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Perspective

Redox regulation for sustainable water purification and risk management

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A B S T R A C T

Sustainable detoxification and advanced treatment of toxic organic pollutants (TOPs) in wastewater are essential for water reclamation and ecosystem security. Although biological treatment is a low-carbon and eco-friendly approach for TOPs degradation, its effectiveness is often limited by the high toxicity and recalcitrance of TOPs. Oxidative and reductive reactions can degrade TOPs according to their intrinsic redox potentials. However, conventional biological or chemical oxidation treatment often fails to efficiently or purposefully cleave key functional groups, which leads to unsatisfactory performance of biological reactions or excessive chemical oxidation costs. This perspective proposes redox regulation as a strategy to moderately catalyse the oxidation or reduction of TOPs and thereby generate low toxicity and increased biodegradable intermediates, which will improve subsequent biological treatment. We summarize strong redox regulation techniques, including advanced oxidation and reduction processes, and weak redox regulation through low-energy electrical potential, along with the corresponding mechanisms and applications. Additionally, we explore the integration of redox regulation with biological treatment, either in a sequential mode or *in situ*. This study emphasizes the need for future research to focus on targeted and durable catalytic detoxification processes and to optimize balancing the carbon footprint, process control, operational efficiency, and economic feasibility. By integrating chemical reactions with microbial metabolism, redox regulation has the potential to transform wastewater treatment from isolated process optimization to a holistic approach. This perspective advocates for innovation of conventional wastewater detoxification technologies to achieve sustainable water purification and ecological risk control.

1. Introduction

More than 204 million registered chemicals exist, and this number increases by millions annually [1]. Many synthetic chemicals, including antibiotics, pesticides, halogenated compounds, and organic nitrogen compounds, are classified as toxic organic pollutants (TOPs) [2]. These chemicals often enter the environment unintentionally through industrial discharge, agricultural runoff, and improper waste disposal [3]. Because of their complex chemical structures, featuring electron-withdrawing groups (e.g., nitro, azo, and halogen groups), and benzene or heterocyclic rings, TOPs are refractory, persistent, and bioaccumulative [4]. More critically, TOPs are a major source of emerging contaminants (ECs), which pose carcinogenic, teratogenic, and mutagenic risks to aquatic organisms and humans [5].

Biological treatment, which leverages microbial metabolism, is a widely used cost-effective technique for TOP removal. However, the inherent toxicity and refractory properties of TOPs can disrupt enzyme activity, alter the structures of extracellular polymeric substances, damage cell membranes, and inhibit microbial metabolic activity processes [6]. Moreover, the concentrations and types of TOPs also greatly affect the carbon and nitrogen conversion processes in activated sludge systems [7]. For instance, antimicrobial compounds such as triclocarban can inhibit the production of volatile fatty acids, NH_4^+ assimilation, nitrification, and denitrification

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processes [8,9]. Consequently, conventional biological treatments often fail to fully remove TOPs and they persist in treated effluent and enter receiving water bodies such as rivers, groundwater, and marine environments [10]. TOPs pose direct threats to aquatic ecosystems by inducing oxidative stress, reducing biodiversity, and impairing ecological functions. Additionally, TOPs contribute to the occurrence and spread of antimicrobial resistance in receiving water bodies [11]. Therefore, sustainable detoxification and advanced treatment of TOPs in wastewater are essential for water reclamation and ecosystem security.

Oxidative and reductive transformations are key processes in TOPs degradation that mitigate toxicity through dehalogenation, ring cleavage, and nitro reduction, and enhance bioavailability [12]. The thermodynamic feasibility of redox reactions depends on the functional groups and redox potentials of TOPs. Generally, heterocyclic compounds (e.g., pyrazine, 2.44 V vs. the standard hydrogen electrode [SHE]), aromatic amines (e.g., aniline, 0.42 V), and carboxylic acids favour oxidation reactions, while halogenated organics (e.g., 2,4,6-trichlorophenol, −0.27 V; florfenicol, −0.65 V, and perfluorooctane sulfonic acid, −2.0 V) and nitro/azo compounds (e.g., nitrobenzene, −0.36 V; alizarin yellow R, −0.56 V) are more susceptible to reduction [13–18]. From the intrinsic redox potentials and thermodynamic and kinetic favourability of TOPs, we propose redox regulation as a novel strategy to enhance the selective deconstruction of functional groups and detoxification of TOPs in wastewater (Fig. 1). Redox regulation involves creating strong oxidation/reduction by generating reactive free radicals, or weak oxidation/reduction. Weak redox regulation is defined as the application of an external voltage or electrode potential below the theoretical thresholds for the hydrogen evolution reaction (HER, −0.41 V vs. SHE, pH = 7) and the oxygen evolution reaction (OER, 0.82 V vs. SHE) [19]. Under these conditions, the system's current primarily originates from the degradation and transformation of TOPs, rather than from side reactions such as HER and OER. Strong oxidation regulation is defined as a standard electrode potential higher than O_3 (2.07 V vs. SHE), and the transition oxidation region is defined as an electrode potential between 0.82 V and 2.07 V, including $S_2O_8^{2-}$, H_2O_2, etc. Strong reduction regulation is defined as a standard electrode potential below H· (−2.31 V vs. SHE), and the transition reduction region is defined as an electrode potential between −0.41 V and −2.31 V, including HS^{2-}, $S_2O_3^{2-}$, etc. [20,21]. Acidic and basic conditions generally promote oxidation and reduction respectively, and the concentration of oxidants/reducing agents can be used to regulate the redox in actual reactions, according to the Nernst equation.

