



Lewis acid-assisted near-neutral hydrolysis of organophosphorus pesticides via a CuMn coordination polymer: Kinetics and mechanism

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ABSTRACT

Organophosphorus pesticides (OPPs) pose severe environmental and human health risks owing to their inherent persistence, slow spontaneous hydrolysis, and strong inhibitory activity against acetylcholinesterase. However, conventional remediation approaches for OPPs suffer from low neutral-condition efficiency, poor reaction selectivity, and limited practical environmental applicability. Herein, a self-supported Mn-doped Cu-C-N-based coordination polymer (CuMn@CN) with tailored Cu⁺ active sites using ligand anchoring was fabricated for the efficient hydrolysis of representative OPPs and colorimetric detection of methyl parathion (MP) under environmentally relevant neutral conditions. Structural characterization confirms the uniform dispersion of Cu and Mn sites within the C-N framework, which constructs stable metal-N and metal-O coordination configurations and mixed-valence active centers. Under neutral conditions, CuMn@CN exhibits prominent hydrolytic performance toward typical OPPs (e.g., methyl parathion and chlorpyrifos) and complies with typical Michaelis-Menten kinetics with a low K_M value of 0.04675 - 0.6313 mM, indicative of excellent substrate affinity. Meanwhile, the catalyst exhibits robust durability and environmental adaptability in complex systems containing coexisting inorganic anions and real water matrices, as well as during cyclic catalytic operations. With the in-situ generation of 4-nitrophenol, a sensitive colorimetric sensing platform was established, achieving quantitative MP detection over a wide linear range of 0.1 - 200.0 $\mu\text{mol L}^{-1}$ and facilitating rapid visual screening of MP in water samples without reliance on sophisticated instrumentation. Integrated experimental results and DFT/Fukui function analyses reveal a unique Lewis acid-assisted hydrolysis mechanism, where the synergistic effects of bimetallic sites enable substrate adsorption, P-O bond polarization, and nucleophilic attack by surface-activated H₂O/metal-OH species.

1. Introduction

Organophosphorus pesticides (OPPs) have been widely used in agricultural fields due to their broad-spectrum and highly efficient insecticidal activity, contributing substantially to global food security. However, the long-term and improper application of OPPs has led to the continuous accumulation of pesticides in soil, surface water, and groundwater, posing persistent threats to ecosystems and human health through agricultural runoff, sediment transport, and food chain accumulation (Bu et al., 2026; Pathak et al., 2022; Wang et al., 2026). The toxicity of OPPs primarily stems from their irreversible inhibition of acetylcholinesterase (AChE), resulting in the excessive accumulation of

acetylcholine at neuronal synapses and neuromuscular junctions, which may subsequently induce severe adverse effects, including neurotoxicity, genotoxicity, and cardiovascular dysfunction (Edwards and Tchounwou, 2005; Fu et al., 2022).

Currently, remediation strategies for the removal and detoxification of OPPs mainly include advanced oxidation processes (AOPs) (Karimi et al., 2023; Saini et al., 2017; Zhang et al., 2019), biological/enzymatic catalysis (Taxeidis et al., 2024; Tiwari et al., 2017), and chemical hydrolysis (Chen et al., 2021). AOPs generally rely on highly reactive oxygen species, including hydroxyl radicals ($\cdot\text{OH}$), singlet oxygen ($^1\text{O}_2$), and sulfate radicals ($\text{SO}_4\cdot^-$), to rapidly degrade contaminants. Nevertheless, AOPs often suffer from poor selectivity,

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complex byproduct formation, and uncontrollable mineralization pathways. Furthermore, natural organic matter and coexisting anions in complex aqueous matrices may competitively scavenge reactive oxygen species, thereby substantially reducing treatment efficiency (Lee et al., 2020; Wang and Wang, 2020). Alternatively, catalytic detoxification systems based on organophosphorus hydrolase (OPH) or artificial enzyme mimics exhibit high selectivity. However, their practical application remains hindered by limited stability, high preparation costs, inadequate environmental tolerance, and poor reusability (Li et al., 2022; Wang et al., 2024a). Therefore, developing an efficient catalytic system capable of achieving the rapid detoxification and safe removal of OPPs under environmentally benign conditions remains a critical challenge in environmental remediation.

Nanozymes have attracted increasing attention in pollutant remediation, biocatalysis, and environmental monitoring owing to their enzyme-mimicking catalytic functions, as well as the superior stability, tunability, and cost-effectiveness of nanomaterials (Chen et al., 2024; Li et al., 2022). Driven by the increasing demand for environmental remediation, nanozyme research has gradually expanded from conventional redox catalysis to hydrolytic catalysis associated with phosphoester bond cleavage and organophosphorus pollutant detoxification. In particular, the construction of artificial Lewis acid catalytic sites to mimic the catalytic behavior of natural OPH has emerged as a promising strategy for organophosphorus detoxification (Hou et al., 2023; Tan et al., 2020). Meanwhile, with the rapid development of single-atom catalysis and coordination engineering, metal-N-C coordinated nanozyme systems, including single-atom nanozymes and bimetallic atomic site catalysts, have gained increasing attention because of their highly dispersed metal centers, tunable local electronic structures, and coordination microenvironments resembling those of natural metalloenzymes (Guo et al., 2024; Huang et al., 2023; Wang et al., 2025; Ye et al., 2026). Previous studies have shown that atomically dispersed metal sites not only maximize atomic utilization efficiency but also enhance substrate adsorption and catalytic activity through modulation of the electronic states and coordination environments of metal centers (Huang et al., 2023; Ma et al., 2019).

Most reported nanozyme systems remain focused on oxidative catalysis, biosensing, and peroxidase-like reactions, whereas studies on the selective hydrolysis and efficient detoxification of OPPs under near-neutral conditions remain limited. Bimetallic coordination polymer-based nano-hydrolase systems capable of integrating efficient detoxification with auxiliary process monitoring have rarely been reported. Furthermore, considering the structural diversity of OPPs, evaluating the substrate applicability of nano-hydrolase systems toward representative pesticides is essential for assessing their broader environmental remediation potential. The non-enzymatic hydrolysis of OPPs generally proceeds more readily under alkaline conditions, whereas hydrolysis under near-neutral conditions is kinetically hindered by the limited nucleophilicity of water molecules. Consequently, strategies relying on strongly alkaline environments often exhibit limited applicability in realistic environmental systems (Li et al., 2022; Zhang et al., 2025a). In recent years, Coordination polymers have emerged as versatile platforms for constructing functional catalytic materials because their metal compositions, coordination environments, and ligand configurations can be flexibly regulated (Liu et al., 2024; Maeda et al., 2022; Wang et al., 2024b; Zhou et al., 2024). Such structural tunability enables modulation of the electronic properties and catalytic behaviors of metal centers, providing opportunities for designing hydrolytic catalysts under mild aqueous conditions.

Herein, a self-supported Cu-Mn bimetallic coordination polymer (CuMn@CN) was prepared via a mild solvothermal method. Cu serves as the primary metal, as Cu-based materials facilitate organophosphate hydrolysis via Lewis acid-driven substrate activation and surface hydroxyl/water-assisted nucleophilic processes (Rizo et al., 2020b; Zheng et al., 2019), while Mn was incorporated as the secondary metal, whose multivalent nature and heterometallic coupling with Cu enable

modulation of Cu oxidation-state distribution as well as its local coordination and electronic environment (Wang et al., 2023). XPS and Cu K-edge XAS confirm that Mn doping increases the Cu⁺ fraction and reconstructs the local Cu-N/O coordination environment, thereby modulating the Cu-centered Lewis-acidic catalytic site and the catalytic hydrolysis of representative OPPs, together with product-based mechanistic understanding and auxiliary colorimetric monitoring of MP. Collectively, this work presents a Cu/Mn bimetallic coordination catalytic strategy for near-neutral OPPs hydrolysis, offering mechanistic insights and auxiliary colorimetric monitoring for MP, and delivers new perspectives for designing sustainable catalysts toward OPPs hydrolysis and toxicity reduction.

