

Electrodegradation of Acid Red B by N-doped Graphite Cathode in Electro-Peroxone Process

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Abstract

Textile dyeing wastewater is characterized by complex composition and high toxicity. Conventional advanced oxidation technologies like the electro-Fenton process are often constrained by pH range limitations and iron sludge contamination in practical applications. In contrast, electro-peroxone (EP), as an emerging high-efficiency and environmentally friendly technology, demonstrates promising prospects. Although heteroatom doping has been proven to enhance cathode performance, its application in EP processes remains largely underexplored. This study employs a composite strategy combining electrochemical pretreatment with nitrogen doping via melamine pyrolysis to develop a cathode material with broad pH adaptability and high salt tolerance. Results indicate that the optimized electrode achieves favorable configurations of active nitrogen species, exhibiting excellent oxygen reduction electrocatalytic activity with stable degradation performance across a wide pH range (3.0 ~ 11.0) and high salinity conditions. This provides novel insights for developing high-performance electrocatalytic cathodes suitable for complex water quality conditions.

1. Introduction

The textile printing and dyeing industry is one of the major sources of industrial water pollution. According to statistics, approximately 10,000 different types of commercial dyes are produced globally each year, with a total volume of 700,000 tons, of which about 280,000 tons are ultimately discharged into surface water [1]. Azo dyes, the most widely used dyes in the textile industry, account for over 60% of global dye consumption [2]. These dyes are toxic and carcinogenic [3, 4], and improper treatment can release large amounts of pollutants into natural water bodies, causing environmental pollution and severe ecological damage. In response, Advanced Oxidation Processes (AOPs) were developed, which generate highly oxidative hydroxyl radicals ($\cdot\text{OH}$) in water through physical or chemical means. $\cdot\text{OH}$ exhibits an exceptionally high redox potential (2.80 eV), enabling non-selective attack and destruction of molecular structures in most organic compounds, thereby achieving efficient degradation and mineralization of pollutants [5]. In advanced oxidation processes, ozone oxidation and electro-Fenton processes are widely applied, yet both are constrained by inherent limitations that restrict their treatment efficiency and versatility. For ozone oxidation technology, its mechanism involves two pathways: direct oxidation by ozone molecules and indirect oxidation via free radicals. In actual water treatment processes (particularly under acidic or neutral conditions), direct oxidation by ozone molecules predominates. This pathway selectively targets organic compounds, making it difficult to fully mineralize some recalcitrant pollutants, while posing a risk of generating carcinogenic byproducts such as bromates [6]. On the other hand, while the electro-Fenton process efficiently generates hydroxyl radicals ($\cdot\text{OH}$), it heavily relies on a strongly acidic reaction environment to sustain the catalytic activity of ferrous ions. This not only increases operational costs but also generates substantial iron-containing sludge, resulting in secondary pollution and disposal challenges [7].

The electro-peroxone (E-peroxone, EP) process is a novel electrocatalytic advanced oxidation technology developed to address the aforementioned challenges collaboratively. This process ingeniously couples

ozone oxidation with the electrochemical in-situ generation of hydrogen peroxide (H_2O_2), utilizing the continuously produced H_2O_2 at the cathode to initiate an efficient chain reaction with the introduced O_3 (Eq. 1) [8] shifted the oxidation mechanism from "predominantly selective direct oxidation" under ozone alone to "predominantly non-selective free radical oxidation" [9, 10]. This not only significantly improved oxidation efficiency and versatility for complex pollutants, but also effectively avoided the potential bromate formation issues associated with single ozone oxidation [6]. Meanwhile, compared with the electro-Fenton process, the EP process is not reliant on ferrous ions and strongly acidic conditions, resulting in simpler and more environmentally friendly operation [7]. As a result, the EP process has garnered significant attention as a highly promising water treatment technology [11, 12].



The degradation efficiency of electro-peroxone process is largely determined by the oxygen reduction reaction (ORR) at the cathode, specifically the efficiency of oxygen (O_2) reduction to produce hydrogen peroxide (H_2O_2) on the cathode surface. Therefore, enhancing the performance of the electro-peroxone process hinges on optimizing the ORR at the cathode interface, with the core focus being the promotion of O_2 molecule adsorption, activation, and reduction at the catalyst's active sites. In recent years, carbon-based materials such as carbon felt, activated carbon fibers, and graphite felt have garnered significant attention from researchers due to their excellent conductivity, high specific surface area, good chemical stability, diverse tunable surface chemical properties, and relatively low cost [13–17]. However, the surface catalytic activity of original commercial carbon-based materials remains limited. By employing modification techniques such as oxidation, doping, or catalyst loading, the surface properties of these materials can be effectively optimized, thereby enhancing their ORR performance and ultimately improving the overall pollutant degradation efficiency of the system.

Studies have demonstrated that heteroatom doping (particularly nitrogen) can effectively modulate the electronic structure of carbon-based materials, significantly enhancing their oxygen reduction reaction (ORR) catalytic performance [18–20]. Currently, most heteroatom-doped cathode materials are primarily applied in water treatment processes such as electro-Fenton [21, 22] and electrocoagulation. Dong et al. employed electrochemical oxidation to modify graphite felt cathodes. Compared to the original graphite felt cathodes, those modified within 5 minutes achieved a 2.6-fold increase in hydrogen peroxide yield, exhibiting remarkable efficiency and stability in removing ozone-resistant organic pollutants [23]. In 2018, Zhu et al. proposed a highly porous nitrogen-enriched graphite carbon cathode derived from melamine and applied it to the electro-Fenton process. The results show that the 900°C carbonization samples have the best H_2O_2 generation capacity, which can be attributed to the pyrrole nitrogen structure and the improved conductivity. He et al. developed cobalt/nitrogen co-doped carbon composites using melamine and 2,6-pyridine formaldehyde polymerized nitrogen-rich porous polyamines as precursors. Through cobalt ion coordination and subsequent high-temperature pyrolysis, these materials demonstrated high catalytic activity in reducing organic dyes and nitrobenzene compounds [25]. The electro-peroxone process fundamentally requires efficient in-situ hydrogen

