_2$ with adjustable dual-crystal structure from peroxytitanic acid by soft template method. Because the catalytic activity of one-dimensional and two-dimensional nanomaterials tends to weaken when organic pollution is degraded, Li[34] prepared three-dimensional TiO$_2$ nanotubes on ZnO template with TiO$_2$(P25) and NaOH as raw materials. The results showed that the degradation rate of methylene blue could reach 98%, showing strong catalytic performance. The template method is simple to prepare, but its disadvantage is that the morphology of the generated nanotubes depends on the template pores used. In addition, during the separation process of the template and nanotubes, the morphology of the nanotubes may be easily destroyed due to operation or other reasons, so the reproducibility is relatively poor.

2.1.3 Anodic Oxidation

Anodic oxidation process is after pretreatment of the anode materials (mostly titanium plate), add fluoride ion electrolyte, with Pt and Cu, graphite, the material such as stainless steel as cathode, the anode oxidation corrosion orderly system of titanium dioxide nanotube structure, is one of the main methods in the preparation of TiO$_2$ nanotube arrays[23]. Liu[35] prepared TiO$_2$/Ti by anodic degradation method and studied the kinetics and degradation mechanism of OG degraded by photoelectric oxidation. Wang[36] used anodic oxidation method to prepare TiO$_2$ nanotube by using titanium plate as anode and red copper plate as cathode and using constant voltage dc power supply to provide applied voltage. It was found that the diameter of nanotube was affected by voltage. Liu et al.[37] studied the influence of anodic oxidation preparation process on the formation of TiO$_2$ nanotubes, and the study showed that the nanotubes obtained at different voltages have the characteristics of bamboo structure. The results show that there is a good linear relationship between the oxidation voltage and the average diameter of nanotubes. In addition, oxidation time, electrolyte solution composition, temperature and other experimental conditions have certain effects on the morphology, length and diameter of TiO$_2$ nanotubes, which are also research hotspots in recent years[23]. The research results of Zou[38] showed that the critical anodic oxidation time of the nanotube array was 5min, and the length of the nanotube increased with the extension of the oxidation time. When the oxidation time increased to 2h, the nanotube did not increase. Du[39] compared the effects of three electrolytic liquid systems on the morphology of nanotube arrays, and the results showed that nanotube arrays with different aspect ratios were prepared by three different electrolytic liquid systems. According to previous research results, a highly ordered and uniform TiO$_2$ nanotube array can be obtained in an organic system. Li et al.[40] studied the effect of temperature on the nanotube array and found that temperature mainly affected the growth rate of TiO$_2$ nanotube, and the length of nanotube increased rapidly with the increase of temperature. On the other hand, temperature has a great impact on the surface morphology of the array. It can be found that when the temperature is 0°C, the nanopores on the top of the nanotube are uniform and orderly without any impurities, but the surface impurities increase with the increase of temperature, which are mainly caused by the tearing of the top nanotube under the action of electric field[41]. Studies have shown that most studies[42] used primary anodizing method to prepare TiO$_2$ nanotubes by anodizing. In this way, although nanotube arrays can be obtained, the regularity of nanotubes is not very good. So Lin[43] number of anodic oxidation of nanotube arrays is studied, the influence of willow embankment[37], Xiao[44] and Xie[45] secondary anodic oxidation was studied and an anodic oxidation preparation of TiO$_2$ nanotubes, and the results show that an anodic oxidation was prepared by TiO$_2$ nanotube arrays to relatively uneven surface, has the floc, and improved secondary anodic oxidation method can produce surface level off.
the orderliness of TiO$_2$ nanotube arrays, and showed higher catalytic efficiency.$^{[43-45]}$

2.2 Preparation of Ti/ TiO$_2$-NTs/PbO$_2$ surface layer

The Ti/TiO$_2$-NTs/PbO$_2$ electrode material is a novel composite material for surface modification of titanium matrix. The purpose is to load the nanoparticles PbO$_2$ onto the surface of a titanium substrate having TiO$_2$ nanotubes. This not only solves the problems of poor mechanical strength, brittleness and easy detachment of PbO$_2$ electrode, but also has a large specific surface area, a large number of active sites and a strong directional electron transport capability, and its special structure makes TiO$_2$-NT have photoelectrocatalytic oxidation. Strong ability to degrade organic pollutants.$^{[46]}$. Among them, Duan et al.$^{[47]}$ showed that TiO$_2$-NTs improved the catalytic activity of PbO$_2$ electrode. P-NP is better than PbO$_2$/SnO$_2$-Sb$_2$O$_3$/Ti on PbO$_2$/TiO$_2$-NTs/Ti electrode surface. The surface of the electrode is more prone to oxidation. After degradation by electrocatalytic oxidation for 120 min, the degradation rate of p-NP can reach 97.8%, which is obviously higher than the degradation rate of PbO$_2$/SnO$_2$-Sb$_2$O$_3$/Ti electrode is 87.6%. Therefore, PbO$_2$/TiO$_2$-NTs/Ti electrode materials have great research significance in water treatment. At present, there are many researches on the modification of titanium dioxide at home and abroad, but the research methods of PbO$_2$ loaded Ti/TiO$_2$-NTs electrode have not been uniformly discussed. The author will do the preparation method of PbO$_2$ loaded Ti/TiO$_2$-NTs electrode. A more detailed summary.