2. Materials and methods

2.1. Chemicals and reagents

The chemicals and reagents used in this study are listed in Text S1.

2.2. Preparation of CuMn@CN nanozyme

CuMn@CN was synthesized via a facile one-step hydrothermal method. Typically, 0.1 g of SDS and 0.3 g of P-123 were dissolved in 20 mL of DI water under continuous magnetic stirring to form a transparent and homogeneous aqueous solution. Afterwards, 1 g of dicyandiamide and 2 g of cyanuric acid were introduced into the above solution, and the mixture was stirred vigorously to achieve uniform dispersion. The resulting mixture was then transferred to a Teflon-lined autoclave to form the CN precursor. In parallel, a mixture of CuSO₄·5H₂O and (CH₃COO)₂Mn·4H₂O with a series of Cu/Mn ion mass ratios (1:1, 1.5:1, 2:1, 2.5:1, 3:1, 1:2, 1:0, and 0:1) was fully dissolved in 20 mL of DI water in a conical flask via ultrasonic treatment. The total Cu and Mn input was fixed at 0.75 g. The amounts of CuSO₄·5H₂O and (CH₃COO)₂Mn·4H₂O were calculated according to their corresponding elemental metal contents. After digestion using HNO₃/H₂O₂ in a microwave digestion system, the actual Cu/Mn compositions of the resulting materials were then determined by using inductively coupled plasma optical emission spectrometry (ICP-OES, PerkinElmer Optima 8300). The obtained metal precursor solution was dropwise added into the pre-prepared CN precursor system under sustained magnetic stirring, and the mixed solution was further stirred for 30 min to guarantee thorough and homogeneous mixing. The sealed Teflon-lined reactor was heated at 150 °C for 12 h. After naturally cooling down to room temperature (approximately 30 °C), the solid product was collected by centrifugation. The precipitate was repeatedly rinsed with deionized water and absolute ethanol to eliminate residual inorganic ions and organic impurities. Finally, the purified sample was dried in a vacuum oven at 60 °C for 12 h, and the purple CuMn@CN composite material was successfully obtained.

2.3. Material characterization

The morphological and microstructural features of the as-prepared CuMn@CN were characterized via a Hitachi SU8000 field emission scanning electron microscope (SEM). Energy-dispersive X-ray spectroscopy (EDS) equipped with an Octane Super Det detector integrated within the SEM system was applied to analyze the elemental composition and spatial distribution of the samples. The crystal structure and phase composition of the samples were examined by X-ray diffraction (XRD) on a Bruker D8 ADVANCE diffractometer with Cu K α radiation. The scanning range was set from 5° to 90° at a scanning rate of 2°/min, and the structural configuration and phase information were identified by analyzing the characteristic peak positions, intensities, and full width at half maximum (FWHM).

Fourier transform infrared spectroscopy (FTIR, Nicolet iS 10) was performed to detect the surface functional groups of the materials. X-ray

photoelectron spectroscopy (XPS, Thermo VG ESCALAB 250) with non-monochromatic Al K α radiation was used to investigate the surface elemental composition and chemical states. The C 1s peak at 284.8 eV was adopted for spectral calibration. Both survey spectra and high-resolution spectra were recorded to clarify the elemental composition, oxidation states of Cu, Mn, C, N, and O species, and surface chemical environments of the composites. The specific surface area and pore structure parameters of the materials were measured using an ASAP 2460 automatic surface area and porosity analyzer (Micromeritics, USA). Cu K-edge X-ray absorption fine structure (XAFS) spectra were collected at room temperature using a laboratory-based XAFS/XES spectrometer (easyXAFS300+, easyXAFS, LLC, USA) equipped with a Mo-anode X-ray source and a Si(553) crystal analyzer. The operation details are provided in **Text S2**.

2.4. Phosphatase-like property evaluation of CuMn@CN nanozyme

The phosphatase-like catalytic activity of CuMn@CN nanozyme was evaluated by using MP as a chromogenic substrate. A standard reaction mixture was prepared by adding 50 μ M of MP solution and 100 μ L of CuMn@CN suspension (0.2 mg/mL) to 800 μ L of Tris-HCl buffer (50 mM, pH = 8.0). Following incubation, the colorimetric change of the solution was monitored over time using UV-vis spectroscopy. The effects of buffer pH, reaction temperature, nanozyme dosage, coexisting anions, and water matrices on catalytic performance were systematically investigated, as detailed in **Text S3** and **Text S4**.

Additionally, the batch-to-batch reproducibility and storage stability of the CuMn@CN material were assessed under similar conditions. After each recycling cycle, the reaction supernatant was collected and analyzed by ICP-OES to quantify Cu and Mn leaching. Through enzymatic reaction kinetics analysis, the Michaelis-Menten constant (K_M) and the maximum reaction rate (V_{max}) of the CuMn@CN toward MP were determined, as detailed in **Text S5**.

The residual MP and generated 4-NP were simultaneously quantified using a high-performance liquid chromatography system (HPLC, Shimadzu, Japan) equipped with an Agilent C18 column (4.6 mm $\times$ 250 mm, 5 μ m). To further identify the hydrolysis products of MP, LC-HRMS/MS analysis was performed using a Q Exactive Orbitrap mass spectrometer, with the detailed analytical conditions provided in the **Supporting Information Text S6**. The potential aquatic toxicity of MP and its identified hydrolysis products was further predicted using the U. S. EPA Ecological Structure-Activity Relationships (ECOSAR) model. Detailed information on the evaluated toxicity endpoints and toxicity-index calculations is provided in the **Supporting Information Text S7**.

The pH, total organic carbon (TOC), and major inorganic ion composition of the detailed analytical procedures and water-quality parameters are provided in **Text S8**. To evaluate the analytical reliability of the colorimetric method in real water matrices, MP spike-recovery experiments were conducted in river water, tap water, lake water, and seawater at spiking levels of 5, 20, and 50 μ M. Detailed procedures for the matrix-matched calibration and spike-recovery experiments are provided in **Text S9**.

2.5. Catalytic hydrolysis of chlorpyrifos by CuMn@CN nanozyme

To evaluate the substrate applicability of the CuMn@CN nanozyme toward structurally distinct organophosphorus pesticides, chlorpyrifos (CPF) was selected as a representative substrate. The CPF hydrolysis experiments were conducted under experimental conditions identical to those established for MP, unless otherwise specified. The residual concentration of CPF was quantified using high-performance liquid chromatography (HPLC, Shimadzu) equipped with an Agilent C18 column (4.6 mm $\times$ 250 mm, 5 μ m) to determine the overall degradation efficiency. Because CPF hydrolysis does not generate 4-nitrophenol and is therefore not suitable for the 4-NP-based colorimetric readout.

3. Results and discussion

3.1. Synthesis and characterization of CuMn@CN nanozyme

To elucidate the morphology, elemental composition, and surface chemical states of CuMn@CN, a comprehensive characterization was conducted. Low-magnification SEM images (**Fig. S1**) reveal an interconnected network composed of abundant elongated nanobelts. High-magnification SEM images (**Fig. 1a**) further demonstrate this distinct interwoven nanobelt architecture. TEM observation (**Fig. 1b**) further reveals thin and partially transparent ribbon-like structures that interconnect with each other, confirming the cross-linked nanobelt network observed in SEM, which likely facilitates the exposure of accessible active sites and enhances mass transfer during catalytic reactions. Furthermore, EDS elemental mapping (**Fig. 1c**) confirms the uniform distribution of Cu, Mn, C, N, and O throughout the material without apparent metal-rich domains, indicating the successful incorporation and homogeneous dispersion of bimetallic species within the CN framework.