peroxide (H_2O_2) generation via the oxygen reduction reaction (ORR) at the cathode. Nitrogen-doped carbon materials are widely recognized as effective means to enhance ORR catalytic activity in carbon materials, indicating strong theoretical compatibility between these requirements. However, empirical studies directly applying nitrogen-doped cathodes to EP systems remain scarce over extended periods, creating a notable research gap. Regarding nitrogen source selection, melamine emerges as an efficient nitrogen-rich precursor due to its molecular structure containing up to 67% theoretical nitrogen content. This characteristic enables post-pyrolysis introduction of high-concentration nitrogen atoms into the carbon framework, thereby generating abundant catalytic active sites. Studies indicate that melamine-derived nitrogen-doped carbon materials exhibit high nitrogen content, with the formed graphite nitrogen and pyridine nitrogen serving as key active centers capable of efficiently catalyzing oxygen reduction reactions [26]. Therefore, melamine was selected as the nitrogen source for subsequent research in this paper.

Although nitrogen-doped carbon materials have demonstrated potential in conventional wastewater treatment, there remains a significant gap in research on high-salinity wastewater—a unique and challenging domain. The presence of abundant inorganic salt ions (e.g., Na^+ , Cl^- , SO_4^{2-}) in high-salinity wastewater exerts complex dual effects on advanced oxidation processes. On one hand, high-concentration background electrolytes may inhibit the primary reaction pathway through competitive adsorption or radical quenching. On the other hand, specific components (e.g., Cl^-) may be converted into active chlorine species, providing additional oxidation pathways [27]. Consequently, the net effect of high-salinity environments on degradation efficiency—whether inhibitory or promoting—depends on the dominant mechanism, which is closely related to the characteristics of the electrode material and the chemical composition of the saline solution. Notably, the surface properties of carbon materials are critical in determining their salt ion interference resistance. We hypothesize that precise nitrogen doping can establish stable catalytic active centers (e.g., graphite nitrogen and pyridine nitrogen) on graphite felt surfaces. By inducing electronic effects such as localized positive charges in the carbon framework, this approach enhances the specific interaction between the catalyst and reactant (O_2) in the ORR reaction. It, in turn, partially mitigates the competitive adsorption effects of non-specific ions (e.g., Na^+ , SO_4^{2-}), thereby improving the structural stability and catalytic selectivity of the electrode in high-salinity environments. Existing studies have primarily evaluated these materials in simple single-electrolyte systems (e.g., low-concentration Na_2SO_4), with insufficient research on their performance and tolerance in complex high-salinity environments. Therefore, it is not only necessary to evaluate the performance of nitrogen-doped cathodes in high-salinity environments, but also important to understand the interaction between the surface chemistry of carbon materials and complex medium environment.

Based on this, the study proposes that optimizing electrode surface chemistry through nitrogen doping strategies could establish a stable catalytic interface resistant to salt ion interference while maintaining high activity. The research will systematically investigate the preparation of nitrogen-doped graphite felt cathodes (NEGF) and their pollutant degradation performance in various salt solutions with different concentrations. This aims to clarify the practical potential and influencing factors of NEGF in high-

salinity wastewater treatment, providing a cost-effective and efficient solution for treating complex industrial wastewater with diverse components.

2 Materials and Methods

2.1 Materials

All reagents used in this study, except melamine, were of analytical grade and used as is. All solutions were prepared with deionized water. The graphite felt was purchased from Beihai Carbon (China). Acid Red B and acetone were obtained from Shanghai Aladdin Biochemical Technology Co., Ltd. Anhydrous sodium sulfate, sodium chloride, sodium hydroxide, and melamine (chemical grade, CP) were supplied by Sinopharm Chemical Reagents Co., Ltd. Concentrated sulfuric acid (70%) was procured from Chengdu Kelong Chemical Co., Ltd.

2.2 Preparation of Nitrogen-Doped Electrochemically Modified Graphite Electrode (NEGF)

A 3×5 cm² graphite felt with a thickness of 0.3 cm was selected as the substrate for the modified doped material. The graphite felt was pre-treated with acetone and deionized water under ultrasonic conditions to remove surface contaminants such as grease. The pre-treated graphite felt was then subjected to electrochemical modification using graphite felt as the anode, graphite plates as the cathode, and a 0.05 mol/L Na₂SO₄ electrolyte solution. The current was maintained at a constant 0.1 A for 10 minutes, resulting in an electrochemically modified graphite felt electrode (EGF). A detailed schematic of the apparatus is shown in Fig. S1

N-doped EGF was prepared using melamine as the nitrogen source through high-temperature pyrolysis [28]. The EGF was first immersed in a melamine-water-ethanol mixture (melamine : water : ethanol = 5 g : 50 mL : 50 mL) for 1 minute under ultrasonic control. The melamine-coated EGF was then placed in a tubular furnace and heated at a rate of 3.3°C/min under N₂ atmosphere to 600°C, 700°C, and 800°C, with holding times of 1 h, 2 h, and 3 h, respectively, to prepare the corresponding nitrogen-doped electrochemically modified graphite felt electrode (NEGF). For example, the sample prepared at 700°C with a holding time of 2 h is designated as NE700-2h.

2.3 Morphological and Structural Characterization of NEGF

The surface morphology of the electrodes was characterized by scanning electron microscopy (SEM, ZEISS Sigma 300, Germany). Surface functional groups and N-doping content and morphology were analyzed by X-ray photoelectron spectroscopy (XPS, Thermo Scientific K-Alpha, USA).

2.4 NEGF Electrochemical Performance Testing

The electrochemical properties were characterized using a three-electrode system electrochemical workstation (CHI 660E, Shanghai Chenhua Instrument Co., Ltd., China). The cyclic voltammetry (CV)

measurements were performed at a scan rate of 100 mV/s. The linear scanning voltammetry (LSV) measurements were performed at a scan rate of 10 mV/s.

