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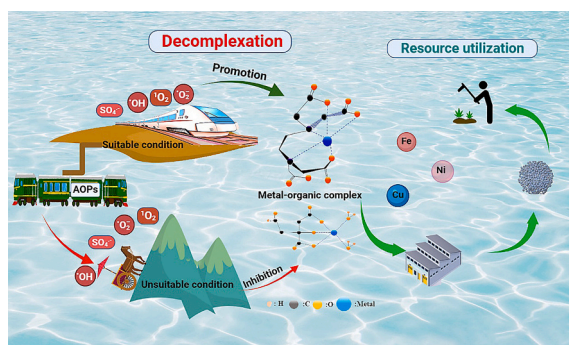
Decomposition of metal-organic complexes and metal recovery in wastewater: A systematic review and meta-synthesis

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- Spatial configurations and properties of metal-organic complexes are reviewed.
- Cleavage mechanisms of metal-organic complexes are explained.
- Synergetic and competitive effects of coexisting ions and pH are discussed.
- Applications and limitations of various decomplexation methods are presented.



ABSTRACT

Metals are rarely found as free ions in natural and anthropogenic environments, but they are often associated with organic matter and minerals. Under the context of circular economy, metals should be recycled, yet they are difficult to extract for their complex forms in real situations. Based on the protocols of review methodology and the analysis of VOS viewer, there are few reviews on the properties of metal-organic complexes, decomplexation methods, the effect of coexisting ions, the pH influence, and metal recovery methods for the increasingly complicated metal-organic complexes wastewater. Conventional treatment methods such as flocculation, adsorption, biological degradation, and ion exchange fail to decompose metal-organic complexes completely without causing secondary pollution in wastewater. To enhance comprehension of the behavior and morphology exhibited by metal-organic complexes within aqueous solutions, we presented the molecular structure and properties of metal-organic complexes, the decomplexation mechanisms that encompassed both radical and non-radical oxidizing species, including hydroxyl radical ($\cdot\text{OH}$), sulfate radical (SO_4^-), superoxide radical (O_2^-), hydrogen peroxide (H_2O_2), ozone (O_3), and singlet oxygen ($^1\text{O}_2$). More importantly, we reviewed novel aspects that have not been covered by previous reviews considering the impact of operational parameters and coexisting ions. Finally, the potential avenues and challenges were proposed for future research.

Keywords:
Metal-organic complexes
Decomplexation
Radicals
Coexisting ions effect
Resource recovery

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1. Introduction

Water pollution ranks among the top ten global environmental issues of concern (E.R. Wang et al., 2019). Consequently, stringent regulations on effluent discharge are enforced to prevent contamination of natural resources (Mondal and Palit, 2022). Industries commonly use cobalt (Co), chromium (Cr), manganese (Mn), nickel (Ni), copper (Cu), and zinc (Zn) to produce valuable goods at low cost (Kumar et al., 2023). For example, the printed circuit board industries employ ethylenediaminetetraacetic acid (EDTA) to chelate Cu^{2+} and to form a stable octahedron structure. Similarly, ferrous-ethylenediaminetetraacetic acid (Fe(II)-EDTA) modified $\text{g-C}_3\text{N}_4$ nano-sheets serve as catalysts for solar light-induced degradation of tetracycline (Khaing et al., 2020). Other than EDTA, there are amino tris methylene phosphonic acid (ATMP), 1-hydroxy ethylidene-bis phosphonic acid (HEDP), citric acid, and nitrilotriacetic acid. These industrial applications have aroused health concerns due to the toxic effects exhibited by both metals and organic ligands, such as carcinogenicity, teratogenicity, and mutagenicity (W. Li et al., 2022).

Another challenge arises from the refractory nature of certain metal-organic complexes that cannot be completely degraded or biodegraded using conventional wastewater treatment methods such as flocculation, adsorption biological degradation, and precipitation (Nguyen et al., 2021). These traditional approaches are time-consuming with high energy consumption while resulting effluents remain toxic in lakes and rivers (Sashkina et al., 2016). These drawbacks pose threats to aquatic ecosystems, soil environments, and health through various pathways (Fig. 1) (Ustaoglu and Islam, 2020). As a consequence, high-mineralization, low-cost, high-recovery, and low-energy technologies have been recently explored to degrade recalcitrant metal-organic complexes and recycle metals (Li et al., 2021).

Various technologies, such as ozone oxidation, Fenton oxidation, persulfate oxidation, and electrochemical advanced oxidation, are commonly employed for the decomposition of metal-organic complexes by utilizing reactive species such as hydroxyl radicals ($\cdot\text{OH}$), sulfate

radicals ($\text{SO}_4\cdot^-$), singlet oxygen ($^1\text{O}_2$), ozone (O_3) and superoxide radicals ($\text{O}_2\cdot^-$) (P. Chen et al., 2022). Electro-deposition and electro-adsorption have shown high potential in recovering metal ions due to advantages such as high mineralization efficiency, low-cost operation with high recovery rates versatility, and low energy consumption (Wu et al., 2017).

To date, the utilization of a systematic review methodology, such as Preferred Reporting Items for Systematic Reviews and Meta-analyses (PRISMA), stands as a prominent approach offering comprehensive research insights derived from the breadth of published literature. Additionally, visualization tools like VOS viewers have been instrumental in transforming this extensive literature data into visually understandable presentations. Notably, recent reviews centering on the decomplexation and recovery of metal-organic complexes have primarily emphasized chemical analyses and treatment mechanism elucidation (Wu et al., 2017; Q.Q. Xu et al., 2022; Z. Xu et al., 2022). However, a systematic synthesis encompassing the nuanced properties of metal-organic complexes, the influential role of pH variations, and the intricacies of metal recycling remain conspicuously absent from the current literature landscape.

The degradation and recovery technologies for heavy metal-organic complexes hold significant potential for environmental protection and resource sustainability. Therefore, this article reviewed the properties, mechanisms, methods, and metal recovery associated with metal-organic complexes while addressing current limitations and future development directions from various perspectives.

2. Methodology

2.1. Systematic literature review

Utilizing a rigorous methodology grounded in the Preferred Reporting Items for Systematic Reviews and Meta-Analyses (PRISMA) guidelines (Moher, 2009), an exhaustive examination of literature spanning the past decade was undertaken. The comprehensive search for

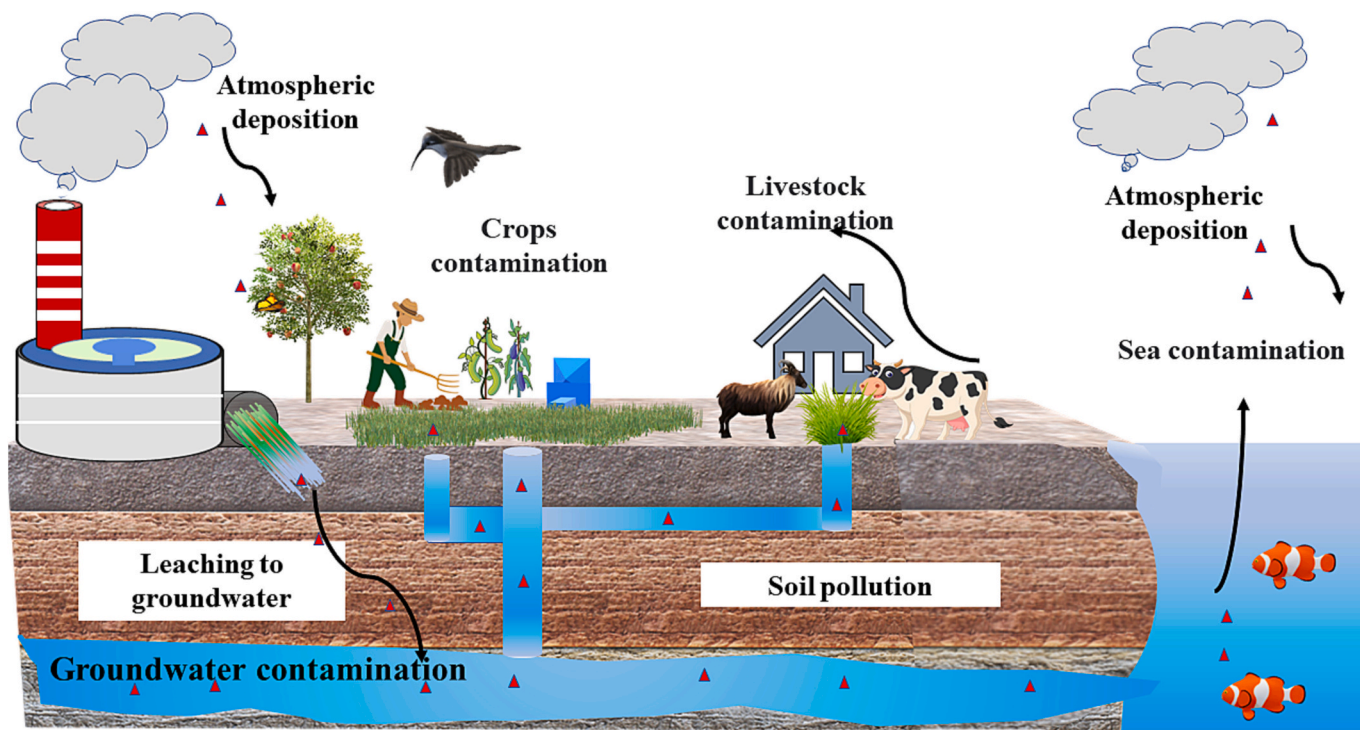


Fig. 1. Pollution pathways by industrial wastewater containing heavy metal-organic complexes. Once released in water, metal-organic complexes diffuse to the entire ecosystem, e. g. soils, groundwater, crops, livestock, food, atmosphere, and sea.

scholarly articles and journal proceedings across diverse fields commenced in June 2022. This exploration was conducted meticulously utilizing both the Web of Science Core Collection database and Google Scholar within our research group. Subsequently, a refined search strategy was employed, utilizing targeted keywords such as “metal-organic complexes removal,” “metal-organic complexes removal and recovery,” “chelates decomplexation,” “metal-organic degradation,” and “Cu(II)-EDTA removal” to curate a refined and pertinent search list.