In this perspective, we outline two primary redox regulation strategies: strong redox interventions, which encompass advanced oxidation and reduction processes; and weak redox regulation, which involves the application of a small amount of electrical energy. These approaches enable targeted and moderate transformation of TOPs to improve their biodegradability and achieve synergistic enhancement of both physical and biochemical wastewater treatment processes. We examine the underlying mechanisms by which both strategies enhance the degradation and detoxification of TOPs, and further explore their application modes, including sequential combinations and *in situ* integration with biological treatment systems. Additionally, we highlight future research priorities focused on developing targeted and sustainable detoxification approaches that optimize trade-offs among the carbon footprint, process control, operational performance, and economic feasibility.

2. Mechanisms and strategies of redox regulation

The core mechanism of redox regulation involves constructing a thermodynamically and kinetically favourable reaction environment by applying external energy and catalysts. This redox potential-dependent transformation reduces molecular stability by breaking refractory functional groups and converting TOPs into bioavailable intermediates. This process alleviates biological toxicity and stimulates microbial metabolism, which ultimately bridges the energy barrier between TOPs degradation and subsequent biological treatment. According to the redox potential requirements of different TOPs, redox regulation strategies can be

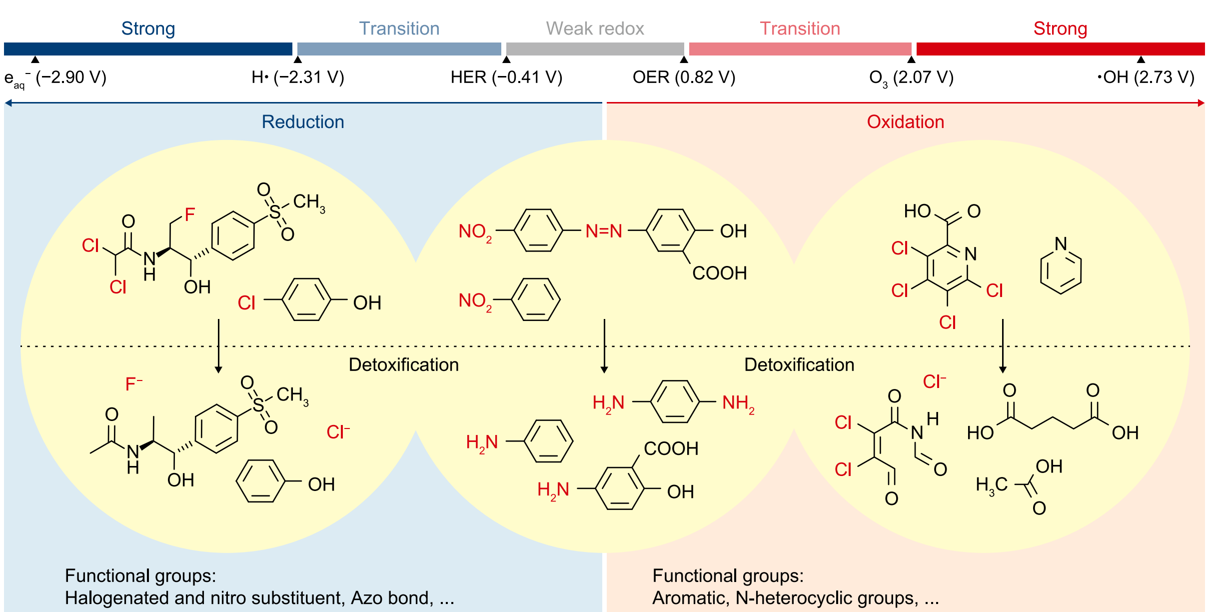

Fig. 1. Redox regulation for toxic organic pollutant (TOP) detoxification. Redox regulation involves creating strong reduction (<−2.31 V), strong oxidation (>2.07 V), or weak oxidation/reduction (−0.41–0.82 V). The selection between strong and weak redox regulation depends on the intrinsic redox potential of TOPs, as well as their thermodynamic and kinetic favourability of TOPs, aiming at specific functional group deconstruction. All the potential is against the standard hydrogen electrode (SHE). HER: hydrogen evolution reaction; OER: oxygen evolution reaction.

categorized into strong and weak redox regulation (Fig. 2).

