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Research Progress on Anode-Enhanced Electro-Fenton for the Degradation of Organic Pollutants

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Abstract: Organic pollutants in water bodies such as domestic sewage, agricultural runoff, and industrial wastewater present significant challenges to environmental protection due to their persistence, toxicity, and potential for bioaccumulation. The electro-Fenton (EF) technology has emerged as one of the most effective methods for the degradation of organic pollutants. This review aims to provide an updated understanding of anode-enhanced electro-Fenton in the degradation of organic pollutants. We outline the core principles and mechanisms of the electro-Fenton process, followed by a detailed discussion of the factors influencing its performance, including electrode materials, current density, Fe^{2+} concentration, and pH conditions. Furthermore, we systematically explore various strategies involving anode materials for efficient pollutant removal under different operational conditions. The review also examines the mechanisms of the anode-enhanced electro-Fenton process, explaining how organic pollutants are broken down into non-toxic or low-toxicity products. Finally, we identify the future challenges and prospects in the development and application of this advanced oxidation process, emphasizing its potential in large-scale industrial applications.

Keywords: Electro-Fenton; Anodic enhancement; Organic pollutants; Modification; Degradation mechanism.

1. Introduction

In recent years, rapid industrialization and economic growth have significantly impacted water resources[1,2]. Among the various types of pollutants, organic pollutants—such as phenols, dyes, and pharmaceuticals found in industrial wastewater—have become a major environmental concern[3,4]. These pollutants are not only difficult to degrade, but also exhibit high toxicity, persistence, and potential for bioaccumulation in aquatic ecosystems[5]. As a result, effective methods for removing organic pollutants from wastewater are urgently needed.

Traditional methods for treating organic pollutants include physical, biological, and chemical techniques[6]. While physical methods like adsorption and membrane filtration can concentrate pollutants, they do not address the issue of pollutant degradation. Biological treatment methods, although effective in some cases, are limited by their slow reaction times and the potential toxicity of certain pollutants to microorganisms[7]. On the other hand, chemical treatments, particularly advanced oxidation processes (AOPs), have gained significant attention due to their high oxidation efficiency, ability to degrade a wide range of organic pollutants, and minimal secondary pollution[8].

Among various AOPs, electro-Fenton (EF) technology has gained widespread attention due to its high efficiency, relatively low energy consumption, and minimal secondary pollution. The core of the electro-Fenton process lies in the electrochemical generation of hydrogen peroxide (H_2O_2) at the cathode through the reduction of dissolved oxygen. Its principle lies in the reduction reaction occurring at the cathode under the influence of direct current, leading to the formation of H_2O_2 from oxygen in the aqueous phase. This then rapidly reacts with Fe^{2+} from the anode or externally supplied Fe^{2+}, producing •OH and Fe^{3+}. On the electrode surface, Fe^{3+} ions are directly converted back to Fe^{2+} ions, initiating a new cycle of the Fenton reaction and ensuring its continuous progression[9].

$$O_2 + 2H^+ + 2e^- = H_2O_2 \quad (1)$$

$$H_2O_2 + H^+ + Fe^{2+} = \bullet OH + Fe^{3+} + H_2O \quad (2)$$

$$Fe^{3+} + e^- = Fe^{2+} \quad (3)$$

These hydroxyl radicals (•OH) are highly reactive and play a key role in the oxidative degradation of organic pollutants. In addition to •OH, other reactive oxygen species (ROS) such as superoxide anions ($\bullet O_2^-$) and hydrogen peroxide (H_2O_2) may also be involved, depending on system conditions. These radicals work synergistically to break down the pollutants into simpler, non-toxic compounds such as carbon dioxide and water.

