

RESEARCH ARTICLE

Intermetallic Bond Mediated Singlet Oxygen Generation System for Emerging Pollutants Detoxification in Carbon-Neutral Water Purification

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Received: 25 June 2026 | **Revised:** 5 August 2026 | **Accepted:** 21 August 2026

Keywords: carbon neutrality | detoxification | low carbon emissions | transformation-AOPs

ABSTRACT

Mineralization-driven advanced oxidation processes (AOPs) effectively remove emerging pollutants but often require substantial energy input and generate considerable carbon emissions, conflicting with carbon-neutrality goals. Here, we develop a transformation-focused AOP based on cobalt-doped lanthanum oxycarbonate (Co-LC), which activates peroxymonosulfate (PMS) to selectively generate singlet oxygen (¹O₂). Experimental and theoretical results reveal that Co–La bonding interactions reconfigure the local electronic environment, stabilize high-valent O* intermediates, and lower the energy barrier for ¹O₂ formation. The Co-LC/PMS system exhibits a transformation rate 49.23 times that of pristine LC and selectively destroys the carcinogenic amino and naphthalene moieties of 1-naphthylamine. Ecotoxicological assays using *Chlorella vulgaris* confirm complete elimination of biological risks, with physiological indicators returning to baseline levels after treatment. A continuous-flow packed-bed reactor maintained >94% removal efficiency for 37 days and increased the BOD₅/COD ratio of real wastewater from 0.25 to 0.50. Life-cycle assessment further shows 85.6% lower CO₂ emissions and reduced operating costs compared with the Co₃O₄/PMS system. This study establishes a low-carbon detoxification strategy that prioritizes toxicity elimination over complete mineralization for sustainable water purification.

1 | Introduction

The long-term development of human society depends on secure water supply systems, but industrialization has introduced complex toxic chemicals—such as polycyclic aromatic hydrocarbon

(PAH) derivatives—that threaten aquatic ecosystems [1–3]. These derivatives exhibit high polarity, environmental persistence, and mutagenicity. A typical example is 1-naphthylamine (1-NA), a carcinogenic naphthalene derivative widely used in the production of dyes, pharmaceuticals, and rubber products [4, 5]. During the

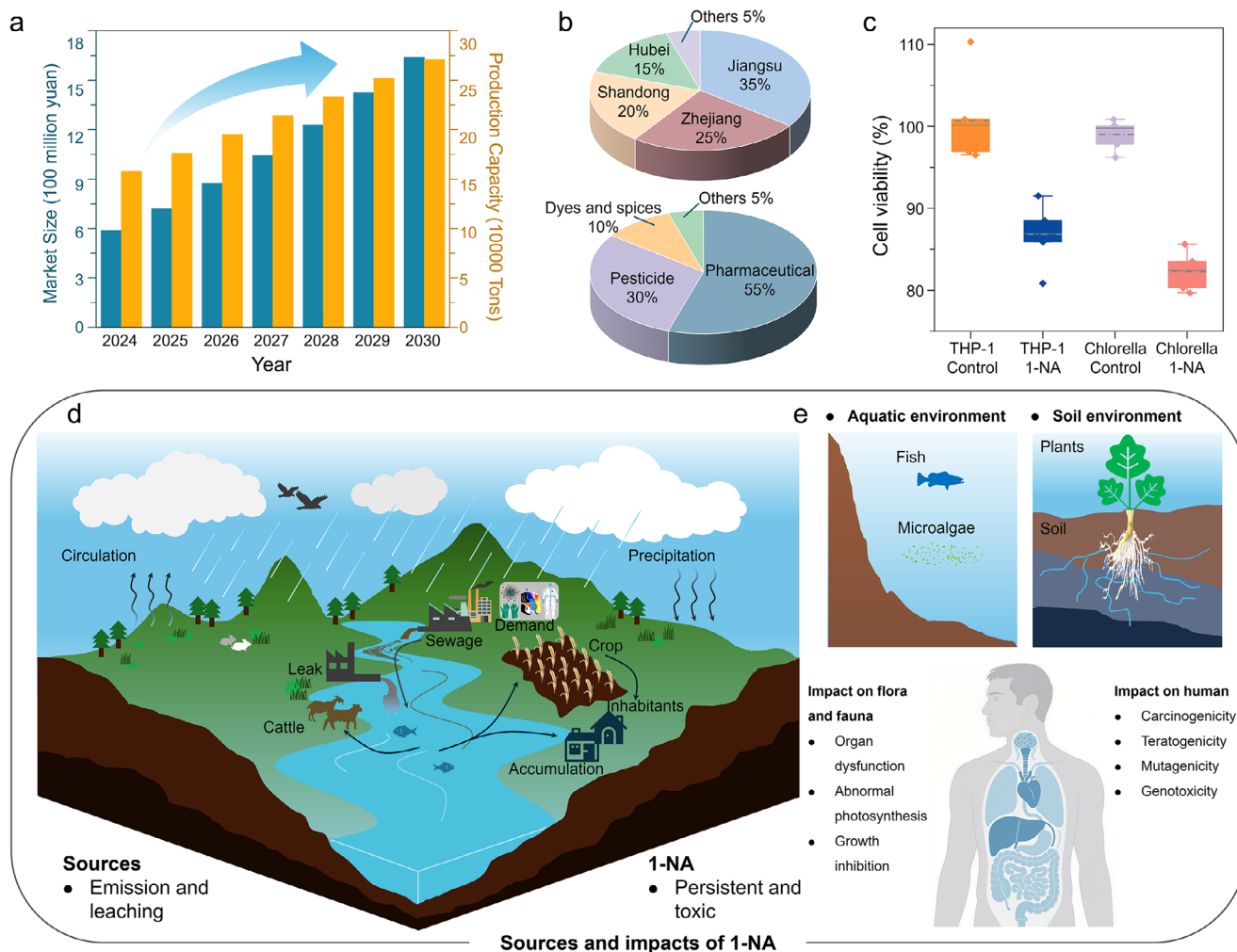


FIGURE 1 | Market size and toxicological impact of 1-NA. (a) Market size and production capacity forecast for 1-NA in the Chinese market by 2030. (b) Primary production areas and application fields of 1-NA in the Chinese market. (c) Toxicity expression of 1-NA in THP-1 cells and *Chlorella*. The experimental group was exposed to a 1-NA solution at a concentration of 1 $\mu\text{g/L}$, while the control group received an aqueous solution instead of the 1-NA solution. (d) The transfer process of 1-NA-containing wastewater in the natural environment. (e) The release of 1-NA into the environment adversely impacts water bodies, soil, and diverse plant species. This contamination further leads to 1-NA accumulation in the human body, triggering a range of health problems and diseases. Additionally, the discharge or leakage of wastewater containing 1-NA poses substantial risks to both ecosystems and human health, highlighting the need for effective and timely remediation measures.

COVID-19 pandemic, global demand for rubber products (e.g., medical supplies) surged dramatically. Malaysia, a major rubber glove manufacturer, saw its rubber glove exports grow by 31.8% year-on-year in 2020 [6]. In China, 1-NA production capacity and market scale are projected to expand steadily through 2030, with production primarily concentrated in Jiangsu and Zhejiang provinces and applications focused on the pharmaceutical industry (Figure 1a,b). This trend further intensifies the risk of 1-NA exposure in aquatic environments. Currently, 1-NA has been detected in rivers and various wastewater streams at concentrations reaching the milligram per liter (mg/L) level [7, 8]. Toxicity tests using human monocyte leukemia (THP-1) cells and *Chlorella* (Figure 1c) show that exposure at 10 $\mu\text{g/L}$ significantly reduces cell viability within 24 h, providing direct evidence of its high toxicity. When 1-NA-contaminated wastewater infiltrates soil and ultimately enters rivers, the compound accumulates in organisms across multiple trophic levels through the food chain. Agricultural irrigation further facilitates its environmental

transport within agricultural systems (Figure 1d). In this process, microalgae at the base of the food chain are directly contaminated, potentially disrupting energy transfer and triggering the collapse of aquatic ecosystems. Concurrently, 1-NA entering the soil disrupts microbial communities, induces phytotoxicity in plants, and transfers through the food chain to humans, causing diseases (Figure 1e). Therefore, the effective control of 1-NA pollution is urgently required [9, 10].