2.1. Strong redox regulation

Advanced oxidation processes (AOPs) and advanced reduction processes (ARPs) are chemical treatments in which TOPs are oxidized or reduced by strong redox radicals. These active species can effectively attack electron-carrying groups or unsaturated bonds, and undergo substitution, oxidation–reduction, or elimination reactions to achieve mineralization or dehalogenation.

2.1.1. AOPs

AOPs degrade pollutants using active species such as ·OH and $SO_4\cdot^-$ [22]. Key to AOPs is the efficient production of ·OH, which acts as a non-selective oxidant with a standard electrode potential of 2.73 V vs. SHE and a rate constant between 10^7 and 10^{10} M^{-1} s^{-1}. Hydroxyl radicals tend to attack electron-rich functional groups and capture the hydrogen atoms of -NH_x, -OH, and -CH_x groups [23]. Sulfate radicals are usually generated in reaction systems using persulfate as an oxidant and have a standard oxidation potential of 2.60 V vs. SHE and a secondary rate constant between 10^5 and 10^9 M^{-1} s^{-1}. These radicals are relatively stable. They participate in selective reactions with organic molecules containing unsaturated bonds or delocalized π electrons through electron transfer [24].

Oxidants (mainly O_3 and/or H_2O_2) have been combined with different catalysts and/or radiation (ultraviolet [UV], sunlight, or artificial light) to generate multiple active species. Treatments such as O_3/H_2O_2, UV/persulfate, and Fe^{2+}/H_2O_2/UV provide great removal of pharmaceutical and personal care products, endocrine disrupting chemicals, polycyclic aromatic hydrocarbons, and other ECs [22,25,26]. Pollutants undergo various degradation processes, including demethylation, deamination, hydroxylation, dehydration, hydrolysis, ring opening, bond cleavage, and dehalogenation, to form transformation products, including organic acids, alcohols, ketones, aldehydes, carboxylic acids, and peroxides [20,27]. However, the transformation products of partial compounds such as nitrobenzene, quinolones, methomyl, *N*-nitroso-pyrrolidine, and *N*-nitroso-di-*n*-propylamine undergoing AOPs may have higher toxicity, for example, mutagenicity and estrogenic activity, than the parent compounds [26].

2.1.2. ARPs

Similarly to AOPs, ARPs combine various activation methods with reducing agents to produce reducing substances (e_{aq}^- and H·). Sulfite is a common reducing agent and is more efficient than other reducing agents (i.e., bisulfite, sulfide, and ferrous compounds) under UV catalysis because of its high yield of e_{aq}^- [12]. The e_{aq}^- are key active species in the reduction process, with a standard electrode potential of −2.9 V and a short half-life of 300 μs. These species exhibit extremely high reactivity towards halogenated compounds, unsaturated bonds, and a range of ketones [28]. The e_{aq}^- can decompose stubborn organic pollutants into compounds with simple chemical structures [29,30]. The oxidation–reduction standard potential of ·H (the conjugated acid of e_{aq}^-) is −2.3 V [31].

The e_{aq}^- generated during the UV/sulfite process can effectively decompose perfluoroalkyl and polyfluoroalkyl substances by defluorination, desulfonation, and breaking of the centremost C–C bond. This is difficult for AOP of ·OH and $SO_4^{\cdot-}$ [29,30]. More importantly, e_{aq}^- can greatly reduce the toxicity of halogenated TOPs and enhance their biodegradability by attacking C–*X* bonds (*X* = F, Cl, or Br) by dechlorination, defluorination, or removal of sulfomethyl group [32,33]. However, the effectiveness of ARPs in TOPs degradation is greatly influenced by the pH in the environment. Alkaline conditions are more conducive to generating hydrated electrons, whereas under acidic conditions, hydrated electrons are more likely to react with protons to generate ·OH with weak reducing abilities [12]. Additionally, water in enriched oxygen or containing other end electron acceptors (e.g., nitrate, nitrite, and O_2) can also remove e_{aq}^- [29].

2.2. Weak redox regulation

Electrical stimulation through weak electrical energy intervention (WEEI), a weak regulation strategy, involves the integration of solid electrodes into biological treatment systems and application of a minimal external voltage (<1.0 V). This is particularly effective for the reductive transformation of electron-withdrawing TOPs, such as nitroaromatic compounds and azo dyes [34–37]. Because of the activity of electroactive bacteria at the anode and the facilitation of extracellular electron transfer, the cathode can achieve more negative redox potentials, depending on the applied voltage. For instance, bioanodes may provide −0.16 V (vs. SHE) and cathodes can reach −0.66 V (vs. SHE) under a 0.5 V external voltage. Initial studies used bioanodes and chemical cathodes to reduce nitrobenzene to aniline [38,39]. Although abiotic cathodes offer thermodynamically favourable conditions for the reduction of nitroaromatics and azo dyes with typical redox potentials ranging from −0.06 to −0.26 V (vs. SHE), their reaction kinetics are often

