Applications of electro-catalysis municipal wastewater treatment

Xuanlin Yu

College of Chemistry and Chemical Engineering, Xiamen University, Xiamen 361005, China

20420172201970@stu.xmu.edu.cn

Abstract. In the context of developing a more livable environment, people are paying more attention to the pollution problem. As the consumption of water resources increases, water pollution is one of the most serious problems people need to pay attention to the most. However, traditional methods cannot meet the requirements of treating wastewater while recovering resources. In this review, the application of electrocatalytic technology in municipal wastewater treatment is discussed. Specifically, the comparison between electrocatalysis and traditional methods is shown in this review. Various literatures on different types of materials of electrodes are included. Besides, two different types of electrodes and mechanisms of electrocatalysis and their application in multiple types of wastewater are also summarized. This review aims to arouse people's attention to the wastewater problem and explore the further application of electrocatalytic technology in the future in order to rationally design new electrocatalytic systems for the recovery of energy and resources.

Keywords: electrocatalysis, municipal wastewater, three-dimensional electrode.

1. Introduction

Along with the rapid development of industry and economy, sewage problems have become a common challenge for people all over the world. Among these, the urban sewage problem is the most serious because of the large number of emissions and emerging contaminants [1]. The classification of municipal sewage can be considered as four main types: organic wastewater, heavy metal ion wastewater, wastewater with ammonia or nitrogen, and domestic wastewater. Many methods have been taken to solve the problem. However, traditional technologies like the activated sludge (AS) process or the anaerobic biological system process are considered unsustainable. Urban wastewater also contains various substances, such as organic nutrients, metal ions and lots of non-metallic elements like carbon, oxygen and hydrogen. Energy and resources contained in wastewater cannot be recycled but only converted to H_2O and CO_2 during these processes, while they have long duration and high energy consumption [2]. It has been reported that municipal wastewater with organic matter concentration of nearly 450 mg of chemical oxygen demand per litre (COD/L) contains about 1.7 kWh/m^3 of potential chemical energy of sewage, which is as twice as the requirement of an anaerobic biological system [3]. Thus, there is a demand for searching and developing a renewable and sustainable system to manage wastewater and gather energy and resources simultaneously.

According to the final goal, the development of managing wastewater can be divided into the following parts: water recovery, nitrogen and phosphorus recovery and utilization, organic substance recovery and metal ions recovery. At the first stage, previous studies have shown that AS processes have the advantage of odor controlling [4]. However, traditional AS processes have high energy consumption, because long-term and/or large-scale operations of AS diffusion are required to examine possible adverse effects on wastewater treatment, effects on process fluctuations and operational failures, and removal efficiency of various volatile organic compounds (VOCs). Membrane bioreactors may solve the problem, but they will also consume a lot of energy. For better management of degrading nutrition, that is, nitrogen and phosphorus, several systems have been designed to achieve the goal [5]. Recently, some progresses have been made in the utilization of machine learning for nutrient recovery. This may make some breakthroughs in the future but it is currently lacking of studies for nutrient recovery in many fields [6]. Despite the recovery of water resources and nitrogen and phosphorus, it is also significant to recover the carbon and hydrogen of wastewater. Traditional treatments like metal-based catalysts for photocatalytic will emit unexpected free radicals and convert carbon into CO_2 [7]. Converting carbons in wastewater into fuels is a significant topic now. Electrocatalysis has been paid attention to because of its potential application in H_2O reduction and CO_2 reduction [8].

Electrocatalysis as technology of a high efficiency and mild reaction condition process has been used for solving environmental problems throughout modern and contemporary history accompanied by renewable electric energy. The reaction usually takes place in an electrolytic cell made up of an anode, cathode and electrolyte solution. For wastewater, the waste is oxidized near the anode, while the CO_2 and other resources produced are reduced near the cathode. The most critical part is the choice of electrodes and catalysts. Nanomaterials, carbon nanofibre and metal-oxide membranes have been used as electrodes in the treatment of wastewater, considering the absorbability and electric potential difference [9-11]. Electrocatalysis can also be combined with other techniques easily, such as ionization or photocatalysis. Herein, two types of mechanisms of electrocatalysis and the three-dimensional electrode system are presented in this article. To enrich the theme, various utilizations of electrocatalysis in different types of wastewater are also introduced.

