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Environmental significance

The Fe-N₅ SAC for enhanced PMS activation in degrading various CPs, especially 4-CP, in a wide pH range holds significant environmental implications. Fe-N₅ exhibited remarkable performance in degrading various CPs and resistance to the interference of coexisting substances, suggesting that Fe-N₅ is an ideal candidate for actual wastewater treatment. This work emphasizes the potential of Fe-N₅, with axial N coordination responsible for modulating the electron distribution density around metal active centers as a profound and sustainable approach for enhanced PMS activation. This work also provides a promising and eco-friendly solution for eliminating organic pollutants, ultimately ensuring improved water quality.

Introduction

The treatment of toxic and recalcitrant organic pollutants in wastewater has become increasingly challenging, necessitating innovative approaches to meet stringent

promoted peroxymonosulfate activation for degradation of 4-chlorophenol[†] Manoj Kumar Panjwani, ^{(D) abc} Feiyu Gao,^b Ting He,^a Pan Gao,^b Feng Xiao^a and Shaoxia Yang ^(D)*^a

Highly coordinated Fe–N₅ sites effectively

 $M-N_x$ single-atom catalysts (SACs) with a high coordination number (x > 4) are effective catalysts for eliminating organic pollutants, while the origin of SACs with high activity still remains elusive. In this work, we successfully synthesized an Fe-N₅ SAC with axial N coordination, which exhibited exceptional catalytic performance by peroxymonosulfate (PMS) activation for degrading 4-chlorophenol (4-CP) in a wide pH range (4.0–10.0). The rate constant of Fe-N₅ (2.99 min⁻¹) was 6.36 times higher than that of Fe-N₄, and the turnover frequency (TOF) of Fe-N₅ was found to be 4–149 times higher than those of state-of-the-art SACs and nanocatalysts reported in the literature for 4-CP degradation by PMS activation. Moreover, Fe– N_5 was not significantly affected by coexisting substances (HA, HCO3⁻, SO4²⁻, H2PO4⁻, NO3⁻, and Cl⁻) and had satisfactory degradation efficiency for various chlorophenols. Electron paramagnetic resonance (EPR), quenching experiments, and radical probe experiments demonstrated that ¹O₂ played a key role in the Fe-N₅/PMS system for 4-CP degradation. Density functional theory calculations confirmed that a narrower gap between the Fe-3d band center and Fermi level enhanced the electron transfer in Fe-N₅, which resulted in promoted PMS activation. In addition, the Fe-N₅/PMS system showed good potential for application in real wastewater. The above findings offer important implications for the future of coordination chemistry in designing M-N_x-C SACs (x > 4), highlighting their practical applications in environmental remediation

> environmental standards. Advanced oxidation processes (AOPs) have emerged as effective technologies to generate a broad range of reactive oxygen species (ROS) for efficiently degrading a variety of refractory contaminants, making AOPs wastewater treatment.^{1–5} promising option for Peroxymonosulfate (PMS)-based AOPs have recently attracted extensive attention due to their advantages, which include enhanced reaction rates, more robust oxidation capacity, and relatively simpler operation.⁶ Moreover, PMS-based AOP studies have reported organic contaminants decomposing into low or non-toxic substances and even completely mineralizing into carbon dioxide (CO₂) and water (H₂O).⁶⁻⁸ However, the agglomeration of nanocatalysts with low metal atom utilization significantly inhibits PMS activation,



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resulting in lower degradation efficiency for the pollutants in wastewater.⁹ Therefore, the development of highly dispersed and stable catalysts is crucial to overcome this limitation and achieve efficient PMS activation for wastewater treatment.

Carbon-supported single-atom catalysts (SACs) have exhibited a new frontier in heterogeneous catalysis for environmental remediation.¹⁰ The unique advantage of SACs lies in their single metal active sites, providing maximum metal atom utilization efficiency and precisely controlling the coordination structure of metal atoms.^{11,12} Metal single atoms anchored through N atoms on carbon materials are employed for PMS-based AOPs and show good catalytic performance to destroy refractory organic pollutants.^{13,14} Importantly, the coordination number of the $M-N_x$ moieties has a strong influence on the catalytic performance of SACs by PMS activation for removing the pollutants, because different coordination numbers at the metal center remarkably alter the geometry and electronic structure of the metal atom, leading to the improved performance of SACs.^{15,16} Therefore, a thorough understanding and precise adjustments of the coordination structure, including the coordination number of the $M-N_x$ moieties, are crucial for improving the PMS activation for effective pollutant removal.