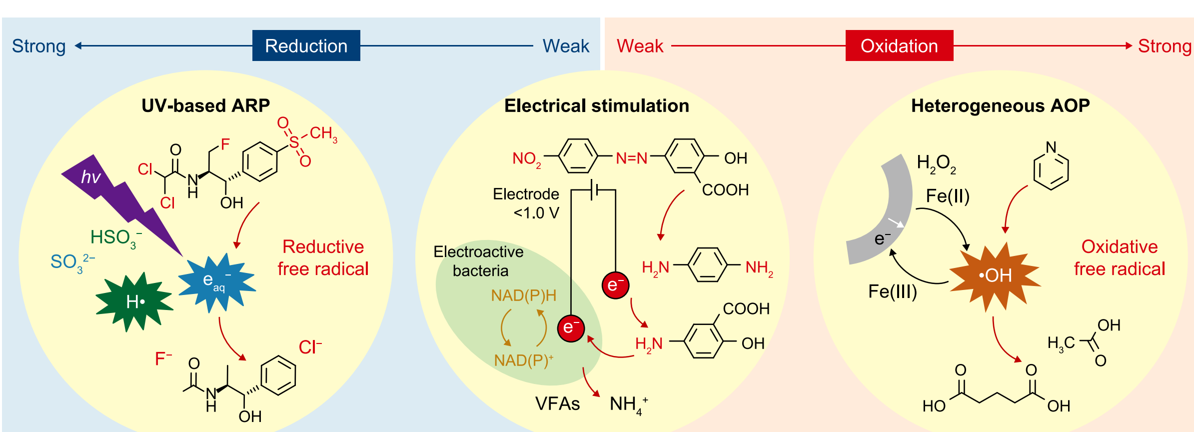

Fig. 2. Mechanisms and strategies of redox regulation for toxic organic pollutant (TOP) detoxification. Strong reduction/oxidation by generating reactive free radicals, such as hydroxyl radicals (·OH, 2.5–2.8 V), sulfate radicals ($SO_4\cdot^-$, 2.5–3.1 V), and hydrogen radicals (·H, −2.3 V) through various chemical reactions. Weak oxidation/reduction applyies a minimal external energy (<1.0 V). UV: ultraviolet; ARP: advanced reduction processes; VFAs: volatile fatty acids; AOP: advanced oxidation processes.

constrained in the absence of chemical catalysts on the cathode surface. By contrast, biocathodes can catalyse the reduction of TOPs by harnessing electrical energy to drive microbial respiration and ATP synthesis [40]. TOPs such as nitro/azo and halogenated organic compounds can act directly as electron acceptors in these systems, with biocatalytic enhancement resulting in increases of over twofold in the degradation efficiency [41]. Additionally, aniline, phenols, and carboxylic acids with weak oxidation potentials can act as electron donors and be readily oxidized at the anode, which produces intermediates such as volatile fatty acids and ammonia (NH_4^+). Although WEEI requires a small energy input and primarily relies on microbial metabolism, the use of modified electrode materials and redox mediators can further improve the performance by addressing the overpotentials inherent to electrode materials.

3. Application modes of redox regulation

In engineering practice, redox regulation achieves technical synergy with biological treatment through differentiated application modes. Free radicals cause inactivation and oxidative stress in microbial communities, and strong redox regulation (e.g., AOP) is applied as a pretreatment step in combination with biological processes to detoxify TOPs. Weak redox regulation is often integrated directly with biological treatment systems to enhance microbial metabolism and facilitate TOPs degradation while preserving system stability. These two modes establish a regulatory network gradient that transitions from chemical deconstruction via strong redox regulation to microbial activation through weak redox intervention. These approaches mitigate excessive carbon loss associated with over-mineralization during AOPs and also address the limitations of conventional biological treatments in transforming TOPs. Consequently, redox regulation demonstrates broad engineering applicability for the treatment of industrial wastewater, including from coking and pharmaceutical industries.

3.1. Combination of strong redox regulation with biological treatment processes

Combining advanced oxidation/reduction processes with biological treatment in a sequential batch reduces the material input, required residence time, and long-term water treatment costs. These changes should be balanced with optimizing the degradation efficiency of TOPs in the entire system.

3.1.1. Moderate oxidation and subsequent biotreatment

Pretreatment of most pollutants with AOPs can increase biodegradability and/or reduce toxicity [42]. This does not result in complete mineralization. Instead, the by-products formed after moderate oxidation are further biodegraded through subsequent biological treatment. Overall, this is a more cost-effective system than complete mineralization. Ozone, Fenton, or electrochemical processes are often used in the oxidation step [43]. These processes exhibit high removal rates (69−86%) for target TOPs in wastewater containing pharmaceuticals (e.g., sulfamethoxazole, amoxicillin, ampicillin, and tetracycline), insecticides (e.g., lindane, dichlorvos, and linuron), industrial compounds (e.g., polychlorinated biphenyls, bisphenol A, phthalates, and ethanolamine), and dyes, and greatly improve the biodegradability (>70%) [44]. These changes promote reactions in subsequent biological treatments (e.g., membrane reactors, fixed bed reactors, activated sludge, and biochar) and provide high removal rates (92−97%) for target pollutants [45].