2.5 NEGF Degradation Assay for Acid Red B

The NEGF degradation dye device mainly consists of three parts: an ozone generator, a DC power supply, and a reaction device. Among them, NEGF serves as the cathode, and the graphite plate acts as the anode. The ozone generator is responsible for delivering the O_2/O_3 mixed gas to the reaction device. Acidic Red B was selected as the dye to be degraded for testing, and the detailed device diagram is shown in Fig. S2. The electrode to be tested was installed at the indicated position, connected to the power supply and ozone, and the reaction could then begin. Samples were taken at regular intervals, and the concentration of Acidic Red B in the sample solution was measured at a wavelength of 514 nm using a dual-beam UV-visible spectrophotometer (TU-1901, Beijing Puxi General Instrument Co., Ltd., China).

The procedures for H_2O_2 generation performance test and energy consumption analysis were listed in the Supporting Materials.

3 Results and Discussion

Using raw graphite felt (GF) as the anode, we modified it with a DC power supply to obtain an electrically modified graphite felt electrode (EGF). Subsequently, melamine was employed as the nitrogen source to prepare nitrogen-doped electrically modified graphite felt electrodes (NEGF). Samples under different operating parameters were labeled with the notation "NE + calcination temperature ($^{\circ}C$) -calcination time (h)" (e.g., NE700-1h). First, we observed the surface morphology changes of electrodes at different modification stages using scanning electron microscopy (SEM) to investigate the effects of modification on electrode structure.

3.1 Electrode Morphology Characterization and Structural Analysis

The SEM images of NEGF, EGF, and GF (Fig. 1a-c) demonstrate the surface morphology of the fabricated electrodes.

At 5 μm magnification (Fig. 1), the fibrous structure characteristic of graphite felt becomes clearly visible. Compared to the original graphite felt (c), the anodized modified graphite felt (b) exhibits a rougher surface due to oxygen-containing functional groups introduced by electrochemical modification, which also creates surface defects [23, 29]. Nitrogen doping on the electrochemically modified graphite felt (a) reveals uniformly distributed carbon fibers coated with solid powder, confirming that the catalysts are loaded on the graphite fiber surface. The rough surface structure and nitrogen doping provide additional active sites, both of which enhance the oxygen reduction reaction (ORR) [30].

Furthermore, the rough morphology of the anodized modified graphite felt provides more active sites for nitrogen doping, which also lays a foundation for subsequent performance optimization.

3.2 Optimization of Sintering Temperature and Time for NEGF Electrode Performance

To optimize the distribution and quantity of nitrogen doping on graphite felt, five types of NEGF electrodes were prepared by adjusting two parameters: calcination temperature and holding time. The calcination temperatures were set at 600°C, 700°C, and 800°C, with holding times of 1 hour, 2 hours, and 3 hours, respectively. Through systematic literature review on nitrogen doping using melamine as the nitrogen source, it was found that the optimal performance temperature and holding time vary across different application fields. Based on this, parameter screening was conducted [23, 28, 29].

The electrochemical CV, LSV, and dye degradation test results of three NEGF electrode materials prepared at different calcination temperatures are shown in Figs. 2a, b, and e. Compared to the 600°C and 800°C samples, the NE700-1h sample exhibited the highest current response, demonstrating a distinct reduction peak, indicating its optimal catalytic performance in the ORR reaction [24]. Additionally, Fig. 2e illustrates the degradation of Acid Red B dye solution at a concentration of 50 mg/L on both NEGF and EGF electrodes. The nitrogen-doped electrochemically modified graphite felt (NEGF) electrode showed significantly superior degradation performance against Acid Red B compared to the undoped electrode (EGF), directly proving that the introduction of heteroatom nitrogen effectively enhances the electrode's catalytic activity. This is attributed to nitrogen's high electronegativity (3.04), which, upon incorporation into the carbon matrix, attracts electrons from adjacent carbon atoms, generating partial positive charges on the carbon atoms. This not only promotes O_2 adsorption on the catalyst surface but also accelerates electron transfer to O_2 , thereby significantly improving the efficiency of oxygen reduction to H_2O_2 [30, 31]. Consistent with the electrochemical characterization results, the NE700-1h sample exhibited the best degradation performance.

After determining the optimal calcination temperature at 700°C, this study systematically investigated the effects of holding time. The electrochemical CV, LSV, and dye degradation test results of NEGF electrode materials prepared with three different holding times are shown in Figs. 2c, d, and f. The NE700-2h material with a 2-hour holding time exhibited the highest current response. In the dye degradation test, it also demonstrated a higher degradation rate, but no significant difference was observed compared to electrochemical characterization. This is likely because once the electrode's catalytic activity reaches a certain level, the overall dye degradation rate shifts from being controlled by surface reactions to being governed by mass transfer and diffusion of O_2 to the electrode surface [32]. At this stage, the supply rate of O_2 becomes the rate-limiting step, so further optimization of surface nitrogen parameters has limited contribution to overcoming the O_2 diffusion bottleneck, resulting in insignificant improvement in degradation rate.

In addition to electrochemical CV, LSV, and dye degradation tests, this study also measured the H_2O_2 generation performance of different NEGF electrodes, and the results are shown in Fig. S4. The H_2O_2 yield and the dye degradation efficiency show generally consistent trends. In the EP system, the generation of $\cdot\text{OH}$ not only comes from the reaction between H_2O_2 and O_3 , but also involves the direct reduction of O_3 at the cathode and the reaction of O_3 with free OH^- in water. Therefore, the degradation performance of the electrode is governed by both its H_2O_2 production capability and the O_3 activation efficiency, and these data serve only as a reference for auxiliary evaluation of the material performance.

In conclusion, nitrogen doping can significantly enhance the intrinsic activity of electrodes. However, once the catalytic activity reaches a certain level, the mass transfer process becomes the key limiting factor for further performance improvement.

3.3 Nitrogen Doping Chemical State Analysis and Its Structure-Activity Relationship with Catalytic Activity

Fourier transform infrared spectroscopy (FT-IR) was employed to characterize the surface functional groups and chemical structures of a series of nitrogen-doped carbon materials, confirming the successful incorporation of nitrogen into the carbon framework and the formation of various doping configurations, including pyridinic N, pyrrolic N, and graphitic N. The detailed FT-IR spectra are shown in Fig. S5.

