

Mini Review

Development in electrochemical technology for environmental wastewater treatment

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Electrochemical methods can enhance the rate and efficiency of environmental interface processes through the directional transfer and precise regulation of electrons. Its extraordinary characteristics and advantages can be applied in water treatment, which is an important technical means to crack water crisis and water pollution. In the past 10 years, electrochemical water treatment technology has been developed rapidly and tends towards electrode efficiency, process coupling as well as low carbon and green development. It will further focus on important directions such as functional electrode material design, high-efficiency reactor and combined process development, and directional transfer and recovery of resources and energy in the future. This review describes the current research status and practical applications of electrochemical technology in different kinds of wastewater treatment, while analyzing the basic working principles of different water treatment technologies of electrochemistry. Despite a generally environmentally friendly and efficient treatment method, electrochemistry as a water treatment technology still has certain drawbacks. This review suggests that future research should be strengthened regarding the reduction of energy consumption of the overall water treatment system, the overall system cost should be reduced based on various aspects of the application, and attempts should be made to combine the application with traditional processes.

Keywords: Electrocoagulation flocculation; Electrochemical oxidation; Photoelectrochemistry; Electro Fenton method; Electrosorption

1. INTRODUCTION

Currently, water resources are in serious shortage around the world, and with the rapid development of industrial technology, a large amount of industrial wastewater has been produced, which in turn has brought more serious problems to this unfavorable situation. Therefore, the purification of industrial wastewater is of great importance in the process of environmental protection [1]. Generally, electrochemical water treatment technology does not require the introduction of other substances, because the reaction substance is electrons, which fundamentally reflects the characteristics of

electrochemistry in producing low pollution and promoting environmental protection in the treatment process [2,3]. The reactants directly enter the reaction system, and more types of organic substances can be involved in the reaction, while the efficiency of energy utilization is improved. The reaction device of electrochemical technology is simple and easy to operate, and the reaction conditions are milder, which means that the whole process is simpler with easier automation control, thus leading to a bright future of industrial application [4].

Treatment of wastewater with electrochemical technology is a complex process. In a specific electrochemical reactor, electrons in the reactor undergo a directional transfer due to the effect of electric field, thus the pollutants in the water are removed by specific physical and chemical reactions [5–7]. Physical processes mainly contain adsorption, flocculation and separation of pollutants. while chemical processes can be divided into direct electrolysis and indirect electrolysis. Direct electrolysis means that the pollutant is directly reduced or oxidized in the electrode, which includes anodic and cathodic treatment processes. When the reaction takes place on the surface of the anode, the pollutant is oxidized to a substance that is less toxic, easily biodegradable or even directly mineralized. In this way, the contaminant content in the water is reduced or completely removed [8–10]. Cathodic processes are mainly adopted to recover heavy metals and reduce halogenated hydrocarbons, and pollutants are reduced and eliminated on the cathode surface. Indirect electrolysis means that the pollutants are transformed or degraded with strong oxidation products or intermediate reducing substances produced by electrochemical reactions.

2. ELECTROCOAGULATION WATER TREATMENT TECHNOLOGY

Electrocoagulation water treatment technology, also commonly referred to as electrofloatation, is applied in removing colloidal impurities from wastewater, as well as in dyeing and galvanizing wastewater treatment [11,12]. The mechanism is that an external voltage is applied to the soluble anode to produce cations, which then react with the colloidal contaminants in the water. As a result, the colloidal contaminants with steady state would lose their stability and settle after coagulation. At this point, a certain amount of hydrogen is released from the cathode of the current. With less density than that of water, hydrogen can carry the deposited contaminants to the water surface during the uplifting process. In this way, the contaminant and the water body can be separated [13,14]. However, the cathode and anode materials in this method will be dissolved, and in practice, a large amount of electrical and metallic materials will be consumed. Hence it cannot be widely promoted at present [15,16].

Al₁₃ form is the most effective component of flocculants. The electrochemical synthesis of high content Al₁₃ flocculation forms is the key to improve the efficiency of electroflocculation water treatment. Polymeric aluminum chloride (PACI) with Al₁₃ content up to 90% can be prepared with aluminum plates being anodes and by adjusting the solution chemical conditions and electrochemical parameters during electrolysis. Applying a similar principle of action, Hu et al.[17] investigated the optimal conditions for the generation of Al₁₃ forms during the electroflocculation process. It was found that the electroflocculation time of 5-15 min, pH=5-7, low current density and induction electrode conditions were favorable for the formation of Al₁₃ morphology. The Al₁₃ content was more than 60%

at the highest. In addition, the floc morphology determines the water treatment effect during the electroflocculation process. Current density and water pH value are the most important parameters affecting floc morphology structure. Higher current density and pH value are beneficial for the generation of large-size flocs. However, the specific surface area of flocs produced at low current density and pH value is larger and more loose and porous. Since the flocs generated in a weakly acidic environment have a high adsorption capacity, the highest rate of removing humic acid with electroflocculation method can be achieved.