The XRD patterns (**Fig. 1d**) display characteristic diffraction peaks at approximately 13.78° and 28.08°, these broad reflections indicate the formation of a low-crystallinity ordered polymeric framework rather than a highly crystalline inorganic phase. Considering the use of cyanuric acid and dicyandiamide as the organic building units, the reflections at 13.78° and 28.08° can be reasonably assigned to the periodic packing of cyanurate/dicyandiamide-derived C-N/O heterocyclic units and the interlayer stacking of coordination-polymeric domains (CP-I and CP-II). Cyanurate ligands are known to form robust hydrogen-bonded ribbons and metal-coordinated network structures through N/O donor sites, providing a structural basis for the ordered domains observed in this system (Ghorbani-Choghamarani et al., 2023; Meng et al., 2020). In addition, a weak diffraction feature observed at 16–18° may be associated with local structural modulation induced by Cu/Mn incorporation and metal-support interfacial interactions (Choi et al., 2018). Notably, no discernible diffraction peaks attributable to crystalline CuO or MnO_x phases were observed. This suggests that no detectable large-sized crystalline metal/oxide aggregates are formed (Ma et al., 2019; Zhang et al., 2021).

The FTIR spectra (**Fig. 1h**) further confirm the CN framework structure and the interaction between metal species and the support. The broad absorption band at 3000–3500 cm⁻¹ is assigned to the stretching vibrations of -NH/-OH groups, indicating the presence of residual amino/hydroxyl groups, adsorbed water, or surface hydrophilic functionalities (Niu et al., 2023; She et al., 2016). A weak band near 2850 cm⁻¹ is attributed to aliphatic C-H stretching vibrations, possibly arising from residual soft-template species or edge organic groups formed during hydrothermal condensation (Basak et al., 2023). The absorption bands within the 900–1800 cm⁻¹ region are assigned to the C=N and C-N stretching vibrations of triazine/heptazine units, while the characteristic peak at 810 cm⁻¹ can be attributed to the ring-breathing vibration of triazine/cyanurate-like heterocyclic structures (Sangeetha et al., 2013). Moreover, the low-wavenumber bands at 602 and 530 cm⁻¹ are attributed to metal-oxygen-related vibrations, suggesting strong interactions between the bimetallic species and the CN matrix (Basak et al., 2023; Shahsavani et al., 2016).

XPS analysis further elucidated the elemental composition and surface chemical states of the material. As shown in **Fig. 1e**, the survey spectrum confirms the presence of C, N, O, Cu, and Mn elements. In the high-resolution Cu 2p spectrum (**Fig. 1f**), peaks at 932.7 and 952.5 eV are assigned to Cu⁺ species, whereas peaks centered at 934.6 and 954.4 eV, accompanied by satellite peaks, indicate the coexistence of Cu²⁺ species (Tai et al., 2025). In the Mn 2p spectrum (**Fig. 1g**), characteristic peaks at 642.3 and 644.3 eV correspond to Mn²⁺ and Mn³⁺ species, respectively. The coexistence of mixed-valence Mn centers may contribute to the formation of surface Lewis acid sites and metal-bound hydroxyl/water coordinations, thereby facilitating water activation and

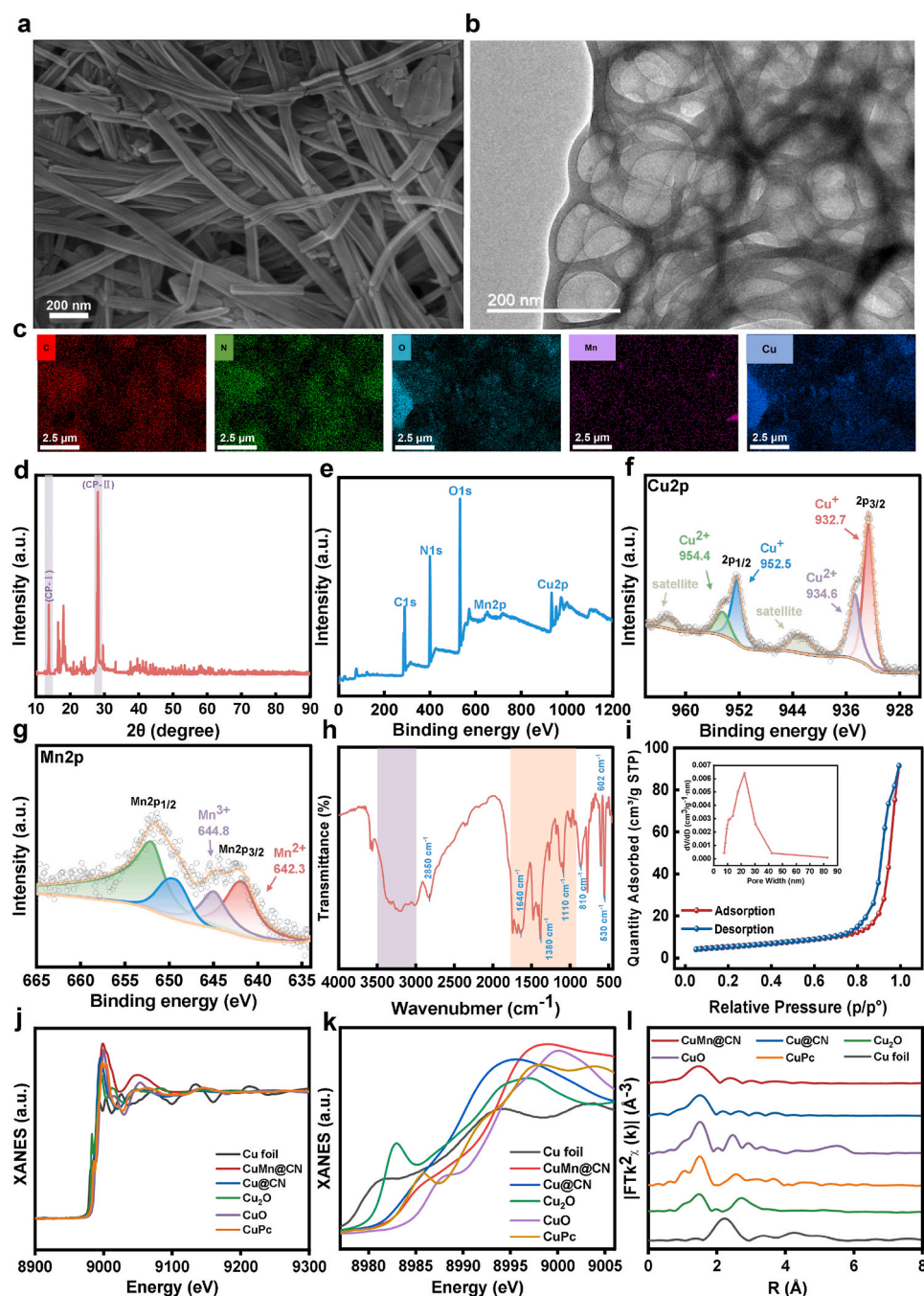


Fig. 1. Characterization of CuMn@CN nanozyme. (a) SEM image, (b) TEM image, (c) EDS mapping, (d) XRD pattern, (e) XPS full spectrum, (f) Cu2p high-resolution XPS spectrum, (g) Mn2p high-resolution XPS spectrum, (h) FTIR spectrum, (i) N₂ adsorption-desorption isotherm and pore size distribution curves, (j) Cu K-edge XANES spectra of CuMn@CN, Cu@CN, and reference samples, (k) enlarged Cu K-edge XANES spectra in the near-edge region, and (l) Fourier-transformed k²-weighted Cu K-edge EXAFS spectra.

subsequent nucleophilic attack on phosphorus centers during hydrolysis (Štátný et al., 2016). To further examine whether Mn incorporation influences the electronic state of Cu, the Cu 2p spectra of Cu@CN and CuMn@CN were comparatively analyzed (Fig. S2). Mn incorporation did not induce a consistent or pronounced shift in the binding energies of the fitted Cu 2p components. Based on the deconvoluted Cu 2p_{3/2} peak areas, the Cu⁺ fraction increased from approximately 37.5% in Cu@CN to 61.0% in CuMn@CN, while the corresponding Cu⁺/Cu²⁺ area ratio increased from 0.60 to 1.57. Collectively, these results suggest that Mn incorporation primarily regulates the Cu⁺/Cu²⁺ distribution rather than inducing a pronounced shift in the Cu 2p binding energies, thereby favoring the formation and/or stabilization of Cu⁺ species.