2.2.1 Spin coating method$^{[48-49]}$

Also known as thermal decomposition. Firstly, Ti/ TiO$_2$-NTs substrate needs to be polished and corroded, etc., and then the intermediate layer is uniformly coated with Pb(NO$_3$)$_2$ aqueous solution, which is then dried in an oven at 120 °C for 20 min, and then transferred to a muffle furnace at 500 °C for 20 min. After repeated sample feeding, the electrode material of PbO$_2$ active layer is prepared. Liu et al.$^{[50]}$ coated saturated Pb(NO$_3$)$_2$ solution containing N-butanol after substrate pretreatment, and then put it into an oven with a temperature set at 80 °C and kept the reaction until 10 min. After that, the temperature was set to 500°C for thermal decomposition for 10 min. Studies have shown that the electrode prepared by spinning coating method has good electro-catalytic performance, and a large amount of OH• will be produced in the process of degrading the target pollutant phenol, and the cell voltage is significantly reduced in the experiment.

2.2.2 Compression Molding$^{[51]}$

Compression molding is prepared by mixing PbO$_2$ powder with inert binder under high pressure. Cao et al.$^{[52]}$ mixed a small amount of FDPF-1 organic adhesive into the prepared β-PbO$_2$ powder, and shaped the mixed powder tablet under the pressure of 20MPa. The degradation of nitrobenzene and alizarin red wastewater by electrocatalytic degradation of the obtained electrode plates was found to be the best for the β-PbO$_2$ electrode prepared by Compression molding, and the problem of coating shedding was completely solved, and it had good corrosion resistance. Relaxation, etc.$^{[53]}$ doped lanthanum and activated carbon prepared by high compression slice method and polytetrafluoroethylene (PTFE), a new type of lead dioxide electrode, and its catalytic organic dyes wastewater treatment was studied, the study found that high molding method of electrode corrosion resistance is strong, high degradation rate of methylene blue, compared with ordinary method of lead dioxide electrode, the dye with good decolorization and removal of COD has obvious advantages, at the same time, the research shows that the electrode in electrolysis chlorine organic wastewater has good application prospect.

2.2.3 Electrodeposition method

The selected substrate is the anode, and materials such as stainless steel or titanium plate are used as the cathode. Under the action of direct current, Pb ions in the electrolyte are oxidized or reduced by gaining and losing elec-
trons, and PbO₂ nanoparticles or thin films are precipitated on the anode. Yang\[54\] prepared high-performance PbO₂-TiO₂ nanocomposite electrode under the condition of pulse electrodeposition with pulse frequency of 10 Hz, deposition current density of 0.05 A/cm² and duty cycle ratio of 0.2. Li\[55\], Wang\[56\], Yao\[57\] such as high-performance titanium base prepared by electrodeposition method respectively lead dioxide electrode, Li\[56\] and nodules in the actual preparation of production in large surface roughness, catalytic activity and stability improvement, the first screening of Mn²⁺ and Ni²⁺, Al³⁺ three kinds of ions on the doping modification of catalytic oxidation of phenol waste water action to improve the performance of the electrode. Pr-PbO₂ was deposited into TiO₂-NTs by pulsed electrodeposition method\[58\] to prepare Pr-PbO₂/TiO₂-NTs/Ti electrode. The electrocatalytic degradation of methylene blue showed that the electrode had good electrocatalytic ability, and the degradation rate of methylene blue reached 98% in 120 min. Similarly, Chen \[59\] also doped CeO₂ and Ce(NO₃)₂ in the electrolyte to improve the catalytic performance of Ti/ PbO₂-TiO₂ anode. The results showed that the electrocatalytic activity of Ti/ PbO₂-TiO₂ plus CeO₂ electrode was good, and its electrolytic life also increased. According to the latest research trends, the doping of some oxides or ionic elements on Ti/PbO₂-TiO₂ matrix can greatly improve the photoelectric catalytic performance of the electrode, which plays a good role in promoting the application of this kind of electrode in the actual electrocatalytic water treatment technology and widens its application scope. Therefore, doping on Ti/PbO₂-TiO₂ matrix is a research hotspot at present. Sahar Boukhchina\[60\] obtained Ti/ TiO₂-NTs /PbO₂ electrode with electrolyte of 0.5M Pb(NO₃)₂, 0.5 M HNO₃ and 0.04M NaF by using a three-electrode system, and used to treat pharmaceutical pollutants. Wang et al. \[61\] also prepared Ti/ TiO₂-NTs electrode by anodic oxidation method, and prepared Ti/ TiO₂-NTs electrode by pulse electrodeposition method and direct current electrodeposition method respectively. After comparing the degradation ability of methylene blue, it was found that the degradation rate of methylene blue obtained by pulse electrodeposition method was higher than that obtained by direct current electrodeposition method. This is the same as the research results of Wang\[62\], indicating that the catalytic performance of PbO₂ loaded on the substrate by pulse electrodeposition is better than that by direct current electrodeposition.

3. Technology for morphology and electrochemical analysis of Ti/TiO₂-NTs/PbO₂ electrodes

3.1 Morphology and structure characterization method

Electrocatalytic reactions are heterogeneous reactions that occur between two phases (solid and liquid). Therefore, the surface morphology and structure of the electrode, as well as the crystallization, will have a significant impact on the electrocatalytic reactions. The same electrocatalytic reaction will have different reaction results in different electrode materials, and the degradation ability of organic compounds will also be reflected differently. Therefore, it is very important to study the internal relationship between the structure of electrode materials and electrocatalytic mechanism. Therefore, the author will mainly introduce several common methods to study the characterization of electrode morphology, composition and structure.

(1) Scanning electron microscopy (SEM) The principle of SEM is to use electron microscope to scan the thin electron beam on the surface of the sample, and then enlarge the image according to the principle of television, and then the surface morphology of the detected electrode materials can be clearly seen on the screen.

(2) Transmission electron microscope (TEM) TEM is different from SEM in that it projects a beam of accelerated and concentrated electrons onto a sample. The electrons collide with the atoms in the sample and change direction, resulting in solid angular scattering. The result-

AJBAS: https://escipub.com/american-journal-of-basic-and-applied-sciences/
ting light and dark images are then aggregated and displayed on the imaging device. Thus, the internal structure of the electrode material can be seen by TEM.