At present, M–N_x–C SACs ($x \le 4$) are reported in PMSbased AOPs. M–N_x–C (x = 4) exhibited significantly higher levels of activity and stability for pollutant degradation.^{14,17,18} For example, M–N₄–C SACs (M = Fe, Co, and Cu) notably improved PMS activation for enhanced pollutant removal.¹⁹ However, the M–N₄ structure still faces an unsatisfactory catalytic activity due to the symmetrical coordination configuration, which causes strong adsorption between SACs and reactants and/or intermediates.^{20–22} Meanwhile, metal atoms in M–N_x–C (x < 4) have more 3d electrons that easily transfer to active species adsorbed on the SACs *via* feedback π bonds. This makes it difficult for these species to further obtain electrons from the pollutants during the reaction, ultimately resulting in a lower catalytic activity for the pollutant degradation.^{23,24}

The exploration of coordination chemistry to improve PMS activation in M–N_x–C SACs (x > 4) has gained increasing attention, while a few studies have reported M–N₅–C SACs in PMS-based AOPs to remove organic contaminants.^{25–31} M–N₅ has shown superior activity for pollutant degradation in a heterogeneous Fenton-like reaction. For example, the Mn–N₅–C SAC utilized axial N coordination to modulate the electron density around metal atoms, thereby improving PMS activation and enhancing the pollutant removal.²⁵ However, understanding the mechanism of M–N_x SACs (x > 4) with a high coordination number to activate PMS in pollutant degradation remains elusive.

In this work, 4-chlorophenol (4-CP) widely detected in wastewater, one of the persistent organic pollutants, was chosen as the target pollutant. We experimentally and theoretically investigated the feasibility and superiority of the Fe– N_5 –C SAC in PMS activation to degrade various chlorophenols (CPs) in a wide pH range. Moreover, the

interference of coexisting substances (HA, HCO₃⁻, SO₄²⁻, H₂PO₄⁻, NO₃⁻, and Cl⁻) in natural water in the 4-CP degradation was also discussed. Electron paramagnetic resonance (EPR) trapping and radical scavenger experiments were used to determine ROS produced in the Fenton-like reaction over Fe-N₅ by PMS activation. Density functional theory (DFT) calculations proved that Fe-N₅ was more prone to PMS activation due to the axial N coordination modulating the electron density around Fe atoms, which played an essential role in the electron transfer, thereby significantly enhancing the catalytic performance of Fe-N₅ in the degradation of organic pollutants. The results underscore the remarkable performance and broad applicability of Fe-N₅-C SACs in water and wastewater treatment.

Experimental section

Materials

Dicyandiamide (C₂H₄N₄, 99.0%), polyethylene glycol (PEG, >99.9%), iron(II) chloride tetrahydrate (FeCl₂·4H₂O, 99.5%), iron(m) chloride hexahydrate (FeCl₃·6H₂O, 99.5%), cobalt(n) hexahydrate $(Co(NO_3)_2 \cdot 6H_2O,$ 99.5%), nitrate 1,10phenanthroline (C₁₂H₈N₂, 97.0%), zinc chloride (ZnCl₂, 99%), formamide solution (HCONH₂, 99%), ethanol (75%), potassium peroxymonosulfate (PMS, KHSO₅·0.5KHSO₄·0.5K₂-SO₄, 98%), 2-chlorophenol (2-CP, 99%), 4-chlorophenol (4-CP, 2,4-dichlorophenol (2,4-DCP, 2,4,6-99%). 99%), trichlorophenol (2,4,6-TCP, 99%), bisphenol A (BPA, 99%), o-nitrophenol (2-NP, 99%), p-nitrophenol (4-NP, 99%), phenol (99%), sulfamethazine (SMT,99%), sulfadiazine (SDZ, 99%), benzoic acid (BH₃O₃, 99%), nitrobenzene (NB, 99%), para-chlorobenzoic acid (p-CBA, 99%), furfuryl alcohol (FFA, 99%), *tert*-butanol (TBA, >99%), chloroform (CF, \geq 99.0%), humic acid (HA, >99%), methyl phenyl sulfoxide (PMSO, 98%), sulfuric acid (H₂SO₄, \geq 99.5%), sodium bicarbonate (NaHCO₃, \geq 99.8%), sodium sulfate (Na₂SO₄, >99%), sodium dihydrogen phosphate (NaH₂PO₄, >99%), sodium nitrate (NaNO₃, >99%), sodium chloride (NaCl, \geq 99.5%), potassium iodide (KI, 99%), potassium thiocyanate (KSCN, 98.5%), sodium thiosulfate (Na₂S₂O₃, >99%), boric acid (BA, \geq 99.5%), 5,5-dimethyl-1-pyrrolidine N-oxide (DMPO) and 2,2,6,6-tetramethylpiperidine (TEMP) were obtained from Macklin Co. Ltd. and Aladdin Biochemical Technology Co. Ltd. without further purification.