2. Mechanisms

2.1. Oxidation-reduction electrocatalysis

Oxidation-reduction electrocatalysis is the most common method. This type of catalysis is also known as mediator electrocatalysis. The catalyst fixed on the electrode or existing in the electrolyte itself has undergone a redox reaction, becoming the charge transfer medium of the substrate and promoting the electron transfer of the substrate. The oxidation state form (Ox) of the electrocatalyst fixed on the electrode surface or existing in the solution generates a reduction state form (Re) under the action of the applied electric field, and the Re reacts with the substrate A in the solution to generate the product B, and the oxidation form Ox of the catalyst is regenerated, and so on (Figure 1).

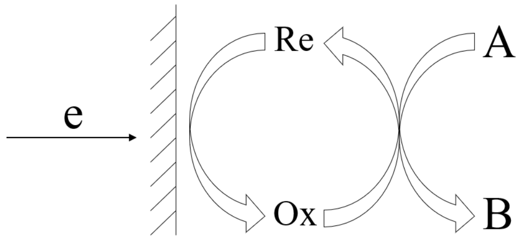

Figure 1. Oxidation-reduction electrocatalysis.

A good electron transport agent has the following properties: it can be adsorbed or rented on the electrode surface stably; the kinetic characteristics of reversible electrode reaction are presented, and both oxidation state and reduced state can exist stably; rapid electron transfer can occur between the catalyzed substance and the transport agent. In addition, there are two types of mediator electrocatalysis.

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One is heterogeneous catalysis. The catalytic action of the electrode reaction is carried out by attaching a trimmer to the electrode indication. Many studies have been completed. Recently, highly efficient methods of glucose oxidation have been reported, using different metals, metal oxides or carbon nanorods to modify electrodes [12, 13]. The other one is homogeneous catalysis, which is less used than the former. Heterogeneous catalysis is widely used due to its less usage of catalysts and higher reaction rate. It can improve the selectivity and sensitivity of the reaction based on thermodynamics.

2.2. Non-oxidation-reduction electrocatalysis

Non-oxidation-reduction electrocatalysis refers to the catalyst fixed on the electrode surface itself in the process of catalysis without the redox reaction. The total electrochemical reaction produces some chemical adducts or some other electroactive intermediates. The total activation energy is reduced by the catalyst (Figure 2). Metal oxides and precious metals are usually used to manufacture electrodes.

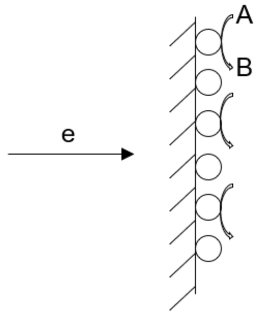

Figure 2. Non-oxidation-reduction electrocatalysis.

Such techniques are regularly used for researches on biochemical analysis, like the reaction between proteins and enzymes. Some of the latest studies show that some kinds of bimetallic alloys play a significant role in CO_2 reduction. Recently, a copper–antimony bimetallic porous alloy has been reported in the area of CO_2 reduction. It shows that porous alloy has a great advantage in gathering and reducing CO_2, benefits from its electronic configuration, large surface area, high CO_2 adsorption rate, and fast charge transfer rate [14]. Other metals like Au and Sn with Cu also have a high efficiency in CO_2 reduction and recovery. Bimetallic alloy demonstrates high Farady efficiency, current density and yield. Some of the nanomaterials have even 1.9-2.9 times of yield higher than normal alloy [15]. Except for the two-dimensional structural catalysts, some researches on three three-dimensional structural catalysts have been done in order to enhance the cycle stability and rate performance of nanomaterials and the ability of recovery. A kind of $MnCo_2S_4/NiCo_2S_4$ (MCS/NCS) composites with three-dimensional network structures have been reported to have better capacitive and conductive properties compared with the two-dimensional network structures. Still and all, the selection of metal elements and the manufacturing of nanomaterials need further study.