2. Factors Affecting Electro-Fenton Performance

2.1. Reaction conditions

2.1.1. pH

In the electro-Fenton reaction process, the pH value significantly influences both the reaction efficiency and the generation of free radicals[10]. Excessively high or low pH levels can reduce the regeneration rate of Fe^{2+}. When the pH is too low, the following hydrogen evolution side reaction occurs at the cathode:

$$H_2O + Fe^{3+} \rightarrow H^+ + Fe^{2+} + HO_2\bullet \quad (4)$$

$$\bullet OH + H^+ + e^- \rightarrow H_2O \quad (5)$$

In cases of excessively high pH, Fe^{2+} and Fe^{3+} ions readily react with OH^-, forming precipitates of $Fe(OH)_2$ and $Fe(OH)_3$, respectively:

$$2OH^- + Fe^{2+} \rightarrow Fe(OH)_2 \quad (6)$$

$$3OH^- + Fe^{3+} \rightarrow Fe(OH)_3 \quad (7)$$

The formation of these precipitates significantly reduces the effectiveness of iron ions as catalysts, leading to a decline in the efficiency of the electro-Fenton reaction.

At a pH of 3, the highest concentration of •OH is generated in the electro-Fenton reaction. Donadelli et al used zero-valent iron (ZVI) as the cathode and introduced hydrogen peroxide to form an electro-Fenton system for the degradation of refractory organic pollutants[11]. The experimental study examined the impact of solution pH on the degradation efficiency, revealing that the most effective pollutant degradation occurred at a pH of 3.

2.1.2. Current density

The influence of current density on the electro-Fenton process is primarily reflected in the rate of hydrogen peroxide generation, the reaction rate, and the catalytic role of iron ions[12]. A higher current density can enhance the generation rate of hydrogen peroxide, thereby improving the degradation efficiency of the reaction. However, excessive current density may trigger side reactions, such as the formation of oxidation by-products and gas release, which can inhibit the catalytic function of iron ions and potentially cause electrode surface corrosion or clogging. Therefore, an optimal current density is essential for enhancing the efficiency of the electro-Fenton reaction, while excessively high current density may diminish its effectiveness, necessitating the identification of the optimal current density during the reaction optimization process. Ruiz et al used a single-chamber electrochemical system with a boron-doped diamond (BDD) anode and an air-diffusion electrode (ADE) as the cathode, investigated the degradation and mineralization of azo dyes[13]. They found that at current densities of 25, 50, 100, and 150 mA cm^{-2}, TOC was almost completely mineralized within 360, 330, 240, and 180 minutes, respectively, with a removal rate reaching 95%. However, as the current density increased, the efficiency gradually declined, with the highest value of 96% achieved within 120 minutes at 25 mA cm^{-2}, dropping to 34% within 40 minutes at 150 mA cm^{-2}.

2.1.3. Fe^{2+} Concentration

The concentration of Fe^{2+} directly impacts the production of hydroxyl radicals, which are responsible for the oxidative degradation of organic pollutants[14]. However, excessive Fe^{2+} can lead to side reactions where Fe^{2+} itself scavenges •OH radicals, thus reducing their availability for pollutant degradation. Long Y. et al. utilized carbon felt and BDD as the cathode and anode, respectively, to degrade Microcystis aeruginosa[15]. They investigated the impact of Fe^{2+} concentration on the degradation efficiency. The study revealed that as the Fe^{2+} concentration increased, the degradation efficiency improved. However, when the concentration exceeded the optimal level, the efficiency decreased, primarily due to the excess Fe^{2+} consuming •OH, leading to the following reaction:

$$\bullet OH + Fe^{2+} \rightarrow Fe^{3+} + OH^- \quad (8)$$

2.2. Electrode materials

2.2.1. Cathode Material

In the Fenton system, the cathode material plays a crucial role in the catalytic kinetics and removal mechanism, serving as the key element in the activation of H_2O_2 production on the electrode surface. It is an essential carrier for the reduction and regeneration of Fe^{3+}/Fe^{2+}. Currently developed cathode catalytic materials include precious metals and alloys, metal oxide electrodes, and carbon-based synthetic materials[16].

Precious metal cathode materials, such as platinum, gold, and lead, along with their alloys, efficiently catalyze the high-selectivity generation of H_2O_2 from O_2 and are the preferred catalytic materials for electrochemical reactions. However, their low cost-effectiveness and the potential for secondary pollution from certain metals, due to their reactive chemical properties, limit the large-scale application of precious metal catalysts[17].