Following the structured guidelines of the PRISMA checklist, meticulously designed to augment the transparency and cohesiveness of review methodologies, a multi-tiered filtration process was implemented as illustrated in Fig. S1a. The systematic review established stringent criteria for inclusion and exclusion, meticulously curated to encompass the most pertinent articles (Table 1). In essence, the selected documents were required to delve into the realms of metal-organic complexes removal, metal-organic complexes removal and recovery, chelates decomplexation, metal-organic degradation, or Cu(II)-EDTA removal, while specifically excluding those associated with metal-organic frameworks (MOFs). Furthermore, documents featuring statistical tests or substantiated claims through data validation were considered favorably. Patents, unpublished manuscripts, abstracts, and dissertations were eliminated from this process. Moreover, with a minimum page length requirement of eight pages, this scholarly endeavor embarked upon an exploration of pioneering methodologies, innovative approaches, and theoretical frameworks meticulously designed to bolster the efficacy and comprehension of removing metal-organic complexes.

2.2. Quality of literature assessment

In the last round of screening, the evaluation process involved a comprehensive examination of the article's key contributions to ascertain its suitability for inclusion in studies about metal-organic complexes' properties, decomplexation, and recovery (J.B. Li et al., 2023). Quality benchmarks are established in Table S1 extracted from the criteria of PRISMA guidelines (Page et al., 2021) and reference (J.B. Li et al., 2023). More specific appraisal frameworks and subcategories are shown in Table S1.

A total of 10 subcategories was incorporated by emphasizing different aspects, including objective, methodology for data collection, contextualization, analytical approaches employed, discussion nuances, limitation and future research, adaptation strategies, reliability of evidence, availability and spatial scale of impacts on the decomplexation and recovery of metal-organic complexes and practicality and temporal scale of metal-organic complexes decomplexation and recovery (J.B. Li

Table 1
Inclusion and exclusion criteria for the systematic review.

Classification	Included	Excluded
Wastewater type	Industrial wastewater containing metal-organic complexes	Metal-organic frameworks
Publication dates	Within dozen years	/
Minimum length	More than three pages	Less than three pages
Publication language	English	Non-English
Document types	Published and peer-reviewed journal articles, conference proceedings	Key studies, commentary, book reviews, editorials, letters, clinical trials, perspectives, opinions
Contribution	Focusing on the practical and theoretical dimensions of properties, decomplexation, or recovery for metal-organic complexes	Review papers and advocacy pieces that have no innovative contribution

et al., 2023). As shown in Table S2, Scores assigned to documents within each subcategory hinged upon the comprehensive depiction of information and the adequacy and scientific rigor demonstrated in the approaches utilized. A total of 85 articles were selected and analyzed for this review. Documents achieving a score of 7.5 or above were classified as “convincing documents” and were highlighted in pale orange and other studies were highlighted in blue within Table S2.

2.3. VOSviewer analysis

The voluminous collection of literature on metal-organic complexes presents a challenge in exploring the hotspots and trends of decomplexation and metal recovery. Therefore, it is necessary to utilize clustering techniques to extract meaningful insights from the data. It is acknowledged that VOSviewer is a powerful visualization tool used in bibliometric analysis to explore and map relationships among scholarly data. This robust analytical approach unveils intricate connections and relationships among scholarly documents (Ali et al., 2021). By harnessing the capabilities of VOS Viewer, researchers gain a comprehensive understanding of the interlinkages within the academic literature, identifying and delineating strong associations between related documents. In our review, we collected 1269 records in the first round, then, we used VOSviewer 1.6 to construct a keyword co-occurrence network diagram based on the 252 keywords that occurred more than three times. Besides, the color and size denote the cluster type and the frequency of occurrence for keywords respectively, the interconnecting lines among words serve as graphical representations of links or associations between them. Based on the visual representation and analysis of VOSviewer (Fig. S1b), the removal, degradation, complexes, heavy metal and oxidation were the main research aspects, however, no record associated with the properties of metal-organic complexes, coexisting effects, and the influence of pH has been explored and reviewed.

3. Results and discussion

3.1. Metal-organic complexes

The nature of metals and the organic ligands determine the contribution of different treatment methods (Wang et al., 2023). Transition metals are readily and stably combined with organic matter to form metal-organic complexes that possess one or more polydentate ligands by coordination and agglomeration (Wang et al., 2021; Zhao et al., 2022). The central ion, with electron pairs, provides a vacant orbital while the organic groups act as ligands and employ various interactive effects to bind with heavy metal ions (Baccaro et al., 2023).

3.2. Structures of common heavy metal-organic complexes

It is acknowledged that citric acid contains three carboxylic groups and one hydroxyl group, rendering citric acid uniquely suitable for chelating heavy metal ions in solution (Fig. 2A). Different forms of complexes can be formed between heavy metal ions and citric acid. Specifically, calcium ion (Ca^{2+}), Ni^{2+} , and ferric ion (Fe^{3+}) can form bidentate complexes with citric acid whereas cadmium ion (Cd^{2+}), Cu^{2+} , lead ion (Pb^{2+}), and Fe^{2+} form tridentate complexes with citric acid (Fig. b, c) (Francis et al., 1992). In the case of EDTA, the ligand possesses two ammonia nitrogen atoms and four carboxyl oxygen atoms which provide six coordination sites exhibiting strong complexing ability towards heavy metal ions (Fig. 3D). Whether the heavy metal ions are monovalent or divalent/trivalent, they predominantly form a 1:1 complex upon undergoing a complexation reaction with EDTA (Novoa-Ramírez et al., 2023).

3.3. The properties of metal-organic complexes

Some of the metal-organic complexes have a significant effect on the

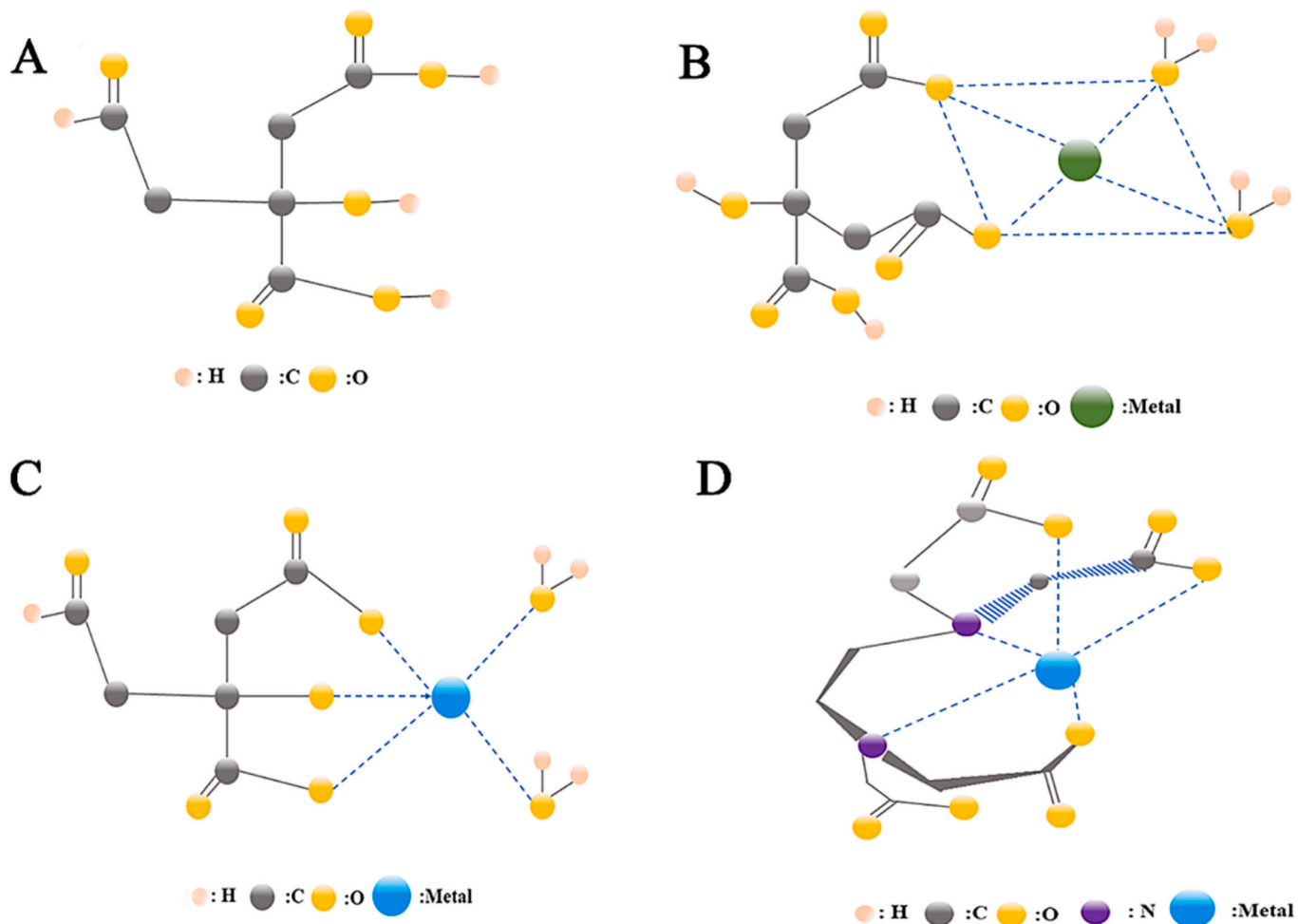


Fig. 2. Spatial configurations of citric acid (A), calcium, ferric and nickel citrate (B), cadmium ion, lead, and ferrous and copper citrate (C), and copper, nickel, manganese, cobalt - EDTA with five-membered chelate ring (D).