3. Three-dimensional system

The three-dimensional electrode, also known as a bed electrode or particle electrode, is based on the traditional two-dimensional electrode with the introduction of granular and fragmentary electrode material, which can be charged on the surface. The three-dimensional electrolytic bed is composed of a power source, an electrolytic cell, a cathode plate, an anode plate and a particle electrode. Among them, the power supply is generally a direct current (DC) regulated power supply. The anode plate is generally made of materials that can generate OH radicals. The particle electrode is made of conductive material. In the 1950s and 1960s, due to the limitation of the development level of the power industry, the electrochemical reaction can only be limited to the interface between the ionic conductor and the electronic conductor, that is, the two-phase interface between the electrode and the electrolyte. Since the reaction space is a two-dimensional plane, this greatly limits the electrochemical reaction speed. With the development of industry, the three-dimensional electrode is born, which is the electrochemical reaction that can get rid of the two-dimensional limitation. There are many kinds of three-dimensional electrode classifications, among which the way of filling particles is more practical. The product of the electronic reaction is related to the electrode material. The treatment of the same electrode material can change the corresponding reaction path and reaction rate. For example, when iron is embedded on the surface of the electrode, the corresponding yield will be greatly improved and the treatment effect of sewage will be improved.

The three-dimensional electrode system can be better used for managing organic wastewater compared with the two-dimensional electrode especially because of the oxidation of H_2O_2 and the OH radical it generates through the process. The removal rate of benzene and chlorobenzene is very high, as well as other organic substances by controlling oxidation time, the distance between the electrodes and the pH of the solution. An electrode called the Dimensionally Stable Anode (DSA) is widely used in the system, too. It is to coat the surface of the titanium matrix with some metal oxides which have an electrocatalytic activity to make a coating anode. Many of the titanium-metal oxide couples have been successfully studied, such as Ti/SnO_2; Ti/PhO_2; Ti/RuO_2; Ti/MnO_2; Ti/IrO_2, etc. However, with the rapid development of the electrochemical industry, people put forward higher requirements for the preparation of DSA electrodes. Methods have emerged for adding an intermediate layer or to the coating. The Ti/IrO_2/Sb-SnO_2 electrode can enhance the performance and stability of the Ti/Sb-SnO_2 electrode. According to Li et al.’s research, the titanyl manganese dioxide electrode with the interlayer of IrO_2 could decrease the influence of electrical resistance observably, and the accelerated service life of Ti/IrO_2/Sb-SnO_2 electrode was about 30 times longer than that of the Ti/Sb-SnO_2 electrode [16]. Other methods like doping rare earth elements or electro-depositing rather than thermal decomposition can also significantly improve the performance of the DSA electrode. A team from Dalian Institute of Chemical Physics, Chinese Academy of Sciences has prepared different kinds of PbO_2 electrodes using titanium mesh and tin-antimony oxide layer by electrodeposition. Their experiments have shown that the best degradation effects can achieve a 85.56% conversion rate of m-cresol and a 16.51% removal rate of total organic carbon (TOC) with the lowest energy consumption of about 0.97 kW·h/g, measured in TOC [17]. Nowadays, the DSA electrode is one of people’s first choices for managing wastewater with a large amount of organic substance. Other kinds of wastewater can also be treated using a three-dimensional electrode system.

4. Applications

Three-dimensional electrodes have been widely used all over the world for degrading organic wastewater. Industrial effluents not only contain toxic organic compounds but also contain some heavy metal ions. Electrocatalysis combined with the Fenton oxidation process has a remarkable effect on the degradation or removal organic substances in wastewater. In recent years, the combination of three-dimensional electrode methods with different working materials and other water treatment technologies has become a research hotspot. Application of such 3D electrodes with DSA becomes more and more common in industrial production.

4.1. Printing and dyeing wastewater

Printing and dyeing wastewater is a kind of industrial wastewater, with a high concentration of organic pollutants, high alkalinity, high chroma, and high difficulty of treatment. Using DSA electrodes to treat printing and dyeing wastewater has the advantages of no secondary pollution, simple equipment, high chroma removal rate, complete degradation of pollutants and so on. A novel porous Ti/SnO_2-Sb_2O_3/CNT-PbO_2 electrode was prepared by electrochemical deposition method using a porous titanium matrix and carbon nanotubes (CNTs). It has a prominent higher COD removal rate than traditional non-DSA electrodes [18]. Di et al. prepared Ti/α-PbO_2/β-PbO_2 electrodes by electrodeposition [19]. The COD removal rate and decolorization rate of printing and dyeing wastewater were 68.23% and 79.21%, respectively.