(3) X-ray diffraction (XRD) By conducting X-ray diffraction on electrode materials and analyzing their diffraction patterns, the research means to obtain the information of the composition of the material and the structure or morphology of atoms or molecules inside the material. XRD can be used to analyze and identify the phase of the electrode coating, and the grain size can be estimated according to Scherrer formula.

(4) X-ray photoelectron spectroscopy (XPS) XPS is one of the most advanced and useful techniques for the characterization of electrode materials. The principle is to use X-ray radiation sample, so that atoms or molecules of inner or valence electrons excited out. XPS can provide elemental analysis of electrode surface, as well as qualitative and quantitative information of element oxidation state in surface compounds.

3.2 Electrochemical analysis method
The electrochemical analysis method can analyze the intrinsic relationship between the electrocatalytic activity and the structure of the electrode and provide convincing basic data for the study of electrocatalytic mechanism. Electrochemical analysis methods are often performed at electrochemical workstations in three-electrode systems.

(1) cyclic voltammetry (CV) is a common electrochemical analysis method. The method is to control the motor potential at different rates, with time to the triangular waveform once or repeatedly scanning. The obtained current-potential curves can be used to determine the range of oxidation potential and reduction potential in the motor reaction, as well as the reversibility of the motor reaction, the possibility of intermediates, phase boundary adsorption or new phase formation.

(2) linear polarization curve method (LSV) the so-called polarization phenomenon refers to a state of deviation from equilibrium. The electrochemical polarization of the electrode is the electrode polarization phenomenon caused by the slowest electrochemical reaction step reflecting the loss of electrons on the surface of the electrode The polarization curve shows the relationship between electrode potential and polarization current or polarization current density. It can react electrode material oxygen evolution potential, oxygen evolution potential is high, electrode material electrocatalytic performance is good, and vice versa.

(3) electrochemical impedance spectra of the electrode system can be obtained by a set of frequency response function values measured by alternating current impedance method (EIS) at a series of different angular frequencies. According to the measured EIS spectra, can determine the equivalent circuit or EIS mathematical model, which can analyze the dynamic process and mechanism of the electrode system contains the equivalent circuit can estimate the dynamic parameters of the motor system, such as electric double layer capacitor electrode, the resistance of the charge transfer process, diffusion and mass transfer process parameters, etc.

Generally, electrode materials are used for electrocatalysis in practical studies, and the basic data indexes required are obtained by using the electrode morphology analysis and electrochemical analysis methods described above. See Table 1 for details.

| Index                  | Characterization method | Function                                                                 |
|------------------------|-------------------------|---------------------------------------------------------------------------|
| Microscopic appearance | SEM, TEM                | Observe the fine morphology of the electrode surface layer and the distribution inside the coating |
4. Research progress of Ti/TiO$_2$-NTs/PbO$_2$ in electrocatalytic toxic wastewater treatment

4.1 Basic principle of electrocatalysis
The basic principle of electrocatalytic oxidation treatment is REDOX reaction. In the electrolytic cell, the reaction is carried out at the electrode/solution interface through the action of the applied electric field, and the organic matter is degraded directly on the anode or the strongly oxidizing substances such as hydroxyl radical (OH•)\(^{[63]}\), Cl\(_2\)\(^{[64]}\) and H$_2$O\(_2\)\(^{[65]}\) are produced to degrade the organic matter. The degradation pathways can be divided into direct oxidation stage and indirect oxidation stage.

(1) Direct oxidation stage
It is the direct catalytic oxidation of organic pollutants on the surface of the anode, the conversion of large molecular organic matters into non-toxic small molecular organic matters or direct mineralization into CO\(_2\) and H\(_2\)O. The specific reaction is: metal anode material reacts with hydroxyl radicals formed by H\(_2\)O or OH• to form high-priced oxides, as shown in equations (1) ~ (2):

\[
\begin{align*}
\text{MO}_x + \text{H}_2\text{O} & \rightarrow \text{MO}_x[\cdot \text{OH}] + \text{H}^+ + e^- \quad (1) \\
\text{MO}_x[\cdot \text{OH}] & \rightarrow \text{MO}_{x+1} + \text{H}^+ + e^- \quad (2)
\end{align*}
\]

Organic pollutants R in wastewater react with high-priced oxides generated above, and organic pollutants are degraded, as shown in equations (3) ~ (4):

\[
\begin{align*}
\text{R} + \text{MO}_x[\cdot \text{OH}] & \rightarrow \text{CO}_2 + \text{MO}_x + \text{yH}^+ + e^- \quad (3) \\
\text{R} + \text{MO}_{x+1} & \rightarrow \text{MO}_x + \text{RO} \quad (4)
\end{align*}
\]

(2) Indirect oxidation stage
It is the use of the active substances produced in the electrolysis process: hydroxyl radical OH•, Cl\(_2\), HClO, H\(_2\)O\(_2\) and other intermediates to react with organic pollutants in the water to achieve the purpose of degradation of pollutants \(^{[66]}\).

\[
\begin{align*}
\text{MO}_x + \text{H}_2\text{O} & \rightarrow \text{MO}_x[\cdot \text{OH}] + \text{H}^+ + e^- \quad (5) \\
\text{R} + \text{MO}_x[\cdot \text{OH}] & \rightarrow \text{CO}_2 + \text{MO}_x + \text{yH}^+ + e^- \quad (6)
\end{align*}
\]

When Cl\(^-\) is present in the solution, the following reactions will occur under certain conditions \(^{[67-69]}\):

\[
\begin{align*}
2\text{Cl}^- & \rightarrow \text{Cl}_2 + 2e^- \quad (7) \\
\text{Cl}_2 + \text{H}_2\text{O} & \leftrightarrow \text{HClO} + \text{Cl}^- + \text{H}^+ \quad (8) \\
\text{HClO} & \leftrightarrow \text{ClO}^- + \text{H}^+ \quad (9)
\end{align*}
\]

When the pH value reaches 3, the active substance in the solution is Cl\(_2\). When the pH value is 3-8, the main performance of Cl is HClO. When the pH value reaches above 8, the active substance in the solution is ClO\(^{[70-73]}\).