Synthesis of the Fe-N₅ SAC

Dicyandiamide (2.0 g) and polyethylene glycol (0.2 g) were dissolved in deionized water (40 mL) under stirring at 30 °C for 30 min, referred to as solution A. Subsequently, FeCl₂·4H₂O (0.048 g) was dissolved in deionized water (2 mL), and then added to solution A. Then, 1,10-phenanthroline (0.1298 g) dissolved in ethanol (8 mL) was loaded into the above solution. The resulting solution was vigorously stirred for 4 h and dried at 60 °C for 24 h. The precursor was calcined at 900 °C for 2 h under N₂ at a heating rate of 5 °C min⁻¹. The obtained solid was impregnated with H₂SO₄ solution (1 mol L⁻¹) at 80 °C for 2 h, filtered, washed with deionized water, and dried at 60 °C overnight to obtain the Fe–N₅ SAC. A metal free-NC catalyst was prepared using a similar method in the absence of an iron source, and the Fe–N₄ SAC was prepared using a previously reported literature method, and the preparation process is detailed in the ESI,†³²

Characterization of the SACs

High-angle annular dark field scanning transmission electron microscopy (HAADF-STEM) was performed on an atomic resolution analytical microscope JEM-ARM 300F (JEOL Ltd., Japan) operating at 300 kV. X-ray diffraction (XRD) was performed on a SmartLab SE (Rigaku, Japan) to determine the crystal structure of the catalysts in the range from 20° to 90° at a scanning rate of 5° min⁻¹. X-ray photoelectron spectroscopy (XPS) was performed on an EscaLab Xi⁺ (Thermo Fisher Scientific, USA), with a monochromatic Al Ka source (hv = 1486.6 eV) to obtain the composition and chemical state of the catalysts. X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) at the Fe K-edge were carried out in a transmission mode at the Spring 8 beamline of the synchrotron radiation facility in Japan (Spring 8, Sayo, Japan). Fe-K-edge X-ray absorption spectroscopy (XAS) was performed with Si (111) crystal monochromators. Before the analysis at the beamline, samples were placed into aluminum sample holders and sealed using a Kapton tape film. X-ray absorption fine structure (XAFS) spectra were recorded at room temperature using a 4-channel silicon drift detector (SDD) Bruker 5040. The electrochemical properties of the catalysts were measured on a CHI760E electrochemical workstation (Chenhua Instrument Co., China). The detailed information is described in the ESI.[†]

Catalytic activity evaluation

4-CP was used as the target contaminant to evaluate the activity of Fe-N5 in the heterogeneous Fenton-like reaction. Experiments for 4-CP degradation were carried out at room temperature. Initially, 2.5 mg of catalyst was introduced into 50 mL of 4-CP solution (20 mg L^{-1}) under stirring for 30 min establish an adsorption-desorption equilibrium. to Subsequently, 1 mL of PMS solution (10 g L^{-1}) was added to initiate the reaction. At specific time intervals, a sample was withdrawn, promptly quenched with sodium thiosulfate, and filtered through a 0.22 µm filter for analysis. Other CPs and pollutants, including 2-CP, 2,4-DCP, 2,4,6-TCP, BPA, phenol, SDZ, SMT, 2-NP, and 4-NP, were compared to further assess the performance of Fe-N5. The concentration of the contaminants was measured using high-performance liquid chromatography (HPLC, Agilent1260, USA) with a C18 column, and additional details are described in Table S1.† Additionally, the concentration of PMS in the solution was determined by the colorimetric method, and the details are stated in the ESI.[†] The initial pH of the solution was adjusted

by adding HCl and NaOH solution. The total organic carbon (TOC) of the solution in the reaction was used to evaluate the mineralization of the pollutants on a TOC-L_{CPH} (Shimadzu, Japan). In quenching experiments, methanol, TBA, CF, and FFA were used as scavengers to analyze ROS generated in the Fenton-like reaction. Measurement of the concentration of leached iron was carried out using inductively coupled plasma mass spectrometry (ICP-MS, ICAP PRO X, Thermo Fisher Scientific, USA). EPR (JES-FA200, JEOL Ltd, Japan) was used to further verify ROS generated in the reaction on a Bruker EMX 10/12 spectrometer with DMPO as the trapping agent for SO_4 . O_4 . and O_2 . and TEMP as the trapping agent for ¹O₂. The experiment was set as follows: center field of 3500 G, sweep width of 100 G, microwave frequency of 9.853 GHz, microwave power of 20 mW, modulation amplitude of 1G, and modulation frequency of 100 kHz.

DFT calculations

All calculations were performed within the framework of DFT as implemented in the Vienna ab initio software package (VASP). The exchange-correlation energy was treated by adopting the Perdew-Burke-Ernzerhof generalized gradient approximation (GGA-PBE) and the projected augmented wave (PAW) method. The DFT-D3 method of Grimme with a zerodamping function was used for dispersion correction. The calculations considered DFT+U, the magnetic moment of Fe was 2.5, and for the rest, it was 0. The cutoff energy for the plane-wave basis set was 400 eV. A vacuum layer of 15 Å was introduced to avoid interactions between periodic images. The Brillouin zone of the surface unit cell was sampled by Monkhorst-Pack (MP) grids for catalyst structure optimizations. The convergence criteria for the electronic self-consistent iteration and force for the atom were 1.0 \times 10^{-6} eV and 0.02 eV Å⁻¹, respectively. The catalyst surface was determined by a $1 \times 1 \times 1$ Monkhorst–Pack grid. The *k*-point used for self-consistent calculation was $3 \times 3 \times 2$. The climbing image nudged elastic band (CI-NEB) method was used to confirm the transition states along with the reaction coordinates.