To further clarify the metal-support coordination environment, high-resolution C 1s, N 1s, and O 1s spectra (Fig. S2) were then analyzed. In the C 1s spectrum, the components assigned to C-C (284.8 eV), C-N (286.2 eV), and C=O/O-C=O (288.4 eV) indicate the presence of a cyanuric acid/dicyandiamide-derived C-N/O polymeric matrix (Alman et al., 2020; Tai et al., 2025). The N 1s spectrum exhibits peaks at 398.5 and 400.8 eV, corresponding to C-N=C and N-H, respectively. The N 1s spectrum also exhibits a peak at 399.5 eV corresponding to metal-N bonding, suggesting the formation of stable metal-N coordination structures within the nitrogen-rich CN framework (Tai et al., 2025). Such metal-N coordination configurations can modulate the electronic configuration of metal active centers and induce the formation of Lewis

acid hydrolytic sites, thereby promoting the catalytic hydrolysis of organophosphorus pesticides (Li et al., 2022). Additionally, deconvolution of the O 1s XPS spectrum confirms the presence of metal-oxygen (M-O) and metal-hydroxyl (M-OH) species, implying that surface-bound hydroxyl groups may facilitate water adsorption and subsequent activation throughout the catalytic reactions.

To further elucidate the local coordination environment of Cu centers, Cu K-edge XAS measurements were performed using Cu foil, Cu₂O, CuO, and CuPc as reference samples (Fig. 1j–l and Fig. S4). The XANES spectra of CuMn@CN exhibited distinct absorption-edge and white-line features compared with those of Cu@CN, indicating that Mn incorporation modulates the local electronic and coordination environment of Cu centers. The FT-EXAFS spectra showed dominant first-shell features at approximately 1.50 and 1.47 Å for Cu@CN and CuMn@CN, respectively, consistent with scattering from light N/O atoms coordinated to Cu. Notably, Mn incorporation shifted this first-shell feature from approximately 1.50 to 1.47 Å and decreased its amplitude from approximately 0.945 to 0.794, indicating reconstruction of the local Cu-N/O coordination environment, accompanied by increased coordination

heterogeneity and/or local structural disorder. In contrast, Cu foil exhibited a pronounced Cu-Cu scattering feature at approximately 2.24 Å, whereas no comparable strong Cu-Cu contribution was observed for CuMn@CN, supporting the predominant presence of highly dispersed N/O-coordinated Cu centers rather than aggregated metallic Cu species (Gao et al., 2021). Consistently, WT-EXAFS revealed that the dominant scattering contribution of CuMn@CN was concentrated in the lower-*k* region, characteristic of neighboring light N/O atoms, and was clearly distinct from the high-*k* Cu-Cu scattering feature of Cu foil (Fig. S4).

N₂ adsorption-desorption isotherms (Fig. 1i) exhibit a typical Type-IV isotherm with an H3 hysteresis loop, indicating the presence of a mesoporous architecture originating from particle aggregation or interlayer stacking. Quantitative BET analysis yields a specific surface area of 18.77 m² g⁻¹, a micropore volume of 0.00107 cm³ g⁻¹, and an average pore diameter of 22.2 nm, respectively. This relatively low specific surface area and limited micropore volume further verify that the catalytic transformation of organophosphorus pesticides is dominated by surface-exposed Cu/Mn active centers participating in catalytic

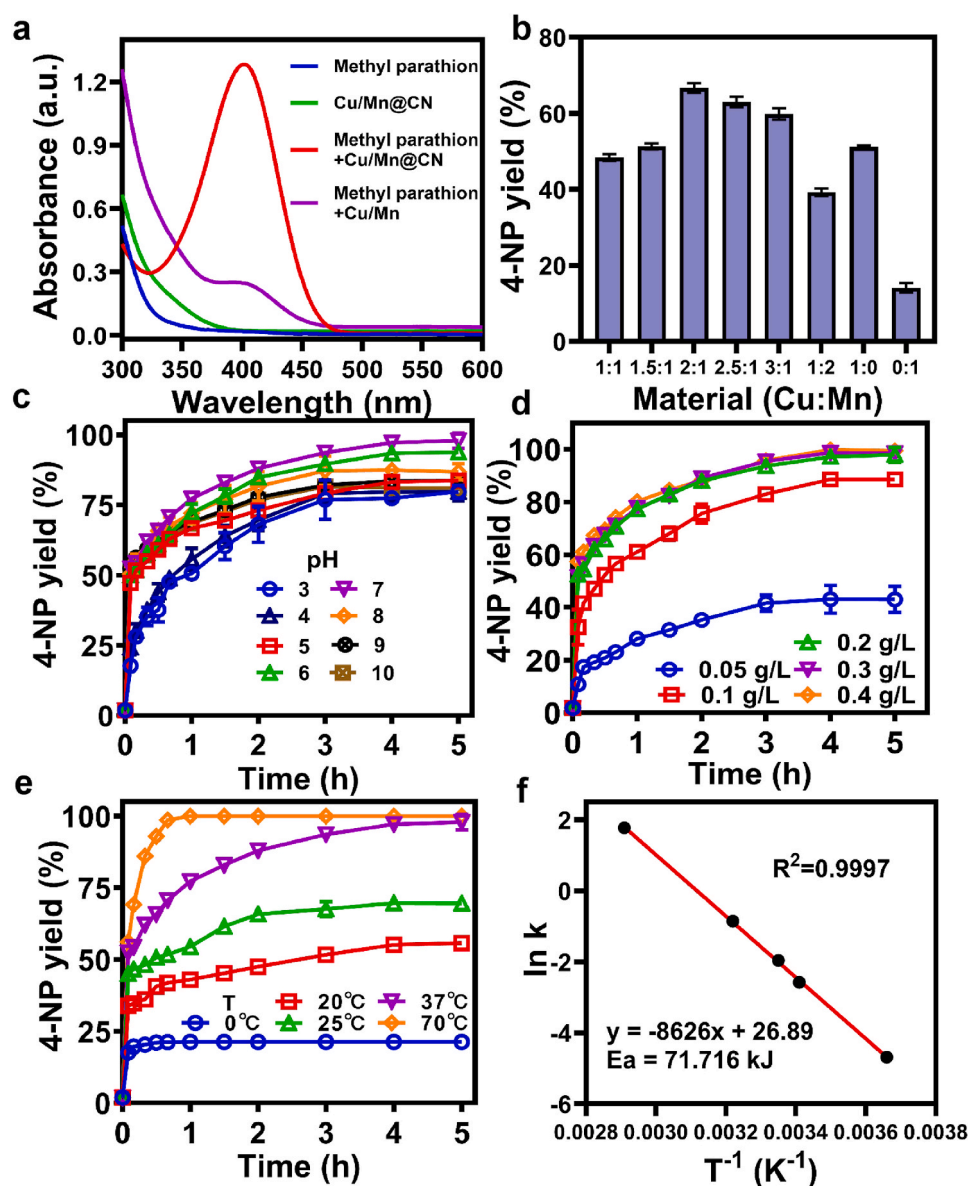


Fig. 2. Evaluation of MP hydrolysis performance via CuMn@CN catalytic reactions. (a) UV-visible absorption spectra of different reaction mixtures after 120 min incubation, effects of (b) Cu: Mn ratios, (c) pH, (d) CuMn@CN dosage, and (e) temperatures on MP hydrolysis, as well as (f) Arrhenius plot of CuMn@CN derived from apparent rate constants at different temperatures.

hydrolysis, rather than substrate enrichment via physical pore adsorption.

ICP-OES confirmed that the final metal compositions deviated from the nominal feed ratios (Fig. S5). For CuMn@CN-2:1, the Cu and Mn contents were 204.88 and 31.73 mg g⁻¹ (20.49 and 3.17 wt%), respectively, corresponding to an actual Cu/Mn mass ratio of 6.46:1. Therefore, Cu/Mn ratios used throughout this study denote nominal elemental-metal feed ratios unless otherwise specified.