Despite these positive findings, the nitrification system in biochemical treatment may fail to degrade TOPs if the wastewater toxicity exceeds the tolerance threshold, and the traditional Fenton process may fail because of the consumption of ·OH by halide ions. The heterogeneous Fenton process effectively avoids ion concentration at the reaction interface and enhances the reduction of Fe^{3+}, thereby restoring functionality to subsequent nitrification processes (Fig. 3a) [46].

3.1.2. Targeted reduction and subsequent biotreatment

Compared with AOPs, ARPs exhibit specificity in the dehalogenation of halogenated organic compounds. These processes selectively react with easily reducible substances instead of coexisting with easily oxidized organic compounds, which maintains the carbon source content at a high level [47,48]. The combination of UV/sulfite and biological processes is considered an effective method for treating wastewater containing high concentrations of toxic compounds [49,50]. A study on trichlorophenol showed that before entering biological treatment, ARP did not effectively mineralize pollutants but degraded and targeted dehalogenated parent pollutants through $\cdot SO_3^-$ and e_{aq}^-. The intermediates generated by UV/sulfite, such as 1,3-cyclohexadiene, 2-chloro-1-benzoquinone, 2-chlorophenol, benzene, 2-hydroxybenzoquinone, and cyclohexene, were simple organic compounds that were effectively biodegraded in subsequent biological treatments to ultimately achieve complete degradation of trichlorophenol and 98% dechlorination [51]. We obtained similar findings in our previous research on vacuum UV/UV/sulfite degradation of florfenicol (Fig. 3b) [33]. The dehalogenation rate for florfenicol was approximately 83.0%, the mineralization performance was 8.0%, and chemical oxygen demand (COD) removal was 1.1%, which enhanced the biochemical processing capability by providing sufficient bioavailable carbon sources. Moreover, the abundance of antibiotic resistance genes (55.4%) and the relative abundance of mobile genetic elements (e.g., integrons, 22.9%) caused by florfenicol stress were reduced before biological treatment. This decreased the risk of antibiotic resistance and antibacterial activity [33,52].

3.1.3. Economics of combined treatment

In practical engineering applications, the balance between cost and effectiveness determines the combination of processes, and depends on the type and concentration of wastewater. Optimizing the selection of the pretreatment processes and operating conditions reduces the cost and energy consumption of chemical treatment and also helps to shorten the treatment time. A treatment plant located in Singhöfen (Germany) has been in operation since 1994 using a combination of UV/O_3 and biological aeration-packed bed processes. This increases the biodegradability after ozone treatment and reduces ozone consumption, which decreases the overall treatment technology cost and ensures that emission requirements are met [53].

Combination with biological treatment is beneficial because only moderate oxidation−reduction needs to be completed in chemical treatment to achieve detoxification and a tolerable influent concentration for organisms. This reduces the consumption of chemical reagents and optimizes the system. In a combined process with the Fenton reaction, biological anaerobic filtration, and aerated biological filtration, the Fenton reagent dose decreased by 10% [54], but the COD reduction increased by 35%, compared with the single Fenton [55]. When using an O_3/H_2O_2 advanced oxidation process (USD 6.27 per ton) to treat leachate from garbage, the cost was reduced by approximately 24% compared with separate O_3 and H_2O_2 processes (USD 8.24 per ton) [56]. Multiple studies have shown that moderate chemical processes promote the removal of organic nitrogen and ammonia nitrogen and form the carbon source required for biological treatment [44,45,47,48],