Metal oxide electrodes, including RuO_2, IrO_2, SnO_2, and PbO_2, have varying characteristics[18]. RuO_2 and IrO_2 exhibit low oxygen evolution potentials of 1.5 V and 1.4 V, respectively, leading to high oxygen production but low current efficiency. SnO2 has poor conductivity, structural instability, and a short lifespan. PbO_2, on the other hand, offers good conductivity, ease of preparation, low cost, and a relatively high oxygen evolution overpotential (1.8 V). However, under the influence of an electric field, PbO_2 loses electrons and forms Pb^{2+}, which can damage brain neurons and cause blood and brain disorders, thereby restricting the application of PbO_2 electrodes in water treatment[19].

Carbon-based synthetic cathode materials, such as gas diffusion electrodes, graphite, and glassy carbon, are inexpensive, non-toxic, exhibit high hydrogen evolution potential, large surface area, abundant availability, environmental friendliness, ease of modification, and good stability and conductivity[20]. These characteristics make them promising candidates for electrochemical advanced oxidation processes, with widespread research interest from scholars worldwide. Researchers have focused on modifying carbon-based materials to enhance H_2O_2 production, employing techniques like nitrogen, sulfur, oxygen, co-doping, and metal doping, yielding promising results. Liu et al developed a heterogeneous electro-Fenton system, utilizing an oxygenated carbon nanotube/iron oxychloride natural air-diffusion electrode (OCNTs/FeOCl NADE) as the cathode, achieving rapid degradation of ciprofloxacin (CIP) across a wide pH range (3–9)[21].

2.2.2. Anode Material

Anode materials must possess corrosion resistance, excellent conductivity, catalytic activity, and the ability to form a passive layer. Common anode materials include noble metal electrodes (Pt, Au, Ir, Ru, etc.), metal oxide electrodes (TiO_2, PbO_2, SnO_2, etc.), and carbon electrodes (graphite, glassy carbon electrodes, etc.).

Platinum (Pt), known for its stability and outstanding electronic conductivity, has long been used as an anode material. Due to the absence of active sites for hydroxyl radicals (•OH) to bond with, •OH directly reacts with organic compounds. Additionally, Pt exhibits a relatively low oxygen evolution overpotential (1.6 V), enabling selective conversion of organic pollutants at lower current efficiencies[22]. It has been demonstrated that pure Pt and Pt electrodes supported by Ti can effectively degrade organic pollutants. For instance, Brillas and colleagues investigated the degradation of diclofenac using Pt anodes, following pseudo-first-order kinetics. Their results showed that the initially colorless diclofenac solution in a neutral buffer (pH 6.5) was degraded under a 300 mA current, gradually turning a strong brown over 180 minutes, continuing until the electrolysis ended (360 minutes), at which point the TOC had decreased by 46%[23]. Pimentel and collaborators explored electro-Fenton oxidation degradation of phenolic aqueous solutions in acidic media ($2.5 < pH < 3.0$) using a carbon felt cathode and Pt anode. When 0.1 mM Fe^{2+} was employed as a catalyst, the

electrolysis for 4 hours resulted in an 80% TOC removal rate[24].

Carbon anodes are regarded as ideal candidates due to their high conductivity, corrosion resistance, and cost-effectiveness. Sopaj F. et al. discovered that graphite felt (GF), when used as both an anode and cathode, exhibited high degradation efficiency for the antibiotic sulfamethazine at low current densities. After 90 minutes of electrolysis, the degradation efficiency reached 100%[25]. Huang et al. employed graphite felt (GF) as an anode for the removal of microcystin-LR, achieving a removal rate 15 times greater than that of a platinum anode[26]. Guivaerh et al. investigated the oxidation degradation products and kinetics of three azo dyes using an electro-Fenton method, revealing that the degradation intermediates on the carbon anode primarily included hydroquinone, ortho-phenylphenol, and 1,3,5-tri-nitrobenzene, with the electro-Fenton degradation of azo dyes following first-order kinetics[27]. However, basic carbon materials exhibit no significant degradation or removal effect on refractory pollutants.