Results and discussion

Synthesis and structural characterization of the Fe-N5 SAC

The synthesis procedure of the Fe– N_5 SAC is illustrated in Fig. 1a. Dicyandiamide, PEG, FeCl₂·4H₂O, and 1,10phenanthroline were well mixed to produce a homogeneous solution. The solution was dried, and then the resulting solid was pyrolyzed under a N_2 flow to obtain Fe single atoms anchored on a carbon support. HAADF-STEM analysis confirmed the uniform distribution of Fe atoms on the carbon substrate, where individual bright dots corresponded to isolated Fe atoms (Fig. 1b and c). Moreover, the elemental mapping of the Fe SAC showed a homogeneous distribution of Fe, N, and C on the surface of the catalyst (Fig. 1d and e). Consequently, the atomically dispersed Fe-based SAC was obtained. Furthermore, no characteristic signals for Fe

Paper



Fig. 1 (a) Illustration of the synthesis procedure of $Fe-N_5$, (b) HAADF-STEM image of $Fe-N_5$, (c) enlarged intensity of (b), and (d and e) EDS mapping images of $Fe-N_5$.

crystals were detected in the XRD patterns, in addition to the two diffraction peaks at 26.1 and 44° corresponding to the (002) and (101) planes of amorphous graphitic carbon in the Fe-based SACs, respectively (Fig. S1[†]), in consistence with the HAADF-STEM results.³² Additionally, ICP-MS measurements illustrated that the actual Fe content in Fe-N₄ and Fe-N₅ was 3.06 and 3.20 wt%, respectively. The XPS spectra revealed the chemical compositions of Fe, N, and C in Fe-N₄ and Fe-N₅ (Fig. S2a⁺). Five distinct nitrogen peaks at binding energies of 398.8, 399.2, 401.3, 406.2, and 400.0 eV were identified and corresponded to pyridinic N, pyrrolic N, graphitic-N, NO_x, and Fe-N, respectively.³⁰ Pyridine-N was chosen as the axial ligand in Fe-N5 due to its structural and electronic properties that favored metal-ligand interactions. The lone pair on the pyridine-N was more freely available for bonding, as it was less involved in the aromatic stability of the molecule compared to other nitrogen-containing heterocycles like pyrrole-N.33 The results revealed significantly higher Fe-N bonds in Fe-N5 compared to Fe-N₄, suggesting a more abundant or favorable coordination which likely contributed to its enhanced catalytic activity (Fig. S2b[†]). Meanwhile, the peaks located at 711.6/724.8 eV and 714.1/726.0 eV in the Fe 2p XPS

spectrum were assigned to Fe(11) and Fe(111) species in Fe–N $_4$ and Fe–N $_5$ (Fig. S2c†). 30,34

XAS analysis was used to further explore the chemical state and the coordination environment of the Fe atom in the Fe-N₅ SAC. The Fe absorption edge XAS spectra of Fe-N₅ and Fe₂O₃ nearly coincided, indicating a higher Fe valence of about +3 (Fig. 2a).^{35,36} The Fourier-transformed k³-weighted EXAFS spectra of Fe-N5 exhibited one prominent peak at ~1.53 Å (Fig. 2b), corresponding to the Fe-N first coordination shell. Only one intensity was observed at 4 $Å^{-1}$, which was assigned to the Fe-N bond, while no Fe-Fe signal was observed in the Fe-N5 wavelet transform (WT) contour plots (Fig. 2c).³⁶ The above results demonstrated that the Fe species in the Fe-based SAC existed as single atoms, in agreement with the XRD results. Moreover, EXAFS curvefitting parameters revealed that the average coordination number of Fe was 5.2, as shown in Fig. 2d and Table S2.† In order to determine the coordination structure of the Fe-based SAC, we compared our XAS results which included the coordination number and bond distance with the findings in the literature.^{31,37} The results revealed that the prepared Fe-N5 included four N coordinations in the horizontal plane and one N coordination in the axial direction. The coordination



Fig. 2 (a) Fe K-edge XANES spectra of Fe foil, Fe_2O_3 , and $Fe-N_5$, (b) the corresponding Fourier transform spectra of Fe foil, Fe_2O_3 , and $Fe-N_5$, (c) WT analysis of Fe K-edge EXAFS spectra of Fe foil, Fe_2O_3 , and $Fe-N_5$, and (d) EXAFS fitting of $Fe-N_5$.

number of more than 5 can be attributed to the occurrence of –OH on the Fe active site, and other oxygen species were present as hydroxyl (–OH) and carbonyl (C==O) functional groups in the Fe–N₅ substrate.^{30,31,37} The above results convincingly confirmed that the atomically dispersed catalyst with the Fe–N₅ coordination environment was successfully synthesized.