4.2. Phenol wastewater

Phenol is a highly toxic, carcinogenic and teratogenic organic compound. It is common in industrial effluents used in the production of petroleum and rubber, which means the treatment is urgent. Fan et al. designed an electrochemical reactor with MnO_x/Ti membrane electrode modified with Sb-SnO_2 interlayer, which reached 98.98% and 89.38% of phenol and COD removal rates, respectively [20]. Samarghandi et al. also researched a kind of three-dimensional electrochemical system with Ti/SnO_2–Sb/β-PbO_2 anode and activated carbon particles. The removal rate of 2,4-dichlorophenol reached 99.8% in their experiments [21]. There are many other studies of removal phenol. Most of all have reached a high rate level of removal expectedly with DSA and/or three-dimensional electrode reactors.

4.3. Organic wastewater with heavy metal ions

Organic wastewater containing heavy metal ions has a complex composition and poor biodegradability. The development and processing of natural gas will produce a lot of organic pollutants and heavy metals in gas field wastewater. However, the traditional treatment methods such as adsorption and coagulation cannot meet the current requirements of wastewater treatment. The recovery of ions is usually done by combining three-dimensional electrodes with other methods. The technology of three-dimensional electrodes with foam separation was adopted. In addition, the combined process of activated carbon three-dimensional electrode and electroadsorption was adopted to treat oil refining wastewater. Most of the heavy metal ions, especially ions of Ni, Cu, Zn and Mn, can be removed at a rate of about 85%. Tang et al. reported that a complex three-dimensional electrode reactor with graphite as cathode and Ti/RuO_2-IrO_2 as anode can reach a 98.3% removal rate of mercury and a 94.7% removal rate of COD [22]. However, the process may reduce the durability of electrodes quickly because of the erosion of electrodes during the redox process. Further studies are needed in this area.

4.4. Other organic wastewater

4.4.1. High chlorine concentration organic wastewater. The concentration of chloride ions in some of the organic wastewater is very high, which has the characteristics of wide source, serious pollution and difficult biodegradation. High concentrations of chloride will lead to the decrease of dissolved oxygen content in water and will seriously affect the growth of microorganisms. A common method is that convert chloride ions to effective chlorine by electrocatalysis so that it can be used for organic oxidation. The Ti/IrO_2-RuO_2 electrode system can convert chloride ions into Cl_2 or ClO^- so that the generated Cl_2 and ClO^- can be returned to the degradation and decolorization of organic wastewater.

4.4.2. Wastewater with nitrobenzene. There are biological, chemical and physical methods for the treatment of nitrobenzene in wastewater. Among them, electrocatalysis has the characteristics of environmental protection, simple operation and high efficiency. A kind of DSA electrode like Ru-Pd/Sn-Sb/Ti electrode can be used for degradation. Under the condition of specific current density, electrolyte concentration, plate spacing and pH value, the removal rate of nitrobenzene can exceed 90%, and the TOC can be removed by nearly 90% [23].

5. Conclusion

Wastewater treatment with electrocatalysis has been extensively investigated. This review has shown some development in the composition of electric catalysts and electrodes, especially the DSA electrode. Furthermore, the three-dimensional electrode has been introduced as a substitute for traditional two-dimensional electrodes. It can be manifested that electrocatalysis with such a system has been widely used around the world, from the printing and dyeing industry to the petrolic and natural gas industry. Nevertheless, the technology for this is still immature in terms of commercialization. Several serious problems are needed to solve: reduction of the cost of manufacturing; enhancement of the oxidation resistance of the electrode; reduction of the impedance of the electrode, etc. It is also an interesting area of combining three-dimensional electrocatalysis with traditional methods or some other efficient and mature techniques. Along with the development of the economy and productivity, the problem of water pollution will be accompanied by almost all of the production activities and people's life. This review

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may drive researchers to design various compounds or alloys under the demand of more stable and more efficient techniques of electrocatalysis in the future.

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