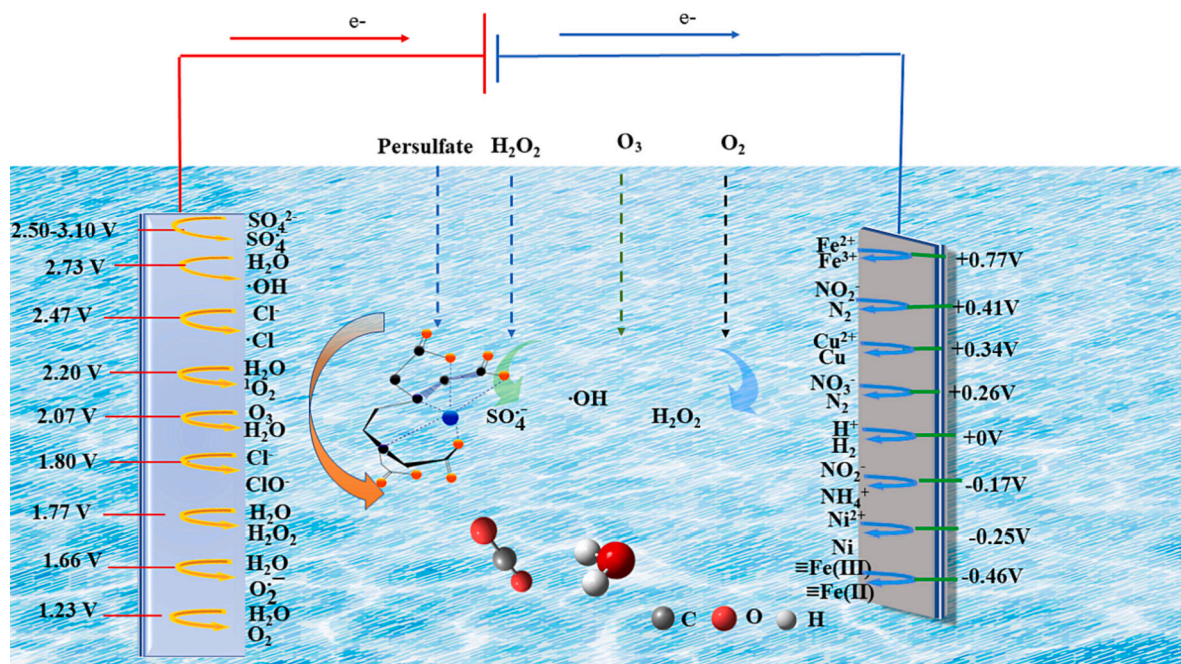


Fig. 3. The mechanism of electrochemical removal and recovery of metal-organic complex in solution: the redox potential of various active species (SO₄²⁻, ·OH, ·Cl, ¹O₂, ClO⁻, H₂O₂, O₂, O₂) at the anode and the redox potential of metal ions (Fe²⁺, Cu²⁺, Ni²⁺) at the cathode.

oxidation kinetics of the decomplexation process, but the specific “promotion” mechanism is not clear yet. Noteworthy, many daughter complexes derived from the decomplexation of parent complexes exhibit catalytic abilities to enhance degradation processes through the Fenton/Fenton-Like reaction and/or electrochemical reduction of active metal intermediates (Baldrian et al., 2005). Li and his co-authors reported that weak signals could be observed for Cu(II)-N-(2-hydroxyethyl) ethylenediamine-N, N', N'-triacetic acid (Cu(II)-HEDTA) and Cu(II)-imino diethyl acetic acid (Cu(II)-IDA) while strong peak intensities were present for Cu(II)-ethylenediamine-N, N'-diacetic acid (Cu(II)-EDDA) and Cu(II)-glycine (Cu(II)-Gly) in the electron paramagnetic resonance experiments, accordingly, the Cu(II)-EDDA and Cu(II)-Gly boosting the H₂O₂ to transform to •OH (Li et al., 2020). Besides, the Cu(I)-complex can be generated from the Cu(II)-complex by intramolecular charge transfer, and in turn, react with chlorine to generate chlorine radicals (Cl•) that accelerate the degradation of Cu(II)-EDTA (Huang et al., 2019). Similar autocatalytic decomplexation was observed during the electrochemical oxidation of the Ni(II)-complex, where chlorine radicals promoted the degradation of Ni-ethylenediaminetetraacetic acid (Ni(II)-EDTA) (Li et al., 2017). Wu et al. (2023) found that the self-enhanced oxidation associated with Fenton-Like reactions of Ni(II)-EDTA in the process of electrocatalysis was undistinguished, whether the presence of O₂ or not, the removal rate of EDTA and Ni ions had no significant difference. Ipso facto, the catalytic performance of metal-organic complexes, mostly depends on the decomplexation methods and reactive species. Therefore, it is recommended to investigate the impact of different metal centers and ligands on catalytic activity and develop a novel self-strengthening process to enhance the efficiency of pollutant removal.

3.4. Reactive species and degradation mechanism

Reactive species such as •OH, SO₄⁻, Cl•, ¹O₂, O₃, and O₂⁻, generated by various advanced oxidation processes, exhibit diverse effects on decomplexation efficiency, total organic carbon removal (TOC) rate, degradation mechanism, and pathway (S. Li et al., 2023; T. Li et al., 2022) (Table 2). It has been previously demonstrated that the main degradation mechanisms of non-radicals' oxidative species, such as H₂O₂, O₃, and ¹O₂, are the direct electrophilic attack to abate the toxicity of heavy metal-organic complexes (Loganathan et al., 2023). In other words, H₂O₂, O₃, and ¹O₂ act as electrophilic agents that target nucleophilic positions in organic substances and functional groups in aromatic molecules such as oxyhydryl (-OH), nitro (-NO₂), and chlorine (-Cl) (J.L. Chen et al., 2022). These non-radical oxidative species possess advantages for wastewater treatment due to their good anti-interference effect on natural organic matter (Dai et al., 2022).

In contrast, SO₄⁻, Cl•, •OH, adsorbed hydroxyl radical (•OH_{ad}), secondary oxidants (•OOH) and O₂⁻ function as radicals' oxidative species capable of converting heavy metal-organic complexes into biodegradable low molecular weight organic matter (Malvestiti et al., 2023). To be specific, •OH and O₂⁻ generated in advanced oxidation processes (AOPs) and electrochemical advanced oxidation processes (EAOPs) would readily react with heavy metal-organic-complexes through hydrogen abstraction, while •OH is a non-selective radical and more readily reacts with organics through hydrogen abstraction and O-transfer reactions than O₂⁻ (Fayyaz et al., 2021). Moreover, the SO₄⁻ exhibits higher selectivity and efficiency when reacting with unsaturated bonds-containing organic compounds through electron transfer reactions (Glaze et al., 1987). This allows effective treatment of metal-organic complex wastewater without compromising the natural components presence (Anipsitakis and Dionysiou, 2003; Cuerda-Correa et al., 2019). Cu(II)-EDTA is a common heavy metal-organic complex that undergoes two distinct degradation pathways (García et al., 2021). In the decomplexation process, the first pathway involves •OH attacking the C of -CH₂-COOH due to its high electron density, while the second pathway

involves -N-CH₂-CH₂-N- being attacked and generating C-center radicals, both of which involve different intermediates (Zhu et al., 2019).

Nevertheless, different active oxidative species exhibit various efficiencies in decomplexing heavy metal-organic complexes. Undoubtedly, these treatment effects and degradation pathways become more intricate when interacting with other operating conditions such as initial pH, temperature, stirring rate, and potential side reactions of heavy metal-organic complexes in solution e.g., adsorption at electrodes and catalysts (Du et al., 2020).

4. Methods for decomplexation

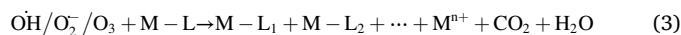
Advanced oxidation techniques have exhibited considerable efficacy in the mitigation of metal-organic complexes through the generation of highly reactive species, thereby aiding in the elimination of heavy metals. Notably, reactive species such as SO₄⁻, •OH, O₂⁻ and ¹O₂ bring about increasing attention in environmental remediation and wastewater treatment. Their exceptional selectivity and robustness in navigating complex water environments, especially those containing inorganic anions, underscore their significance. This review aims to fill gaps left by prior studies, focusing on novel facets unexplored in existing literature. Specifically, it delves into the nuanced impact of operational parameters and coexisting ions in ozone oxidation, Fenton oxidation, persulfate oxidation, and electrochemical advanced oxidation. Additionally, the review scrutinizes technologies pertinent to the feasibility assessments of these methodologies and proposes potential trajectories for future research endeavors.

4.1. Ozone oxidation

The treatment of metal-organic complexes involves two steps: firstly, the breakdown of the organic ligand to release free heavy metal ions; secondly the capture of metal ions to mitigate environmental risks (Du et al., 2020). Among various advanced oxidation processes disrupting organic ligands' structures in metal-organic complexes wastewater, ozone oxidation stands out as a widely recognized method (Chen et al., 2021) due to its high oxidation-reduction potential and selectivity in acidic media and easy decomposition in alkaline conditions (Eq. (1)); ozone oxidation contributes significantly to decomplexing metal-organic complexes (S. Li et al., 2022).