TiO_2 is regarded as a promising metal oxide electrode material due to its low cost, excellent conductivity, chemical stability, and high overpotential for the oxygen evolution reaction[28]. Efforts have been consistently focused on enhancing the electrocatalytic activity and stability of TiO_2. However, the application of TiO_2 electrodes is challenged by electrochemical corrosion. Some research teams have reported the superiority of Ti/SnO_2-Sb and Ti/SnO_2-Sb/PbO_2 with β-PbO_2 as an inert coating in promoting •OH generation. Li et al., using K_2SO_4 as the electrolyte at a pH of 9.0, discovered that after 6 hours of reaction, the Ti/SnO_2 anode exhibited twice the removal efficiency of aniline compared to the Pt anode[29]. Dong et al. synthesized TiO_{2-x} using a hydrogen plasma etching strategy, and compared to the original TiO_2, TiO_{2-x} displayed a significantly increased oxygen vacancy (O_v) content, resulting in higher selectivity for the $2e^-$ WOR to produce H_2O_2[30].

3. Mechanism of Anode-Enhanced Electro-Fenton System

In the anode-enhanced electro-Fenton system, the oxidation of organic pollutants primarily occurs through free radical oxidation. Initially, dissolved oxygen migrates to the cathode surface, where it is reduced to H_2O_2. This electro-synthesized H_2O_2 is then activated to generate •OH, which are the main oxidizing agents responsible for degrading organic pollutants. In addition to •OH, other free radicals, such as superoxide radicals ($•O_2^-$) and hydroperoxyl radicals ($HO_2•$), also play significant roles in the oxidation process. These free radicals work together through two main oxidation pathways: direct oxidation via electron transfer and indirect oxidation mediated by hydroxyl radicals (•OH). These combined reactions can efficiently degrade most organic pollutants, eventually mineralizing them into carbon dioxide (CO_2), water (H_2O), and inorganic ions.

In high-salinity wastewater treatment, the electrolytes (mainly NaCl, Na_2SO_4, and $NaNO_3$) not only increase the conductivity of the reaction system but also generate oxidizing agents such as chlorine species (ClO^-) and sulfate radicals ($SO_4^-•$) through oxidation reactions, thus enhancing the overall oxidation efficiency of the electro-Fenton system[31]. Moreover, different anode materials can influence the activation ability and mechanism of the free radicals. For example, using Ti_4O_7 as an anode material generates a large amount of •OH with low physical and chemical adsorption properties, which can efficiently work alongside Fe^{2+} and H_2O_2 generated •OH to degrade and mineralize pollutants[32].

Despite research on free radical activation mechanisms, current studies mainly focus on free radical quenching experiments and electron spin resonance (ESR) spectroscopy, which provide limited insight into the detailed activation mechanisms. In particular, the interactions between liquid-phase reactions and heterogeneous interface reactions, as well as the variety and activation mechanisms of free radicals generated from molecular oxygen, differ significantly, making it challenging to predict the dominant free radical species and their activation mechanisms accurately.

4. Conclusion

Wastewater containing organic pollutants is challenging to treat using traditional microbiological methods, as they often fail to meet discharge standards. In contrast, the electro-Fenton technology, with its strong mineralization capability, ease of operation, high efficiency, and cleanliness, has garnered increasing attention for the treatment of refractory organic pollutants. However, electro-Fenton technology still faces significant challenges, including high energy consumption, the need for additional electrolytes, low H_2O_2 generation and accumulation, and low Fe^{3+} reduction rates. These issues highlight the need for substantial improvement and development, necessitating the exploration of superior anode and cathode materials. The anode material should exhibit low physical adsorption of O_2, while the cathode material should demonstrate high two-electron redox activity. Additionally, the electrode materials must possess excellent corrosion resistance to ensure energy efficiency and effectiveness. It is also essential to focus on the development of low-carbon energy sources to prevent secondary environmental pollution caused by the materials. Furthermore, establishing a high-efficiency, low-energy electro-Fenton system is a pressing requirement. Currently, electro-Fenton technology has yet to be widely implemented in practical wastewater treatment, but the advancements presented in this study offer new perspectives and references for future development and real-world applications.

References

[1] K. H. D. Tang, R. Li, Z. Li, D. Wang, Environ Chem Lett. 22 (2024) 1155–1183.