To ensure safe water supply, advanced oxidation processes (AOPs) have been employed in the water treatment industry as a supplement to conventional processes, with the aim of comprehensively removing most organic pollutants [11]. Currently, AOPs that generate highly oxidizing species (e.g., $\cdot\text{OH}$ and $\text{SO}_4^{\cdot-}$) to achieve thorough pollutant mineralization are defined as mineralization-oriented advanced oxidation processes (M-AOPs) [12]. While treating pollutants, the non-selective oxidation of free radicals typically leads to high operational costs and unregulated carbon

emissions. In addition, polymerization-based advanced oxidation processes (P-AOP) have emerged as an alternative to M-AOPs [13]. This approach converts organic pollutants in aqueous solutions into recoverable solid products via polymer transfer (PT) reactions, offering significant advantages in energy conservation and emission reduction [14]. However, polymerization reactions are often restricted by pollutant types—current research primarily focuses on phenols, anilines, pyrroles, and thiophenes—and challenges such as secondary treatment of polymeric products remain unresolved [15]. In terms of water treatment technology application, considerations should go beyond end-of-pipe treatment to address pollution at its source. Furthermore, treatment methods should be selected based on the intrinsic properties of pollutants. Taking 1-NA as an example, its high toxicity poses a threat to aquatic environments. Therefore, by specifically deconstructing 1-NA to transform it into non-toxic or low-toxic substances with the target of selective destruction of specific toxic structural moieties, pollution can be eliminated while avoiding mineralization and the associated byproducts. This approach constitutes a transformation-focused AOP (T-AOP).

Herein, an alloy catalyst was selected as the catalytic medium. By constructing highly efficient intermetallic bonds, peroxy-monosulfate (PMS) was rapidly activated to selectively generate singlet oxygen ($^1\text{O}_2$)—a reactive species with moderate oxidizing capacity. This process specifically targeted the electron-rich toxic moieties in 1-NA, namely the amino group and naphthalene ring, to achieve deconstructive transformation of the pollutant. First, experimental results combined with theoretical calculations were used to elucidate the detailed transformation mechanism. Subsequently, toxicity experiments using *Chlorella* were conducted to evaluate changes in the toxicity of transformation products. Comprehensive monitoring of *Chlorella*'s physiological activity indicators confirmed that this system can completely transform 1-NA into non-toxic products without inducing mineralization. Finally, a pilot-scale device was constructed for long-term operation stability tests, which verified the system's potential for practical application. In summary, this work represents the first study to eliminate pollutant toxicity via transformation while clarifying the underlying mechanism, providing novel insights for advanced water treatment technologies.

2 | Results and Discussion

2.1 | Synthesis and Characterization of Catalysts

As shown in Figure 2a, the catalyst was prepared via a hydrothermal process followed by calcination (designated as LC and Co-LC). X-ray diffraction (XRD) spectra (Figure S1) confirmed that both LC and Co-LC maintained the $\text{La}_2\text{O}_2\text{CO}_3$ structure, and the incorporation of Co endowed Co-LC with higher crystallinity. The absence of characteristic crystal peaks of Co in the Co-LC ruled out the presence of Co crystalline particles. This finding indicated the atomic-level dispersion of Co within the $\text{La}_2\text{O}_2\text{CO}_3$ matrix while simultaneously promoting the ordering of the crystal structure [16]. The FTIR and BET results further demonstrate the superior structural characteristics of Co-LC (Figures S2 and S3). Microscopic characterizations via scanning electron microscopy (SEM) and transmission electron microscopy (TEM) further elucidated the morphological features of LC and Co-

LC. Both samples exhibited smooth spherical morphology, with Co-LC showing a slightly smaller particle size compared to LC (Figures S4–S6). Elemental mapping confirmed the uniform distribution of La in LC and La and Co in Co-LC (Figures S7 and S8). Aberration-corrected high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) images (Figure 2b; Figure S9) revealed that Co-LC displayed the (1 0 3) lattice plane corresponding to $\text{La}_2\text{O}_2\text{CO}_3$, where La and Co atoms are atomically dispersed. Specifically, Co atoms are embedded between adjacent La atoms.

As shown in Figure 2c, LC contains abundant oxygen vacancy (OV) structures, whereas Co-LC contains almost none. We found that the incorporation of Co into the $\text{La}_2\text{O}_2\text{CO}_3$ lattice can effectively increase the energy barrier of OVs, and Co tends to replace O atoms or fill OVs to form a “perfect lattice” (Figure 2d; Figure S10). To investigate the structure of Co-LC in depth, the coordination environments of Co in Co-LC were confirmed by x-ray absorption fine structure (EXAFS) spectroscopy (Figure 2e,f; Figure S11). As presented in Figure 2e, the white-line energy absorption intensity of Co-LC is higher than that of Co foil and lower than that of CoO, indicating that the valence state of Co atom lies between Co^0 and Co^{2+} . The lower valence state of Co compared with its precursor implies a significant metal-support interaction within the Co-LC [13]. The weak peak at 1.53 Å in the Co EXAFS spectrum corresponds to Co–O bonding, which is ascribed to the coordination of a small fraction of Co and O [17]. Notably, the peak at 2.17 Å is attributed to the Co–La bonding, and no Co–Co bonding is observed. This confirms the atomic dispersion of Co in $\text{La}_2\text{O}_2\text{CO}_3$ and the formation of Co–La intermetallic bonds [18]. Quantitative local coordination information for Co-LC was obtained via EXAFS fitting (Figure 2e; Table S2). The fitting results yielded an average Co–La coordination number of 3.2 and a bond length of 2.52 Å, suggesting a dominant $\text{Co}_1\text{-La}_3$ coordination mode [19]. This result further verifies that the Co–La configuration is predominant in Co-LC. The wavelet transforms of the EXAFS spectra (Figure 2f) further confirm the metallic nature of the Co–La intermetallic bonding. Furthermore, the projected density of states (PDOS) calculation results (Figure 2g) demonstrates that the PDOS of the La 5d orbitals in LC is nearly zero at the Fermi level (E_F), which indicates a relatively inert chemical state [20]. In contrast, the PDOS of the Co 3d orbital in Co-LC features a prominent peak of electronic density of states near E_F , and this peak crosses E_F . This suggests that electrons in the Co 3d orbital are highly localized near the E_F , with a considerable number of electrons available to take part in the reaction process [21]. At the same time, the PDOS of the La 5d orbital in Co-LC also shows distribution and overlaps with the Co 3d orbital near E_F , further bolstering the formation of intermetallic bonds [22]. Moreover, the differential charge density distribution (Figure 2g) reveals that when Co incorporation into the $\text{La}_2\text{O}_2\text{CO}_3$ lattice, electron-deficient regions are generated around La atoms (blue area) while electron-rich regions form around Co atoms (yellow area). Consistent with this observation, XPS results (Figures S12–S16) demonstrate that the intrinsic La peak undergoes a blue shift after Co incorporation [23]. These findings collectively confirm that the formation of Co–La bonds induces electronic interactions between metal atoms, leading to the generation of distinct sites with significant charge differences. This observation further corroborates the formation of Co–La intermetallic bonds.