Considering that O₃ exhibits lower oxidation potential (1.24 V) under alkaline conditions (Eq. (2)) and that O₃ oxidation reaction shows greater selectivity with pollutants in acidic conditions, achieving complete decomplexation and satisfactory results through O₃ oxidation alone is unlikely. Numerous methods have been developed aiming at enhancing the oxidizing ability of O₃, such as combining with H₂O₂, ultraviolet light, ultrasound, and alkaline reagents. Meanwhile, •OH, H₂O₂, •OH_{ad}, O₂⁻ and ¹O₂ were yielded in the synergistic process. The equation for decomposing heavy metal-organic complexes is as indicated by (Nidheesh et al., 2022):



S.Y. Xu et al. (2020) illustrated the synergistic effect between Cu(II)-EDTA and Ni(II)-EDTA using the ozone-oxidation process to accomplish the total decomplexation, and they further proved that Ni(II)-EDTA had a higher decomplexation kinetics than Cu(II)-EDTA. Nguyen et al. (2021) reported 99.70 % removal of Ni²⁺ and 99.72 % of Cu²⁺ from the plating wastewater through Fenton/ozone-based oxidation and coagulation. Based on their complementary advantages, Fenton is likely more effective in decomposing heavy metal-organic complexes, while O₃ oxidation under alkaline conditions is more efficient for mineralization.

Table 2

Redox potential, production, and common methods of decomplexation using radical reactive oxidative species and non-radical oxidizing reactive species. M^{z+} represents the heavy metal ion.

Radical reactive oxidative species	Redox potential E (V _{NHE})	Reactions	Undesired reactions	Advanced oxidation processes	References
·OH	1.8–2.7	$M^{z+} + H_2O_2 \rightarrow M^{(z+1)+} + \cdot OH$ $Mn^{2+} + O_2^- + RNHNH_2 \rightarrow \cdot OH + Mn^{3+} + RNHNH$ $Cr(V) + H_2O_2 \rightarrow \cdot OH + Cr(III)$ $TiO_2 + hv + e^- \rightarrow \cdot OH$ $SO_4^- + H_2O \rightarrow SO_4^{2-} + \cdot OH + H^+$ $SO_4^- + OH^- \rightarrow SO_4^{2-} + \cdot OH$ $e_{aq}^- + H_2O_2 \rightarrow \cdot OH + OH^-$ $H^+ + H_2O_2 \rightarrow \cdot OH + H_2O$ $O_3 + \cdot HO_2 \rightarrow 2O_2 + \bullet OH$ $O_3^- + H_2O \rightarrow \bullet OH + O_2 + OH^-$ $O_2^- + 2H^+ \rightarrow 2\bullet OH$ $HO_3^* \rightarrow \bullet OH + O_2$ $2H_2O_2 \rightarrow 2\bullet OH$ $HSO_5^- + O_3 \rightarrow SO_4^- + O_2$ $HSO_5^- + M^{z+} \rightarrow SO_4^- + M^{(z+1)+} + OH^-$	$\bullet OH + HOO^- \rightarrow H_2O + O_2$ $\bullet OH + O_2^- \rightarrow OH^- + O_2$ $2\cdot OH \rightarrow H_2O_2$ $\bullet OH + OH^- \rightarrow H_2O + O^{\bullet -}$ $Cl^- + \bullet OH \rightarrow ClOH^-$	O_3/H_2O_2 , ultraviolet light/ H_2O_2 , Fenton, Fenton-Like, ultraviolet light / TiO_2 , wet air oxidation, ultrasound oxidation, photocatalysis oxidation	Saravanan et al., 2022
		$S_2O_8^{2-} + M^{z+} \rightarrow M^{(z+1)+} + SO_4^-$ $S_2O_8^{2-} + Fe^0 \rightarrow Fe^{2+} + SO_4^- + 2SO_4^{2-}$ $Heat + S_2O_8^{2-} \rightarrow 2SO_4^-$ $HSO_5^- \rightarrow SO_4^- + \cdot OH$ $S_2O_8^{2-} \rightarrow 2SO_4^-$	$HSO_5^- + SO_4^- \rightarrow SO_5^- + SO_4^{2-} + H^+$ $HSO_5^- + \cdot OH \rightarrow SO_5^- + OH^- + H^+$ $SO_4^- + \cdot OH \rightarrow SO_4^{2-} + 1/2O_2$ $SO_4^- + SO_4^- \rightarrow S_2O_8^{2-}$ $S_2O_8^{2-} + H_2O \rightarrow 2HSO_4^- + 1/2O_2$ $SO_4^- + H^+ + e^- \rightarrow HSO_4^-$	Peroxymonosulfate (PMS) activation; peroxydisulfate (PDS) activation; photolysis, activation reaction with PDS or PMS with heat, chelated or non-chelated transition heavy metal, and ultraviolet light	Tian et al., 2022
Cl [•]	1.1–2.5	$SO_4^- + Cl^- \rightarrow SO_4^{2-} + Cl^{\bullet}$ $Cl^{\bullet} + Cl^{\bullet} \rightarrow Cl_2$ $Cl^- + Cl^{\bullet} \rightarrow Cl_2^{\bullet -}$ $Cl_2^{\bullet -} + Cl_2^{\bullet -} \rightarrow Cl_2 + 2Cl^-$ $HSO_5^- + 2Cl^- + 2H^+ \rightarrow SO_4^- + Cl_2 + H_2O$ $Cl^- + HSO_5^- \rightarrow SO_4^- + HClO$ $HClO \rightarrow \bullet OH + Cl^{\bullet}$ $Cl_{2(aq)} + H_2O \rightarrow HClO + H^+ + Cl^-$	$6ClO^- + 3H_2O \rightarrow 6ClO_3^- + 2H^+ + 4Cl^- + 3/2O_2 + 6e^-$ $Cl^- + 3H_2O \rightarrow ClO_3^- + 6H^+ + 6e^-$ $ClO^- + H_2O + 2e^- \rightarrow Cl^- + 2OH^-$ $Cl^- + 2H_2O \rightarrow ClO_2 + 4H^+ + 5e^-$ $Cl^- + 2H_2O \rightarrow HClO_2 + 3H^+ + 4e^-$ $2Cl^- \rightarrow Cl_2 + 2e^-$ $HOCl \leftrightarrow H^+ + OCl^-$ $Cl^- + \cdot OH \rightarrow ClOH^-$ $ClOH^- + H^+ \rightleftharpoons \cdot Cl + H_2O$	Electrogenenerated chlorine; Photoelectrochemical solar energy	Zeng et al., 2020
		$\cdot HO_2 \rightarrow H^+ + O_2^-$ $e_{aq}^- + O_2 \rightarrow O_2^-$ $\bullet OH + H_2O_2 \rightarrow H_2O + H^+ + O_2$ $S_2O_8^{2-} + HO_2^- \rightarrow SO_4^- + O_2^- + SO_4^{2-} + H^+$ $O_3 + OH^- \rightarrow O_2^- + HO_2^{\bullet}$ $O_2 + e^- \rightarrow O_2^-$ $H_2O_2 + HO_2^- \rightarrow \bullet OH + O_2^- + H_2O$	$O_2^- + H^+ \rightarrow \bullet OOH$ $O_2^- + O_2^- \rightarrow 2O_2$ $\bullet OH + O_2^- \rightarrow OH^- + O_2$	Photocatalysis oxidation; activation reaction with PDS or PMS with heat, chelated or non-chelated transition heavy metal, and ultraviolet light	Zhang et al., 2023a
•OOH	/	$\bullet OH + O_3 \rightarrow \bullet OOH + O_2$	$\bullet OOH + Fe^{3+} \rightarrow Fe^{2+} + O_2 + 2H^+$ $\bullet OOH \leftrightarrow O_2^- + H^+$ $2\bullet OOH \rightarrow O_2 + H_2O_2$ $O_2^- + HO_2 \rightarrow O_2 + HO_2^-$	O_3/H_2O_2 , ultraviolet light/ H_2O_2 , Fenton, Fenton-Like, ultraviolet light / TiO_2 , wet air oxidation, ultrasound oxidation, photocatalysis oxidation	Saravanan et al., 2022
Non-radical reactive oxidative species	Redox potential E (V _{NHE})	Reactions	Undesired reactions	Advanced oxidation processes	References
H_2O_2	1.8	$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2$ $HO_2 + Fe^{2+} \rightarrow H_2O_2 + Fe^{3+}$ $HO_2^- + H^+ \rightarrow H_2O_2$	$Fe^{3+} + H_2O_2 \leftrightarrow Fe - OOH^{2+} + H^+$ $Fe - OOH^{2+} + H_2O_2 \rightarrow Fe^{2+} + HO_2 \cdot$ $H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O$ $H_2O_2 \rightarrow \bullet OOH + H^+ + e^-$ $Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO_2 + H^+$ $2H_2O_2 \rightarrow 2H_2O + O_2$	O_3/H_2O_2 , ultraviolet/ H_2O_2 , Fenton, Fenton-Like, wet air oxidation, ultrasound oxidation, photocatalysis oxidation	Liu et al., 2021b

Table 2 (continued)