To further investigate the effects of nitrogen doping morphology and content on the catalytic performance of NEGF electrode materials, and to elucidate the evolution patterns of nitrogen species under different optimization conditions (temperature and time), XPS measurements were performed on five types of NEGF electrode materials. Figures 3f and 3g present the XPS spectra of NEGF electrode materials within the binding energy range of 0 ~ 1200 eV, while Figs. 3a ~ e show the high-resolution XPS spectra of NEGF electrode materials at the N 1s energy level along with their peak-fit results. Detailed information on nitrogen species content is provided in Table 1.

XPS analysis confirmed that this study successfully achieved nitrogen doping in graphite felt materials using melamine as the nitrogen source through pyrolysis. The N1s spectrum of the NEGF electrode material consists of four subpeaks, corresponding to pyrrole N (398.1 ~ 398.5 eV), pyrrole N (399.5 ~ 399.9 eV), graphite N (400.5 ~ 401.0 eV), and oxidation N (> 402.0 eV) [29, 32].

The edge structure and nitrogen doping near the edge have been demonstrated to enhance oxygen adsorption and the catalytic activity of the oxygen reduction reaction (ORR). Pyridine nitrogen can contribute a p-electron to the aromatic π system and possesses a lone pair of electrons in the carbon matrix plane, which enhances the electron-donating ability of the catalyst. Consequently, it weakens the O-O bond through the bonding of oxygen with nitrogen and/or adjacent carbon atoms, thereby promoting the reduction of O_2 , density functional theory (DFT) calculations by researchers have demonstrated that carbon atoms adjacent to graphite N [34] and the second-adjacent carbon of pyridine N [35] serve as

active sites for the oxygen reduction reaction (ORR), both exhibiting high catalytic activity [33, 36]. For other N-doped forms, most studies indicate that they have minimal impact on ORR activity [37, 38].

In this series of samples, NE800-1h (total N 6.52%) and NE700-3h (total N 6.41%) exhibited the poorest catalytic activity due to significant nitrogen loss caused by high temperature or prolonged heat treatment, resulting in a low number of active sites. As temperature increased and holding time extended, the content of pyridine N and pyrrole N decreased, while the graphite N content remained largely unchanged. This is attributed to the superior stability of graphite N, whereas pyridine N and pyrrole N are less stable and prone to loss or conversion to graphite N under high-temperature and prolonged heat treatment conditions [39]. Although NE600-1h demonstrated the highest total N content (11.99%), its graphite N content (1.78%) was relatively low, indicating limited intrinsic activity. The total N content of NE700-1h and NE700-2h samples was similar, with slight differences in the ratio of pyridine N to graphite N. This variation likely contributed to the minor fluctuations in catalytic activity. NE700-2h samples exhibited the optimal catalytic activity, achieving a balanced combination of high activity (graphite N) and high selectivity (pyridine N) while maintaining sufficient active sites (total N).

3.4 Degradation Performance and Stability Evaluation of NEGF Cathode in EP Process

The prepared NEGF electrode was used for the degradation of acid red B in EP process, and its catalytic performance and stability were tested under different salt solution concentrations and acidic or alkaline conditions.

In high-salinity environments, the potential quenching of hydroxyl radicals caused by competitive adsorption from high-concentration salt ions [40] may lead to reduced electrode catalytic activity. This study systematically investigated the effects of different electrolytes (pure sodium sulfate, pure sodium chloride, and their 1:1 mixture, Fig. 3a ~ c) and their concentrations on the degradation efficiency of acid red B. In the pure sodium sulfate system, when the degradation time was 20 minutes, the degradation rate decreased from 98.8% to 93.6% as the solution concentration increased from 0.05 mol/L to 0.6 mol/L. Specifically, compared to the 0.05 mol/L baseline, the degradation rates at 0.2 mol/L, 0.4 mol/L, and 0.6 mol/L decreased by 3.6%, 3.9%, and 5.3%, respectively, indicating a slight inhibitory effect of sulfate ions. This may be related to competitive adsorption caused by high-concentration salt ions, which could occupy active sites for the ORR reaction, though the impact was limited. Fig. S6a shows the degradation capability and energy consumption analysis of the solution at 8 min. The variation under different concentration conditions is relatively small, further indicating that the NEGF electrode exhibits good adaptability over a wide range of sodium sulfate concentrations.

In contrast, in the pure sodium chloride system, the degradation performance slightly improved with increasing salinity, maintaining a degradation rate above 97.5% at all concentrations after 10 minutes of reaction. The enhanced degradation performance in the sodium chloride system is primarily attributed to

the oxidation of chloride ions during the electrochemical process, generating active chlorine species that provide additional oxidation pathways [26]. Consistent with the trend of degradation rate, the degradation capability increases with the concentration of sodium chloride, while the energy consumption decreases accordingly (Fig. S6b). In a 1:1 mixed electrolyte, the degradation efficiency initially increases and then decreases with rising total salinity, yet maintains a 99% degradation rate at 0.4 mol/L total concentration and 20-minute reaction time, with minimal overall variation.

In conclusion, the NEGF electrode demonstrates excellent tolerance and application potential in high-salinity wastewater treatment.

The solution pH is one of the most critical operational parameters for controlling EP process performance, as it directly influences the oxidation pathways of ozone in acidic and alkaline environments, as well as the generation and stability of H_2O_2 . Studies have shown that optimal EP process conditions can be achieved at different pH levels, with acidic conditions (pH = 3.0), neutral conditions (pH = 7.0), and alkaline conditions (pH = 9.0) reported as effective pH ranges for EP processes, depending on specific operational parameters [5].

Figure 4d shows the degradation performance of the NEGF electrode for Acid Red B under different pH conditions. The corresponding degradation efficiency and energy consumption analysis results are shown in Fig. S7. The results indicate that the NEGF electrode exhibits optimal degradation performance under alkaline conditions at pH = 9.0. This is attributed to the alkaline environment's favorable conditions for H_2O_2 generation, accelerated ozone decomposition, and enhanced hydroxyl radical production, which collectively contribute to the electrode's peak performance at pH = 9.0 [5, 41]. However, in excessively alkaline environments, the rapid reaction between hydroxide ions and hydroxyl radicals leads to radical quenching and reduced degradation efficiency [42]. Consequently, the NEGF electrode demonstrates the poorest degradation performance at pH = 11.0.