In addition, other researchers believe that the anode can produce O\(_3\), which can effectively degrade organic matter in solution Thanos et al. \(^{[74]}\) found that O\(_3\) can be produced on the lead electrode by the following reaction:

\[
\begin{align*}
3\text{H}_2\text{O} & \rightarrow \text{O}_3(\text{g}) + 6\text{e}^- + 6\text{H}^+ \quad (10) \\
\text{O}_2 + \text{H}_2\text{O} & \rightarrow \text{O}_3(\text{aq}) + 2\text{e}^- + 2\text{H}^+ \quad (11)
\end{align*}
\]

Ozone has a strong oxidation ability, can oxidize cyanide and organic compounds, such as phenol.

4.2 Application of Ti/TiO\(_2\)-NTs/PbO\(_2\) to electrochemical oxidation in wastewater treatment
Due to its strong catalytic activity and chemical inertia, Ti/TiO$_2$-NTTs/PbO$_2$ electrode is now widely used in the experimental study of wastewater degradation of refractory organic substances, such as phenolic substances, dyes, pesticides, and the treatment of chemical wastewater and other practical refractory organic wastewater.

4.2.1 Degradation of model wastewater

**1) Wastewaters containing Phenols**

Phenolic compounds are mainly used in pesticide, dye plastics, paint, petrochemical and pharmaceutical industries. Therefore, waste water from these industries contains a large number of phenolic substances that are difficult to degrade. Phenolic substances do great harm to environmental quality and human health and safety.

Duan et al. [47] studied the electrocatalytic degradation of target pollutant p-np (p-nitrophenol) by PbO$_2$/TiO$_2$-NTs/Ti electrode. The results showed that the degradation rate of p-np by PbO$_2$/TiO$_2$-NTs/Ti electrode prepared by anodic oxidation was 97.8% after 120 min of electrolysis. Hong [75] evaluated the catalytic activity of the β- PbO$_2$/TiO$_2$-NTs/Ti electrode by electrocatalytic degradation of phenol. The experimental results showed that the electrodeposition of β- PbO$_2$/TiO$_2$-NTs/Ti improved the electrocatalytic activity of the electrode, and the degradation of phenol reached 83% in the electrolysis for 180min, while the degradation of phenol by pure TiO$_2$-NTs/Ti only reached 27.4%.

**2) Wastewaters containing dyes**

Nowadays, with the development of economy, synthetic dyes are widely used in textile, cosmetics, leather and other major industries. Data show that the printing and dyeing processes adopted by printing and dyeing enterprises consume 100 ~ 200 m$^3$ of pure water per 1 t of products, 80% ~ 90% of which become waste water because they cannot be recycled [76]. The composition of dye wastewater is complex, the content of organic pollutants is high, and the amount of water is large. Among them, azo dyes, which are the most widely used ones, are difficult to degrade and do great harm to biology.

Dayanne [77] studied the effect of electrocatalytic oxidation of acidic blue-113 wastewater by Pb/PbO$_2$, Ti/PT, PbO$_2$/TiO$_2$-NTs/Ti electrode. The results showed that under the same experimental conditions, PbO$_2$/TiO$_2$-NTs/Ti electrode could better degrade the acidic Blue-113 wastewater, and the chroma and COD degradation rate could reach 98% and 92.5% respectively. Moreover, compared with Pb/PbO$_2$, Ti/PT, PbO$_2$/TiO$_2$-NTs/Ti electrode has higher current efficiency and lower energy consumption. Wu [77] used the prepared PbO$_2$/Sb-SnO$_2$/TiO$_2$NTs/Ti electrode to treat simulated rhodamine B wastewater, and investigated the effects of different initial concentrations of rhodamine B, initial pH, temperature and chloride ion concentration on electrocatalysis. Yang [54] also used PbO$_2$-TiO$_2$ nanocomposite electrode to study the photoelectric catalytic degradation performance of rhodamine B on dye, and pointed out that the degradation rate of rhodamine B and COD was in line with the first-order reaction kinetics model. The results showed that rhodamine B’s uv-visible spectral absorption decreased gradually with the progress of photocatalytic degradation, and the solution color became lighter and colorless gradually. After continuous degradation for 90 min, the ultraviolet absorption of rhodamine B at 553 nm basically disappeared. After degradation of rhodamine B to 75 min, rhodamine B removal rate and COD removal rate of PbO$_2$/TiO$_2$-NTs/Ti electrode were 98.2% and 71.8% respectively. Wang [61] used pulsed electrodeposition of Co- PbO$_2$/TiO$_2$-NTs/Ti electrode to electrocatalyze the degradation of methylene blue, an organic pollutant. 0.2mol/LNa$_2$SO$_4$ was added as an applied electrolyte. Under the condition of pH=3, current density of 50mA/cm$^2$ and solution containing 30mg/L methylene blue, the degradation rate of methylene blue reached 100% and COD degradation rate reached 74% after 2 hours of electrolysis. Meanwhile, Wang
also electrocatalyzed methylene blue with Pb-O₂/ TiO₂-NTs/Ti electrode under the same conditions, and found that the electrocatalysis effect of Co- PbO₂/ TiO₂-NTs/Ti electrode was better. Obviously, combining other active elements on PbO₂/ TiO₂-NTs/Ti electrode can improve the electrocatalytic ability.