Non-radical reactive oxidative species	Redox potential E (V _{NHE})	Reactions	Undesired reactions	Advanced oxidation processes	References
¹ O ₂	2.2	$\cdot\text{O}_2^- + 2\text{H}^+ \rightarrow {}^1\text{O}_2 + \text{H}_2\text{O}_2$ $\cdot\text{O}_2^- + \cdot\text{OH} \rightarrow {}^1\text{O}_2 + \text{OH}^-$ $\text{O}_2 + \text{h}\nu \rightarrow 3\text{O}_2 \rightarrow {}^1\text{O}_2$ $3\text{H}_2\text{O} \rightarrow \text{O}_3 + 6\text{e}^- + 6\text{H}^+$	/	O ₃ /H ₂ O ₂ , ultraviolet/H ₂ O ₂ , Fenton, Fenton-Like, ultraviolet/TiO ₂ , Photocatalysis	Zhang et al., 2023b Manna and Sen, 2023
O ₃	2.07/1.24	$\text{O}_2 + \text{H}_2\text{O} \rightarrow \text{O}_3 + 2\text{e}^- + 2\text{H}^+$	$\text{O}_3 + \cdot\text{OH} \rightarrow \text{O}_2 + \cdot\text{OOH}$ $\text{O}_3^- + \text{H}_2\text{O} \rightarrow \text{O}_2 + \text{OH}^- + \cdot\text{OH}$ $\text{O}_3 + \text{H}_2\text{O} \rightarrow \text{O}_2 + \text{H}_2\text{O}_2$	O ₃ /H ₂ O ₂ , ultraviolet light/H ₂ O ₂ , photocatalysis oxidation	Zhang et al., 2023c

J. He et al. (2021) synthesized magnesium oxide/expanded graphite catalyst with excellent catalytic activity, stability, and reusability to boost the oxidation of O₃ by forming MgO^{-sOH} (surface active radicals) resulting in nearly complete removal of Cu ions. Zong et al. (2023) demonstrated that the overlooked Ni(III) species, i.e., NiOOH, generated from the reaction between Ni(OH)₂ and •OH, also played an indispensable role in enhancing the EDTA mineralization. However, how to enhance the reactivity and production of •OH, HO₂⁻, O₂⁻ and ¹O₂ during the decomposition of heavy metal-organic complexes have been the research hot point for several years. Adequate treatment measures along with sufficient funding, resources, and manpower should be considered to achieve the goals set by pilot projects.

4.2. Influence of the initial pH on ozone oxidation

Several investigations were conducted from different perspectives to elucidate the impact of pH on the treatment of heavy metal-organic complexes. One approach involved adjusting the initial pH to a fixed value, while another method maintained a consistent pH throughout the decomplexation process by adding acid and alkaline solutions. Visual MINTEQ 3.1 was commonly employed to calculate the chemical equilibrium model at various pH values, providing insights into the behavior and morphological distribution of metal-organic complexes during the ozone treatment (Zhao et al., 2014).

Numerous studies have demonstrated that the decomplexation efficiency of O₃ was mostly dependent on pH; the decomposition efficiency of heavy metal-organic complexes was maximized under alkaline conditions due to more potent reactive oxidative species generated in an alkaline medium compared to the acidic environment. Simultaneously, an increase in the •OH concentration and other oxidants (H₂O₂, •OH_{ad}, O₂⁻ and ¹O₂) triggered a spontaneous chain reaction within the bulk solution (Malik et al., 2020).

Guan and co-workers studied how initial pH influences O₃ oxidation of organic Ni and Cu complexes from electroless plating effluent using a continuous pilot-scale system (Guan et al., 2022). Under neutral and weak alkaline conditions with an ozone flow velocity of 3 L/min, faster removal rate for total nickel concentration reached 98 %, whereas inferior removal rates were observed at pH levels below 7.0 or above 11.0 due to accelerated decomplexation caused by dissociative •OH generation from insufficient alkali addition; otherwise, small carboxylic acid molecules would be produced rapidly leading to acidic shifts in pH values. From the economic perspective, there are factors such as the maintenance of the ozone generator, the energy consumption, and the treatment cost. Hence, to live up to the green standard in reality and to achieve the best performance, the developments and application of O₃ oxidation need more exploration (Pourakbar et al., 2022).

4.3. Fenton oxidation

The Fenton reaction is an attractive and straightforward oxidative technique due to the strong oxidizing ability of the mixture of H₂O₂ and ferric ions, which effectively decomposes numerous hazardous

pollutants with less input of toxic reagents (Fenton and Kim, 2013). The continuous production of •OH and •OOH in this reaction enables indiscriminate oxidation of metal-organic complexes at a low cost and a simple operation process. The activation of H₂O₂ by high valent cationic species (Fe²⁺, Co²⁺, etc.) generates •OH in Fenton or Fenton-Like oxidations, which have been widely employed for effective decomplexation of metal-organic complexes without selectivity (W. Sun et al., 2022). Homogeneous and heterogeneous catalysts play a crucial role in these reactions. For instance, iron-based catalysts such as FeNx/g-C₃N₄, iron ore like hematite, and loaded iron types like Fe₂O₃/CuO/γ-Al₂O₃ can activate H₂O₂ through chain reactions to generate •OH. Xie et al. (2019) synthesized oxygen vacancies-based Cu-Doped Fe₃O₄@g-Al₂O₃ catalyst using a Fenton-Like reaction for the degradation of Ni(II)-EDTA, which exhibited excellent Fenton-Like activity even in neutral or alkaline conditions. Sashkina et al. (2016) utilized Fe-silicalite nanocrystals along with added H₂O₂ to achieve a 27.0 % removal rate of Co⁶⁰ from the Co⁶⁰-EDTA solution. Wang and his co-workers reported that microwave irradiation can improve the •OH radical generation for Ni(II)-EDTA degradation while accelerating ferric speciation transformation from ionic oligomeric species to high polymeric species within 10 min and achieving 94.0 % decomplexation efficiency (Wang et al., 2020). Jiang et al. (2023) employed a mixture of magnetic biochar derived from phoenix tree leaves and FeSO₄·7H₂O to activate H₂O₂ for the decomposition of Cu(II)-EDTA, achieving a breaking efficiency of 78.5 %. Some advantages of the Fenton reaction include its ability to function with reduced H₂O₂ as an oxidant, eliminating the requirement for additional electric energy, light energy, or other forms of energy. Despite utilizing Fenton oxidation for metal-organic complex decomposition, challenges such as excessive alkali requirement, hazardous sludge production, and side reactions persist. Among them, alkaline precipitation is inevitably required to neutralize the solution and/or remove heavy metal ions in compliance with discharge standards (e.g., Ni²⁺, Co²⁺, iron filings).

4.4. Influence of the initial pH on Fenton oxidation

The variation in the decomplexation efficiency of the Fenton reaction is primarily influenced by two main factors: hydrogen peroxide concentration and iron speciation, both of which are sensitive to changes in solution pH (Patil et al., 2023). Due to the redox potential of •OH is higher under acidic conditions (E₀ = 2.7 V) compared to alkaline conditions (E₀ = 1.8 V) and the chemical equilibrium model of Cu(II)-EDTA at lower pH using Visual MINTEQ (version 3.1). The formation of CuH₂EDTA and CuHEDTA⁻ in an acid environment enhances their reactivity with •OH through hydrogen abstraction, thereby improving decomplexation efficiency. However, excessive Fe²⁺ content contributes to chemical waste generation and the formation of the complex species [Fe(II) (H₂O)₆]²⁺ at pH < 3 (Ren et al., 2021). Conversely, when the pH of the solution exceeds 3, the effectiveness of the Fenton reagent diminishes due to the presence of relatively inert iron oxyhydroxides and the creation of iron precipitates in the form of hydroxide derivatives, specifically Fe(OH)₃ (Liu et al., 2021b). Consequently, this results in a lower concentration of free Fe ions, leading to the reduced generation of

•OH. Moreover, at higher pH levels, an accelerated auto-decomposition of hydrogen peroxide into water and gaseous byproducts (Table 2) and hydroxyl ions (OH⁻) may react with •OH to inhibit the formation of reactive species (Table 2).

4.5. Persulfate oxidation

Another important approach to effectively remove metal-organic complexes from wastewater and facilitate their subsequent removal is SO₄⁻-mediated AOPs, or persulfate oxidation. Researchers have found that the key to degrading refractory heavy metal-organic complex pollutants is to activate PDS/PMS (L. Wang et al., 2019). In other words, solely exerting PDS/PMS with an electrode potential of 2.01 V is not sufficient to degrade most heavy metal-organic complexes (Han et al., 2015). Therefore, various methods and materials combined with PDS/PMS to generate SO₄⁻ have been reported, such as radiolysis, photolysis, heat treatment, heavy metal oxides, transition metals like Co(II), Fe(II), Ni(II), Mn(II), Fe(III), etc. The generated SO₄⁻ readily reacts with unsaturated bonds and exhibits better performance over a wide pH range, thereby achieving partial or complete mineralization.

Hong et al. (2022) reported that the synergistic effect of alkali-activated PDS with CuO showed excellent reusability and long-lasting catalytic activity in decomposing Cu(II)-EDTA complexes. Experimental results demonstrated nearly complete removal of Cu(II) through synergistic effects at pH = 11 after 2 h of decomplexation. Z. Xu et al. (2020) investigated the use of Co²⁺ as an activator for PMS in degrading 0.3 mM Cu(II)-EDTA complexes, resulting in about 90 % release of Cu ions within 120 min. Lee and his co-workers demonstrated that PMS-based Co(II)-EDTA decomplexation was superior and more environmentally friendly than the Fenton reaction, the removal efficiency of Co (II) ions was 99.3 %, while the TOC removal efficiency was 81.5 % (Lee et al., 2022).

Liu et al. (2022a) concluded that non-thermal plasma, activated by endogenous PDS, effectively decomposed Cu(II)-EDTA with the destruction of Cu—O and Cu—N bonds, resulting in a decomplexation efficiency of 95.3 %. Wang et al. (2022) observed a decomposition efficiency of 96.6 % for Cu(II)-EDTA and a complete reduction of Cr(VI) within 90 min using the PDS/formate system at pH = 3.6, achieving simultaneous decomplexation of Cu(II)-EDTA and reduction of Cr(VI). Zu et al. (2022) prepared Ti₃C₂T_xMXene which exhibited high catalytic performance in enhancing the production of SO₄⁻ and •OH, enabling self-catalyzed decomplexation to remove Cu(II)-EDTA complexes.