Evaluation of the catalytic performance of the Fe-N₅ SAC

The catalytic activity of various catalysts in the Fenton-like reaction for 4-CP degradation as a target pollutant was evaluated. In Fig. 3a, PMS alone could not degrade 4-CP directly. However, the N/C could not degrade 4-CP, suggesting that the metal-free N/C failed to activate PMS for 4-CP removal. Fe^{2+} , Fe^{3+} , and Co^{2+} are widely recognized homogeneous catalysts in the Fenton-like reaction. Fe^{2+} , Fe^{3+} , and Co^{2+} salts were substituted as comparison catalysts to further evaluate the catalytic activity, and 48%, 43%, and 51% 4-CP removal was obtained after 10 min, respectively. It was noticed that $Fe-N_4$ and $Fe-N_5$ yielded 56% and 100%

degradation efficiency after 10 min, respectively. Negligible adsorption (less than 10% 4-CP removal) was obtained for the Fe SACs (Fig. S3[†]). In addition, ca. 65.7% TOC removal was obtained in the Fe-N5/PMS system for 4-CP degradation (Fig. S4[†]), which indicated that some intermediates were accumulated in the reaction. The apparent pseudo-first-order kinetic rate constant (k) of Fe-N₅ was 10, 11, 7.3 and 6.36 times higher than that of Fe^{2+} , Fe^{3+} , Co^{2+} , and $Fe-N_4$ in the Fenton-like reaction for 4-CP degradation by PMS activation, respectively (Fig. 3b). Meanwhile, the PMS consumption rate over Fe-N5 was 65% after 10 min (Fig. 3c and S5⁺), which was obviously higher than those of other catalysts in the reaction. The above results proved that Fe-N5 showed good catalytic performance for 4-CP removal in the Fenton-like reaction by activating PMS. Notably, the k of Fe-N₅ was ca. 1.76-78 times higher than those of the reported SACs and nanocatalysts (Fig. S6 and Table S3[†]). The turnover frequency (TOF) has emerged as a critical parameter in assessing the degradation efficiency of different catalysts in the Fenton-like process. Fe-N5 outperformed state-of-the-art SACs and nanocatalysts, and the TOF of Fe-N5 was ca. 4-149 times

higher than those reported in the literature (Fig. S6 and Table S3†). The above findings further confirmed that Fe–N₅ exhibited exceptional catalytic performance in the Fenton-like reaction for the degradation of 4-CP by PMS activation.

The stability of Fe–N5 was assessed through recycling experiments. The degradation efficiency of 4-CP decreased to 63% after the 3rd recycling experiment (Fig. S7†), likely due to intermediate adsorption on the catalyst surface and

the leaching of active metals causing Fe–N5 deactivation. Remarkably, minimal Fe leaching (*ca.* 0.098 mg L^{-1}) was observed in the reaction. After calcination of the used Fe–N5, the 4-CP degradation efficiency recovered to 91%, indicating that intermediate adsorption primarily resulted in the lower 4-CP removal efficiency in the recycling reaction. Hence, Fe–N5 demonstrated good stability in PMS activation for the 4-CP degradation. To gain insight into the



Fig. 3 Catalytic evaluation of the Fe-N₅/PMS system. (a) 4-CP degradation with various catalysts, (b) initial reaction rates of various catalysts, (c) PMS consumption with various catalysts after 10 min, (d) effect of pH on 4-CP degradation in the Fe-N₅/PMS system, (e) effect of temperature on 4-CP degradation in the Fe-N₅/PMS system, (f) effect of coexisting substances on 4-CP degradation in the Fe-N₅/PMS system, (g) 4-CP degradation in different water matrices, and (h) degradation of various CPs in the Fe-N₅/PMS system. Reaction conditions: $[4-CP]_0 = [2,4-DCP]_0 = [2,4,6-TCP]_0 = 20 \text{ mg } \text{L}^{-1}$, $[\text{Catalyst}]_0 = 0.05 \text{ g } \text{L}^{-1}$, $[\text{PMS}] = 0.2 \text{ g } \text{L}^{-1}$, pH = 7.0, T = 25 °C, coexisting substance = 7.8 mM, if not otherwise specified.

Paper

catalytic behavior of Fe–N₅ for PMS activation, the effect of initial solution pH on the 4-CP degradation efficiency was investigated in a wide pH range (Fig. 3d). The catalyst exhibited a high 4-CP removal, and *k* was *ca.* 2–3 min⁻¹ in a wide pH range. The 4-CP removal in acidic solution was slightly higher than that in basic solution in the reaction, (in the likely due to the catalyst's enhanced adsorption at a lower expH level (Fig. S8†), making the pollutant more accessible for subsequent oxidation, in agreement with the literature.^{38–40} The result proved that Fe–N₅ is an effective material for 4-CP degradation *via* PMS activation across a

wide pH range in the Fenton-like reaction. The effect of reaction temperature (5, 15, and 25 °C) on the 4-CP degradation efficiency was evaluated in the heterogeneous Fenton-like reaction over Fe-N₅ (Fig. 3e). With increasing reaction temperature, 4-CP removal was significantly improved, and k increased from 1.73 to 2.99 min⁻¹ in the Fe-N₅/PMS system. At high reaction temperatures, the kinetic energy of the molecules increases, leading to more frequent and energetic collisions between the reactants and metal active sites on the catalyst, thereby improving the generation of reactive species in the reaction.⁴¹ The activation energy (Ea) for 4-CP degradation, calculated *via* the Arrhenius equation, was *ca.* 18.78 kJ mol⁻¹ over Fe–N₅ at neutral pH. The activation energy was nearly identical to the result reported previously in the literature (17.83 kJ mol⁻¹) for activating PMS to degrade 4-CP.⁴² The results proved that the prepared Fe-N5 is promising for 4-CP degradation in a broad-temperature range.