The effectiveness of electroflocculation water treatment can be affected by the selection and arrangement of electrodes. For oily wastewater, the efficiency of COD removal with aluminum electrodes is slightly lower than that of iron electrodes. Bayramoglu et al. [20] found that the rates of removing COD and SS with aluminum and iron electrodes are relatively similar, but the cost of iron electrodes is lower. The optimum conditions include current density of 30 A/m^2 , electrolysis time of 15 min, and optimum pH of 7, and the optimum pH of the aluminum electrode is 5. Usually, the arrangement of the electrode plates can be either monopolar mode or complex mode. Yu et al. [18] investigated the efficacy of monopolar and complex electroflocculation for removing silicate ions from brackish water, and the results show that the treatment efficiency of complex electroflocculation process is higher. Under optimal conditions, a removal rate of up to 80% can be achieved as the feed water silicate mass concentration is 80-200 mg/L.

In addition, direct current tends to cause passivation of the electrode plates in the electroflocculation process, thus more studies focus on the application of AC. Vasudevan et al. [19] compared the effect of DC and AC on the removal of cadmium ions from water, finding that the removal of cadmium with AC is 1.3% higher and the energy consumption is 55% lower than that of DC at an electrode current density of 0.2 A/dm^2 and $\text{pH}=7$. Eyvaz et al. [20] studied the performance of AC electroflocculation for the treatment of dye wastewater. The result reveals that the removal of dyestuff increases with the operation time. The opposite is true for DC and the operating cost of DC is 30% higher than that of AC per 1 kg of dye treated.

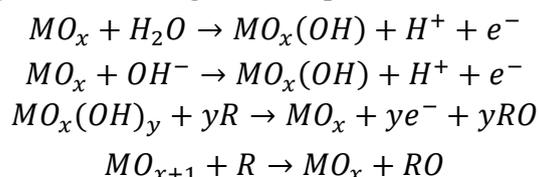
With a capacity of effectively removing soluble organic matter such as particulate matter and humic acid from water, electroflocculation has been widely adopted as a pretreatment technology in membrane separation processes in recent years. Electroflocculation produces flocs that form a loose and porous cake layer on the membrane surface to reduce membrane contamination and remove contaminants more efficiently [21]. Sari et al. [22] studied electroflocculation-microfiltration to reduce membrane contamination and improve water quality, with the results presenting that the membrane flux increases from 51% to 72% in microfiltration compared with electroflocculation-microfiltration. Electroflocculation controls the generation of disinfection byproducts by removing natural organic matter and forming large flocs to mitigate microfiltration membrane contamination [23]. Compared with the separated electroflocculation and membrane separation process, Sun et al. [24] made a further improvement on the conventional technique. They developed a novel electroflocculation membrane reactor (ECMR) by placing an ultrafiltration membrane assembly between two electrodes, and both electric field effect and electroflocculation were applied. Compared with the separated electroflocculation-ultrafiltration process, the ECMR membrane flux can increase by about 15%.

Moreover, with the advantages of small footprint and energy saving, ECMR can save energy consumption by up to 6.4% at a current density of 10 A/m².

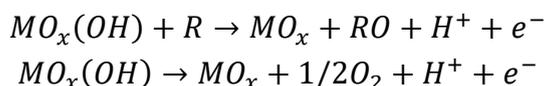
3. ELECTROCHEMICAL OXIDATION TREATMENT TECHNOLOGY

Electrochemical oxidation water treatment technology is mainly adopted to effectively change certain organic types of pollutants in water, leading to a change in the activity of the functional groups, as a result of which their chemical properties can also change to a certain extent. Electrochemical oxidation technology can effectively reduce the toxicity of organic pollutants in the water to be treated, which reduces the difficulty of subsequent treatment, thus the biodegrading of certain macromolecular pollutants becomes easier [25,26]. Direct and indirect electrolysis are two methods of treating wastewater with electrochemical oxidation [[27,28], but there is no absolute boundary between the classification of direct and indirect oxidation. Generally, both oxidation processes occur at the electrode during the electrochemical decomposition of organic matter, while experimental conditions and changes in the control parameters during the experimental process can lead to different degrees of changes in the decomposition mechanism [29].