4.6. Effect of the initial pH on persulfate oxidation

The solution pH is a critical reaction parameter for PMS/PDS activation as it determines the types of reactive species that play a significant role in the reactor and influence the reactions and equilibria. Several studies have reported on the generation and impact of SO₄⁻ under different pH conditions. In an acid environment, activating PMS to produce sufficient SO₄⁻ and •OH for effective oxidative decomplexation of metal-organic complexes was challenging. H⁺ plays a role in SO₄⁻ scavenger by a rather steady reaction (Table 2). However, increasing solution pH promoted hydrolysis reaction of heavy metal ions leading to the formation of hydrolysates, which activated PMS and significantly improved decomplexation efficiency effectively. It has been demonstrated that NiOH⁺ possesses the ability to activate PMS (Lu et al., 2022). When the solution at pH above 10.0, the production of ¹O₂, O₂⁻, SO₄⁻, and •OH was facilitated (Table 2), which can be advantageous for the decomposition of metal-organic complexes through selective and non-selective oxidation processes. Additionally, compared to protonated Cu complexes, complete deprotonation of CuEDTA³⁻ and CuEDTA²⁻ at alkaline conditions requires higher energy consumption when reacting with reactive species. Therefore, side-effect reactions (Table 2) occurred to hinder the decomplexation process when pH exceeds 12.0 during

alkaline activation.

4.7. Synergy of different advanced oxidation processes

Prominent synergetic methods that have gained widespread application in recent years include ultraviolet/H₂O₂, ultraviolet/Cl₂, O₃/H₂O₂, O₃/ultraviolet, O₃/PMS, and other methods. These methods offer the advantage of complementarity in decomposing heavy metal-organic complexes. The key advantages of hybrid methods treating such complexes are their synergistic effects, moderate technological conditions, user convenience, flexibility, low cost, and less energy consumption (Du et al., 2023). The feasibility of synergetic technologies has been demonstrated through experiments with various artificial wastewater types containing target compounds such as Cu(II)-EDTA, Ni(II)-EDTA and Co(II)-EDTA (Adam et al., 2022), resulting in a multitude of outcomes that enable the regulation of suitable operating parameters for complete decomposition and resource recovery from actual effluents (Bokare and Choi, 2014; Epelle et al., 2022).

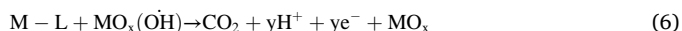
One intriguing feature of combining different advanced oxidation processes is their ability to operate over a wide pH range without requiring strict regulation or continuous control of acidity/alkalinity. Zhao et al. (2014) reported that coupling photo-electrocatalytic oxidation with electrodeposition not only decomposed Cu(II)-EDTA but also exhibited high performance in recovering Cu²⁺. Integrating degradation methods with water-splitting processes not only recovers heavy metal elements from organic complexes but also produces clean energy sources like hydrogen (H₂) or oxygen (O₂), thereby reducing carbon emissions (Z.J. Chen et al., 2022). Several other factors including decomplexation efficiency, dominant reactive species, and optimal pH were summarized in Table 3. Despite these aforementioned benefits, some limitations still exist that hinder industrial applications (Bertolini et al., 2021). Apart from inadequate duration and excessive expenditure of certain catalysts and reagents, AOPs suffer from inherent deficiencies such as side-effect reactions and mass transport limitations, which impede the decomplexation of heavy metal-organic complexes (Garcia-Rodriguez et al., 2020).

4.8. Electrochemical advanced oxidation

Electrochemical advanced oxidation methods, characterized by their catalytic activity, oxygen evolution potential, and electrochemical performance, have emerged as a highly influential technology for pollutant degradation. The decomplexation of heavy metal-organic complexes is primarily determined by direct oxidation and indirect oxidation (Zhuo et al., 2022).

4.8.1. Direct oxidation

Direct oxidation refers to the reaction between pollutants and electrons at the anode surface, resulting in their conversion into various simple organic compounds (Eqs. (4)–(7)) (Shestakova and Sillanpaa, 2017). The efficiency of direct oxidative degradation depends on both the nature of the pollutants and the generation of reactive species on the anode surface. For instance, Ni(II)-EDTA has been effectively degraded through anodic oxidation near the anode surface via its interaction with •OH radicals generated during water splitting (Sun et al., 2023).



H.L. Xu et al. (2022) successfully decomposed Ni(II)-EDTA using a dual mixed heavy metal oxide/Fe anode system, which not only reduced chlorinated intermediates' toxicity but also exhibited high removal

Table 3

Predominant reactive substances, decomplexation efficiency, heavy metal icon removal rate, TOC removal rate, energy efficiency, and energy consumption on metal-organic complexes decomposition based on different advanced oxidation processes.

Type of pollutant	Complex	Initial concentration	Optimal pH	TOC (mg/L)	Methods	Predominant reactive substances	Decomplexation efficiency (%)	Heavy metal icon removal rate (%)	TOC removal rate (%)	Energy efficiency (g/kWh)	Energy consumption (kWh/m ³)	Ref.
Model compound	Cu(II)-EDTA	0.2 mmol/L	9.3	\	Bicarbonate-activated hydrogen peroxide/chemical precipitation	\dot{O}_2^-	92.0 % in 60 min	68.3 %	78.4 %	\	\	T.C. Wang et al., 2019
Model compound	Cu(II)-EDTA	1000 mg/L	2	\	Discharge plasma oxidation and alkaline precipitation	$^1O_2, \dot{O}_2^-, O_3,$ and $\cdot OH$	99.6 % in 60 min	78.1 %	82.1 %	0.62	\	Wang et al., 2018
Model compound	Cu(II)-EDTA	0.3 mmol/L	3	31.71	Electron beam irradiation accompanied with autocatalytic Fenton-like	$\dot{O}_2^-, \cdot OH$	99.0 % in \ min	98.5 %	52 %	\	\	Zhao et al., 2023
Model compound	Cu(II)-EDTA	0.05 mmol/L	\	\	Glow plasma electrolysis	$\cdot OH$ and $\cdot H$	87.0 % in 90 min	64.0 %	30.0 %	\	1.80	Liu et al., 2022b
synthesized wastewater	(Cu(II), Ni(II))-EDTA	3440 mg/L (COD)	3 and 6	\	Fenton/ozone-based oxidation and coagulation processes	\	\	99.7 % of Ni ²⁺ and 99.72 % of Cu ²⁺	\	\	\	Nguyen et al., 2021
Model compound	Cu(II)-EDTA	0.30 mmol/L	8	\	Ultraviolet/chlorine	Cl ⁻	~70 % in 15 min	~60 %	70 %	\	\	Huang et al., 2019
Model compound	Cu-citrate	0.30 mmol/L	6	\	Non-woven cotton fabric-based	$\dot{O}_2^-, \cdot OH$	\	94 % in 5 h	\	\	\	Ye et al., 2022
And real water	tap water	0.3 mmol/L	6	\	intimacy coupling of photocatalysis and biodegradation system	$\dot{O}_2^-, \cdot OH$	\	81.3 % in 5 h	55 %	\	\	
	Yangtze River water	0.3 mmol/L	6	5.05		$\dot{O}_2^-, \cdot OH$	\	83.9 % in 5 h	55 %	\	\	
Model compound	Cu(II)-EDTA	0.3 mmol/L	\	\	Cu-mediated photo-Fenton reactions	$\cdot OH$	\	77.2 %	\	\	\	Zhang et al., 2019
Model compound	Cu(II)-EDTA	0.1 mmol/	5.5	\	Multifunctional piezoelectric heterostructure of BaTiO ₃ @Graphene	$\cdot OH, h^+$	100 % in 180 min	~64.8 %	~10.0 %	\	\	Pan et al., 2019
Model compound	Cu(II)-EDTA	0.30 mmol/L	4	\	Photocatalytic decomplexation by MIL-53(Fe)	$\cdot OH, ^1O_2, h^+$	~91 % in 60 min	\	64 %	\	\	S.T. He et al., 2021
	Fe(III)-EDTA						82 % in 120 min	\	\	\	\	
	Ni(II)-EDTA						87 % in 120 min	\	\	\	\	
Model compound	Cu(II)-EDTA	0.3 mmol/L	2-4	\	Non-thermal plasma coupled with Fe/C micro-electrolysis	$\cdot OH, \dot{O}_2^-, ^1O_2$	\	~100 % in 10 min	64 %	0.67	\	Liu et al., 2022a
Model compound	Cu(II)-EDTA	0.3 mmol/L	\	\	Ag/AgCl modified MIL-53(Fe) under Xe lamp	h^+	93 % in 120 min	\	60 %	\	\	T. Li et al., 2023
Model compound	Cu(II)-EDTA		1-12	\	Nanoscale zero valent iron	$\dot{O}_2^-, \cdot OH$	99 % in 10 min	70-90 %	~70 %	\	\	Zou et al., 2023
Model compound	Cr(III)-EDTA	10 mg/L	3	\	Al-containing ferrihydrite	\	99.8 % in 60 min	\	85.72 %	\	\	Zhang et al., 2022

efficiency for Ni²⁺, achieving 98.41 % removal after further alkaline precipitation. Lian and his co-workers, in their investigation on the effects of anode geometry on electrochemical degradation, found that reducing electrode aperture size enhanced Ni(II)-EDTA degradation rate by up to 1.4 times due to increased mass transfer rate from bulk solution to electrode surface (Lian et al., 2023). It should be noted that only pollutants located near the electrode surface can undergo direct oxidative degradation; thus, this process is influenced by mass transfer efficiency.