Although degradation performance is influenced by pH, degradation can be essentially completed within 30 minutes across all tested pH ranges ($\geq 97\%$). This indicates that the system is insensitive to pH variations in the reaction environment, demonstrating good adaptability. It operates efficiently without precise pH control in practical applications, showcasing broad applicability prospects.

Figure 4e shows the degradation curve of NEGF electrode after five cycles of acid red B dye degradation under pH = 7.0 and 0.05 mol/L Na_2SO_4 conditions. The results indicate that while the electrode exhibits minor fluctuations in degradation performance, its stability remains well-established without significant performance decline.

3.5 Degradation Effect of NEGF Cathode in EP Process on Actual Wastewater

To evaluate the practical application of the NEGF cathode in the EP process, we conducted field tests using three wastewater samples from the Deke Industrial Park (China): dye vat effluent, comprehensive discharge water, and treated water. Figure 5 illustrates the degradation progress and COD changes for these samples. Notably, the Deke comprehensive discharge water and treated water exhibited a light coloration approaching transparency with minimal color variation during the degradation process, hence the color change charts are omitted. The complete three-dimensional fluorescence spectra are shown in Figs S8 ~ S10.

Figure 5a presents the UV-Vis absorption spectrum of decolored dye effluent as a function of degradation time. The initial wastewater (0 min) exhibited high absorbance and pronounced chromaticity, with a distinct absorption peak in the 250 ~ 350 nm short-wave UV region corresponding to aromatic ring structures, alongside a significant absorption peak in the 500 ~ 700 nm visible region indicating the presence of large conjugated chromophores. This wastewater, a typical high-concentration complex organic effluent, was rich in refractory aromatic compounds and chromogenic components. After 180 minutes of degradation, all wavelengths showed marked absorbance reduction. The 500 ~ 700 nm visible region absorption peak virtually disappeared, achieving decolorization as dye molecules were oxidized into small intermediates or molecular fragments. The COD decreased from 29,222 mg/L to 6,329 mg/L, representing a 78.3% reduction.

Figure 5b and 5c demonstrate the UV-Vis absorption spectra of Deke comprehensive effluent and Deke treated effluent versus reaction time. The initial wastewater (0 min) exhibited no significant coloration, with absorption peaks predominantly in the UV region, indicating aromatic compounds as the primary constituents. As degradation progressed, UV absorbance progressively decreased, reflecting the gradual breakdown of aromatic structures into smaller molecules and subsequent mineralization, accompanied by a marked reduction in COD. The COD values of Deke comprehensive effluent and Deke treated effluent decreased by 54.6% and 79.1%, respectively.

Furthermore, Figs. 5e ~ 5m demonstrate three-dimensional fluorescence variations during the degradation of three wastewater types. The regions with $E_x < 400$ and $E_m < 500$ primarily correspond to tryptophan-like proteins, furic acid-like substances, and humic acid-like substances [43]. As degradation progresses, the fluorescence intensity in these regions significantly diminishes, characteristic peaks gradually disappear, and fluorescent groups are disrupted, thereby enhancing the mineralization of the solution. This change also aligns with the COD data before and after degradation.

In summary, the results demonstrate that the EP process employing NEGF cathodes exhibits outstanding degradation performance and broad applicability in treating real wastewater. For high-concentration complex wastewater with a COD of 29,229 mg/L, the process achieved a 78.3% removal rate within 3 hours, reducing COD to 6,329 mg/L, highlighting its strong resistance to shock loads and high mineralization potential. For low-COD index wastewater, the maximum removal rate reached 79.1% after 1 hour of reaction, further validating the system's deep treatment capability for residual refractory components. Combined with three-dimensional fluorescence spectroscopy analysis, the significant

weakening or disappearance of characteristic fluorescence peaks such as protein-like, fulvic acid-like, and humic acid-like spectra during degradation confirmed at the molecular level that the EP process effectively disrupts aromatic structures and conjugated chromophore systems in wastewater, achieving efficient degradation and transformation of organic pollutants. This process holds broad application prospects for treating both high-concentration and low-concentration complex organic wastewater.

4. Conclusion

This study successfully developed a melamine pyrolysis nitrogen doping strategy for constructing high-performance graphite felt cathodes (NEGF). Through systematic optimization, the optimal preparation conditions were determined as a calcination temperature of 700°C and a holding time of 2 hours. The resulting NE700-2h electrode exhibited outstanding oxygen reduction reaction (ORR) catalytic activity due to its appropriate pyridine nitrogen-to-graphite nitrogen ratio, demonstrating a distinct reduction peak and the highest current response. When applied to the electro-peroxone (EP) process for the degradation of acid red B dye, experimental results showed that the electrode maintained efficient and stable degradation performance across a wide pH range (3.0 ~ 11.0) (degradation rate > 98.0% at 20 minutes) and exhibited excellent tolerance to high-salinity environments up to 0.6 mol/L Na₂SO₄ (degradation rate > 98.1% at 30 minutes). In practical wastewater applications, the NEGF cathode also demonstrated excellent potential, achieving a removal rate of 78.3% within 3 hours for high-concentration complex wastewater, reducing COD from 29,229 mg/L to 6,329 mg/L.

These advantages highlight the electrode's significant application potential in treating complex textile wastewater with high salinity fluctuations. In summary, this work not only provides an efficient and stable cathode material but also offers new insights and theoretical foundations for designing advanced oxidation process catalytic electrodes suitable for complex water conditions.

Declarations

Supplementary details

Supplementary Information The online version contains supplementary material available at <https://doi.org/####-#>.

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Conflict of interest

The authors declare no competing interests.

Author Contribution

Authorship contributions Yu-jia Gao: Investigation, Formal analysis, Writing-original draft. Xu-yan Bai: Formal analysis. Shuai-cong Huo: Software. Bo-lun Yu: Formal analysis. Ying Yang: Supervision, Funding acquisition, Writing-review & editing, Software. All authors have read and agreed to the published version of the manuscript.