After energization, the anode produces physisorbed active oxygen and chemisorbed active oxygen. The electrode discharge forms adsorbed hydroxyl radicals on the surface. The higher valence state of the oxide MO_x is formed by the reaction between the hydroxyl radical and the oxygen preexisting on the anode, as well as the transfer of oxygen from the hydroxyl radical to the metal oxide. As organic matter is present in the wastewater solution, the activated oxygen is able to oxidize the organic matter on the electrode surface through the following reaction process:



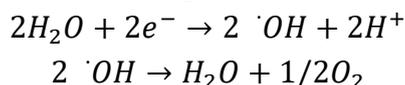
For inert electrodes, the ·OH does not bind well to the electrode since there is no active site for binding to free radicals. The ·OH will react directly with the organics it contacts, and a competitive oxygen precipitation reaction also occurs.



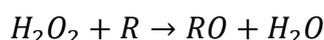
Anode material is the most important factor affecting the reaction rate and selectivity of anode direct oxidation. High oxygen precipitation superpotential, high stability and high catalytic activity are required for anode materials. DSA electrodes have good stability and catalytic activity, and are usually doped to improve their oxygen precipitation potential and catalytic performance. For example, in the printing and dyeing wastewater treated with Ti/SnO₂-Sb₂O₅, Ti/RuO₂, and Ti/IrO₂-RuO₂ anode, most of the organic matter can almost be completely removed. Turro et al.[30] achieved 90% and 65% removal of COD and TOC, respectively, from electrolytic waste leachate using T/IrO₂-RuO₂ as an anode. In their study, the removal of chromaticity and phenols reached 100%, and the treatment energy consumption was 35 kWh/kg (in terms of COD). The results show that the BDD electrode not only has good electrical

conductivity, chemical stability, and corrosion resistance, but also has extremely strong oxidation activity and a good removal effect on pollutants. Perez et al.[31] investigated the degradation effect of BDD electrode on a variety of pollutants in reverse osmosis concentrated water. It was found that in addition to ammonia nitrogen and COD, many new environmental pollutants (e.g., nicotine, caffeine, furanic acid) can also be effectively removed. The presence of $\cdot\text{OH}$ in the free state on the surface of the BDD electrode is the main reason for the strong oxidative activity of the BDD electrode. Different from the bound $\cdot\text{OH}$, the free $\cdot\text{OH}$ is less likely to combine with each other and undergo oxygen precipitation side reactions, thus having a stronger oxidation capacity.

Indirect oxidation reaction anode reaction produces:



The cathode produces a polar inverse:



Jackson et al.[32] suggested that the small amount of oxygen produced on the anode surface is reduced by the cathode to produce H_2O_2 , which is converted to $\cdot\text{OH}$ under alkaline conditions.

Indirect oxidation is a method for the oxidative degradation of organic pollutants through the intermediate substances with strong oxidizing properties generated by electrode reactions. Both the oxidizing power of the anode and that of the generated oxidant are utilized in the indirect oxidation technology, therefore, the treatment efficiency is substantially increased. Indirect oxidation can be realized in the following two forms.

The first is the indirect oxidation of organic matter using anions in water. The sulfate, chloride and phosphate ions present in the solution produce persulfate, reactive chloride and superphosphate under the action of electrodes. These active intermediate substances have strong oxidizing properties, which can degrade the organic matter with strong oxidation. For example, when sulfate ions are present in the solution, they are oxidized to persulfate ions at the anode. Peroxynitrite ion contains peroxy with strong oxidizing properties. In addition, the persulfate ions can be activated and decomposed into sulfate radicals with stronger oxidation capacity under light and heat conditions. The standard redox potential of sulfate radicals is close to or even exceeds that of the highly oxidizing hydroxyl radicals. All these mechanisms can oxidize and remove most of the organic matter. In the treatment of some complex organic pollutants, the degradation can be promoted by adding several of these anions to the solution. Grgur et al.[33] added NaCl to the electrochemical degradation of methomyl and found that the methomyl degradation rate increased after the addition of NaCl. Under the reaction conditions of current density of 10-20 mA/cm² and NaCl mass concentration of 5 g/L, more than 90% degradation can be achieved within 0.5 h. The rate is comparable to that of the advanced oxidation process, and the main intermediate product, methomyl alum, can be further decomposed in the presence of active chlorine. However, it is worth noting that in the presence of chloride ions, the electrochemical process may undergo reactions in which chlorine combines with organic matter to form more toxic chlorinated organic matter or other by-products of chlorine, such as perchlorate.

The first highlight is the indirect oxidation of organic substances with reversible redox electric pairs. The low valence cations or metal oxides present in the solution can be oxidized to higher valence states in the electrochemical process, and these high-valent metals then oxidize and degrade the organics,

while being reduced to their original valence state. Pollutants are removed by continuous oxidation with a reversible cycle of metal ions in the high and low valence states. Fe(III)/Fe(II), Ni(III)/Ni(II), and Co(III)/Co(II) are electric pairs that are commonly used. Leffrang et al.[34] investigated the degradation of peal-chlorophenol, 4-chlorophenol, and phenol by the Co(III)/Co(II) redox electric pair. The research results show that these pollutants can be degraded to carbon dioxide and carbon monoxide with a degradation rate of more than 98% and a maximum current efficiency of 75%.