4.8.2. Indirect oxidation

Indirect oxidation refers to the anodic reaction that produces substances with strong oxidation properties such as M(•OH), •OH, MO, O₃, ClO⁻, H₂O₂ on the surface of the anode. These substances can decompose metal-organic complexes in wastewater and ultimately reduce the toxicity of pollutants (Song et al., 2010). Zhao et al. (2022) observed complete complexation between Cu(II) and EDTA in a three-dimensional electrolysis system, which facilitated EDTA degradation and achieved a high TOC removal efficiency of 86.2 %. Rong and her colleagues investigated the degradation of Ni(II)-EDTA complexes using PbO₂-Bi electrodes. They observed minimal electrode deterioration and lead leakage after 160 h of electrolysis, indicating that PbO₂(•OH) could enhance Ni(II) removal efficiency (Rong et al., 2022).

Sun and his coauthors studied the degradation performance of an innovative Ni-doped PbO₂ anode, which exhibited excellent electrochemical oxidation activity with a Ni(II)-EDTA removal efficiency of 96.5 ± 1.2 % (Y. Sun et al., 2022). The removal efficiency of Ni(II)-EDTA in the 3D-Electro-Fenton system, utilizing granular activated carbon to generate free •OH, was observed to reach 84.89 % after 120 min at a pH value of 7.0 by Peng et al. (2022). It is worth noting that EAOPs can significantly impact metal-organic complex treatment within a relatively short period; however, researchers have invested considerable effort into preparing electrode materials through doping and modification processes, making it necessary to consider cost-effectiveness and energy consumption when applying these methods to real wastewater treatment.

4.8.3. Electro-flocculation

The electro-flocculation process is an alternative method to treat wastewater containing metal-organic complexes. In this process, an electric field is applied to the electrolyte solution with a soluble anode, typically made of iron (Fe) or aluminum (Al), which generates heavy metal cations in situ (Sun et al., 2021). These cations react with -OH ions produced by water electrolysis at the cathode, resulting in the formation of heavy metal hydroxide and polyhydroxy complexes that form flocculation on top of the reactor. Consequently, pollutants can be settled and removed. The newly formed floc contains abundant surface •OH groups that facilitate aggregation with pollutant particles through electrostatic adsorption and coordination complexation. Some dense flocs settle at the bottom of the electrolytic cell while others float to the top due to hydrogen gas generated by the cathode, achieving solid-liquid separation.

Xie and his co-workers elucidated the decomplexation mechanism involving the reduction of Cu(II)-EDTA to Cu(I)-EDTA under anoxic conditions and pH regulation, primarily precipitating Cu(I) as Cu₂O (Xie et al., 2023). Song and his co-workers combined electrooxidation and electrocoagulation reactors for direct charge transfer, chemisorption of M(•OH), and production of active chlorine species on the anode surface to decompose Cu(II)-EDTA effectively with a copper ion recovery rate reaching 99.85 % (Song et al., 2022). In practical applications, electro-flocculation is commonly employed in major industrial facilities. However, it should be noted that the continuous utilization of electro-flocculation leads to gradual consumption of the anode plate and subsequent formation of a dense oxide film on its surface, as well as precipitation of heavy metal hydroxides throughout the entire process. Consequently, this phenomenon ultimately results in a reduction in

flocculation efficiency (Guan et al., 2018).

4.9. Influence of pH in EAOPs

At the optimal pH, metal-organic complexes not only exhibit favorable species distribution and excellent decomplexation but also enable reactive species to fully realize their potential in EAOPs. Specifically, pH influences (1) the relative concentrations of reactive species, (2) the oxidation potential of ¹O₂, O₂⁻, SO₄⁻ and •OH varies with increasing pH and leads to undesired reactions such as oxygen evolution potential and hydrogen evolution reaction (Eqs. (8)–(9)). One widely acknowledged viewpoint is that protonated forms are more easily oxidized by reactive species during decomplexation (Jiraroj et al., 2006; Guan et al., 2018). For instance, when using Ti³⁺ self-doped TiO₂ nanotube array anode for decomplexation, NiHEDTA⁻ predominates at pH = 2.0–3.5 while Ni-EDTA²⁻ becomes the major species through deprotonation at pH = 5.0–11.0 (Zhang et al., 2021). However, achieving complete mineralization of heavy-metal organic complexes may lead to reduced mass transfer and increased energy consumption over time. Nitrogen mineralization efficiency has become increasingly important in many countries due to eutrophication and ecological imbalances of water bodies (Amirkolaie, 2011).



5. Recovery methods

Recently, significant attention has been focused on the electrochemical degradation and resource recovery of real wastewater, with a particular emphasis on the electro-deposition and electro-adsorption of heavy metal ions as a promising long-term research objective (Liu et al., 2021a). By leveraging the effects of both anode and cathode, the degradation and recovery of heavy metal-organic complexes can be achieved in a single-step operation.

5.1. Electrochemical resource recovery

Depending on different deposition potentials, deposits formed at the cathodes include heavy metals, heavy metal (hydro)oxides, or heavy metallic alloys (Fig. 3). The underlying mechanism involves exploiting electrostatic interactions between the heavy metal-organic complexes and electrode materials to reduce their distance from each other. Consequently, released heavy metals through electrochemical oxidation can be deposited for subsequent recovery and reutilization.

Hu et al. (2022) reported the successful utilization of fixed bed Ni/GO-PAC particle electrodes as a carrier for Cu(II)-EDTA decomplexation via applied electrocatalysis; experimental results demonstrated over 94 % recovery efficiency in forms of Cu⁰ and Cu²⁺. M.Q. Li et al. (2022) employed an electrochemical strategy to treat a 10 mg/L solution of Cu(II)-EDTA in 1.0 M sodium tetrapolyphosphate electrolyte (Na₆TPP). They achieved decomplexation rates exceeding 99.9 % within 8 h, with high-efficiency in situ deposition of recovered Cu ions onto carbon cloth cathodes. Ganzoury et al. (2022) investigated mixed industrial wastewater treatment performance using IrO₂-RuO₂ mixed oxide anodes; although organic content reduction was minimal, Fe reduction rates reached up to 96 % while arsenic (As) reduction rates were approximately 30 %. Similar results were illustrated by recovering Cu ion using electrolysis-O₃-graphite felt-Ti and tunability as much as 90 % in the cathode of graphite felt-coated Ti mesh (Chen et al., 2021). Zhao and co-workers not only studied the oxidation of Cu(II)-EDTA but also recovered Cu(II) by electrodeposition simultaneously (Zhao et al., 2013).

Sun and his coauthors reported that developing a mathematical kinetic model could effectively describe the removal behavior of Ni(II)-

EDTA in the recovery of Ni ions, where Ni²⁺ was subsequently deposited onto the cathode as Ni⁰ (Sun et al., 2023). Yin et al. (2022) reported on a novel electrochemical adsorption method combining an ion exchange membrane with a flow electrode to remove Cu from industrial wastewaters containing Cu(II)-EDTA and Cu(II)-CA, achieving sewage recycling and resource recovery within 75 min. These findings demonstrate that synergistic treatments reduce chemical usage and minimize the generation of secondary pollutants, providing an environmentally friendly approach to decomposing heavy metal-organic complexes and recovering heavy metal elements from wastewater. However, it should be noted that although electrodeposition has satisfactory effects, higher cell voltages result in lower cathode current efficiency, leading to relatively larger power consumption (Wu et al., 2023).

5.2. The limitations and future developmental direction

The current electrochemical treatment of metal-organic complexes faces several technological challenges, including the high cost of electrode materials, expensive equipment, significant energy consumption, and overall high processing costs. Moreover, controlling the by-products and managing the strong toxicity of certain intermediate products remains an issue. To address these challenges, future research in electrochemical treatment should focus on the development of high-performance electrodes. The goal is to enhance the efficient utilization of electrons and improve the selectivity of the reaction. By designing and engineering electrodes with improved catalytic properties and selectivity, the overall performance of electrochemical treatment processes can be enhanced. This would lead to reduced cost, energy consumption, and the generation of unwanted by-products. Additionally, the development of advanced electrode materials and innovative electrode configurations can help overcome the limitations associated with the current technology, paving the way for more efficient and sustainable electrochemical treatment of metal-organic complexes.

6. Effect of coexistent ions

An argument that has sparked extensive debate in recent years is the treatment of real industrial wastewater containing inorganic ions and natural organic matter. The presence of co-existing ions always exerts a significant synergistic and/or competitive effect on the generation of reactive species and the decomplexation of heavy metal-organic complexes, thereby influencing the practicality of different methods. Consequently, considerable attention has been paid to investigating the synergistic and/or competitive effects of anions and cations in various decomplexation methods. The presence of coexisting ions such as carbanion (CO₃²⁻), nitrate ion (NO₃⁻), phosphate anion (PO₄³⁻), Cl⁻, sodium (Na⁺), SO₄²⁻, Fe²⁺ and organic matter leads to diverse impacts on the concentration and speciation of reactive species, degradation efficiency, mechanism, pathway, as well as low-complex formation during different treatment processes.

6.1. Effect of inorganic anions ions on AOPs

As for the persulfate oxidation, 2 mM hypophosphite ion (H₂PO₂⁻) could cause a noticeable inhibitory effect on the Ni removal during the degradation process of Ni(II)-citrate acid by PMS with nickel. Previous studies have shown that H₂PO₂⁻ can scavenge reactive species, particularly •OH (Eq. (10)), which could explain this inhibition effect. However, when 2 mM bicarbonate ion (HCO₃⁻), phosphite ion (HPO₃²⁻), and pyrophosphate ion (P₂O₇⁴⁻) were introduced into the system, it significantly enhanced decomplexation efficiencies while also improving PMS utilization rates (Lu et al., 2022). Nevertheless, it should be noted that high concentrations of HCO₃⁻ may compromise decomplexation efficiency inevitably.