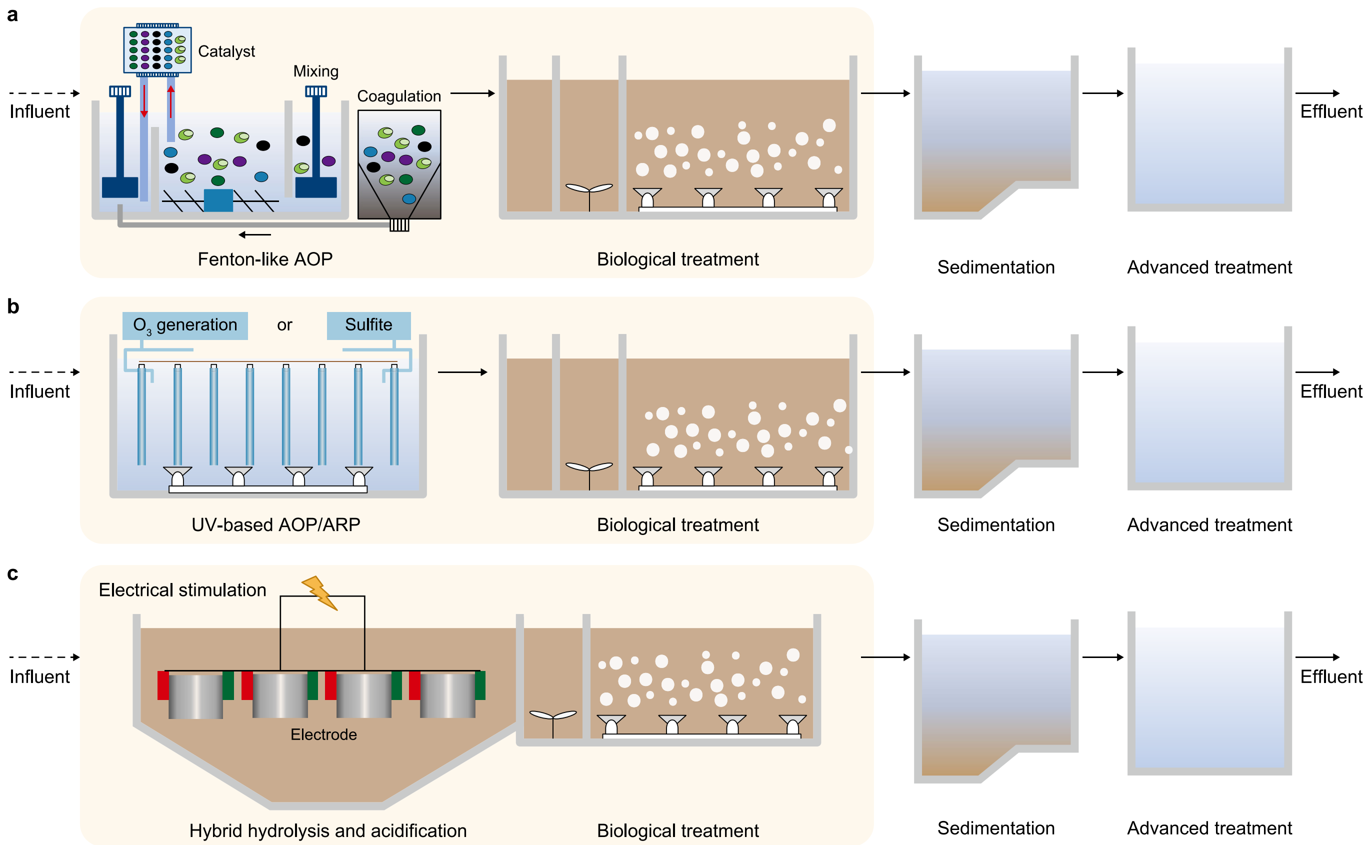

Fig. 3. Schematic diagram of sequential combination of strong redox regulation (**a**, Fenton-like AOP; **b**, UV-based AOP/ARP), and *in situ* integration of weak redox regulation with a conventional biological treatment process (**c**). AOP: advanced oxidation processes; UV: ultraviolet; ARP: advanced reduction processes.

which increase the potential benefits and reduce the actual costs.

3.2. Integration of weak redox regulation with biological treatment processes

The fundamental principle of weak regulation is to stimulate microbial metabolism and enhance bioavailability of TOPs. WEEI introduces electrodes into biological treatment systems to act as electron donors or acceptors to regulate redox potential and function as microbial selectors. This promotes the directional enrichment of electroactive bacteria on the electrode surface and organic-degrading microorganisms in the plankton, which enhances metabolic interactions that favour the detoxification of TOPs. Additionally, WEEI alters the composition of extracellular polymeric substances, which increases the proportion and polarization of electroactive proteins. These changes enhance extracellular electron transfer to further contribute to the efficient biodegradation of TOPs.

The *in situ* integration of WEEI with hydrolysis and acidification processes (hybrid hydrolysis and acidification) is a representative strategy for improving biological wastewater treatment (Fig. 3c). This integration process boosts the decolorization, detoxification, and dehalogenation of diverse TOPs in wastewater, alleviates their inhibitory and toxic effects on the microbial community, and overcomes the rate-limiting constraints of conventional hydrolysis and acidification processes [57]. In a pilot-scale test, we evaluated the performance of hybrid hydrolysis and acidification in a pharmaceutical industrial tank. An electrode module (volume: 1 m^3) was constructed by stacking eight pairs of corrugated electrodes, with each electrode formed by inserting carbon felt between two corrugated stainless steel mesh sheets with the corrugate profile of each sheet matching [58]. Corrugate profiles were alternated between pairs of electrodes to optimize fluid flow, and insulation plastic was placed between the electrodes to minimize interference. Fourteen electrode modules were integrated into an anaerobic baffled reactor consisting of six tanks. Over six months, application of 0.7 V of external power achieved a maximum current density of 1.25 ± 0.11 A m^{-2}, which improved the COD by 16.7 ± 13.2% and the and colour removal efficiency by 59.4 ± 27.9% compared with anaerobic control systems. Operation of hybrid hydrolysis and acidification without a membrane substantially reduces maintenance costs, with membrane-free systems costing < USD 2000 m^{-3} compared with > USD 10,000 m^{-3} for membrane-based electrical stimulation systems. This approach can be seamlessly integrated *in situ* with traditional anaerobic systems (e.g., up-flow anaerobic sludge blankets, anaerobic baffled reactors) by directly installing electrodes, and leads to large reductions in both construction and operational costs [59–62].