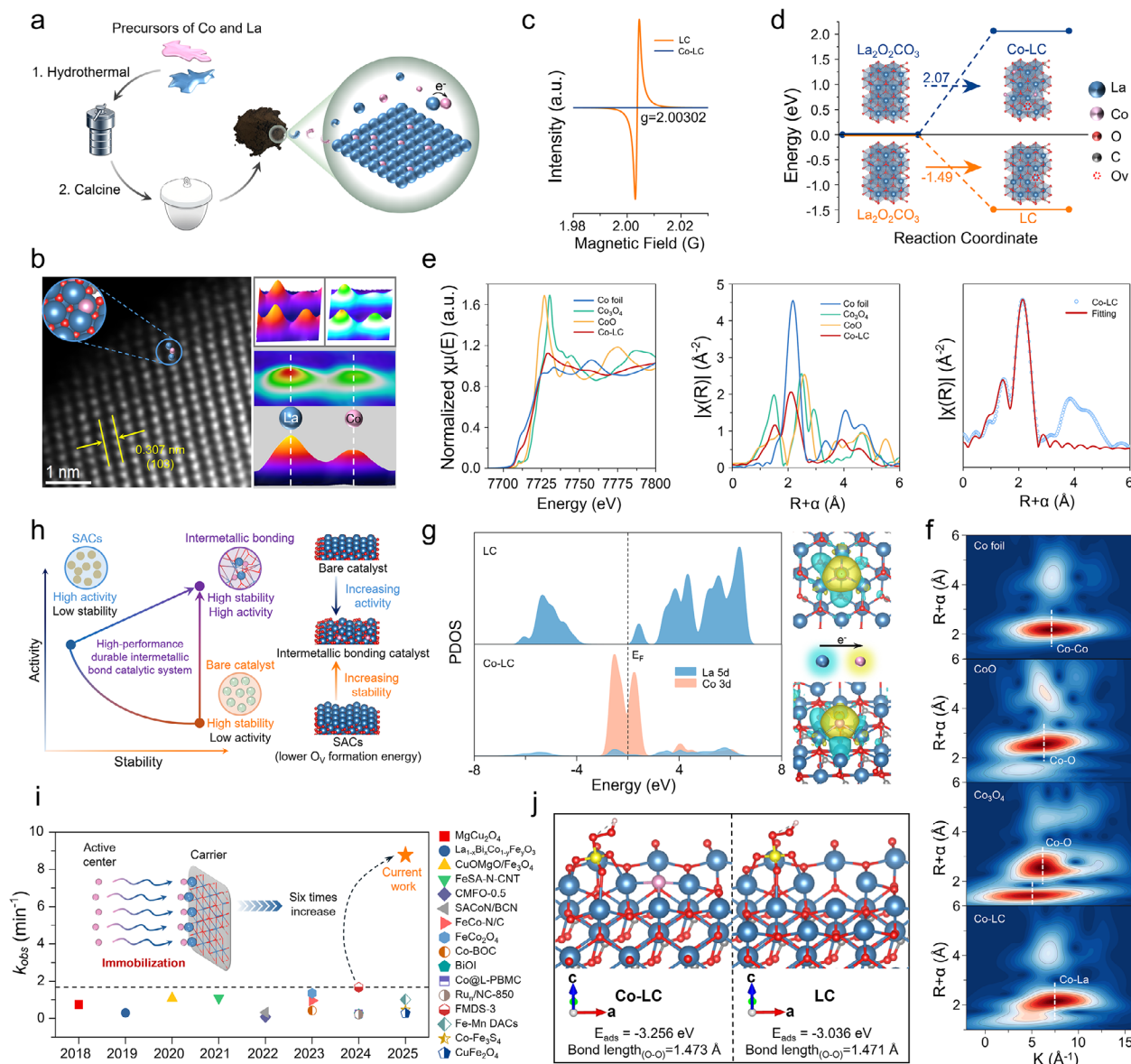


FIGURE 2 | The structure of the catalyst and its interaction with PMS. (a) Preparation of catalysts. (b) An aberration-corrected HAADF-STEM image and corresponding atom overlapping Gaussian function-fitting mapping for Co-LC. (c) EPR spectra of LC and Co-LC. (d) Energy barriers for the formation of OVs on LC and Co-LC. (e) XANES, FT-EXAFS spectra (k^2 -weighted) and corresponding EXAFS R-space fitting curve of Co-LC. (f) WT-EXAFS spectra of Co-LC. (g) PDOS of LC and Co-LC. (h) Schematic diagram of high-performance intermetallic bond catalyst design. (i) Compared with the catalytic performance reported in the literature. (j) The adsorption configuration of PMS on LC and Co-LC.

As noted earlier, to develop highly efficient catalysts, we capitalize on the charge differences between distinct metal atoms to establish strong interactions between the catalytic support and the active metal sites via intermetallic bonding. This approach substantially enhances catalytic stability while introducing activity (Figure 2h) [24]. To validate this dual-functional strategy, we applied the catalyst to an advanced oxidation water treatment system for the degradation of 1-naphthylamine (1-NA). Compared with most previous studies, the catalyst in this work demonstrated significantly superior activity (Figure 2i; Table S3), with its stability to be discussed in subsequent sections. We further investigated the adsorption energy and Bader charge transfer during PMS adsorption on the catalyst surface (Figure 2j; Figures S17–S21). Owing to intermetallic bonds formation, the incorporation of Co into the $\text{La}_2\text{O}_2\text{CO}_3$ significantly increased the

PMS adsorption energy on Co-LC ($E_{\text{ads}} = -3.256$ eV), whereas LC exhibited weaker PMS adsorption ($E_{\text{ads}} = -3.036$ eV). Concurrently, the longer O–O bond length of PMS adsorbed on Co-LC indicates greater propensity for activation to generate reactive oxygen species (ROS) [25, 26].

2.2 | Fenton-Like Catalysis and 1-NA Transformation Mechanisms

The Fenton-like catalytic capabilities of Co-LC and LC were evaluated for the removal of 1-NA in the presence of peroxydisulfate (PMS) (Figure 3a). After optimizing the experimental parameters, control experiments revealed that the reduction in 1-NA concentration was attributed neither to adsorption by