3.2. Optimization of catalytic hydrolysis conditions and kinetic analysis of MP by CuMn@CN

Methyl parathion (MP) was selected as a typical organophosphorus pesticide to systematically characterize the nano-hydrolase-like catalytic performance of CuMn@CN. As shown in Fig. 2a, negligible absorbance around 400 nm was detected for pristine MP or bare CuMn@CN. By comparison, an intense characteristic absorption band centered at ~400 nm emerged after the catalytic reaction of MP with CuMn@CN. This spectral feature originates from 4-nitrophenol released during MP hydrolysis (Rizo et al., 2020; Talebzadeh et al., 2018). Notably, the control material prepared without a C-N/O coordination matrix exhibited much weaker hydrolytic activity, demonstrating that the coordination-polymeric matrix plays a crucial role in stabilizing accessible Cu/Mn active sites and promoting MP hydrolysis.

Catalysts with different nominal Cu/Mn feed ratios exhibited distinct MP hydrolysis performances. Among them, CuMn@CN-2:1 showed the highest catalytic activity, while monometallic Cu@CN also maintained considerable hydrolytic capability, indicating that Cu serves as the primary catalytic component. ICP-OES analysis (Fig. S5) revealed that this activity trend cannot be simply explained by precursor feed ratios. Cu@CN possessed an actual Cu loading of 283.96 mg g⁻¹, in contrast to only 136.68 mg g⁻¹ for CuMn@CN-1:1, which may partially account for its reduced catalytic activity. Compared with other CuMn@CN compositions, CuMn@CN-2:1 achieved an optimal balance between Cu retention and Mn incorporation. Notably, despite containing less Cu than Cu@CN, CuMn@CN-2:1 exhibited enhanced catalytic performance, suggesting that the activity enhancement was not solely determined by Cu loading. Combined with XPS and Cu K-edge XAS results, Mn incorporation was found to regulate Cu⁺/Cu²⁺ distribution and reconstruct the local Cu-N/O coordination environment, demonstrating Mn-mediated modulation of the Cu electronic and coordination microenvironment.

The effects of nanozyme dosage, pH, and temperature on catalytic performance were further evaluated (Fig. 2c–e). Increasing the CuMn@CN dosage gradually enhanced the characteristic absorbance at 400 nm, indicating improved catalytic activity. When catalyst dosage was tuned from 0.05 to 0.2 g L⁻¹, both the formation rate and ultimate yield of 4-NP were drastically boosted, which is ascribed to the increased quantity of exposed accessible Cu/Mn active sites. A further increase in catalyst concentration to 0.3–0.4 g L⁻¹ resulted in negligible activity improvements, demonstrating that the catalytic conversion was gradually restricted by substrate depletion, interfacial mass transfer, or insufficient utilization of intrinsic active centers. Accordingly, 0.2 g L⁻¹ was selected as the optimal catalyst dosage for subsequent experiments.

Over a broad pH range of 3–10, CuMn@CN maintained considerable catalytic activity for MP hydrolysis with maximum efficiency achieved at near-neutral pH (Fig. 2c), whereas catalytic performance decreased under both acidic and alkaline conditions. The relatively low hydrolysis rate under acidic conditions originates from weakened nucleophilic capability of surface-bound M-OH/H₂O species and unfavorable variation of catalyst surface electrostatic potential (Li et al., 2022). Under alkaline conditions, although appropriate OH⁻ facilitates nucleophilic attack on phosphorus centers, excessively high pH disturbs surface charge distribution and the hydroxylation configuration of Cu/Mn sites, further disrupting substrate-catalyst interfacial affinity and depressing catalytic efficiency. Combined with the pH-dependent results, the

outstanding catalytic behavior of CuMn@CN under neutral conditions originates dominantly from Lewis acidic metal-site-mediated synergistic activation of water and MP substrate, instead of spontaneous alkaline-driven non-catalytic hydrolysis.

The effect of temperature on the hydrolysis process was then examined. As shown in Fig. 2e, increasing temperature remarkably accelerated MP hydrolysis. The apparent rate constants acquired at varied temperatures were subjected to Arrhenius linear fitting (Fig. 2f), from which an apparent activation energy (*E_a*) of 71.716 kJ mol⁻¹ was calculated. These results indicate that the CuMn@CN-catalyzed hydrolysis of MP follows a typical temperature-dependent kinetic behavior, while the Cu/Mn bimetallic interface may provide an energetically favorable pathway for P-O-aryl bond cleavage.

3.3. Enzyme-like kinetic behavior toward OPPs hydrolysis

To further evaluate the substrate applicability of CuMn@CN beyond MP, the hydrolytic kinetics of CPF, a structurally distinct representative OPP, were investigated. As shown in Fig. 3a–b, the catalytic reaction rate increases with elevated MP concentration and finally reaches a saturation plateau, showing Michaelis-Menten-type kinetic behavior and demonstrating the intrinsic hydrolase-like behavior of CuMn@CN. The optimized catalyst, CuMn@CN (Cu: Mn = 2:1), exhibited an apparent maximum reaction rate (*V_{max}*) of 1.566 mM h⁻¹ and an apparent Michaelis constant (*K_M*) of 0.6313 mM. The relatively low *K_M* value suggests a strong substrate affinity toward MP, whereas the high *V_{max}* reflects favorable catalytic conversion efficiency. Although Michaelis-Menten kinetics were originally derived for natural enzyme-catalyzed reactions, similar saturation-type kinetic behavior can also occur in heterogeneous nanozymes and artificial hydrolase-like catalysts when the reaction involves substrate adsorption or binding on a finite number of accessible catalytic sites followed by surface reaction (Li et al., 2022; Zhang et al., 2025b). Therefore, the *K_M* and *V_{max}* values obtained herein are treated as apparent kinetic parameters describing the surface saturation process rather than intrinsic enzymatic constants. Similar Michaelis-Menten-type analyses have also been applied to hydrolytic nanozyme (Li et al., 2025). Notably, distinct differences in kinetic parameters were observed among catalysts with different Cu/Mn ratios (Fig. S6 and Table S1), indicating that the bimetallic composition significantly modulates substrate adsorption and interfacial catalytic behavior during MP hydrolysis.

To further verify the universal applicability of CuMn@CN toward diverse organophosphorus pesticides, the hydrolytic kinetics of chlorpyrifos (CPF) were further investigated. As displayed in Fig. 3c–d, CuMn@CN also showed Michaelis-Menten-type saturation kinetics during CPF hydrolysis, with a fitted *V_{max}* and *K_M* of 0.04569 mM h⁻¹ and 0.04675 mM, respectively. Compared with MP, CPF exhibits a lower *K_M* value, indicating a stronger binding affinity between CuMn@CN and CPF molecules. These results demonstrate that CuMn@CN retains hydrolytic activity toward two structurally distinct representative OPP substrates.

The hydrolytic performance of CuMn@CN was further benchmarked against representative reported systems for thio-organophosphorus pesticide transformation (Table S2). Existing non-enzymatic catalysts often require weakly alkaline media, mixed organic solvents, adsorption-assisted processes, or signal-amplification strategies, and their activity is commonly reported as initial rates or removal efficiencies rather than complete enzyme-like kinetic parameters. Enzyme-based systems exhibit high activity but remain constrained by protein stability and narrow operating conditions. By contrast, CuMn@CN directly catalyzes both MP and CPF hydrolysis under near-neutral aqueous conditions and provides clear Michaelis-Menten parameters. Its measurable *K_M*/*V_{max}* values, broad pH adaptability of 3.0–10.0, and efficient performance at pH 7.0 highlight a rare combination of enzyme-like catalytic behavior, non-enzymatic robustness, and environmental compatibility.