Data Availability

The data that support the findings of this study are available in the supplementary material of this article.

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Figures

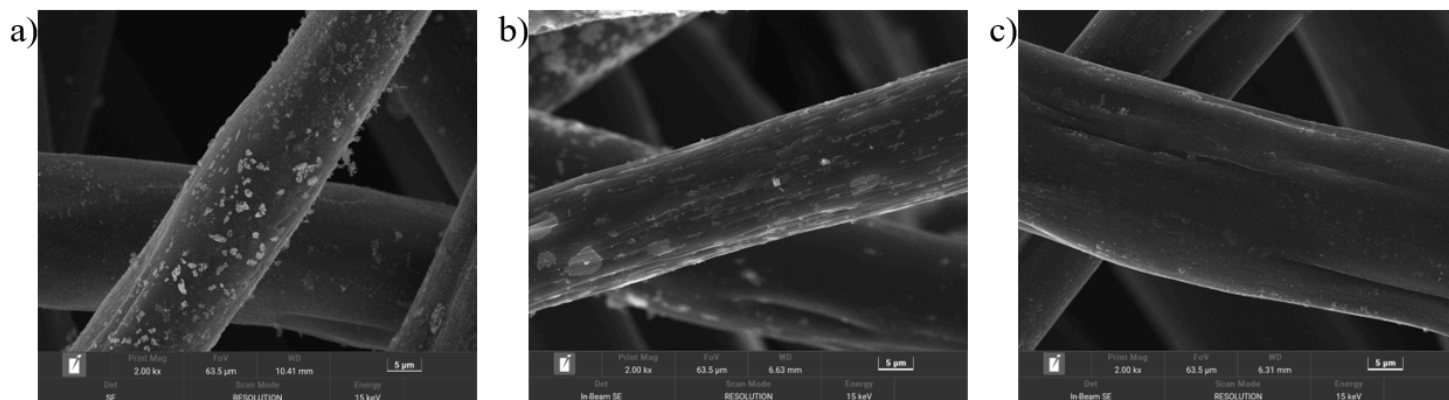


Figure 1

SEM images of NEGF (a), EGF (b), and GF (c)

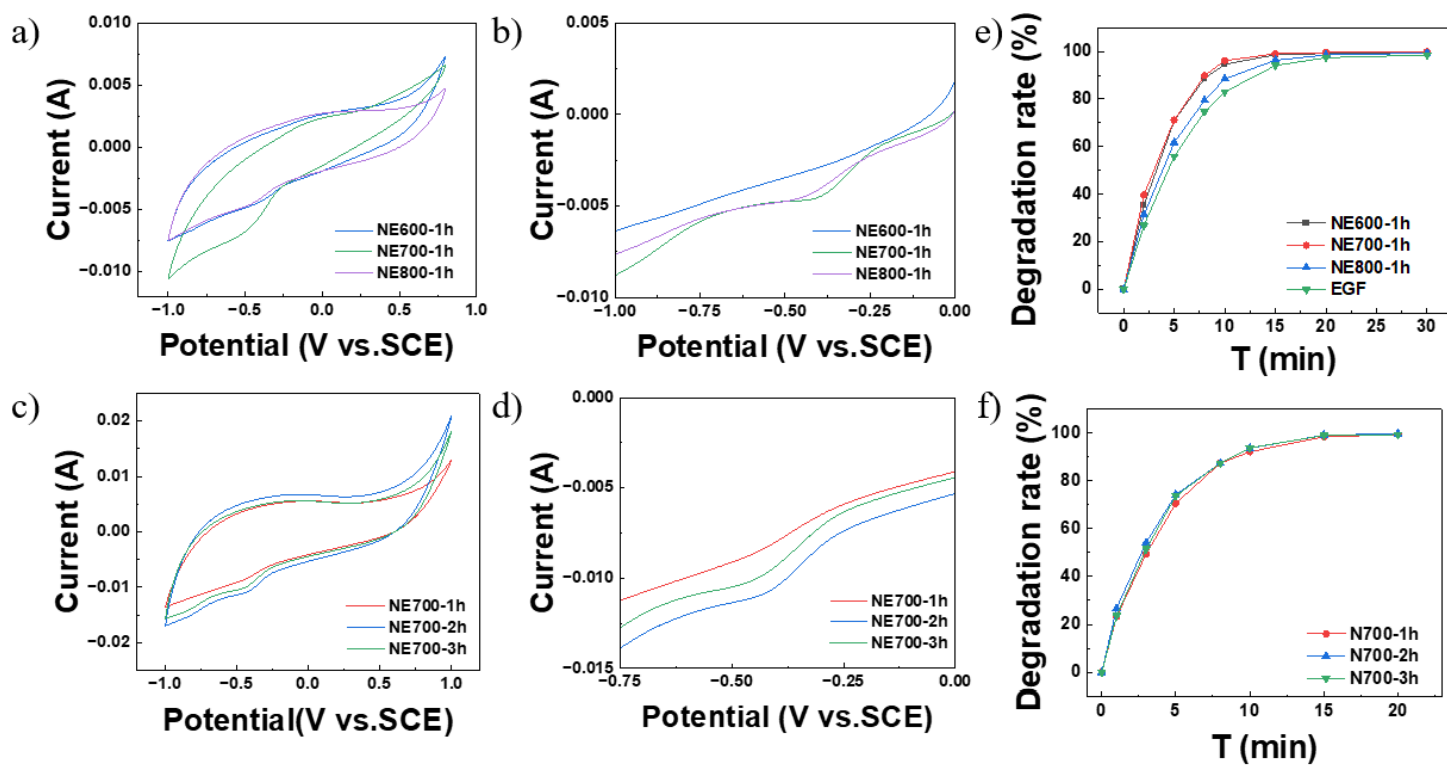


Figure 2

CV (a), LSV (b), and dye degradation tests (e) of NEGF electrode materials prepared at different calcination temperatures; CV (c), LSV (d), and dye degradation tests (f) of NEGF electrode materials prepared at different holding times