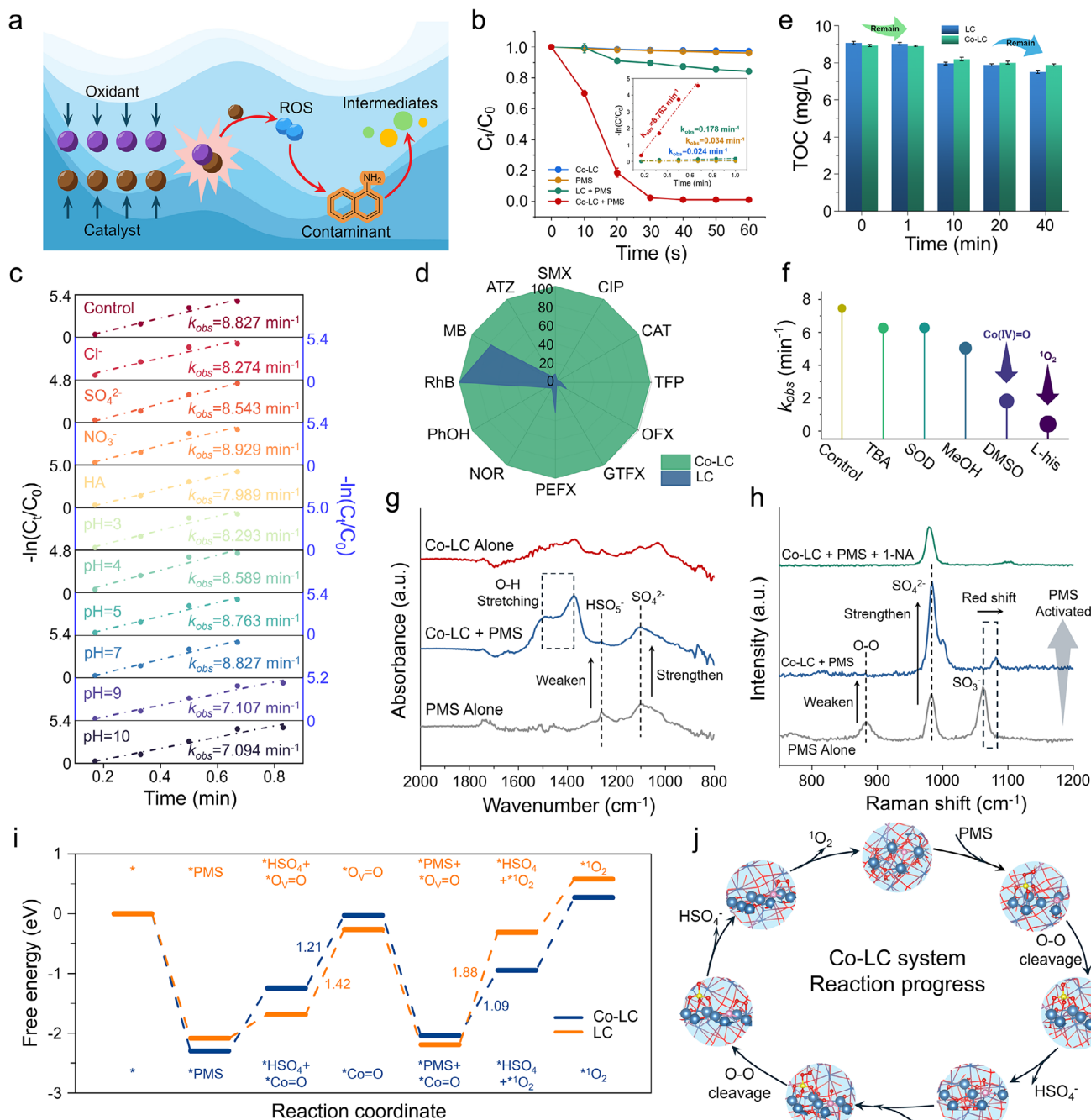


FIGURE 3 | Investigation of transformation efficiency and mechanism of 1-NA in the Co-LC/PMS system. (a) Schematic diagram of Co-LC/PMS transformation of 1-NA. (b) The transformation of 1-NA in different systems. (c) Effects of anions, initial pH, and other factors on the transformation of 1-NA in the Co-LC/PMS system. (d) The universality of LC-PMS and Co-LC/PMS systems for different pollutants. (e) TOC before and after transformation of 1-NA solution. (f) Quenching experiments conducted on the Co-LC/PMS system. Investigating the Activation Process of PMS by Co-LC via In Situ IR (g) and In Situ Raman Spectroscopy (h). (i) Gibbs free energy profiles of two pathways on LC and Co-LC. (j) Activation pathways of PMS. Experimental conditions: [Catalysts] = 0.3 g L $^{-1}$, [1-NA] = 10 mg L $^{-1}$, [PMS] $_0$ = 3 mM, T = 25°C, pH = 7.

the catalyst substrate nor to degradation catalyzed by leached metal ions (Figures S24–S26 and Table S4), which indicates that the Co–La intermetallic bonds play a principal role in the reaction. As presented in Figure 3b, the Co-LC system achieved over 99% 1-NA removal within merely 40 s, which significantly outperformed the LC system. This result clearly demonstrates the superiority of intermetallic bonds in enhancing Fenton-like catalytic performance. Moreover, the Co-LC system maintained high

1-NA removal rates even when subjected to interference from various anions and different initial pH conditions (Figure 3c), highlighting its excellent catalytic stability and promising application potential in complex aquatic environments. Furthermore, the catalytic performance of LC and Co-LC was evaluated using a series of different pollutants and multiple real wastewater samples (Figure 3d; Figure S27). Beyond 1-NA, the Co-LC/PMS system exhibited high removal efficiencies toward a broad range

of structurally diverse organic pollutants, demonstrating its excellent substrate versatility and broad-spectrum oxidation capability. To assess the stability of Co-LC, multiple reuse cycle tests were conducted, which confirmed the broad applicability and practical value of the Co-LC catalyst (Figures S28–S30). The consistently high decontamination efficiency observed in these tests further confirms the broad applicability and practical value of the Co-LC catalyst. It is noteworthy that although the Co-LC system achieved high 1-NA removal efficiency in a short period, the total organic carbon (TOC) content before and after the reaction exhibited minimal variation (Figure 3e; Table S5). This finding suggests that 1-NA in the system was not mineralized into CO₂, but rather transformed into other small-molecule organic compounds that remained in the aqueous phase.

We subsequently investigated the reactive species generated in the Co-LC/PMS system (Figure 3f; Figures S31–S35). The contribution of superoxide radicals (O₂•[−]) to the 1-NA transformation was first ruled out via superoxide dismutase (SOD)-mediated quenching experiments and electron paramagnetic resonance (EPR) measurements. The addition of tertiary butanol (TBA) and methanol (MeOH) only slightly inhibited the 1-NA transformation in the Co-LC/PMS system, indicating that sulfate radicals (SO₄•[−]) and hydroxyl radicals (•OH) make weak contributions to the reaction (Figure 3f; Figures S33–S35) [27–29]. When dimethyl sulfoxide (DMSO) and L-histidine (L-His) were used as quenchers in the experiments, the transformation efficiency of the Co-LC/PMS system was significantly suppressed [30]. Furthermore, the triplet signal detected by EPR spectroscopy and the oxidation of phenylmethyl sulfoxide (PMSO) to phenylmethyl sulfone (PMSO₂) collectively confirm that singlet oxygen (¹O₂) and high-valent cobalt species (Co^{IV} = O) play crucial roles in 1-NA transformation (Figure S32) [31, 32].

The quasi in situ attenuated total reflection (ATR)-FTIR test was conducted to probe the reaction process (Figure 3g). In the spectrum of PMS, the peaks at 1258.01 and 1098.44 cm^{−1} are assigned to the stretching vibration of the S–O bond and the symmetric stretching vibration of the sulfate ion (SO₄^{2−}), respectively. Upon adding Co-LC, the intensity of the S–O bond peak decreased significantly, while that of the SO₄^{2−} peak increased, indicating efficient decomposition of PMS. Additionally, the peaks at 1500.21 and 1373.41 cm^{−1} in the Co-LC/PMS system correspond to O–H bond stretching vibrations, likely originating from deprotonation processes during PMS decomposition [33]. Subsequently, in situ Raman spectroscopy tests were performed to further elucidate the interaction between Co-LC and PMS (Figure 3h). Three distinct peaks at 880, 980, and 1061 cm^{−1} were observed in the PMS solution, corresponding to the stretching vibrations of O–O, SO₄^{2−}, and SO₃[−], respectively [34]. Upon addition of Co-LC, the O–O and SO₃[−] peaks diminished drastically, while the SO₄^{2−} peak increased significantly, manifesting rapid PMS activation. Meanwhile, a red shift of the SO₃[−] characteristic peak was observed, implying the formation of *PMS complexes and Co^{IV} = O [31]. However, no Raman characteristic peaks attributed to Co^{IV} = O (i.e., 571 or 648 cm^{−1}) were detected in quasi in situ Raman spectra, thus excluding the dominant role of Co^{IV} = O [18]. Based on quenching experiment results, Co^{IV} = O is likely a key intermediate in ¹O₂ generation. Hence, quenching Co^{IV} = O also suppresses ¹O₂ production, resulting in a remarkable decrease in the transformation rate of 1-NA in the Co-LC/PMS

system. To clarify the activation pathways of Co-LC and LC toward PMS, density functional theory (DFT) calculations were carried out (Figure 3i,j). Using * to denote the adsorbed state, the optimized free-energy diagram for the Co-LC catalyst surface was *(i) → *PMS(ii) → *HSO₄ + *Co^{IV} = O(iii) → *Co^{IV} = O(iv) → *PMS + *Co^{IV} = O(v) → *HSO₄ + *¹O₂(vi) → *¹O₂ (vii). For LC, OVs catalyze the reaction by generating the *OV = O intermediate to facilitate the ¹O₂ formation, and the detailed minimum energy changes for various steps are documented (Table S6). In these processes, the step vi exhibits the highest energy barrier and is recognized as the rate-determining step for both Co-LC and LC. Notably, the energy barrier decreases from 1.88 eV for LC/PMS to 1.09 eV for Co-LC/PMS, suggesting that Co incorporation optimizes the binding strength of PMS and lowers the energy barrier for ¹O₂ formation. Ideally, catalysts with free energy close to the average value required in reaction steps are deemed optimal, as they ensure the lowest feasible free energy at the rate-determining step [35]. Based on the above analysis, the first PMS adsorbed onto the Co-LC surface undergoes activation, transiently forming a *Co^{IV} = O transition state. Subsequently, a second PMS rapidly adsorbs and activates, binding with *Co^{IV} = O to form *¹O₂. After ¹O₂ is released, the Co-LC reverts to its original state to initiate the next cycle (Figure 3j). Selective generation of ¹O₂ can effectively inhibit undesired side reactions and facilitate the transformation of 1-NA.