4. ELECTRODIALYSIS AND REVERSE ELECTRODIALYSIS

Electrodialysis is easier to operate compared with other methods, which also means simpler maintenance and a longer life [35]. Electrodialysis is the separation of electrolytes in wastewater through the synergistic effect of a direct current field and an ion exchange membrane, which results in the migration of ions in the solution. The selective permeability of the membrane allows the anions and cations to migrate to different electrodes to remove pollutants from water [36]. Kuichang et al.[37] combined electrodialysis with microbial fuel cells to treat organic wastewater at high concentrations and demonstrated a high rate of removing organic matter through experiments.

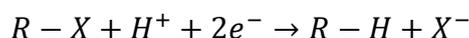
Electrodialysis is not suitable for the desalination of organic wastewater with high concentration directly due to the high concentration of organic matter may lead to membrane clogging and membrane contamination, and is often adopted in combination with other treatment technologies. Zuo et al.[37] developed a multistage microbial fuel desalination cell to treat high-concentration organic wastewater by combining electrodialysis with microbial fuel cells, which achieved simultaneous organic removal and desalination. The results show that when the wastewater flow through two pairs of anodes and cathodes, the rates of removing COD, total nitrogen, and ammonia nitrogen are 97.8%, 90.6%, and 98.4%, respectively. In the electrodialysis process, different charged ions can pass through the ion exchange membrane to achieve separation and concentration. Therefore, it can be applied as a method to recover valuable substances from wastewater. Conventional electrodialysis cannot separate ions with the same charge electrical properties but different valence states, while the application highly selective ion exchange membranes can significantly improve the separation efficiency. Liu et al.[38] developed a selective electrodialysis membrane for the deep treatment of secondary effluent water. In their study, nitrogen and phosphorus were separated by a monovalent selective ion exchange membrane (MVA), NO_3^- plasma entered the brine chamber through the MVA, and HPO_4^{2-} plasma was blocked by MVA to stay in the product chamber, thus realizing the recovery of nitrogen and phosphorus resources and zero wastewater discharge. The results present that the nitrogen and phosphorus recovery rates reach 78.5% and 78.4%, respectively, at a voltage of 3V when 3 membrane pair structures are used, indicating that increasing the voltage and reactor flow rate can improve the recovery rate. Wang et al.[39] applied a modified 3-chamber electrodialysis in recovering petroleum sulfonates from petrochemical dispersants. The fluorinated ion exchange membranes used in the device has a higher crosslinking than heterogeneous ion exchange membranes. The results show that a 99.4% mass fraction of petroleum sulfonate can be recovered from the petrochemical dispersant at an applied voltage of 25 V, a flow rate of 30 L/h, a temperature of 40 °C, and an initial $(\text{NH}_4)_2\text{SO}_4$ mass fraction of 7.5%. In addition, with this

device, petroleum sulfonate-free $(\text{NH}_4)_2\text{SO}_4$ solution can be obtained in the concentration chamber. The process of producing ginger saponin generates a large amount of acidic hydrolysis waste solution. A 3-chamber electro dialysis was used to recover sulfuric acid from the ginger saponin hydrolysis waste stream. The results reveal that the separation efficiencies of H^+ , SO_4^{2-} , and TDS are 81.4%, 81.6%, and 97.9%, respectively, with the current density being 130 A/m^2 . The electricity consumption for separating 1 kg of sulfuric acid is 8.4 k/Wh.

The development of ion exchange membranes with high selectivity and high contamination resistance has been and will continue to be a hot research topic. Moreover, reducing the energy consumption of electro dialysis to expand its application areas will be the focus of future research.

5. ELECTROCHEMICAL DIRECT REDUCTION

In electrochemical water treatment, the major part of direct reduction process of the cathode is reduction dehalogenation. The halogen atoms in the halogen compounds are easily substituted with the adsorbed hydrogen atoms formed on the surface of the cathode through gaining electrons. The reaction process is as follows:



During the reductive degradation of organic matter, cathodic hydrogen precipitation is the main side reaction, which leads to the loss of energy efficiency, thus requiring materials with higher hydrogen precipitation overpotential. The commonly used cathodic reduction electrode materials include carbon materials (activated carbon fiber electrodes, mesh porous carbon electrodes, and carbon nanotube electrodes) [46-48], organic polymer materials (polyaniline film electrodes) [49], etc. To further improve the electroreductive activity of the cathode, modifications with monometal, bimetal, and alloys are required [50-52]. Studies show [53-54] that noble metals (e.g., Pd) have superior hydrogen production and hydrogen fixation properties, thus electrocatalytic reduction systems based on Pd-based materials have also been a hot research topic in recent years.