To explore the potential application of the Fe-N₅/PMS system in actual wastewater treatment, the influence of coexisting substances (HA, HCO₃⁻, SO₄²⁻, H₂PO₄⁻, NO₃⁻, and Cl⁻) on the performance of Fe-N₅ for degrading 4-CP was investigated. Commonly, these coexisting substances in the water matrix compete with the target pollutants for the reaction with ROS.⁴³ It was found that the coexisting substances exhibited negligible suppression in the 4-CP removal (Fig. 3f), suggesting that the Fe-N₅/PMS system exhibited excellent resistance to the interference of both organic substances and inorganic anions. The results validated that Fe-N₅ is a potential material for practical application in actual water and wastewater treatment.

4-CP degradation experiments in actual water matrices, including reclaimed water, river water, and tap water, were also conducted in the Fe–N₅/PMS system (Fig. 3g and Table S4†), and *k* was 2.43, 2.60, and 2.91 min⁻¹, respectively. 4-CP removal was slightly inhibited during the initial stage, and the pollutant was completely removed after 10 min in real water, proving that Fe–N₅ showed potential applicability in actual water matrices. Various CPs as the target pollutants, including 2-CP, 2,4-DCP, and 2,4,6-TCP, were utilized to further evaluate the performance of Fe–N₅ in our study. Fe–N₅ exhibited a robust catalytic capability for degrading CPs by PMS activation (Fig. 3h), and *k* was 2.12, 2.04, and 1.83 min⁻¹ for degrading 2-CP, 2,4-DCP, and 2,4,6-TCP, respectively. Moreover, *k* was significantly higher in the

Fenton-like reaction over Fe–N₅ than that over different catalysts (Table S5†). In addition, Fe–N₅ was applied in the degradation of refractory pollutants, including BPA, phenol, SDZ, SMT, 2-NP, and 4-NP. It was found that Fe–N₅ still maintained higher degradation efficiency for the pollutants (Fig. S9†). The above results further demonstrated that Fe–N₅ exhibited excellent performance in degrading the pollutants by PMS activation.

Identification of the main reactive species

To investigate the main reactive species generated in the Fenton-like reaction over Fe-N5, various quenching and probe agents, i.e., MeOH, TBA, CF, FFA, and PMSO, were used to determine ·OH/SO4⁻⁻, ·OH, O2⁻⁻, ¹O2, and Fe^{IV}=O, respectively (Fig. 4a). MeOH presented significant influence on the 4-CP removal, and 30% inhibition was obtained after 10 min, while only slight inhibition was observed with the addition of TBA. The results suggested that SO₄⁻⁻ contributed more towards 4-CP degradation than ·OH. Notably, considerable 4-CP inhibition was observed using CF and FFA as scavengers, suggesting that both O2- and 1O2 had an essential role in the 4-CP removal in the Fenton-like reaction. Fe^{IV}=O is considered as a potential reactive species especially over the Fe-based catalysts.²⁹ PMSO was used as a probe to determine Fe^{IV}=O, which resulted in slight inhibition indicating a minimal role of Fe^{IV}=O in 4-CP degradation. Thus, the results demonstrated that O_2 and ¹O₂ played a critical role in the Fe-N₅/PMS system for 4-CP removal.

EPR with TEMP and DMPO as the spin trapping agents was introduced to further identify the ROS generated in the Fe-N₅/PMS system. There were no recognizable peaks in the addition of TEMP and DMPO in the PMS alone, which validated the weak self-decomposition of PMS in the absence of the catalyst (Fig. S10[†]). A distinctive triplet signal can be observed in Fig. 4b, revealing the appearance of ${}^{1}O_{2}$ in the PMS activation process over Fe-N5. In addition, tetraplet DMPO/H2O-OH and triplet DMPO/H2O-SO4 signals were detected in the reaction. It is reported that DMPO/H₂O-·OH signals were stronger than DMPO/H₂O-SO₄⁻⁻ signals which can be ascribed to the formation of .OH via the reaction between SO4⁻ and water molecules, in agreement with reported results.³⁹ Moreover, the weak tetraplet signals of DMPO/methanol-O2 - also demonstrated the emergence of O_2 in the reaction. The results indicated that 1O_2 was the dominant ROS generated in the Fe-N5/PMS system for 4-CP degradation, and O_2 acted as a precursor for facilitating the formation of ¹O₂.^{36,42,44,45}