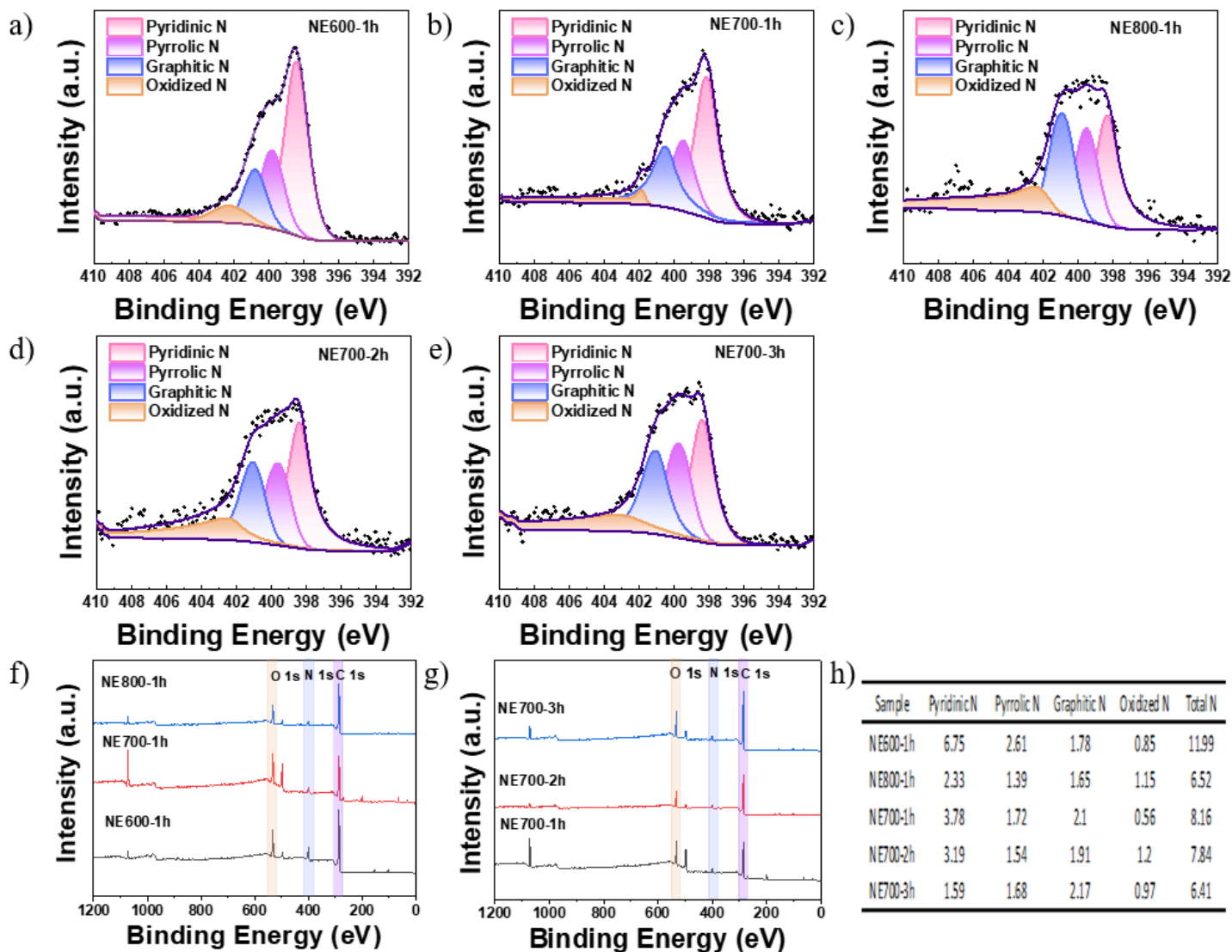


Figure 3

High-resolution XPS spectra of NEGF electrode materials at N 1s energy level (a~e); XPS spectra of NEGF electrode materials prepared at different calcination temperatures (f); XPS spectra of NEGF electrode materials prepared at different holding times (g); Morphological distribution of N-doped NEGF electrode materials (%) (h)