2.3 | Detoxification Pathways and Efficacy Evaluation of 1-NA

Since the Co-LC/PMS system transforms rather than mineralizes 1-NA, the biotoxicity of 1-NA transformation products is crucial for evaluating the suitability of Co-LC as a water treatment catalyst. To further demonstrate the superiority of the ¹O₂-dominated Co-LC/PMS system, a 96-hour cultivation assay was conducted using the sensitive model organism *Chlorella vulgaris* to assess the toxicity of treated water (Figure 4a,b) [36]. Moreover, the performance of the Co-LC/PMS system was comprehensively compared with both the untreated 1-NA solution and a blank aqueous solution. As shown in Figure 4a, the color of each *Chlorella* suspensions exhibited significant changes with increasing cultivation time. By 96 h, the *Chlorella* sample cultivated in the 1-NA solution showed a lighter color than both the control group and the sample treated with the Co-LC/PMS system. This indicates that the 1-NA solution inhibits the normal growth of *Chlorella*, whereas the treated solution does not impede its growth. To analyze the components in the transformed solution, the main intermediates during the transformation process were identified via liquid chromatography-mass spectrometry (LC-MS) (Figure 4c; Figure S37 and Table S7). Initially, 1-NA is attacked by ¹O₂ in the Co-LC/PMS system, leading to the oxidation of the amino group (–NH₂) and the generation of primary intermediates (denoted as N2 and N3). As ¹O₂ continues to oxidize these intermediates, the naphthalene ring undergoes ring-opening, yielding a series of secondary intermediates (e.g., N4, N5, N9, etc.), which are ultimately further oxidized to form the final products (N11 and N17). During this process, the mild oxidizing capacity of ¹O₂ can prevent the complete mineralization of pollutants, thereby minimizing the carbon footprint [37]. Simultaneously, the Co-LC/PMS system continuously generates new ¹O₂ to participate in the oxidation

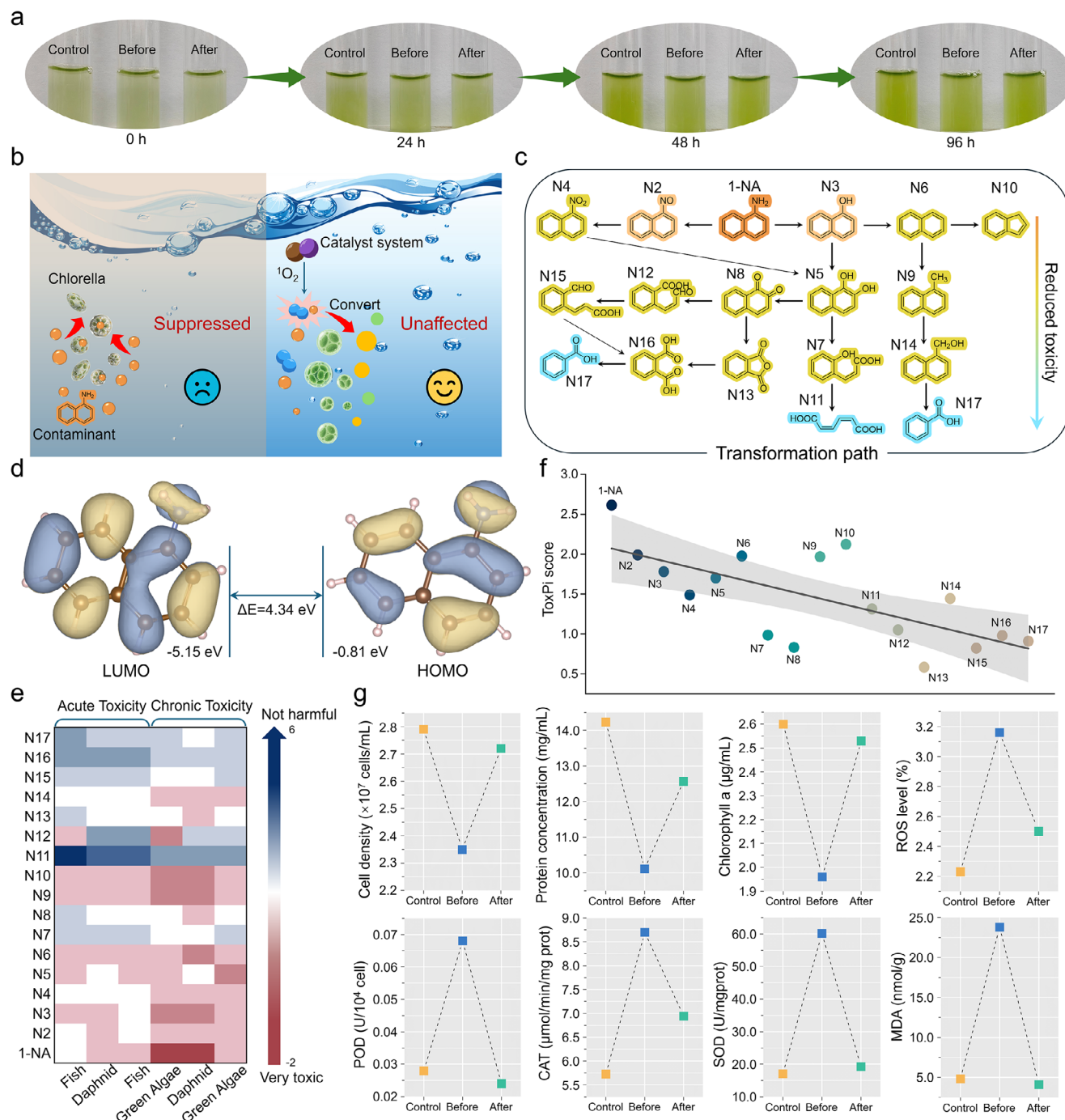


FIGURE 4 | Transformation pathways and product toxicity of 1-NA. (a) Optical photographs of *Chlorella* toxicity experiments at different cultivation times. (b) Schematic diagram of the toxicity test for *Chlorella*. (c) Transformation pathways of 1-NA. (d) Isosurface map of LUMO and HOMO orbitals. (e) Acute and chronic toxicity of 1-NA and its intermediates. (f) ToxPi score of 1-NA and its intermediates. (g) Biological activity indicators of *Chlorella* under different experimental conditions (Including cell density, protein concentration, chlorophyll a, ROS, POD, CAT, SOD, and MDA).

of 1-NA, thereby ensuring its complete transformation without mineralization. Additionally, the intermetallic bonds in Co-LC facilitate the rapid generation of $^1\text{O}_2$. This not only enables the transformation of 1-NA to be completed within an extremely short timeframe but also avoids excessive mineralization that would otherwise occur with prolonged reaction durations. To provide a more in-depth investigation into the transformation mechanism of 1-NA, DFT was employed for wavefunction analysis of the contaminant 1-NA. As depicted in Figure 4d, the lowest unoc-

cupied molecular orbital (LUMO) indicated the region prone to electron acceptance, while the highest occupied molecular orbital (HOMO) indicated the region susceptible to electron donation. The HOMO electron density of 1-NA is primarily concentrated in the conjugated naphthalene ring system and the adjacent amino moiety. As a strong electrophile, $^1\text{O}_2$ tends to attack regions with high electron density. Therefore, the amino group and the α -carbon atom in 1-NA are more susceptible to attack by $^1\text{O}_2$, which is consistent with the previously proposed

transformation pathway of 1-NA [38]. Due to the nucleophilic and reducing properties of the amino group, it can react with electrophilic sites in biomolecules. Meanwhile, the lipophilic nature of the naphthalene ring facilitates the entry of 1-NA molecules into cells or their bioaccumulation within organisms, thereby enhancing their reactivity with intracellular biological targets and amplifying the toxic effects of 1-NA to living organisms [39]. The $^1\text{O}_2$ -dominated Co-LC/PMS system selectively degrades these two toxic moieties, effectively attenuating the toxicity of 1-NA. In addition, the moderate oxidizing capacity of $^1\text{O}_2$ prevents the overoxidation of transformation intermediates derived from 1-NA.