(3) Wastewaters containing pharmaceuticals
The composition of pharmaceutical wastewater is complex, and the drug components and their related metabolites are discharged into the natural water environment, which will have a serious toxic effect on the water. Boukhchina S. used PbO₂/TiO₂-NTs/Ti electrodes prepared by different methods to study the effect of electrocatalytic oxidation on degradation of target pollutant ampicillin. Studies have found that by spin coating method of TiO₂-NTs and electrodeposition method doped PbO₂ nanoparticles obtained by the PbO₂/TiO₂-NTs/Ti electrode electric catalytic activity is stronger, in 300 min, the COD degradation rate of 64%, ampicillin can complete degradation in the space of an hour, and ampicillin pseudo-first-order kinetics model of degradation and the anode oxidation TiO₂-NTs and electrodeposition method doped PbO₂ nanoparticles preparation of Ti/TiO₂-NTs /PbO₂ electrode degradation effect is relatively poor, and ampicillin degradation accords with zero order kinetics model. Boukhchina analyzed the intermediate products of ampicillin degradation by high performance liquid chromatography, and proposed the degradation mechanism of ampicillin based on previous research results.

Chen electrocatalyzed nitrobenzene with Pb-O₂/SnO₂-Sb/TiO₂-NTs/Ti electrode, and kinetic analysis showed that the degradation process of nitrobenzene by the electrode was in line with the pseudo-first-order kinetic model. After 6 hours of electrolysis, the COD degradation rate reached 100%, and it was found by GC-M-S that the intermediate products containing nitro groups in the solution disappeared. Therefore, through the conversion of intermediate pr-

oducts, the authors reasonably proposed the degradation mechanism of the two nitrobenzene. This has very important reference significance to the future research work.

4.2.2 Degradation of real wastewater
In addition to the above simulated wastewater, Ti/TiO₂-NTs/PbO₂ electrode has also been studied in actual wastewater. Yin applied Ti/TiO₂-NTs/SnO₂-Sb/PbO₂, a new type of TiO₂ nanotube modified electrode, to the electrocatalytic oxidation treatment of membrane concentrated water from the tailwater of a sewage plant in a concentrated chemical area. The influences of electrolysis time, current density and pH value on COD removal rate were investigated. The results showed that, with the increase of current density, COD degradation rate significantly increased, electrolysis 1 h, COD degradation rate reached 55%. Li used Ti/TiO₂-NTs/PbO₂ electrode to treat coal chemical wastewater. After 120 min degradation, the removal rate of COD and total phenol by the electrode was 16.13% and 35.48%, respectively, which had good removal effect on refractory phenolic substances.

5. Conclusions and prospects
Ti/TiO₂-NTs/PbO₂ electrode has a good application prospect in the treatment of refractory organic wastewater due to its excellent electrochemical performance and strong degradation ability of organic pollutants. However, at present, the research on Ti/TiO₂-NTs/PbO₂ electrode is only limited to the laboratory, which is quite different from the actual industrial demand. Therefore, it is necessary to promote industry-university-research cooperation among universities, research institutes and enterprises, which will quickly bring cheap and practical electro-catalytic materials to the market, thus accelerating the process of large-scale production. Based on the current research on electrodes, the author puts forward the following two prospects:

(1) develop the preparation technology of Ti/TiO₂-NTs/PbO₂ electrode with large area. At present, the preparation of Ti/TiO₂-NTs/PbO₂ elec-
trode is still in the stage of small area experimental laboratories mainly in universities. Therefore, through technical reform or independent research and development, the preparation equipment and process of Ti/TiO₂-NTs/PbO₂ electrode with intended area is developed, and the formation of large area Ti/TiO₂-NTs/PbO₂ electrode is a major breakthrough to realize its industrial application.

(2) further improve the electrocatalytic performance and stability of Ti/TiO₂-NTs/PbO₂ electrode. Although Ti/TiO₂-NTs/PbO₂ electrode has a good ability to degrade organic matter, it can be found that in the later stage of electrocatalytic reaction, with the decrease of organic matter concentration and the influence of mass transfer process, the current efficiency will decline, which will reduce the degradation rate of organic matter and correspondingly increase the energy consumption. At present, the focus of the current research on electrode materials lies in the synthesis of materials with controllable morphology and reasonable surface doping of rare earth metal elements, which will further improve the electrocatalytic activity and stability of the electrode, improve the overall current efficiency and solve the problem of large energy consumption.

References

1. Wu W, Huang ZH, Lim TT. Recent development of mixed metal oxide anodes for electrochemical oxidation of organic pollutants in water[J]. Applied Catalysis A: General. 2014, 480: 58-78.

2. Zhu DL, Liu SM, Yang Q. Research progress of electrochemical catalytic degradation of organic wastewater[J]. Modern Chemical Industry, 2016, 36(12): 38-41+43.

3. Zhao YY, Wang DJ, Zhao CC. Progress in electrode materials for refractory wastewater treatment by electro-catalytic oxidation[J]. Materials Review, 2019, 33(07): 1125-1132.

4. Feng YJ, Liu JF, Cui YH. Environmental electrocatalytic electrode-structure, properties and preparation[M]. Science press, 2010: 377

5. Mukimin A, Vistanty H, Zen N. Oxidation of textile wastewater using cylinder Ti/β-PbO₂ electrode in electrocatalytic tube reactor[J]. Chem Eng J.2015, 259:430-7.

6. Wu ZF, Cui ZJ. The Preparation and performance analysis of new type Ti/PbO₂ electrode[J]. Technology of Water Treatment, 2012, 38(03): 30-33.