The effectiveness of the hybrid hydrolysis and acidification process is influenced by critical factors such as the applied voltage, electrode durability, and system scalability. If the applied voltage is too small, the cathode may not achieve the required reduction potential to effectively catalyse TOP degradation, which will result in suboptimal treatment efficiency. However, excessively high voltages can lead to increased energy consumption and accelerated electrode corrosion [63]. The selection of electrode materials is also crucial. An ideal electrode should exhibit high biocompatibility, strong chemical stability, low cost, a large specific surface area, and excellent electrical conductivity [64]. Carbon-coated metal electrodes and modular assemblies are promising for advancing the practical application of weak redox regulation [65].

4. Challenges and prospects

The growing prevalence of TOPs imposes high demands on conventional water treatment processes. Because these demands often exceed the capabilities of traditional biological methods, TOPs pose significant environmental risks. Consequently, pretreatment or advanced treatment using redox regulation strategies is essential to ensure the stable operation and efficiency of biological systems. Sustainable detoxification of TOPs requires precise control over treatment combinations and parameter optimization of both system performance and cost-effectiveness. This area is underexplored in current research. Moreover, because TOPs are also present in groundwater and sediments, expanding the application scenarios of redox regulation, such as bioremediation through WEEI, is critical for broader environmental risk control. To address these challenges, we propose a number of strategies, which are detailed in the following sections.

4.1. New catalyst development

Various redox processes rely on catalysts and oxidants/reductants to generate active species with strong redox regulation. The development of efficient, controllable, and durable catalysts has received increasing attention from researchers worldwide. For example, non-metallic components such as sulfur, nitrogen, and carbon can be doped into the material to increase the absorption wavelength range of TiO_2 and enhance photocatalytic activity. The feasibility of using carbon catalysts, which contain adjustable structures, abundant functional groups, structural defects, and other catalytic sites to activate sulfites, should be explored to solve the fundamental problem of metal leaching. In future, the design and calculation of reaction sites for catalysts will rely on the assistance of machine learning (ML) and artificial intelligence to achieve risk reduction-oriented catalyst design. Traditional catalyst development relies on empirical trial and error, while ML enables data-driven screening. This compresses research and development timelines by $> 90\%$. In one case, density functional theory was combined with active learning to dramatically improve the discovery efficiency of a novel Cu-Al catalyst [66].

4.2. Low-carbon development

No water treatment technology can solely solve the problem of organic matter removal efficiently and economically. Most research related to integration processes has overlooked the evaluation of the systemic effects of this multi-component technology, which has resulted in significant expenditure on chemical reagents during actual processing. Therefore, it is essential to recognize that a combination of a moderate redox process with biochemical treatment will optimize the system by reducing complete mineralization and satisfying the redox conditions for sustained microbial treatment. Waste resource utilization is another promising approach that converts various chemicals and intermediates into harmless and valuable raw materials through precise regulation and targeted transformation. Phenol is efficiently reduced to cyclohexanol through an electrocatalytic hydrogenation system constructed with nano Ru/TiO_2 catalytic electrodes, which reduces the product toxicity and resource recovery [67]. The nutrient–energy–water concept has been proposed for traditional carbon, nitrogen, and phosphorus recovery processes in wastewater treatment plants [68]. Extensive research and modelling are essential for the key characteristic functional groups in redox regulation and biological processes to adjust treatment combinations and parameters. This adjustment will help eliminate toxic functional groups while retaining valuable components to achieve toxicity reduction, carbon reduction, and resource cycling in the future.

4.3. Smart process control

The deconstruction pathways and efficiencies of TOPs are closely linked to their chemical characteristics and redox regulation conditions. The goal of redox regulation, particularly in AOPs/ARPs, is not complete mineralization but selective transformation of TOPs into intermediates that enhance microbial metabolism and biological treatment. ML algorithms enable the development of predictive models to analyse the redox properties of TOPs and regulation strategies to reveal complex interactions between degradation pathways, catalytic mechanisms, and product toxicity. Through iterative optimization, ML models can transition from experience-driven to data-driven approaches and balance external energy input, TOPs removal efficiency, and economic feasibility.

4.4. Water ecological security protection

The environmental risks associated with ECs, many of which are classified as TOPs in regulatory databases, have attracted significant global attention. Wastewater is both a source and a sink of these risks in receiving water bodies. Once TOPs enter aquatic ecosystems, their dispersion and dilution make risk mitigation challenging. Therefore, enhancing EC removal and risk reduction during wastewater treatment is both essential and effective. Given the untapped potential of biodegradation, strategies such as microbial co-metabolism, genetic engineering, synthetic biology, and microbiome engineering offer promising solutions for TOP risk control.

CRediT authorship contribution statement

Ai-Jie Wang: Writing - Review & Editing, Writing - Original Draft, Visualization, Methodology, Investigation, Funding Acquisition, Conceptualization. **Rui-Feng Yan:** Writing - Review & Editing, Writing - Original Draft, Methodology, Investigation. **Ke Shi:** Writing - Review & Editing, Methodology, Investigation. **Hao-Yi Cheng:** Writing - Review & Editing. **Jing-Long Han:** Writing - Review & Editing. **Bin Liang:** 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.