To further evaluate the detoxification capacity of the Co-LC/PMS system for 1-NA, the toxicity of 1-NA and its intermediates was initially predicted using the Ecological Structure-Activity Relationships (ECOSAR) system (Figure 4e; Table S8), and calculated the Toxicological Priority Index (ToxPi Score) (Figure 4f; Table S9). Following this, the toxicity of the Co-LC/PMS-treated solution was comprehensively assessed through a comparative analysis of its effects on aquatic organisms. Compared to other transformation products, 1-NA exhibits the highest toxicity with a ToxPi index of 2.613. However, after undergoing the Co-LC/PMS system transformation, the toxicity of all products significantly decreased. The ToxPi indices of the final products N11 and N17 were reduced to 1.315 and 0.910, respectively, and both are biodegradable, demonstrating that this system can effectively transform 1-NA into harmless products. To further validate the effective reduction in toxicity of the 1-NA transformation products, we comprehensively measured key growth indicators of *Chlorella* after 96 h of cultivation, including cell density, protein concentration, chlorophyll *a*, ROS levels, peroxidase (POD), catalase (CAT), superoxide dismutase (SOD), and malondialdehyde (MDA). As shown in Figure 4g, the cell density, protein concentration, and chlorophyll *A* content of the *Chlorella* sample cultured in 1-NA solution (i.e., Before) were significantly lower than normal levels (i.e., Control). In contrast, the *Chlorella* sample cultured in solution and treated with the Co-LC/PMS system (i.e., After) maintained relatively healthy levels for these parameters. ROS, as a metabolic byproduct of *Chlorella*'s physiological activities, is produced in extremely small quantities under normal conditions. However, *Chlorella* samples cultured in 1-NA solution exhibit significantly elevated ROS levels compared to normal states. This indicates that 1-NA induces oxidative stress in *Chlorella*, placing it in a state of oxidative imbalance. Excessive ROS can cause cellular damage and even death in *Chlorella* cells [40].

To further evaluate the physiological status of *Chlorella* under toxic stress, four ROS-related indicators—POD, CAT, SOD, and MDA—were subsequently determined. Under normal physiological conditions, when cells sense ROS accumulation, they actively upregulate the synthesis and activity of POD, CAT, and SOD to form a ROS-scavenging cascade. Specifically, SOD catalyzes the dismutation of superoxide anions ($\text{O}_2^{\bullet-}$) into hydrogen peroxide (H_2O_2), which is then decomposed into H_2O and O_2 by CAT and POD. This coordinated process maintains the normal dynamic balance of intracellular ROS [41]. At this stage, only trace amounts of MDA—an end product of ROS-induced lipid peroxidation in cell membranes—should be detected. As shown in Figure 4g, the activities of the three antioxidant enzymes (POD, CAT, SOD)

in *Chlorella* cultured in the 1-NA solution were significantly higher than those under normal conditions, indicating that the cells had activated a defensive response to counteract the already disrupted ROS balance. However, intracellular ROS levels remained elevated, and excessive MDA was also detected. This phenomenon suggests that despite enhanced activity of antioxidant enzyme, a portion of ROS still evaded the cellular defense mechanisms. These residual ROS further attacked unsaturated fatty acids in the cell membrane, leading to the overproduction of MDA. In conclusion, 1-NA exerted significant oxidative toxicity on *Chlorella*, resulting in both functional disorders (e.g., disrupted ROS homeostasis) and structural damage (e.g., membrane lipid peroxidation). In contrast, *Chlorella* cultured in the 1-NA solution treated by the Co-LC/PMS system exhibited healthy profiles across all tested indicators. The differences in these indicators between the treated group and the blank control group were minimal and within the normal physiological range. This confirms that the Co-LC/PMS system can effectively transform 1-NA into non-toxic metabolites, thereby achieving harmless water treatment characterized by “no mineralization and no carbon emissions”. With comprehensive consideration of aquatic environmental safety, the Co-LC system is more suitable to be deployed as a pre-oxidation unit prior to biological treatment. Discharge after advanced microbial treatment can guarantee zero environmental risks.

2.4 | Practical Application Potential of Transformation Detoxification

The high catalytic activity and stability of the Co-LC/PMS system prompted us to explore its potential for continuous wastewater treatment. First, a cylindrical packed-bed reactor with a volume of 100 cm^3 was designed and fabricated (Figure 5a). A 1.8 mm mesh screen was installed at both the top and bottom ends of the reactor—where the packing material was loaded—to support the packing and retain waste residues at the reactor bottom. Subsequently, Co-LC was loaded onto 2–3 mm diameter molecular sieves, which served as the reactor packing material (Figure 5b; Method S2). Secondary effluent from a residential WWTP located in Tianjin, China, was selected as the actual water matrix. After dissolving 1-NA and PMS in this effluent, a continuous-flow system was established to assess the reactor's treatment performance. The abundant pore channels of the molecular sieve support can endow the catalyst with an effective physical screening effect. With intrinsic acid-base buffering capacity and pore sieving function, molecular sieves assist the catalyst in improving environmental adaptability, alleviating catalyst poisoning, and enhancing the operational stability of the system [42–44].

Using the aforementioned reactor and packing material, a 37-day long-term operation experiment was conducted. As illustrated in Figure 5c, the 1-NA transformation efficiency remained consistently high (>94%) throughout the operation period, while the TOC in the system exhibited a slight reduction compared to the influent (decreasing from 40.35 to below 18 mg/L). This TOC reduction is likely attributed to the mineralization of readily degradable small-molecule organic compounds present in the complex water matrix. As the operation time extends, the effluent TOC remains relatively stable and fluctuates slightly around 15 mg L^{-1} . This phenomenon is possibly caused by the uneven