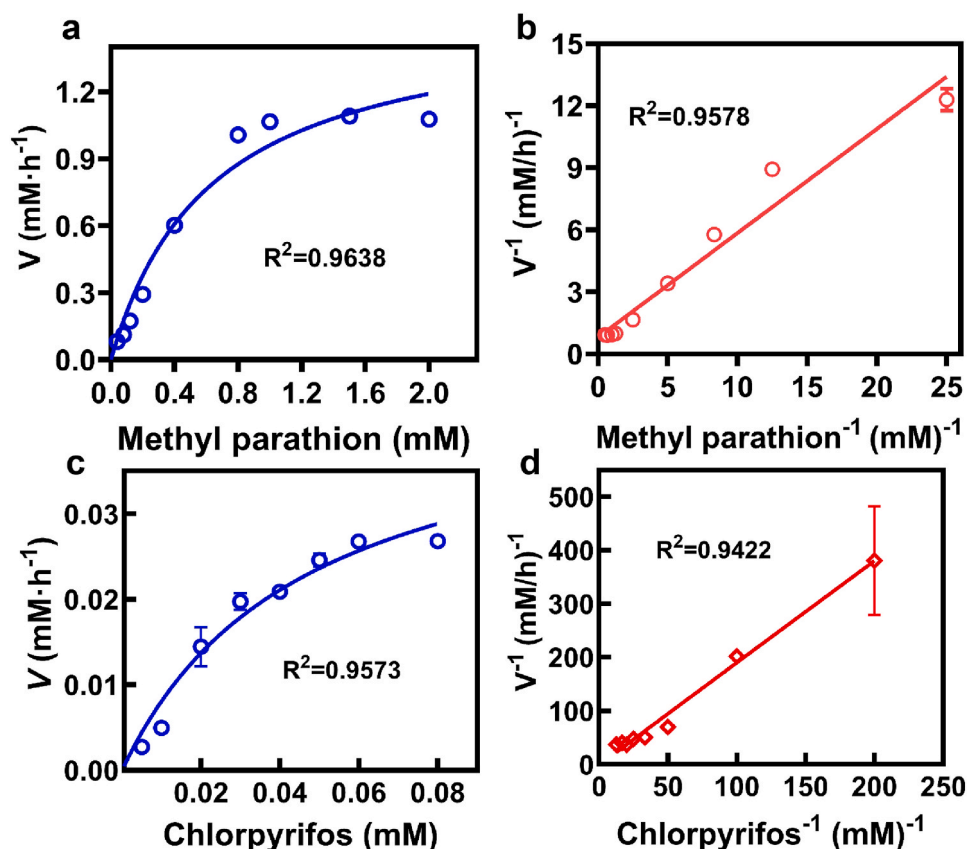


Fig. 3. Michaelis-Menten kinetics measurements of CuMn@CN-mediated MP (a - b) and CPF (c - d) hydrolysis. Reaction conditions: [MP] = 0.04 - 2.00 mM, [CPF] = 0.005 - 0.080 mM; [CuMn@CN] = 0.5 mg mL⁻¹, pH = 7.0, at 25 °C.

3.4. Environmental adaptability and reusability of CuMn@CN

In order to evaluate the practical environmental suitability of CuMn@CN nanozyme, systematic experiments were conducted to clarify how coexisting inorganic anions, authentic natural water matrices, and cyclic operation affect its hydrolytic catalytic performance. As shown in Fig. 4a-e, different anions exerted varying effects on

MP hydrolysis, indicating that the catalytic process is responsive to water chemistry conditions. Among them, Cl⁻ exerted only a negligible influence on 4-NP generation, maintaining relatively high hydrolysis yields even at 100 mM (Fig. 4c), suggesting the good tolerance of CuMn@CN toward saline environments. In contrast, NO₃⁻ (Fig. 4a) and SO₄²⁻ (Fig. 4b) exhibited moderate inhibitory effects on both the hydrolysis rate and final yield at elevated concentrations, which may be

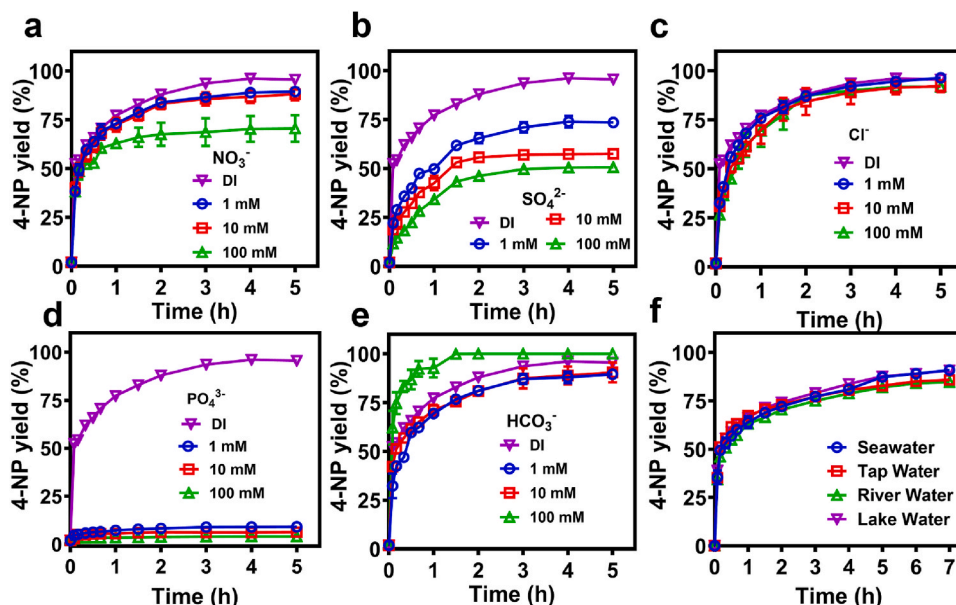


Fig. 4. The effect of (a) NO₃⁻, (b) SO₄²⁻, (c) Cl⁻, (d) PO₄³⁻, (e) HCO₃⁻, and (f) various water matrices on CuMn@CN catalytic performance toward MP degradation.

attributed to increased ionic strength, interfacial charge shielding, and substrate/product mass-transfer limitations. Interestingly, HCO_3^- showed no obvious inhibitory effect within a certain concentration range (Fig. 4e), possibly owing to its buffering capability in stabilizing the local reaction microenvironment. The most pronounced inhibitory effect was observed for PO_4^{3-} (Fig. 4d), which significantly suppressed 4-NP generation even at low concentrations. Considering that Lewis acid metal sites generally facilitate substrate adsorption and bond activation through coordination interactions with phosphate/phosphoester oxygen atoms (Jiang et al., 2020; Tan et al., 2020), exogenous PO_4^{3-} may competitively occupy Cu/Mn active sites, thereby weakening substrate adsorption and interfacial hydrolysis. In addition, the strong affinity of phosphate species toward metal centers may partially block accessible active sites, further decreasing catalytic efficiency (Lin et al., 2026). The applicability of CuMn@CN for MP hydrolysis in real water matrices was subsequently evaluated. Because HA exhibits inherent background absorbance, matrix-matched 4-NP calibration curves were established at HA concentrations of 1, 10, and 20 mg L^{-1} to minimize interference with spectrophotometric quantification (Fig. S7). The influence of humic acid (HA) was further evaluated to simulate natural organic matter interference (Fig. S8). Increasing HA concentration caused only a slight decrease in MP hydrolysis efficiency, indicating the tolerance of CuMn@CN toward organic matrix interference.

To further evaluate the influence of real water matrices on CuMn@CN-catalyzed MP hydrolysis and subsequent 4-NP quantification, the basic water-quality characteristics of river water, tap water, lake water, and seawater were analyzed (Table S3). Matrix-matched calibration curves for 4-NP over 0–50 μM were further established in each water matrix, showing satisfactory linearity with R^2 values of 0.9877–0.9980 (Fig. S9). Given the remaining differences in background absorbance and matrix composition among the water samples, the corresponding matrix-matched calibration curve was used for subsequent MP quantification to minimize matrix-induced analytical bias. As shown in Fig. 4f, continuous MP hydrolysis was achieved in four representative real water samples, with only minor differences in final hydrolysis yields, suggesting that the catalyst maintains favorable catalytic performance in complex aqueous matrices.