The steady state concentration of ROS generation (·OH, SO₄⁻, O₂⁻⁻, and ¹O₂) was quantified by introducing BA, NB, *p*-CBA, and FFA as probe compounds in the Fe–N₅/PMS system (Fig. S11 and S12†). The second-order reaction rate constants of the probe compounds were referred from the literature.^{46,47} The steady-state concentrations of ·OH, SO₄⁻⁻, O₂⁻⁻, and ¹O₂ were 2.467 × 10⁻¹³, 1.099 × 10⁻¹³, 1.22 × 10⁻¹⁴,

Paper



Fig. 4 (a) 4-CP degradation in the presence of various quenching agents and probe agents in the Fe-N₅/PMS system. Reaction conditions: $[4-CP]_0 = 20 \text{ mg L}^{-1}$, $[catalyst]_0 = 0.05 \text{ g L}^{-1}$, $[PMS] = 0.2 \text{ g L}^{-1}$, pH = 7.0, T = 25 °C, [MeOH] = [TBA] = 500 mM, [FFA] = 20 mM, [CF] = 50 mM, $[PMSO] = 50 \mu$ M. (b) EPR spectra in the Fe-N₅/PMS system, (c) EIS results of NC, Fe-N₄, and Fe-N₅, and (d) *I*-T graphs of NC, Fe-N₄, and Fe-N₅.

and 1.74×10^{-12} M, respectively (Table S6†). The quantitative results indicated that a much higher $[^{1}O_{2}]_{ss}$ concentration *ca.* 82.50% was obtained in the Fe–N₅/PMS system, suggesting that $^{1}O_{2}$ was the main ROS in the Fe–N₅/PMS system for 4-CP removal.

Furthermore, KSCN was utilized to capture iron atoms in Fe–N₅ due to its strong binding capacity to iron atoms.⁴⁸ 4-CP removal was dramatically decreased in the presence of KSCN (Fig. S13†), revealing that single iron atoms in Fe–N₅ were the active sites for PMS activation. Meanwhile, KI was used as a quencher for the surface-bound reactive species generated in the Fe–N₅/PMS system (Fig. S14†). The presence of KI almost terminated the 4-CP removal, suggesting that 4-CP degradation happened on the surface of Fe–N₅.^{29,49}

To get insight into the electron transfer properties of Fe-N₅, electrochemical tests, including electrochemical impedance spectroscopy (EIS), linear sweep voltammetry (LSV) plots, and *i*-*t* tests, were conducted. Fe-N₅ displayed a smaller semicircle than NC and Fe-N₄ (Fig. 4c), while Fe-N₅ exhibited a lower charge-transfer resistance (R_{CT}), indicating a faster electron transfer process of Fe-N₅. A marginal increase in current was noticed upon addition of 4-CP or PMS individually to the electrolyte. However, a significant current jump was observed when 4-CP and PMS were simultaneously introduced, indicating that Fe-N5 exhibited excellent electron transfer performance in the presence of 4-CP and PMS (Fig. S15[†]). Moreover, chronoamperometry measurements were performed to verify PMS activation with NC, Fe-N₄, and Fe-N₅ (Fig. 4d). A slight current jump was observed with NC, while both Fe-N4 and Fe-N5 exhibited strong current jumps with PMS and 4-CP injection. The result indicated that NC could not activate PMS, in agreement with its low 4-CP removal. The current jump in Fe-N₅ was more significant than that in Fe-N4, suggesting that Fe-N5 effectively activated PMS, matching well with its high 4-CP removal. The injection of PMS resulted in a distinct current jump, indicating that the electron transfer happened from Fe-N₅ to PMS. Furthermore, a similar trend was noticed with the injection of 4-CP, indicating that the electron transfer occurred from PMS to 4-CP, which led to 4-CP degradation. The injection of 4-CP initiated a low current jump compared to the injection of PMS, suggesting a role of the radical pathway in the Fe-N₅/PMS system, in consistence with the literature.⁵⁰ The results in the electrochemical measurements demonstrated that Fe-N5 possessed enhanced electron transfer capability to facilitate PMS activation, leading to

excellent catalytic activity in the Fenton-like reaction for 4-CP removal.

Theoretical verification concerning PMS activation

DFT calculations were performed to explore the in-depth mechanism of PMS activation over Fe-N5. The electron density distribution around the metal active sites can influence the overall catalytic mechanism.51 The electron density around Fe atoms in Fe-N₄ and Fe-N₅ was higher than that around N atoms, suggesting that electrons around Fe atoms exhibited a higher degree of electron delocalization (Fig. S16[†]). PMS was bound to Fe atoms on the surface of the catalysts through one peroxyl oxygen in a terminal end-on mode (Fig. 5a and b). The PMS adsorption energies (E_{ads}) were calculated to be -2.99 and -2.78 eV for Fe-N4 and Fe-N₅, respectively (Fig. 5c and d), indicating that Fe-N₄ and Fe-N5 had a robust binding affinity with PMS. According to the Bader charge analysis, the electron transfer number from Fe active sites to PMS in Fe-N₅ (0.930 e⁻) was higher than that in Fe–N₄ (0.809 e^{-}), in consistence with the result of electron properties. After adsorption, Fe-O(H)OSO3⁻ was activated with a widespread stretched O-O bond, extending from 1.34 to 1.474 Å in Fe-N₄ and to 1.514 Å in Fe-N₅, respectively. The longer O-O bond was more easily broken to generate ROS. The results indicate that Fe-N₅ was more prone to activating PMS due to axial N coordination modulating the electron density distribution around Fe metal centers, in agreement with the 4-CP degradation efficiency of Fe-N₅.