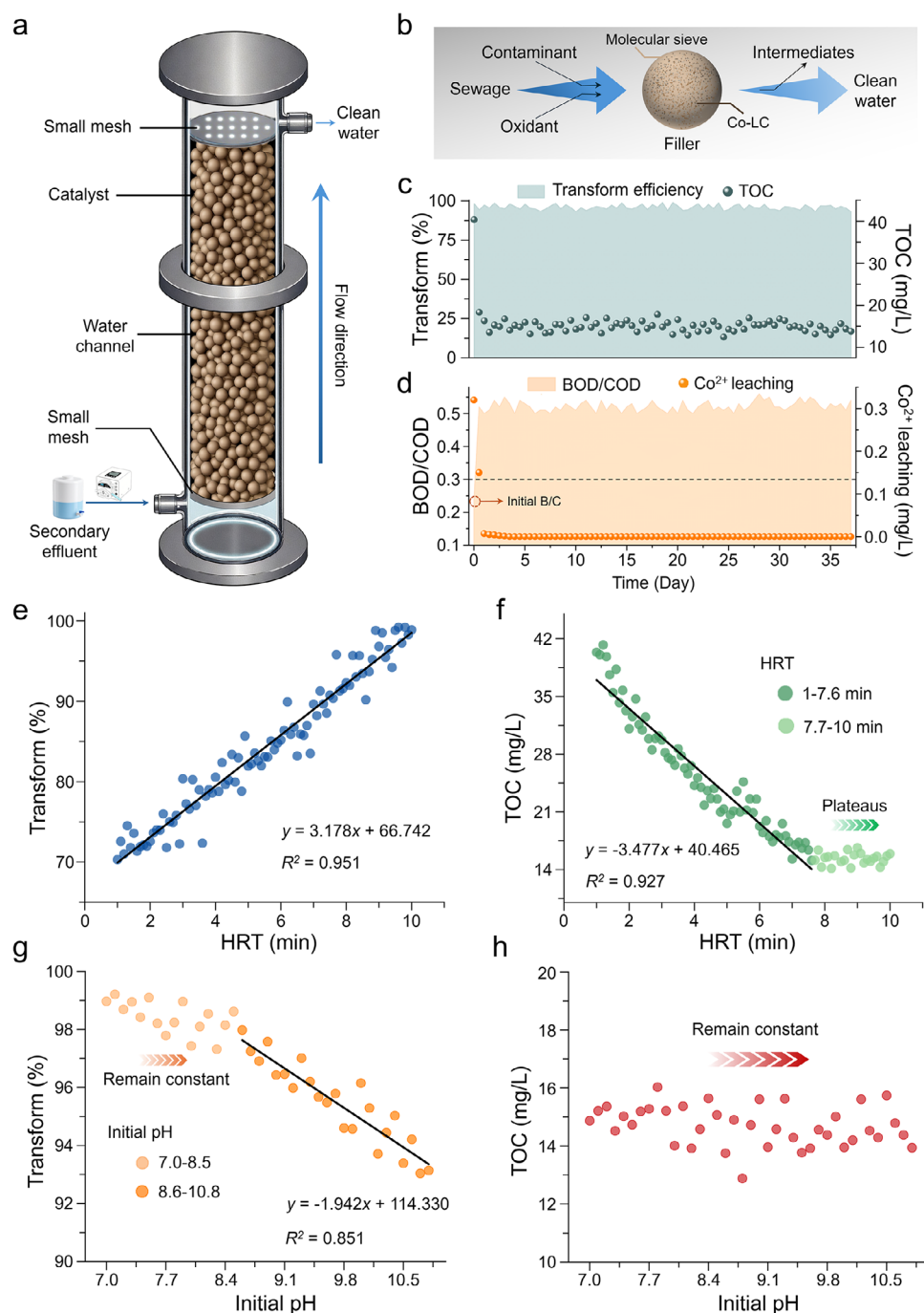


FIGURE 5 | Practical application investigation. (a) Schematic diagram of the Co-LC-packed bed reactor. (b) Schematic diagram of the Co-LC filter media process. (c) Transformation efficiency of 1-NA and variations in water TOC during long-term operation. (d) BOD/COD and Co^{2+} leaching during long-term operation. (e) Transformation efficiency variation with HRT. (f) TOC variation with HRT. (g) Transformation efficiency variation with initial pH. (h) TOC variation with initial pH. Reaction conditions: $[\text{PMS}]_0 = 3 \text{ mM}$, $[\text{1-NA}]_0 = 10 \text{ mg L}^{-1}$, $\text{HRT} = 10 \text{ min}$, $\text{pH} = 7$.

water quality of the actual water sample. This result further demonstrates that stable transformation of 1-NA can still be achieved after treatment by this system under practical application conditions. Subsequently, the BOD_5/COD ratio of the water was determined to assess the system's impact on wastewater biodegradability (Figure 5d). The results indicated that the initial raw water had a BOD_5/COD ratio of only 0.24 (below 0.3), reflecting extremely low biodegradability. After treatment by the reactor, the effluent BOD_5/COD ratio increased to over 0.5. This confirms that the system significantly improves wastewater

biodegradability by transforming highly toxic 1-NA into low-toxicity or non-toxic small-molecule substances [33]. Meanwhile, the concentration of Co^{2+} in the effluent was monitored throughout the experiment. At the start of operation, the leached Co^{2+} concentration in the system was 0.32 mg/L ; as operation time prolonged, Co^{2+} leaching gradually decreased. By the fifth day of operation, no detectable Co^{2+} was found in the effluent. This demonstrates the stability and safety of the system during water purification and validates its application potential in practical water treatment processes.

During the long-term operation of the Co-LC packed bed reactor, the universality of this system for 1-NA transformation was investigated by varying two key influencing factors: hydraulic retention time (HRT) and the initial pH of the feedwater. As illustrated in Figure 5e, HRT exhibited a significant positive correlation with 1-NA transformation efficiency. This observation may be attributed to the competition between 1-NA and other molecules in the water matrix; an excessively short HRT could lead to incomplete 1-NA transformation. Based on this finding, the effect of HRT on TOC was evaluated (Figure 5f). At the start of system operation, effluent TOC was significantly lower than that of the raw water—consistent with previous analyses suggesting the mineralization of other organic compounds in the matrix. As HRT gradually increased, effluent TOC ceased to decrease further and instead showed a gradual plateauing trend. The inflection point observed at 7.6 min may indicate the depletion of other organic compounds. Given the above results, an HRT of 10 min was selected to further investigate the effect of pH on 1-NA transformation. As shown in Figure 3c, alkaline conditions exerted a significant inhibitory effect on the Co-LC/PMS system; therefore, the initial pH of the raw water was adjusted to >7 to examine the reactor's 1-NA transformation performance. As shown in Figure 5g, a negative correlation exists between the conversion efficiency of 1-NA and pH values when the latter exceed 8.5. An increase in pH slightly inhibited 1-NA transformation; at pH 10.8, the transformation efficiency decreased to an average of 93.1% within 10 min. Concurrently, effluent TOC remained nearly constant (Figure 5h), indicating that 1-NA continued to undergo transformation under alkaline conditions. Subsequently, HRT was extended to 15 min (Figure S38), at which point the 1-NA transformation efficiency reached over 98%. This result further confirms that the Co-LC packed-bed reactor maintains stable operation under extreme alkaline conditions, demonstrating considerable potential for practical application. The environmental significance of the Co-LC/PMS system can be further quantitatively compared with the benchmark heterogeneous Co_3O_4 /PMS system via the life cycle assessment (LCA), so as to evaluate the sustainability of the technology relative to alternative or comparable options [45] (Method S8; Figure 6; Tables S10–S12). As shown in Figure 6b, the Co-LC/PMS system exhibits greater environmental friendliness than the Co_3O_4 /PMS system, as evidenced by reduced negative impacts across most environmental metrics. The environmental footprint of the Co-LC/PMS system primarily originates from PMS and electricity consumption during material preparation, whereas that of the Co_3O_4 /PMS system is dominated by Co_3O_4 and electricity consumption during processing. The superior stability of Co-LC allows for its application at lower dosages, thereby reducing both environmental impacts and economic costs. Treating 1 t of wastewater via the Co-LC/PMS system costs only \$1.31—merely one-fifth of that for the Co_3O_4 /PMS system (Figure 6c). Sensitivity analysis of CO_2 emissions (Figure 6d) reveals that energy consumption exerts a more significant influence. In future practical applications, further optimization of synthesis and reaction conditions can be performed to minimize energy consumption.

3 | Conclusions

In summary, this study proposes a transformation-dominant advanced oxidation process (T-AOP) that rapidly activates PMS

via the formation of highly reactive intermetallic bonds, thereby efficiently generating $^1\text{O}_2$. Harnessing the moderate oxidizing capacity of $^1\text{O}_2$ and its selectivity for electron-rich moieties, the toxic functional groups of 1-NA were successfully decomposed. This process transforms 1-NA into non-toxic or low-toxic products, achieving harmless transformation of pollutants. The high efficiency and rapid reaction kinetics effectively suppress side reactions and the formation of toxic intermediates. In contrast to the oxidative stress exerted by 1-NA on *Chlorella*, the generated transformation intermediates support the normal growth of algae. Long-term operation experiments verified the stability of this transformation mechanism, with the biodegradability of treated wastewater increasing threefold. LCA results indicate that the Co-LC/PMS system is environmentally benign and cost-effective, exhibiting strong application potential. This study establishes the first AOP system that replaces “mineralization” with “transformation” and “pollutant removal” with “toxicity elimination,” providing a novel strategy for developing customized water treatment solutions based on the intrinsic properties of target pollutants.

4 | Experimental Section

4.1 | Preparation of Co-LC and LC

First, 0.8 g of CTAB (cetyltrimethylammonium bromide) was dissolved in 60 mL of deionized water at 40°C . Under magnetic stirring, 4 mmol of $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, 4 mmol of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, and 12 mmol of ammonium citrate were sequentially added, followed by further stirring for another half an hour. After thorough mixing, the mixture was transferred into a 100 mL stainless steel autoclave with a Teflon liner, which was then sealed and maintained at 180°C for 12 h. Once the autoclave had cooled down to room temperature naturally, the precipitate was separated by centrifugation. The precipitate was washed several times alternately with deionized water and anhydrous ethanol, and then dried in an oven at 60°C . Subsequently, the powder was calcined at 500°C for 5 h with a heating rate of 5°C per minute. A dark brown powder was obtained and designated as Co-LC. The contents of Co and La in the catalyst were determined via ICP analysis under different Co doping levels. Detailed results are presented in Table S1. The optimal catalyst was selected based on its conversion performance with 1-NA, with results shown in Figure S22. Using the same method but without the addition of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, the resulting black powder was designated as LC.