Korshin et al.[49] reported good electrical reduction of haloacetic acids other than MCAA with Cu and Au electrodes. Zhao et al.[50] applied BDD and counter electrodes (graphite electrode, carbon paper) in the reduction of bromate removal from water. The results show that the BDD electrode has strong reduction performance. Nearly 90% of the bromate can be removed within 2 h under the application of a bias voltage of 1.0 V (vs. SCE). Despite that halogenates are difficult to biodegrade, the electroreduction process can selectively remove halogen atoms under mild conditions, which can improve the biochemical properties of wastewater. Hence the electroreduction halogenated organic matter dehalogenation has received wide attention.

In the academic field, there is no unified explanation for the mechanism of electroreduction of nitrate. One understanding is that during the reduction process, H^* is first reduced to H-atoms and nitrate is indirectly reduced by H atoms adsorbed on the electrode surface. The other is that nitrate is directly reduced by electrons. Langmuir-Hinselwood kinetic studies show that nitrate is adsorbed at different sites on the electrode surface, compared with hydrogen. Therefore, most researchers hold the view that the two mechanisms exist simultaneously.

Peel et al.[51] reported the reduction of nitrate at an electrode potential of -1.5 V (vs. SCE) with 30% Rh-modified carbon cloth being cathode. The nitrate concentration in water is reduced from 73 mg/L to 39 mg/L after 40-60 min of reaction. Wang et al.[52] adopted a PdCu electrode for effective electrocatalytic reduction of nitrate in water. The nitrate removal rate can reach 83.3% with a selectivity of 80.13% within 120 min. In addition, Wang et al.[53] also catalyzed the reduction of nitrate in water using a Pd/Sn bimetallic catalyst with surface modification on an activated carbon fiber electrode. The highest selectivity was shown when Pd:Sn = 4:1 (molar ratio) in the catalytic reaction.

Electrocatalytic reduction of halogenated organics with non-metallic electrode materials (e.g., carbon-based materials) often requires a higher cathodic overpotential. The violently generated hydrogen gas inhibits the migration of contaminants to the cathode surface. In contrast, applying carbon materials as substrates loaded with small amounts of noble metal catalysts (Pd, Rh, Ag, etc.) can achieve higher dehalogenation activity at lower overpotentials. Mao et al.[54,55] established the first in situ characterization of atomic H* with Pd composite electrodes. They captured the nine-fold characteristic peak of atomic H* through ESR and proved the indirect reduction of atomic H* in the electrocatalytic reduction system. Additionally, they developed Pd/graphene composite electrode and Pd/graphene 3D particle electrode continuous flow reactor to study BrO₃⁻ removal in water. According the results of their experiments, at a low voltage of -0.5 V, the Pd/rGO/CFP electrode can completely reduce BrO₃⁻ to Br⁻, and in the three-dimensional continuous flow reactor catalyzed by the main reduction cathode (Pd/rGO) and the particle induction electrode, the BrO₃⁻ effluent concentration of 30 d faucet water is always below 7.5 µg/L, which is lower than 10 µg/L, the standard of drinking water. The above study reveals the promising application of atomic hydrogen H* electroreduction halide for water purification.

In contrast to electrodialysis, reverse electrodialysis (RED) is a process that generates electrical energy by capturing the salt difference energy between concentrated and fresh water. A reverse electrodialysis device consists of an anode, a cathode, and alternating rows of anion and cation exchange membranes [56]. Concentrated and fresh water chambers are between the ion exchange membranes. Driven by the concentration difference, salt ions migrate to form an internal current, which is converted to external current by redox reactions at the electrodes. Reverse electrodialysis equipment is simple, clean and environment-friendly, and its great potential in terms of capacity has received extensive attention. Post et al.[57] predicted that the net power generated per unit membrane area in reverse electrodialysis is 2 W/m² (with a fuel efficiency of 70%), and increasing the net power density would reduce the cost of RED technology.