7. Song S, Fan JQ, He ZQ, et al. Electrochemical degradation of azo dye C.I. reactive red 195 by anodic oxidation on Ti/SnO₂-Sb/PbO₂ electrodes[J]. Electrochimica Acta, 2010, 55: 3603-3613.

8. Amadelli R, Saniolo L, Battisti AD, Velichenko AB. Electro-oxidation of Some Phenolic Compounds by Electrogenerated O₃ and by Direct Electrolysis at PbO₂ Anodes[J]. J Electrochem Soc.2011, 158(7).

9. Han W, Chen Y, Wang L, Sun X, Li J. Mechanism and kinetics of electrochemical degradation of isothiazolin-ones using Ti/SnO₂–Sb/PbO₂ anode[J]. Desalination. 2011, 276(1-3): 82-8.

10. Song S, Zhan L, He Z, Lin L, Tu J, Zhang Z, et al. Mechanism of the anodic oxidation of 4-chloro-3-methyl phenol in aqueous solution using Ti/SnO₂-Sb/PbO₂ electrodes[J]. J Hazard Mater. 2010, 175(1-3): 614-21.

11. Carr J P, Hampson N A. Lead dioxide electrode[J]. Chemical Reviews, 1972, 72(6): 679-703.

12. Abaci S, Tamer U, Pekmez K, Yildiz A. Performance of different crystal structures of PbO₂ on electrochemical degradation of phenol in aqueous solution[J]. Applied Surface Science. 2005, 240(1-4): 112-9.

13. [13] Saez V, Esclapez MD, Frias-Ferrer AJ, Bonete P, Tudela I, Diez-Garcia MI, et al. Lead dioxide film sonoelectrodeposition in acidic media: Preparation and performance of stable practical anodes[J]. Ultrason Sonochem. 2011, 18(4):873-80.

14. Feng YJ, Sheng H, Cui YH, Liu JF. Preparation and evaluation on the electro-catalytic characteristics of Ti-base lead dioxide electrode[J]. Journal of Molecular Ccatalysis (China), 2002(03):181-186.

15. Zhu X, Ni J, Li H, Jiang Y, Xing X, Borthwick AGL. Effects of ultrasound on electrochemical oxidation mechanisms of p-substituted phenols at BDD and PbO₂ anodes[J]. Electrochimica Acta. 2010,55(20) 5: 5569-75.

16. Wang ZN, Li MY, Guo Y, Liang DD, Liu SM. Re-
search progress of preparation and application of nano-TiO$_2$ [J]. China Ceramics Industry, 2018, 25(02): 20-25.

17. Tao L, Xiong Y, Liu H, Shen W. High performance PbS quantum dot sensitized solar cells via electric field assisted in situ chemical deposition on modulated TiO$_2$ nanotube arrays[J]. Nanoscale. 2014,6(2):931-8.

18. Hoid I, González-Pedro V, Tachan Z, Fabregat-Santiago F, Mora-Seró I, Bisquert J, et al. Dye versus quantum dots in sensitized Solar Cells: Participation of quantum dot absorber in the recombination process[J]. The Journal of Physical Chemistry Letters. 2011,2(24):3032-5.

19. Hod I, Zaban A. Materials and interfaces in quantum dot sensitized solar cells: challenges, advances and prospects[J]. Langmuir. 2014,30(25): 7264-73.

20. Huang C, Chen L. Preparation and doping of TiO$_2$ nanotubes[J]. Guangdong Chemical Industry, 2014, 41(09): 85-86+92.

21. KSAUGA T, HIRAMATSU M, HOSON A, et al. Formation of titanium oxide nanotube[J]. Langmuir, 1998, 14(12): 3160—3163.

22. Song JJ. Preparation and Catalytic properties of modified TiO$_2$ nanotubes[D]. Tian Jin: Nankai University, 2013.

23. Liu D, Jiang SQ, Wang G. Study progress on preparation and modification of TiO$_2$ nanotube Array [J]. Surface Technology, 2017, 46(04): 71-78.

24. Liu RB, Liu CH, Xiao Z, Bi S, Hou GL. Preparation and morphology control of TiO$_2$ nanorod arrays[J]. Modern Chemical Industry, 2019, 39(04):108-111 +113.

25. Deng ZH, Jin Y, Zuo ZH. Design of comprehensive experiment on synthesis of anatase-TiO$_2$ by hydrothermal method[J]. Experimental Technology and Management, 2019, 36(01):84-88.

26. Zhang PJ, Qin LH, Zhang YF, Wang JF. Preparation of {001} facets-dominated TiO$_2$ by hydrothermal synthesis[J]. Computers and Applied Chemistry, 2018, 35(05): 385-389.

27. Lv M, Zheng D, Ye M, Xiao J, Guo W, Lai Y, et al. Optimized porous rutile TiO$_2$ nanorod arrays for enhancing the efficiency of dye-sensitized solar cells[J]. Energy & Environmental Science. 2013, 6(5).

28. Fu M, Yuan XX, Ma ZF. Research progress on the preparation and application of titania nanotube[J]. Chemical industry and engineering progress, 2005(01): 42-46.

29. Yang M, Ding B, Lee S, Lee J-K. Carrier transport in dye-sensitized solar cells using single crystalline TiO$_2$ nanorods grown by a microwave-assisted hydrothermal reaction[J]. The Journal of physical chemistry C. 2011, 115(30): 14534-41.

30. Pan F, Zhang W, Zhang D. Research and advance in template-assisted synthesis of TiO$_2$[J]. Materials Review, 2015, 29(01): 22-30.

31. Hoyer P. Formation of a titanium dioxide nanotube array[J]. Langmuir, 1996, 12: 1411-1413.

32. Zhang HC. Templated preparation and photoluminescence of composite structure TiO$_2$ nanotube arrays[D]. Shanghai University, 2014.