The impact of common coexisting anions on Fenton reaction was studied by introducing 10 mM concentrations of HCO₃⁻, CO₃²⁻, SO₄²⁻, and H₂PO₄⁻ during degradation of Cu(II)-EDTA complex. HCO₃⁻, H₂PO₄⁻, and CO₃²⁻ with a high affinity to the Lewis acids would perform the function of the •OH radical scavenger (Eqs. (11)–(13)), which disfavored heavy metal-organic complexes decomposition and Cu elimination efficiency. On the other hand, little inhibition can be seen in the addition of SO₄²⁻. A reasonable explanation is that SO₄²⁻ is conducive to the generation of SO₄⁻ that makes a synergic effect in the process (Zhu et al., 2021).

HCO₃⁻, CO₃²⁻, NO₃⁻ and Cl⁻ were selected by Zhao and his colleagues to examine if the electron beam irradiation accompanied with autocatalytic Fenton-like effect could improve the decomplexation efficiency (Zhao et al., 2023). Their experiments showed the sequence of inhibition effects as CO₃²⁻ > HCO₃⁻ > H₂CO₃. Furthermore, the Cl⁻ had an inferiorly inhibitory effect compared with HCO₃⁻ and CO₃²⁻, because Cl⁻ mostly tended to form dichloride anion radical (Cl₂⁻), which can be combined with heavy metal ions and form stable complexes to resist the attack of some oxidants. The generated ClO₃⁻ and ClO₄⁻ have potentially negative effects on human health and sometimes can even inhibit performance of some treatment processes (T.C. Wang et al., 2019; Gulcin, 2020).



For photocatalytic decomplexation, He and his co-workers investigated the influence of inorganic ions and organic matter on Cu(II)-EDTA decomplexation (S.T. He et al., 2021). The degradation efficiency varied from the concentration of humic acid. Compared with Cu(II)-EDTA, the humic acid with low redox potential (E₀ = 0.7 V) had more superiority to •OH thus contributing to the inhabitation effect. Alternatively, the NO₃⁻ could be decomposed under the ultraviolet light to produce •OH that enhanced the degradation efficiency (Eq. (14)). Unfortunately, the generation of HNO₃ would hinder Cu(II)-EDTA decomplexation because the competitive reaction (Eq. (15)).



Compared to the treatment with the original solution, Hu et al. (2022) illustrated that there is no significant difference in decomposing Cu(II)-EDTA by the addition of SO₄²⁻ and Cl⁻ during the electrocatalytic degradation of Cu(II)-EDTA. Furthermore, NO₃⁻ and CO₃²⁻ were most likely to put a negative effect on the electrocatalytic decomplexation of Cu(II)-EDTA. Mostly because NO₃⁻ could consume active sites. Not only CO₃²⁻ can decrease the decomplexation of Cu-EDTA, but also it influences the composition of the electro-deposition substance. Zhang et al. (2021) reported that [Ni(OH)₂]_{0.75}[H₂O]_{0.16}[NiCO₃]_{0.09} was produced when the endogenous carbonates were put into the solution. The effect of Cl⁻ has dual characteristics in electrochemical degradation reactions which differs from the performance in AOPs. When the heavy metal-organic complexes are actually under the environment of Cl⁻, it might improve the decomplexation because reactive chlorine species, such as HClO, Cl[•], and Cl₂⁻, can be produced by activation of PMS, •OH, and SO₄⁻ (H.L. Xu et al., 2022). Hence, the presence of Cl⁻ slightly promoted the decomplexation of Ni(II)-EDTA in the 3D-electro Fenton system. Cl⁻ generated Cl₂ through chlorine evolution at the anode (Table 2), which was further hydrolyzed to form strongly oxidized ClO⁻ and then promoted the removal of Ni-EDTA (Peng et al., 2022).

6.2. Effect of inorganic cations ions on AOPs

As for cations, the effects of heavy metal ions mostly depend on their stability constants with ligands. The coexisting heavy metal ions might get swapped with the initial heavy metal ions by replacement reactions (Eq. (16)), which results in a change in speciation distribution (Shahedi et al., 2020). With the addition of the heavy metal ions, a fraction of the ligand was complexed with heavy metal ions with diverse complexation stability constants and lost its activity for the original chelate.



7. Conclusion and prospects

The high solubility and stability of heavy metal-organic complexes in a wide pH range pose significant threats to aquatic ecosystems, soil environments, and human health through various pathways. Therefore, the treatment of metal-organic complex wastewater is an important problem that needs to be solved urgently in the current environmental problems.

The spatial disposition and arrangement of ligands play a pivotal role in modulating the establishment and cleavage of coordination bonds with metal ions. Consequently, a comprehensive comprehension of the attributes and spatial orientation of metal-organic complexes facilitates a nuanced analysis of the interplay between the reactivity exhibited by these complexes and their molecular structure and spatial configuration. This understanding serves as a foundational framework for discerning the potential impact on the efficacy of advanced oxidation techniques. By leveraging this knowledge, the screening process for advanced oxidation techniques can be refined, potentially enhancing their efficiency in expediting the breakdown reactions and augmenting the removal rates of metal ions within these complexes. The decomplexation mechanisms of advanced oxidation involving free radicals and non-free radicals (O_3 , $\cdot OH$, SO_4^- , 1O_2 , and O_2^-), the influence of different pH and co-existing substances (CO_3^{2-} , NO_3^- , PO_4^{3-} , Cl^- , Na^+ , SO_4^{2-} , Fe^{2+} and organic matter) empower researchers to judiciously select the most fitting approach by specific circumstances, thereby realizing the objectives of environmentally conscious practices, minimal energy consumption, and cost-effectiveness. While these processes hold the potential to treat heavy metal-organic complexes and recover metal resources with promising results in mechanism research and experimental properties, there are still challenges to be addressed in practical engineering applications.

- (1) The identification of the ratio between ligands and metals in real industrial water.

Until now, the identification of ligands and metals in metal-organic complexes within a real wastewater matrix has posed a challenging problem. Industrial wastewater is characterized by its diverse types and complex components, including non-metallic elements with abundant electrons that exhibit strong bonding abilities. Consequently, the ratios between metals and non-metallic elements vary significantly, as exemplified by $[C_{30}H_{17}O_{11}N_3NiS_7]^-$ and $[C_{11}H_{16}O_2N_3Ni]^-$. It is noteworthy to recognize the catalytic potential of certain metal-organic complexes and explore novel catalysts through processes such as the Fenton-Like reaction or electrochemical reduction of active metal intermediates. To explore the behavior characteristics of metal-organic complex pollutants in the treatment process, it is essential to analyze the water quality of the parent reaction and identify the types and forms of complex metals present in the system. Additionally, it is crucial to clarify the kinetics of the oxidation reactions involving metal-organic complex pollutants. By doing so, we can investigate the degradation mechanism of these pollutants through oxidation and validate the findings using advanced oxidation treatment processes implemented in

real water treatment plants. The research outcomes obtained from this study will contribute theoretical insights and empirical data to optimize the existing urban sewage treatment plants. Furthermore, it will provide valuable insights into the (advanced) oxidation treatment processes employed for raw water used for drinking purposes. The findings will also offer new ideas and methodologies for the advanced treatment and reuse of industrial wastewater containing a high load of complex metal pollutants.

- (2) Factors that affect selectivity for decomplexation.

The selective treatment and recycling of pollutants are crucial in addressing the different adaptation technologies required for various components present in real water quality environments. Additionally, considering the escalating carbon emissions associated with materials, reagents, and energy consumption during advanced oxidation processes and electrochemical advanced oxidation processes, it becomes imperative to incorporate selective pollutant treatment/recycling methods along with low-carbon/negative carbon selective processing strategies into future considerations.

- (3) Predicting the decomplexation performance by machine learning.

In the efficient elimination of metal-organic complexes, the utilization of machine learning stands as a promising tool to craft specialized functional materials that exhibit selective properties, thereby intelligently steering mechanisms for pollution control. Moreover, the amalgamation of visual tracking methodologies with density functional theory calculations serves to validate analyses of the breakdown reaction processes. Ultimately, an integrated approach involving a comprehensive mathematical model, bolstered by insights derived from thermodynamics, could facilitate the development of materials designed with the intent of predicting the performance outcomes in full-scale decomplexation processes under diverse operating conditions.

- (4) The reutilization of the metal resources.

The endeavor to reuse metal resources has been both meaningful and challenging. A multitude of catalytic materials have emerged as suggestions for electrocatalysts in the reduction of carbon dioxide (CO_2), marking a compelling exploration of the latest advancements. This pursuit delves deeply into the design evolution of catalysts, encompassing elements such as Cu, Zn, Mg, and Ru(II). These have been specifically tailored for the electroreduction of CO_2 . An intriguing development lies in the metal-based cathode formed by the electro-deposition of metal elements originating from metal-organic complexes could function as electrocatalysts in the reduction of CO_2 , thereby contributing to the reutilization of metal resources yielding valuable multi-carbon products. Moreover, the coupling of recovered metal elements with processes like hydrogen evolution reaction or oxygen evolution reaction holds promise in enhancing energy utilization within a well-conceived reactor setup. These attainable methodologies stand as pivotal pillars in the innovation of modern industrial wastewater treatment technologies and serve as a pathway to reduce carbon emissions.

CRedit authorship contribution statement

Wenhui Sun: Formal analysis, Methodology, Writing – original draft, Investigation. **Jiao Li:** Formal analysis. **Ziang Chen:** Formal analysis. **Shuwen Wang:** Formal analysis. **Eric Lichtfouse:** Writing – review & editing. **Hongbo Liu:** Conceptualization, Funding acquisition, Project administration, Writing – review & editing.

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.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

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