After five consecutive recycling cycles, CuMn@CN retained approximately 70% of its initial hydrolytic activity (Fig. S10). ICP-OES analysis revealed that Cu concentration gradually increased from 62.39 $\mu\text{g L}^{-1}$ in the first cycle to 608.15 $\mu\text{g L}^{-1}$ in the fifth cycle, whereas the Mn concentration remained consistently low (0.77–3.11 $\mu\text{g L}^{-1}$), indicating that Cu was the major leached metal species during recycling, while Mn exhibited relatively high stability within the CuMn@CN framework (Fig. S11). These results suggest that partial Cu loss may contribute to activity attenuation. Notably, the maximum released concentrations of both Cu and Mn under the tested conditions remained below the corresponding health-based reference values recommended by the WHO drinking-water guidelines (World Health Organization, 2022), suggesting a low potential risk of metal release and favorable

environmental compatibility of CuMn@CN during repeated use.

3.5. Colorimetric sensing platform

Benefiting from the excellent catalytic hydrolysis capability of CuMn@CN toward MP, a 4-NP release-based colorimetric sensing strategy was developed for the visual detection of MP. As shown in Fig. 5a, increasing the MP concentration from 0 to 200 $\mu\text{mol L}^{-1}$ resulted in a progressive enhancement of the absorption peak at approximately 400 nm after alkalization with Na_2CO_3 , indicating the continuous formation of 4-nitrophenolate generated from MP hydrolysis. The absorbance at 400 nm exhibited a strong linear correlation with MP concentration over the range of 0.1–200.0 $\mu\text{mol L}^{-1}$ (Fig. 5b), with $R^2 > 0.99$, demonstrating the favorable quantitative analytical capability and broad linear detection range of the proposed system for effective colorimetric determination of MP. Moreover, the solution color gradually changed from colorless/light yellow to a distinct yellow with increasing MP concentration (Fig. 5c), further confirming the feasibility of this system for visual semi-quantitative detection. Overall, the developed CuMn@CN-based colorimetric strategy offers a simple, rapid, and reliable platform for the on-site screening and environmental monitoring of MP.

To evaluate the analytical performance of the catalytic hydrolysis 4-NP colorimetric method in real water matrices, MP spike-recovery experiments were conducted. At spiking levels of 5, 20, and 50 μM , MP recoveries ranged from approximately 93% to 102% across the four water matrices, with RSDs below 3.5% (Fig. S12). No evident systematic bias was observed in either high-salinity seawater or lake water with relatively high TOC. These results support the reliability of matrix-matched calibration for MP quantification within the tested water matrices and concentration range.

3.6. Mechanistic insights into the hydrolysis of MP catalyzed by CuMn@CN

To verify the product composition and stoichiometry of MP hydrolysis, residual MP and generated 4-NP were simultaneously quantified by HPLC (Fig. S13). Starting from 50 μM MP, the residual concentration decreased to 0.325 μM after 240 min, corresponding to a conversion of 99.35%, while 4-NP reached 49.40 μM , corresponding to a conversion of 98.80%. The molar closure of MP and 4-NP remained within 99.45–102.96%, with 4-NP formation approaching a 1:1 stoichiometric relationship with MP consumption, supporting predominantly near-stoichiometric hydrolysis rather than conversion inferred solely from the colorimetric signal. LC-HRMS/MS further identified 4-NP ($m/z = 138.02$) and the phosphorus-containing hydrolysis product O, O-dimethyl O-hydrogen phosphorothioate ($m/z = 140.98$) (Fig. S14 and Table S4), further supporting MP hydrolysis via P-OAr bond cleavage.

Considering that 4-NP itself remains a potentially hazardous environmental pollutant, a screening-level aquatic toxicity assessment of MP

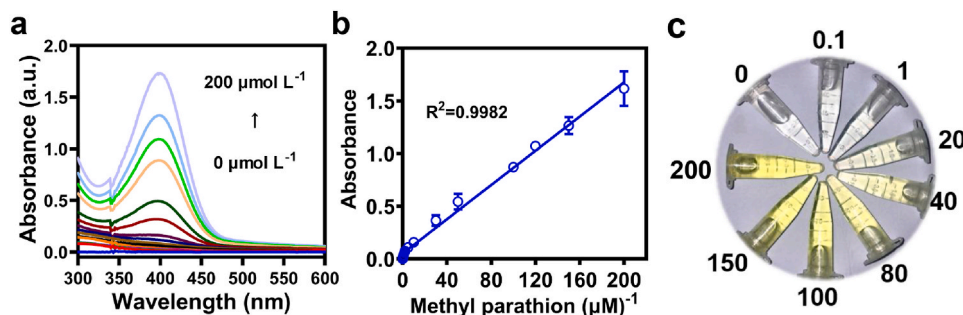


Fig. 5. Colorimetric detection of MP in aqueous solutions. (a) The UV-visible spectra changes of MP at concentrations ranging from 0 to 200 $\mu\text{mol L}^{-1}$, (b) Calibration curve of MP of 0–200 $\mu\text{mol L}^{-1}$, (c) Photo of the assays containing different concentrations of MP.

and its identified hydrolysis products was further conducted using ECOSAR (Fig. S15). The predicted 96-h LC50 for fish and 96-h EC50 for green algae increased from 2.371 to 2.732 mg L⁻¹ for MP to 21.86 and 27.534 mg L⁻¹ for 4-NP, respectively, indicating lower predicted acute toxicity and a corresponding shift from the GHS Acute 2 to Acute 3 range. (Wu et al., 2023). A similar trend was observed for chronic toxicity, with the predicted fish chronic value (ChV) increasing from 0.201 to 2.146 mg L⁻¹. Collectively, these results suggest that selective P-OAr bond hydrolysis can reduce the potential aquatic ecological risk associated with MP.

To further elucidate the mechanism underlying MP hydrolysis catalyzed by CuMn@CN, a comprehensive analysis was performed by integrating DFT/Fukui calculations, pre- and post-reaction material characterization, kinetic behavior, and product identification. Frontier molecular orbital analysis was further performed to understand the electronic characteristics of MP. According to the optimized structure calculated at the B3LYP/6-31G(d,p) level with the SMD water model (Fig. 6b-c), the HOMO and LUMO energies of MP were determined to be -6.87 eV and -2.71 eV, respectively, giving a HOMO-LUMO energy gap of 4.16 eV. The HOMO is mainly distributed over the aromatic π system and the thiophosphoryl/P-O region, whereas the LUMO is predominantly localized on the p-nitrophenoxy moiety and partially extends

toward the P-OAr linkage. This orbital distribution suggests that the electron-withdrawing nitro-substituted phenoxy group plays an important role in stabilizing the leaving group during P-OAr bond cleavage. In addition, Mulliken charge analysis shows that the phosphorus atom carries a significant positive charge, indicating its electrophilic character and susceptibility to nucleophilic attack by activated water or surface hydroxyl species. Collectively, these molecular-level results indicate the electrophilic character of the phosphorus center and the electronic susceptibility of the P-OAr region, providing a molecular basis for understanding the experimentally observed nucleophilic hydrolysis of MP.

Fukui function analysis further revealed the reactive regions within the MP molecule (Table S5). S12 exhibited pronounced electron-donating character, while the phosphorus center and neighboring oxygen atoms showed high electronic responsiveness, suggesting their involvement in substrate polarization and bond activation. Previous studies have demonstrated that Cu-based Lewis acid catalytic systems promote SN2@P-type hydrolysis of MP through metal-mediated substrate activation coupled with nucleophilic attack by surface-associated water/hydroxyl species, leading to P-OAr bond cleavage (Rizo et al., 2020b). Combined with the near-neutral hydrolytic activity of CuMn@CN, the Lewis-acidic coordination environment on the catalyst