33. Nguyen Thanhdong, Wang W, Long HB, Ru HQ. Preparation of mesoporous TiO$_2$ with bi - crystallinity via soft - templating approach from peroxotitanic acid[J]. Journal of Materials and Metalurgy, 2016, 15(01): 53-57.

34. Li XD, Fu L, Liu HL, Wang Y, Wen AH, et al. Template synthesis and the properties of three-dimensional chrysanthemum-like TiO$_2$ nanoflowers[J]. Journal of Harbin institute of technology, 2014, 46(02): 55-60.

35. Liu CF, Huang CP, Hu CC, Huang C. A dual TiO$_2$/Ti-stainless steel anode for the degradation of orange G in a coupling photoelectrochemical and photo-electro-Fenton system[J]. Sci Total Environ. 2019, 659: 221-9.

36. Wang YG, Zhou Bo. Experimental Factors on Preparation of Ordered TiO$_2$ nanotubes by Anodic Oxidation[J]. Journal of Shenyang University (Natural Science), 2017, 29(04): 265-270+293.

37. Liu D, Jisng SQ, Wang G, Zhang QZ. Effects of anodic oxidation process on morphologies of TiO$_2$ nanotube arrays[J]. China Surface Engineering, 2017, 30(06): 67-74.

38. Zou JP, Tang NX, Li HC, Yang HZ, Xiao P, et al. Growing characteristics of TiO$_2$ nanotube array prepared by anodization method[J]. The Chinese Journal of Nonferrous Metals, 2016, 26(02):337 -346.
39. Du JJ, Xi YM, Zhao JW, Chen XM, Wang KS. Influence of electrolyte on the morphology and photocatalytic property of TiO2 nanotube array[J]. New Chemical Materials, 2016, 44(04): 146-148.

40. Li L, Zhang K, Li HL, Wu L, Feng J. et al. Effect of anodic oxidation conditions on the formation of through-hole TiO2 nanotube array membranes[J]. Journal of Wuhan University of Technology, 2016, 38(07): 8-13.

41. Wang J. Freestanding TiO2 nanotube arrays with ultrahigh aspect ratio via electrochemical anodization[J]. Chemistry of Materials, 2008, 20, 1257–1261

42. Yeonmi S. Self-organized regular arrays of anodic TiO2 nanotubes[J]. Nano Letters. 2008, 8(10):317-3173

43. Li XX, Liu J, Fu DG. Effect of two-step anodization on structure and photoelectric performance of TiO2 nanotube arrays[J]. Journal of Synthetic Crystals, 2015, 44(11): 3124-3128.

44. Xiao TX. TiO2 nanotube arrays with regular structure prepared by improved two-step anodic oxidation[J]. New Chemical Materials, 2017, 45(12): 93-95+99.

45. Xie YN, Ma ZM, Shi YB, Tang J,Wang F. et al. Photocatalytic Properties of ordered TiO2 nanotubes Arrays[J]. Micronanoelectronic Technology, 2016, 53(03): 156-160.

46. Ferreira M, Pinto MF, Neves IC, Fonseca AM, Soares OSGP. et al. Electrochemical oxidation of aniline at mono and bimetallic electrocatalysts supported on carbon nanotubes[J]. Chem Eng J. 2015,260:309-15.

47. Duan XY,Liu W, Ru L, Chang LM. Preparation and electro-catalytic properties of PbO2/TiO2-NT /Ti electrode[J]. Acta Scientiae Circumstantiae, 2016, 36(09): 3237-3242.

48. Wang CY. The modification of lead dioxide and its electrocatalytic application research[D]. Anhui University, 2016.

49. Sha HX. Effect of preparation method on the structure and properties of lead dioxide electrode[D]. Yangzhou University, 2008.

50. Liu N, Wang L, Wu D, Mi R, Quan FJ. et al. Comparison of electro-catalytic characteristics of the lead dioxide electrode with different coats[J]. Journal of Jilin University (Earth Science Edition), 2006(S1): 133-137.

51. Sun PZ. Research progress on new lead dioxide electrode[J]. Guangzhou chemical industry, 2018, 46(20): 24-26.

52. Cao CQ. Preparation and modification of beta-PbO2 electrode by high pressure plastic sheet [A]. Shanghai chemical industry association. Abstract collection of papers in 2007 annual academic conference of Shanghai chemical and chemical society[C]. Shanghai chemical industry association, 2007: 3.

53. Zhang C,Wang JQ. Treatment of dye wastewater by a new lead dioxide electrode[J]. Chinese Journal of Environmental Engineering, 2014, 8(06): 2283-2292.

54. Yang Y,Cui LL,Li Y, Yao NW. Preparation and photoelectrocatalytic properties of PbO2-TiO2-nanocomposite Electrode [J]. Plating and Finishing, 2018, 40(11): 42-46.

55. Wang L. Preparation of high performance lead dioxide electrodes and its electro-oxidation degradation of organic wastewater[D]. Xi’an University of Architecture and Technology, 2017.

56. Li CG. Modified preparation of titanium-base PbO2 electrodes for electrochemical oxidation degradation of organic wastewater[D]. Xi’an University of Architecture and Technology, 2017.

57. Yao Y, Li M, Yang Y, Cui L, Guo L. Electrochemical degradation of insecticide hexazinone with Bi-doped PbO2 electrode: Influencing factors, intermediates and degradation mechanism[J]. Chemosphere, 2019, 216: 812-22.

58. Mao YL, Zhang X, Xu M, Wang FW, Wang ZC, Fang WY. et al. Preparation of Ti/TiO2 nanotube arrays /PbO2-Pr electrode and its application in electrocatalytic degradation of organic wastewater[J]. Chinese Journal of Applied Chemistry, 2018, 35(05): 582-588.