[2] Y.-J. He, H. Liao, G. Yang, et al., Environ. Sci. Technol. 58 (2024) 16258–16268.

[3] D. L. Zhao, W. Zhou, L. Shen, et al., Water Research. 251 (2024) 121111.

[4] Y. Wu, J. Bai, X. Wang, et al., Chemical Engineering Journal. 496 (2024) 153698.

[5] J. Georgin, D. S. P. Franco, L. Meili, et al., Advances in Colloid and Interface Science. 324 (2024) 103096.

[6] L. Zhou, N. Li, G. Owens, Z. Chen, Chemical Engineering Journal. 362 (2019) 628–637.

[7] N. Yin, H. Chen, X. Yuan, et al., Journal of Hazardous Materials. 436 (2022) 129317.

[8] Z. Yang, Y. Ma, Y. Liu, et al., Chemical Engineering Journal. 315 (2017) 403–414.

[9] J. Wang, B. Liu, H. Liu, et al., Chemical Engineering Journal. 446 (2022) 137376.

[10] F. Rezaei, D. Vione, Molecules. 23 (2018) 3127.

[11] J. A. Donadelli, L. Carlos, A. Arques, F. S. García Einschlag, Applied Catalysis B: Environmental. 231 (2018) 51–61.

[12] A. Abou Dalle, L. Domergue, F. Fourcade, et al., Electrochimica Acta. 246 (2017) 1–8.

[13] E. J. Ruiz, A. Hernández-Ramírez, J. M. Peralta-Hernández, et al., Chemical Engineering Journal. 171 (2011) 385–392.

[14] M. Li, X. Qin, M. Gao, et al., Environ. Sci.: Nano. 9 (2022) 632–652.

[15] Y. Sun, J. J. Pignatello, Environ. Sci. Technol. 27 (1993) 304–310.

[16] K. Wang, H. Li, Y. Yang, et al., Separation and Purification Technology. 304 (2023) 122302.

[17] Y. Sun, S. Tu, Y. Li, et al., Colloids and Surfaces A: Physicochemical and Engineering Aspects. 690 (2024) 133861.

[18] Y.-X. Guo, D.-W. Wei, L. Zhang, et al., Separation and Purification Technology. 354 (2025) 129174.

[19] X. Wang, C. Xu, Y. Zhu, et al., Surfaces and Interfaces. 44 (2024) 103820.

[20] D. Kubo, Y. Kawase, Journal of Cleaner Production. 203 (2018) 685–695.

[21] Z. Liu, J. Wan, Z. Yan, et al., Chemical Engineering Journal. 433 (2022) 133767.

[22] H. Zazou, N. Oturan, M. Sönmez-Çelebi, et al., Journal of Electroanalytical Chemistry. 774 (2016) 22–30.

[23] E. Brillas, S. Garcia-Segura, M. Skoumal, C. Arias, Chemosphere. 79 (2010) 605–612.

[24] M. Pimentel, N. Oturan, M. Dezotti, M. A. Oturan, Applied Catalysis B: Environmental. 83 (2008) 140–149.

[25] F. Sopaj, N. Oturan, J. Pinson, et al., Applied Catalysis B: Environmental. 199 (2016) 331–341.

[26] C. Huang, W. Huang, J. Xiong, S. Wang, Separation and Purification Technology. 277 (2021) 119502.

[27] E. Guivarch, S. Trevin, C. Lahitte, M. A. Oturan, Environ Chem Lett. 1 (2003) 38–44.

[28] Q. Zhang, J. Duan, Z. Zhu, et al., Chemical Engineering Journal. 497 (2024) 154681.

[29] X. Li, H. Xu, W. Yan, D. Shao, Journal of Electroanalytical Chemistry. 775 (2016) 43–51.

[30] Y. Zhang, J.-X. Liu, K. Qian, et al., Angewandte Chemie International Edition. 60 (2021) 12074–12081.

[31] C. Kim, T. T. Thao, J.-H. Kim, I. Hwang, Chemosphere. 250 (2020) 126266.

[32] N. Oturan, S. O. Ganiyu, S. Raffy, M. A. Oturan, Applied Catalysis B: Environmental. 217 (2017) 214–223.