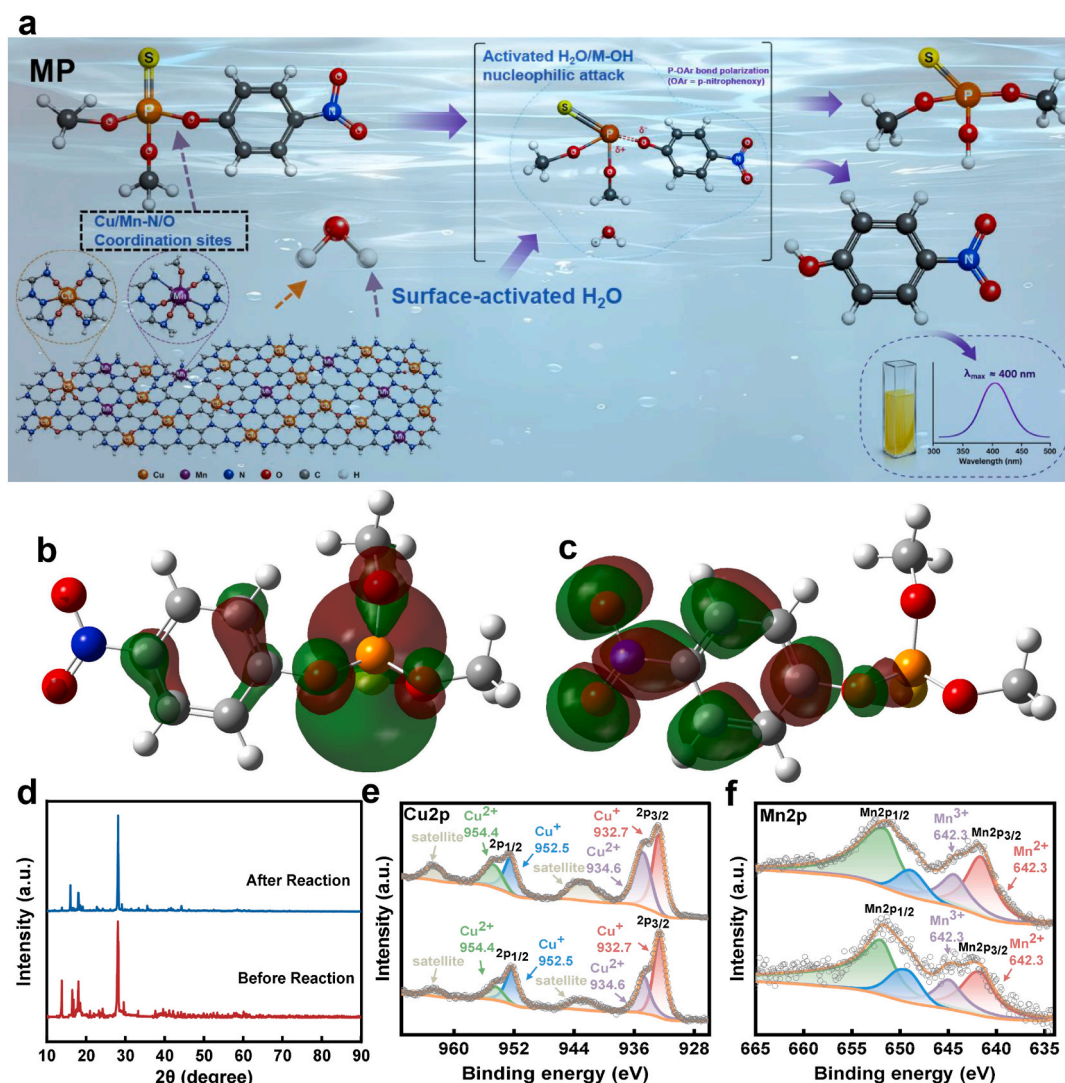


Fig. 6. (a) Schematic illustration of MP hydrolysis via CuMn@CN-catalyzed reactions, (b) The highest occupied molecular orbitals (HOMO), (c) the lowest unoccupied molecular orbitals (LUMO) of the MP molecule. Characterization of CuMn@CN after five cycles of use (d) XRD pattern, (e) Cu2p XPS spectra, and (f) Mn2p XPS spectra.

surface may facilitate phosphorus-center polarization and water activation, thereby promoting nucleophilic attack and subsequent P-OAr cleavage. This pathway is consistent with the formation of 4-NP and the phosphorus-containing hydrolysis product identified by HPLC and LC-HRMS, supporting a Lewis acid-assisted selective hydrolysis mechanism.

Material characterization results further support this proposed mechanism. The principal XRD diffraction peaks (Fig. 6d) remained largely unchanged after reaction, indicating that CuMn@CN maintained structural stability without apparent phase collapse during catalysis. Likewise, the characteristic CN framework peaks in the FTIR spectra (Fig. S16) remained preserved, further confirming the structural integrity of the catalyst. Notably, slight variations in the binding energies and relative peak areas of Cu/Mn species in XPS spectra before and after reaction (Fig. 6e–f) suggest that metal sites may participate in surface coordination and local electronic regulation during catalysis rather than acting merely as inert structural components. In addition, the persistent M-N coordination signal in the N 1s spectra (Fig. S17) indicates that Cu/Mn active centers remained stably anchored within the nitrogen-rich CN framework, thereby providing structural support for the sustained presence of Lewis acid active sites during catalysis.

Based on the above experimental and theoretical evidence, a plausible mechanism for MP hydrolysis catalyzed by CuMn@CN is proposed (Fig. 6a). Cu-centered Lewis-acidic sites within a Mn-modulated Cu/Mn coordination environment may facilitate polarization of the phosphorothioate moiety of MP by withdrawing electron density from the phosphorus-centered region, thereby increasing the electrophilic character of the phosphorus atom and enhancing the susceptibility of the adjacent P-OAr bond to nucleophilic substitution. Meanwhile, coordination of surface-associated H₂O molecules with Lewis-acidic metal centers can promote polarization of the O-H bonds and favor the formation of more nucleophilic hydroxyl-like species. These activated H₂O/M-OH species can subsequently attack the electrophilic phosphorus center, inducing further electronic redistribution within the phosphorothioate group and promoting cleavage of the P-OAr bond. Notably, TMB control experiments showed negligible intrinsic oxidase-like activity of CuMn@CN in the absence of H₂O₂ (Fig. S18), further supporting a Lewis acid-assisted surface nucleophilic hydrolysis pathway rather than ROS-mediated oxidative degradation. Ultimately, cleavage of the P-OAr bond leads to the formation of 4-NP and dimethyl thiophosphate-like products, enabling the selective hydrolysis of MP, producing a characteristic absorption signal near 400 nm and thereby enabling a coupled “catalytic hydrolysis-colorimetric detection” process.

4. Conclusion

In this work, a novel self-supported Mn-doped Cu-C-N-based coordination polymer (CuMn@CN) with tailored Cu⁺ active sites using ligand anchoring was successfully fabricated. It can be used for the efficient hydrolysis of MP with reduced predicted toxicity of the resulting products under near-neutral mild conditions, achieving integrated catalytic hydrolysis and visual detection of MP contaminants. Characterization verified that Cu and Mn active species are uniformly dispersed on the CN framework, constructing stable Cu-centered coordination sites within the Cu/Mn-containing N/O-rich framework. Such unique structural features furnish a favorable structural foundation for efficient catalytic hydrolysis reactions. Kinetic results demonstrated efficient MP hydrolysis by CuMn@CN under near-neutral conditions with Michaelis-Menten-type saturation behavior (apparent $K_M = 0.6313$ mM), suggesting substrate concentration-dependent catalytic saturation. Additionally, CuMn@CN maintained considerable hydrolytic activity in complex aqueous matrices and retained catalytic functionality during repeated use. Taking advantage of the continuous release of 4-NP hydrolysis byproducts, a facile colorimetric sensing platform was established to realize visual semi-quantitative and precise

quantitative detection of MP, enabling auxiliary environmental monitoring of pesticide residues. Furthermore, the successful hydrolysis of CPF, a structurally distinct representative OPP, supports the substrate applicability of CuMn@CN. Compared with conventional advanced oxidation processes and strong alkaline hydrolysis technologies, this CuMn bimetallic nano-hydrolase strategy achieves selective and efficient transformation of organophosphorus pesticides under mild, eco-friendly, and low-consumption conditions. This work provides a feasible and promising method for the remediation of organophosphorus-contaminated water and comprehensive environmental risk early-warning monitoring.

CRediT authorship contribution statement

Yanchun Liao: Writing – original draft, Software, Investigation, Formal analysis, Data curation, Conceptualization. **Yiping Feng:** Supervision, Funding acquisition, Formal analysis, Conceptualization. **Zhu Wang:** Writing – review & editing, Formal analysis, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.envres.2026.125588>.

Data availability

Data will be made available on request.

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