59. Chen Y, Jin BJ, Chen BM, Guo ZC. Effect of Cerium doping on electrocatalytic activity and electrolysis lifetime of lead dioxide - titanium epoxide anode on titanium substrate[J]. Journal of Materials Protection, 2015, 48(04): 16-18+7.

60. Boukhchina S, Akrouh H, Berling D, Bousselmi L.
Highly efficient modified lead oxide electrode using a spin coating/electrodeposition mode on titanium for electrochemical treatment of pharmaceutical pollutant[J]. Chemosphere. 2019, 221: 356-65.

61. Wang C, Wang F, Xu M, Zhu C, Fang W, Wei Y. Electrocatalytic degradation of methylene blue on Co doped Ti/TiO2 nanotube/PbO2 anodes prepared by pulse electrodeposition[J]. Journal of Electroanalytical Chemistry. 2015, 759: 158-66.

62. [Wang YJ. Preparation and research of titanium-substrated lead dioxide electrode for simulated electrocatalytic dye wastewater treatment[D]. Harbin Engineering University, 2016.

63. Chen Z, Zhang Y, Zhou L, Zhu H, Wan F, Wang Y, et al. Performance of nitrogen-doped graphene aerogel particle electrodes for electro-catalytic oxidation of simulated Bisphenol A wastewaters[J]. J Hazard Mater. 2017, 332: 70-8.

64. Wu W, Huang ZH, Lim TT. Recent development of mixed metal oxide anodes for electrochemical oxidation of organic pollutants in water[J]. Applied Catalysis A: General, 2014, 480, 58.

65. Yan L, Ma H, Wang B, Wang Y, Chen Y. Electrochemical treatment of petroleum refinery wastewater with three-dimensional multi-phase electrode[J]. Desalination. 2011, 276(1-3): 397-402.

66. Garcia-Segura S, Ocon JD, Chong MN. Electrochemical oxidation remediation of real wastewater effluents -A review[J]. Process Safety and Environmental Protection. 2018, 113: 48-67.

67. Moreira FC, Boaventura RAR, Brillas E, Vilar VJP. Electrochemical advanced oxidation processes: A review on their application to synthetic and real wastewaters[J]. Applied Catalysis B: Environmental. 2017, 202: 217-61.

68. M. Panizza, G. Cerisola, Direct and mediated anodic oxidation of organic Pollutants[J]. Chem. Rev. 109 (2009) 6541–6569.

69. Szpyrkowicz L, Kaul SN, Neti RN, Satyanarayan S. Influence of anode material on electrochemical oxidation for the treatment of tannery wastewater[J]. Water Res. 2005, 39(8): 1601-13.

70. Szpyrkowicz L, Radaelli M, Daniele S. Electrocatalysis of chlorine evolution on different materials and its influence on the performance of an electrochemical reactor for indirect oxidation of pollutants[J]. Catal Today. 2005, 100(3-4): 425-9.

71. Deborde M, von Gunten U. Reactions of chlorine with inorganic and organic compounds during water treatment-Kinetics and mechanisms: a critical review[J]. Water Res. 2008, 42(1-2): 13-51.

72. de Moura DC, de Araújo CKC, Zanta CLPS, Salazar R, Martínez-Huitle CA. Active chlorine species electrogenerated on Ti/RuO3/TiO2O2 surface: Electrochemical behavior, concentration determination and their application[J]. Journal of Electroanalytical Chemistry. 2014, 731: 145-52.

73. Martínez-Huitle CA, Brillas E. Decontamination of wastewaters containing synthetic organic dyes by electrochemical methods: A general review[J]. Applied Catalysis B: Environmental. 2009,87(3-4): 105-45.

74. Thanos JC, Fritz HP, Wabner D. The Influences of the Electrolyte and the Physical Conditions on Ozone Production by the Electrolysis of Water. Journal of Applied Electrochemistry, 1984, 14(3): 389-399P.

75. Hong P, Wang FW, Xu M, Wei L, Fang WY, et al. Preparation of β-PbO2/TiO2 nanotube arrays electrode and electrocatalytic degradation of phenol[J]. Chinese Journal of Applied Chemistry, 2014, 31(09): 1096-1100.

76. Wang TN, Zu G, Yang L, Cai YT, Li B. Research progress on printing and dyeing wastewater at home and abroad[J]. Environmental Protection and Circular Economy, 2015, 35(04): 28-31.

77. Moura DCD, Quiroz MA, Silva DRd, Salazar R, Martinez-Huitle CA. Electrochemical degradation of Acid Blue 113 dye using TiO2-nanotubes decorated with PbO2 as anode[J]. Environmental Nanotechnology, Monitoring & Management. 2016, 5: 13-20.

78. Wu J, Zhu K, Xu H, Yan W. Electrochemical oxidation of rhodamine B by PbO2/Sb-SnO2/TiO2 nanotube arrays electrode[J]. Chinese Journal of Catalysis, 2019, 40: 917-927.

79. Chen Y, Li H, Liu W, Tu Y, Zhang Y, Han W, et al. Electrochemical degradation of nitrobenzene by anodic oxidation on the constructed TiO2-NTs/Sn O2-Sb/PbO2 electrode[J]. Chemosphere. 2014, 113: 48-55.
80. Yin XD, Chen Y, Lin QQ. Study on Treatment of Reverse Osmosis Concentrate by TiO$_2$ Nano-tubes Modified Electrode[J]. Environmental Science and Technology, 2014, 27(05): 1-4+31.

81. Li JX, Chen Y, Han HJ, Chen ZQ. Preparation of Ti-based PbO$_2$ Electrode and Electrocatalytic Oxidation of Coal Chemical Wastewater [J]. China Water & Wastewater, 2019, 35(03): 111-116.