To promote the application of RED, different teams have been seeking to increase the net power density of reverse electrodialysis. In recent years, tremendous progress has been made in the design of ion exchange membranes and spacers. Conventional spacers used for inter-membrane isolation in RED were non-conductive, which greatly increased membrane resistance and hydraulic friction, limiting the improvement of net power density. This hindrance was overcome by Piotr et al.[58] who applied ion-conductive spacers. Enver et al.[59] developed a special ion-selective membrane for RED, which was prepared from poly(epichlorohydrin) (PECH) and 1,4-diazochloro-octane (DABCO) was used to introduce the anionic group. The membrane material is homogeneous with small thickness and low resistance, which make the power density of RED increase to 1.27 W/m². The increased membrane resistance and decreased permeability caused by membrane contamination reduces the net power density

of RED power production. Actually, it is a major factor that limits the large-scale application of RED. Membrane surface modification is one of the means to control the contamination of RED ion exchange membranes. Mahboobeh et al.[60] coated the AEM surface with polydopamine (PDA) to increase the contamination resistance of AEM. In addition, research on RED membranes mainly covers innovations in membrane materials, preparation and structures. The net power density of reverse electrodialysis can be improved by optimizing the operating conditions, such as concentrated freshwater flow rate, freshwater concentration, number of membrane pairs, and spacer thickness. In recent years, the net power density of RED capacity has increased from 0.7 W/m^2 to 1.5 W/m^2 [61–63], but the expected theoretical value of 2 W/m^2 has not been reached yet.

With the optimization of RED performance, the combination of RED with other technologies also expands its application, such as pollutant degradation and capture of low-grade thermal energy. Scialdone et al.[61] coupled reverse electrodialysis, electro-Fenton, and redox processes to degrade conventional biodegradable wastewater containing acid orange 7 (AO7). According to the results, the production of electricity in the process of treating wastewater reduces the energy consumption of electricity. Anode Cl oxidation generates chlorine gas dissolved in water to produce hypochlorite, while the cathode produces $\cdot\text{OH}$ through electro-Fenton method and in the meantime oxidizes organic matter. 99% chromaticity removal and 55% TOC degradation can be achieved within 1 h. Li et al.[64] investigated a microbial reverse electrodialysis electrolytic cell (MREC) based on Fenton process to treat orange G dye wastewater. The degradation rate is 99.6% and the energy consumption is only 25.93 kWh/kg/ TOC, which is significantly lower compared with the energy consumption of conventional electro-Fenton (865 kWh/kg/TOC) and continuous electro-Fenton (45.8 kWh/kg/TOC) [65,66]. A number of researchers used ammonium bicarbonate for reverse electrodialysis to capture industrial waste heat [67,68]. At a temperature higher than $60 \text{ }^\circ\text{C}$, NH_4HCO_3 decomposes to form fresh water, whereas it dissolves to form concentrated water at a temperature lower than $60 \text{ }^\circ\text{C}$. Hence a closed system is formed, which solves the problem of regeneration of concentrated water and fresh water, and also effectively avoids membrane contamination that is easily caused by the use of natural water sources.

6. PHOTOELECTROCHEMICAL TECHNOLOGY

Photoelectrochemical reactions are redox reactions in which photogenerated electron-hole pairs generated by light irradiation on the surface of a semiconductor in contact with an electrolyte are separated by an electric field at the semiconductor/electrolyte junction and then carried out with ions in solution. TiO_2 is the most widely used photocatalyst, for it is chemically stable, redox-compatible, non-toxic and corrosion-resistant. It absorbs a photon equal to or greater than its band gap energy, which excites a valence band electron to jump from its valence band to the conduction band, thus producing electron (e^-) and hole (h^+) pairs.

The TiO_2 band gap energy is 3.2 eV, thus UV irradiation is required for activation. Negatively charged electrons and positively charged holes can react with water and dissolved oxygen, hydrogen ions, hydroxide ions in water to generate oxygen-containing radicals, such as hydroxyl radicals, superoxide radicals, superoxide radicals, hydroxyl radicals, hydroxide radicals, hydrogen peroxide,

etc., which have extremely strong oxidation capacity. In order to reduce the recombination of electron-hole pairs, oxygen (ozone) or air is generally introduced into the wastewater. Oxygen can rapidly react with electrons to generate superoxide radicals, which react with organic matter to break the unsaturated bonds in the color-forming groups of dyes, producing small molecular weight for decolorization and degradation of organic matter [69]. Ozone is often adopted to remove the organic matter and chromaticity that are difficult to degrade from wastewater [70]. However, problems still exist in applying the oxidation method alone, such as low utilization rate, long reaction time, and insufficient oxidation capacity. Hence the synergy of ozone oxidation technology and photoelectrochemical technology has been widely studied and applied in industrial wastewater treatment [71] and reclaimed water treatment. Boroski et al.[72] treated pharmaceutical wastewater with a combined process of electrocoagulation and titanium dioxide photocatalysis (UV/TiO₂/H₂O₂), and their research results show that the COD of the electrocoagulated effluent is reduced to 160 mg/L as the influent COD is 1753 mg/L, and the COD removal rate reaches 90.87%.