The projected density of states (PDOS) of the Fe 3d band center was located at -1.50 and -0.35 eV in Fe-N₄ and Fe-N₅, respectively. Fe-N₅ was well below the Fermi level in the Fe 3d orbital electrons of the Fe atom (Fig. S17†). A narrower

gap between the Fe-3d band center and Fermi level indicates an enhanced charge transfer rate at the catalyst interface, thus leading to a lower E_a and free energy barrier (ΔG).⁵¹ Therefore, Fe-N5 with PDOS located at a narrower gap was more efficient in promoting PMS activation and generating ROS for degrading pollutants in the Fenton-like reaction. The charge density distribution of PMS adsorbed on Fe-N4 and Fe-N₅ is shown in Fig. 5e and f. There was a noticeable difference in charge density around Fe atoms and PMS. An electron transfer between PMS and Fe atoms, as seen by yellow and cyan color electron clouds, represented electron accumulation and electron depletion, respectively. The electron accumulation was observed around PMS, demonstrating the electron transfer pathway from Fe atoms to PMS, in consistence with the electrochemical results of the Fe-based SACs. Additionally, the electron density surrounding PMS adsorbed on Fe-N5 was richer compared to that on Fe-N₄. In the oxidation of 4-CP catalyzed by Fe-N₄ and Fe-N₅ (Fig. S18[†]), 4-CP was spontaneously adsorbed onto the catalyst surfaces from the surface stage (I) to the adsorption stage (II). This adsorption led to a decrease in the free energies of both systems. Specifically, the adsorption energy of Fe-N₅ was -2.27 eV, compared to -1.34 eV for Fe-N₄, indicating a stronger affinity of 4-CP on Fe-N5 compared to Fe–N₄, in agreement with the 4-CP adsorption results (Fig. $S3^{\dagger}$). Furthermore, the step from the adsorption stage (II) to the transition state (III) was identified as the rate-determining step, with energy barriers of 0.72 eV for Fe-N₄ and 0.55 eV for Fe-N₅. The lower energy barrier suggested that the catalytic reaction occurred more easily and quickly on Fe-N₅, thereby demonstrating that Fe-N5 was efficient in promoting PMS activation and generating ROS for 4-CP degradation in the Fenton-like reaction. Thus, the DFT calculations confirmed that



Fig. 5 DFT calculation of PMS adsorption and activation on $Fe-N_4$ and $Fe-N_5$. Representation of the PMS molecule on (a) $Fe-N_4$ and (b) $Fe-N_5$, adsorption energy and Bader charges (side view) in a PMS molecule adsorbed on (c) $Fe-N_4$ and (d) $Fe-N_5$, and charge density difference (top view) in a PMS molecule adsorbed on (e) $Fe-N_4$ and (f) $Fe-N_5$.

Fe– N_5 exhibited excellent PMS activation capability, which was attributed to the axial N coordination modulating the electron distribution density around Fe atom active centers, resulting in improved catalytic performance.

Conclusions

Herein, an Fe-N5 SAC with axial N coordination was successfully synthesized and exhibited exceptional performance in degrading various CPs, including 4-CP, 2-CP, 2,4-DCP, and 2,4,6-TCP, as well as pollutants such as BPA, phenol, SDZ, SMT, 2-NP and 4-NP. Moreover, Fe-N₅ demonstrated remarkable degradation efficiency across a broad pH range (4.0-10.0) and significant resistance to coexisting substances (HA, HCO_3^- , SO_4^{-2-} , $H_2PO_4^-$, NO_3^- , and Cl⁻), making it a potential candidate for actual wastewater treatment. EPR, quenching experiments, and radical probe experiments revealed that ¹O₂ as the main ROS dominated the pollutant removal in the PMS-based Fenton-like reaction over Fe-N₅. Furthermore, the DFT calculations demonstrated that Fe-N5 sites with axial N coordination modulated the electronic density around single iron atoms and promoted the electron transfer for PMS activation to generate ROS. Overall, developing M-N5 SACs with axial N coordination would be a promising and profound strategy for effective PMS activation to improve the degradation of refractory pollutants. This work has explored the potential of coordination chemistry in M-N_x SACs (x > 4), which modulated the electron density around metal atom centers, thereby improving PMS activation.

Data availability

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

Author contributions

Manoj Kumar Panjwani: conceptualization, methodology, validation, investigation, writing – original draft. Feiyu Gao: investigation. Ting He: investigation. Pan Gao: supervision. Feng Xiao: supervision. Shaoxia Yang: conceptualization, methodology, resources, funding acquisition, writing – review & editing, supervision.

Conflicts of interest

There are no conflicts of interest to declare.

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