4.2 | Preparation of Filler

4A molecular sieves (2–3 mm) were immersed in 0.1 M dilute hydrochloric acid and agitated for 4 h. They were rinsed with water until neutral, and then dried overnight at 120°C . Subsequently, 0.8 g of CTAB was dissolved in 60 mL of deionized water at 40°C . Under magnetic stirring, 4 mmol of $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, 4 mmol of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, and 12 mmol of ammonium citrate were sequentially added. After complete dissolution, the pretreated molecular sieves were added and stirring continued for 30 min. The mixture was transferred to a 100 mL polytetrafluoroethylene-lined stainless-steel autoclave

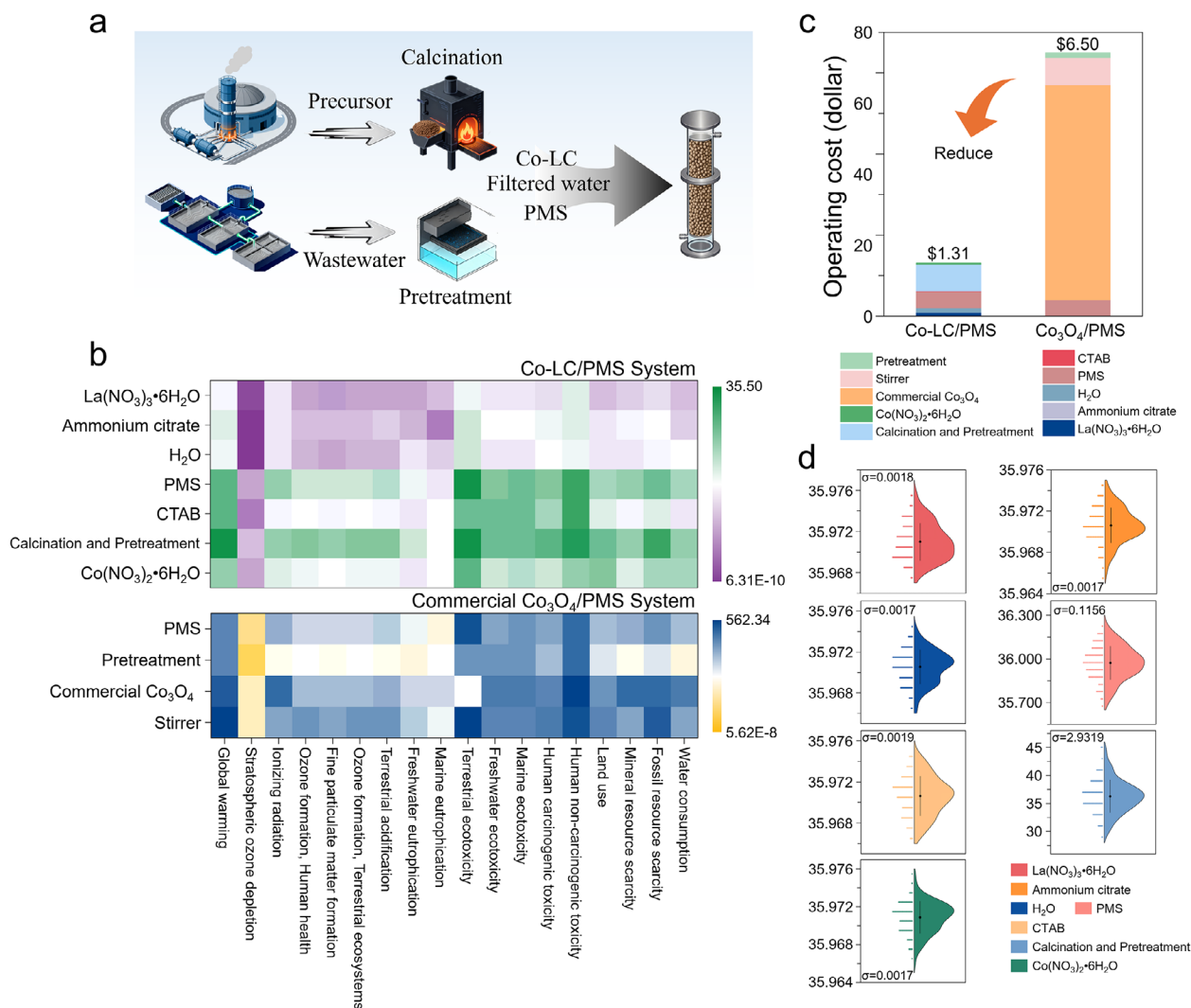


FIGURE 6 | LCA analysis. (a) LCA analysis boundary diagram. (b) Impact assessment of 1 ton 1-NA wastewater remediation using Co-LC/PMS and commercial Co₃O₄/PMS system. (c) Economic evaluation of different systems for water clean-up. (d) Sensitivity analysis of Co-LC/PMS (Global Warming).

and subject to hydrothermal treatment at 180°C for 12 h. Once the autoclave cooled naturally to room temperature, the precipitate was collected via vacuum filtration. The precipitate was washed several times with alternating portions of deionized water and anhydrous ethanol, then dried in a 60°C oven. Subsequently, the molecular sieves were calcined at 500°C for 5 h with a heating rate of 5°C/min to obtain the final filler.

4.3 | 1-NA Transformation Experiments

In a typical experiment, the catalyst was introduced into the target pollutants solution and stirred at room temperature for 10 min to achieve adsorption-desorption equilibrium. After that, the PMS stock solution (0.1 M) was added to the above solution to initiate the oxidation reaction. The mixture was magnetically stirred at 25 ± 0.2°C. At predetermined time intervals, sample aliquots (1 mL) were withdrawn and immediately quenched with 20 µL of Na₂S₂O₃ (0.5 M). Then, it was filtered through a 0.22 µm glass fiber membrane (negligible adsorption for reactants) and injected into a 2 mL amber glass vial for tests. The batch experiments

were conducted at least three times, and the average values with standard deviations were given. The catalytic activity and stability of Co-LC were investigated by activating PMS to degrade 1-Naphthylamine (1-NA) at 25 ± 0.2°C under neutral pH conditions. In addition, the effects of PMS dosages (1, 2, 3, 4 mM), catalyst dosages (0.1, 0.2, 0.3, 0.4 g/L), pH (3, 4, 5, 7, 9, 10), coexisting ions (Cl⁻, SO₄²⁻, NO₃⁻) and organic substance (HA) were also investigated. Adjust the pH using 1 M dilute sulfuric acid and dilute sodium hydroxide solutions. Unless otherwise specified, all experiments were conducted at room temperature with pH = 7.0. The catalyst was used at a concentration of 0.3 g/L, and PMS was used at a concentration of 3 mM.

Acknowledgements

This work was supported by the Natural Science Foundation of China projects (Nos. 22422605, 22225604, U24A20518, U25A20628, 22561160129, 22479074 and 22475096), the Tianjin Commission of Science and Technology as key critical technologies R&D projects (No. 24YFZCSN00050), the Young Scientific and Technological Talents (Level Two) in Tianjin

(No. QN20230206), the Natural Science Foundation of Tianjin (No. 25JCYBJC01450), the Equipment Pre-Research and Ministry of Education Joint Fund (No. 8091B02052407), the Fundamental Research Program Key Project of Jiangsu Province (No. BK20253008), the Science and Technology Major Project of Jiangsu Province (No. BG2024013), the Scientific and Technological Achievements Transformation Special Fund of Jiangsu Province (No. BA2023037), the Academic Degree and Postgraduate Education Reforming Project of Jiangsu Province (No. JGKT24_C001), the Key Core Technology Open Competition Project of Suzhou City (No. SYG2024122), the Open Research Fund of Suzhou Laboratory (No. SZLAB-1308-2024-TS005), the Chenzhou National Sustainable Development Agenda Innovation Demonstration Zone Provincial Special Open Competition Project (Nos. 2023sfq11 and 2025sfq38), and the Fundamental Research Funds for the Central Universities and Nanjing University International Collaboration Initiative (No. 020514380354).

Conflicts of Interest

The authors declare no conflicts of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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Supporting Information

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