7. ELECTRO-FENTON METHOD

The principle of the Fenton method is that H₂O₂ generated by the electrode reacts with Fe²⁺ in an electrochemical reaction to form radical hydroxyl groups, oxidizing and breaking down the hard-to-degrade pollutants into small molecules. Once the voltage and current are controlled, the process can be easily automated. The effectiveness of the electro-Fenton method can be affected by the voltage, current density, aeration rate, and pH of the water to be treated. Iglesias et al.[73] used a voltage of 5.69 V, pH of 2.24, and a concentration of 2.68 mM of iron ions for synthetic dyes. The results of the research show that the decolorization rate can reach 90% and the COD removal rate can reach 56%. Shin et al.[74] treated food wastewater with a constant current at a density of 28.5 mA/cm². 10 mM of phenol in the wastewater was completely degraded after 40 min, and the TOC of the wastewater was reduced by about 75% after continued treatment. Chemical reactions and Fenton reactions are characterized by an extremely strong oxidation capacity. Ayoub et al [38] degraded trinitrotoluene (TNT) at currents of 60 mA and 250 mA and found that the TNT concentration decreased by 70% and 99% after 5 min of electrolysis. Mohajerl et al.[75] treated waste leachate with electrofenton. 94% COD removal and 95.8% color removal were achieved in their study after 43 min at pH 3, H₂O₂/Fe²⁺ of 1 and current density of 49 mA/cm². Kurt et al.[76] treated leather wastewater with electrofenton. The results show that under suitable reaction conditions, the COD removal rate can reach 60%-70% in only 10 min. It can be seen from these experiment results that the electro-Fenton method has high oxidation capacity and low energy consumption, and has been considered as an environmentally friendly treatment method. However, it is currently more suitable for treating acidic wastewater, while for neutral or alkaline wastewater, a large amount of acidic chemicals need to be added to adjust the pH before treatment, which increases the treatment cost. In addition, the low efficiency of H₂O₂ generation at the cathode cannot meet the actual demand in engineering.

8. ELECTROABSORPTION

Electrosorption is a class of electrochemical water treatment technology based on the double layer theory and adsorption separation, also known as capacitive deionization (CDI) [77]. The principle is that by applying a voltage to the electrodes, the anions and cations in water are subjected to an electric field force and migrate towards the electrode with an opposite charge to their own and are adsorbed by the double layer, thus removing ions from the aqueous solution [78]. Under open circuit or opposite voltage conditions, the adsorbed ions are released and discharged, while the electrodes are regenerated. The operating principle and the electrode materials used are very similar to those of supercapacitors [79,80]. Since electrosorption does not involve the gain or loss of electrons, no additional oxidants, flocculants, etc. are needed, and the required current is only applied in charging the double electric layer at the electrode solution interface [81]. Therefore, electrosorption is a process of low power consumption and low cost, and regeneration can be easily obtained by discharging the electrodes.

The selection and preparation of electrode materials is the core of the electrosorption technology. The structural morphology as well as physical and chemical properties of electrode materials directly affect the adsorption capacity and salt removal efficiency of the electrodes. The following requirements should be met for the electrode materials suitable for electrosorption: large specific surface area, high conductivity, good electrochemical stability, easy to shape, and no participation in Faraday reaction within the applied voltage range. Having all the above characteristics, carbon materials are the most important electrode materials in electroadsorption technology, and the commonly used carbon materials include granular activated carbon [82–84], activated carbon fiber [85,86], carbon aerogel [87], carbon nanotubes [88], graphene [89] and composite carbon material electrodes [90,91].

In the early stage of the research on electrosorption, the electrode materials were mainly based on activated carbon particles. Wang et al.[92] compared several commonly used activated carbon materials and found that the adsorption capacity is proportional to the specific surface area. The adsorption capacity of activated carbon electrode with specific surface area of 2030 m²/g can reach 4.6 mg/g. Zornitta et al.[93] obtained activated carbon materials through polyaniline doped with different anions being precursors. In their study, high-performance CDI electrodes were prepared through anion doping as a template, and the highest unit specific adsorption capacities can be up to 14.3 mg/g (1.2 V) and 14.9 mg/g (1.4 V).

Activated carbon fibers emerged in the 1970s. Compared with conventional activated carbon particles, activated carbon fibers have a rich microporous structure and narrow pore size distribution, which means that it is easy for them to adsorb pollutants and facilitates diffusion. Wang et al.[92] synthesized activated carbon fibers (ACF) by electrospinning polyacrylonitrile (PAN) with a specific surface area of 335-712 m²/g. The nanofiber diameter can be adjusted by the activation temperature. The adsorption capacity can reach 4.64 mg/g at an operating voltage of 1.6 V, when activated carbon fibers are used as electrodes for sequential batch electrosorption experiments. Activated carbon fibers, as the third-generation new carbon materials, have been developed rapidly in recent years.