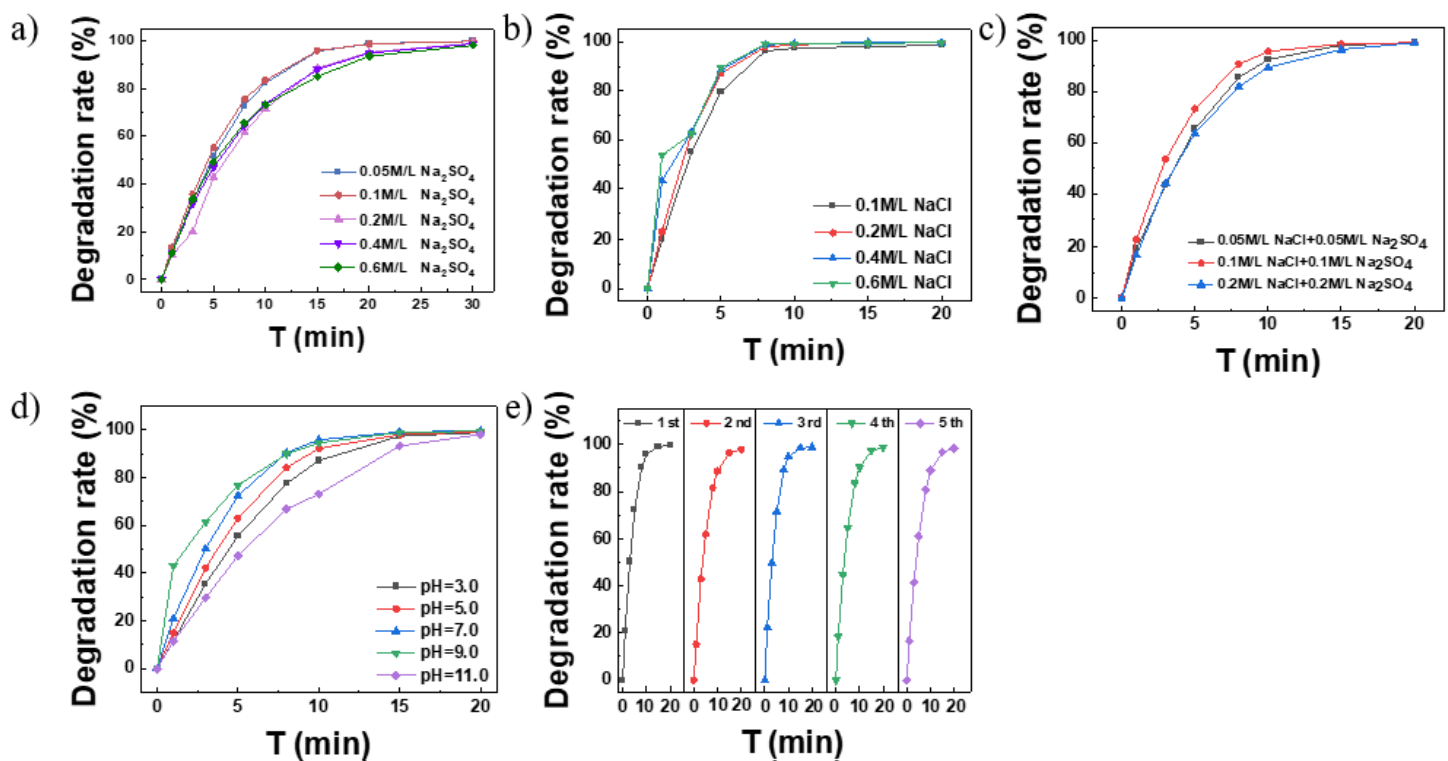


Figure 4

Environmental degradation curves for different salt solution concentrations (a~c); environmental degradation curves for different pH values (d); stability test (e)

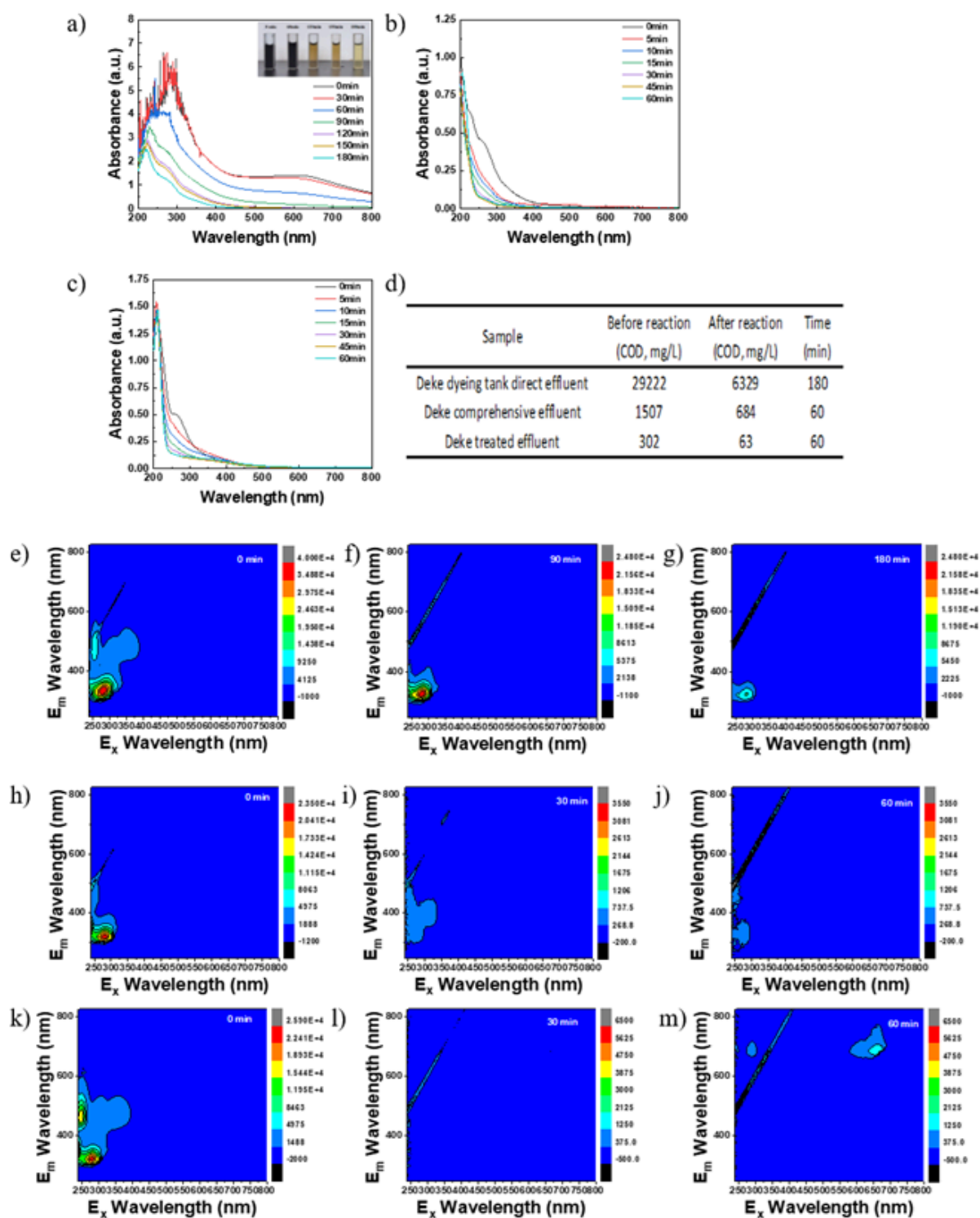


Figure 5

Absorption spectra of Deke dyeing tank direct effluent (a), Deke comprehensive effluent (b), and Deke treated effluent (c) in the UV-visible region; COD changes before and after degradation of the three wastewater streams (e); 3D fluorescence spectra of Deke dyeing tank direct effluent (e~g), Deke comprehensive effluent (h~j), and Deke treated effluent (k~m)

Supplementary Files

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