Carbon nanotubes are a class of carbon materials with a needle-like tubular structure, and have a very high specific surface area and unique pore structure with abundant functional groups. Through certain physical and chemical treatments, the active sites on the surface and inner lumen parts can be

fully utilized, thus improving the adsorption efficiency. Carbon nanotubes can be regarded as convoluted single-layer carbon atomic sheets, and they can be classified into single-walled carbon nanotubes (SWCNTs) and multi-walled carbon nanotubes (MWCNTs) according to the number of sheets. Li et al.[94] compared the electroadsorption effect of these two types of carbon nanotubes as CDI electrodes. The results show that the adsorption efficiency is correlated with specific surface area, pore size structure and hydrophilic groups. Through chemical deposition, Wang et al.[95] obtained carbon nanotube sponge materials, with an adsorption capacity of up to 40 mg/g at an operating voltage of 1.2 V. The result indicates that carbon nanotube sponge materials are excellent for electrosorption with an even higher theoretical adsorption capacity.

Graphene is a well-studied two-dimensional layered carbon nanomaterial in recent years [96]. Due to the extremely excellent physical and chemical properties, graphene-based and graphene-derived materials are widely applied as CDI electrode materials. Liang et al.[97] prepared self-assembled carbon-nitrogen modified graphene hydrogel (CN-GS) by hydrothermal method with melamine and graphite oxide being precursors. An adsorption capacity of up to 9.19 mg/g can be reached in the electrosorption desalination test, thus it is an ideal material for electrosorption. Distinct from the common template and hydrothermal methods, direct lyophilization of graphene oxide solution and annealing under NH_3 atmosphere was adopted by Xu et al.[98] to prepare nitrogen-doped graphene sponge NGS. With this simple way of preparing electrodes on a large scale, NGS materials with high adsorption capacity can be produced. The results show that the adsorption capacity is up to 21 mg/g in 500 mg/L salt solution. Shi et al.[99] constructed a new CDI electrode based on a three-dimensional graphene (3DG) structure. They used planar nanopore structures to construct interconnected graphene sheets (NP-3DG). The results show a very high specific surface area ($445 \text{ m}^2/\text{g}$) and specific capacitance with an adsorption capacity of 17.1 mg/g at 1.6 V.

In addition, metal oxide material electrodes, composite material electrodes, and polymer material electrodes have been widely studied and applied in electrosorption technology. Hu et al.[100] prepared layered metal hydroxide loaded Pd materials as electrode materials by in situ hydrothermal reaction. The materials have high specific capacitance and low mass transfer resistance, being able to efficiently adsorb nitrate ions from the solution during charging. During the discharge process, the adsorbed nitrate is denitrified to produce nitrogen gas through the electric reduction process. Meanwhile, the electrode is regenerated and no concentrated water is produced.

9. CONCLUSION AND PERSPECTIVES

With the continuous development of materials science and electrochemical characterization means in recent years, the electrochemical water treatment technology has been increasingly advanced in the past 10 years. The electrode materials have been evolved from traditional metal electrodes to two-dimensional laminated material electrodes. The target has changed to the removal of new pollutants, while the focus has evolved from water treatment efficiency to simultaneous recovery of energy and resources. The development of electrode materials and the electrochemical regulation of micro-interface processes have always been the topic with great significance in this field. In recent years, research in this field has emphasized the precise regulation of electron transfer processes to achieve the targeted

transformation of pollutants. Moreover, electrochemical water treatment technology has been gradually integrated with other physical and chemical methods such as biological and membrane separation to form a combined process to solve practical water quality problems.

Through the review of the relevant research and consideration of application trends, it can be summarized that the future research of electrochemical water treatment technology will mainly focus on the following 3 aspects:

1) Design and development of functional electrode materials. Efficient and stable electrode materials are the core of electro-oxidation water treatment technology. The development of electrode materials based on optimized electron transfer and micro-interface regulation will directly affect the efficiency of electro-oxidation water treatment and is the focus of current and future research. Additionally, the development of efficient, inexpensive and mass-producible electrode materials will contribute to achieving large-scale practical engineering applications of electro-oxidation technology.

2) Optimization of reactor structure. The optimization of the electrode reactor structure will affect the flow channel and flow field distribution in the reaction process, strengthening the water treatment effect and reducing energy loss. Furthermore, combining multiple processes to achieve synergistic effects can achieve efficient, green and clean production.

3) Recovery of resources and energy. The pollutants of wastewater contain a large amount of chemical energy. How to recover the chemical energy to achieve the degradation and simultaneous production of pollutants is the future trend of water pollution treatment. Through the control of electrode reaction and refinement of micro-interface regulation, the pollutants will be separated and transformed in an efficient and targeted way.

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