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References

[1] Y.W. Wang, L. Jiang, G.B. Jiang, Emerging chemicals in China: historical development, current situation, and future outlook, Environ. Health. 2 (2024) 180–188.

[2] B.I. Escher, H.M. Stapleton, E.L. Schymanski, Tracking complex mixtures of chemicals in our changing environment, Science 367 (2020) 388–392.
[3] Y. Yang, X.R. Zhang, J.Y. Jiang, J.R. Han, W.X. Li, X.Y. Li, K.M.Y. Leung, S.A. Snyder, P.J.J. Alvarez, Which micropollutants in water environments deserve more attention globally? Environ. Sci. Technol. 56 (2022) 13–29.
[4] K. Shi, B. Liang, H.-Y. Cheng, H.-C. Wang, W.-Z. Liu, Z.-L. Li, J.-L. Han, S.-H. Gao, A.-J. Wang, Regulating microbial redox reactions towards enhanced removal of refractory organic nitrogen from wastewater, Water Res. 258 (2024) 121778.
[5] B. Wang, Q. Sui, H.J. Liu, G. Yu, J.H. Qu, Promoting environmental risk assessment and control of emerging contaminants in China, Engineering 37 (2024) 13–17.
[6] K. Shi, J.-M. Xu, H.-L. Cui, H.-Y. Cheng, B. Liang, A.-J. Wang, Microbiome regulation for sustainable wastewater treatment, Biotechnol. Adv. 77 (2024) 108458.
[7] X.-Y. Fan, Z.-X. Zhang, N. Li, X. Li, Molecular ecological insights into the synergistic response mechanism of nitrogen transformation, electron flow and antibiotic resistance genes in aerobic activated sludge systems driven by sulfamethoxazole and/or trimethoprim stresses, Water Res. 270 (2024) 122853, 122853.
[8] H. Wang, L.Y. Zhang, H.L. Cui, X.D. Ma, Z.L. Li, B. Liang, A.J. Wan, Mechanisms linking triclocarban biotransformation to functional response and antimicrobial resistome evolution in wastewater treatment systems, Water Res. 260 (2024) 121909.
[9] L. Zhang, X. Ma, Q. Li, H. Cui, K. Shi, H. Wang, Y. Zhang, S. Gao, Z. Li, A.-J. Wang, B. Liang, Complementary biotransformation of antimicrobial triclocarban obviously mitigates nitrous oxide emission toward sustainable microbial denitrification, Environ. Sci. Technol. 57 (2023) 7490–7502.
[10] F. Rodrigues, L. Duraes, N.E.C. Simoes, A. Pereira, L.J.G. Silva, M.J. Feio, Pharmaceuticals in urban streams: a review of their detection and effects in the ecosystem, Water Res. 268 (2025) 122657.
[11] D.G.J. Larsson, C.-F. Flach, Antibiotic resistance in the environment, Nat. Rev. Microbiol. 20 (2022) 257–269.
[12] S. Zhang, H. Zheng, P.G. Tratnyek, Advanced redox processes for sustainable water, Nat. Water. (2023) 666–681.
[13] L.K. Sviatenko, L. Gorb, F.C. Hill, D. Leszczynska, J. Leszczynski, Theoretical study of one-electron reduction and oxidation potentials of N-Heterocyclic compounds, Chem. Heterocycl. Compds. 50 (2014) 311–318.
[14] A.S. Pavitt, E.J. Bylaska, P.G. Tratnyek, Oxidation potentials of phenols and anilines: correlation analysis of electrochemical and theoretical values, Environ. Sci.-Process Impacts 19 (2017) 339–349.
[15] D. Kong, B. Liang, H. Yun, H. Cheng, J. Ma, M. Cui, A. Wang, N. Ren, Cathodic degradation of antibiotics: characterization and pathway analysis, Water Res. 72 (2015) 281–292.
[16] J.F. King, B.P. Chaplin, Electrochemical reduction of perand polyfluorinated alkyl substances (PFAS): is it possible? Applying experimental and quantum mechanical insights from the reductive defluorination literature, Curr. Opin. Chem. Eng. 44 (2024) 101014.
[17] A.J. Wang, H.Y. Cheng, B. Liang, N.Q. Ren, D. Cui, N. Lin, B.H. Kim, K. Rabaey, Efficient reduction of nitrobenzene to aniline with a biocatalyzed cathode, Environ. Sci. Technol. 45 (2011) 10186–10193.
[18] D. Cui, Y.-Q. Guo, H.-Y. Cheng, B. Liang, F.-Y. Kong, H.-S. Lee, A.-J. Wang, Azo dye removal in a membrane-free up-flow biocatalyzed electrolysis reactor coupled with an aerobic bio-contact oxidation reactor, J. Hazard Mater. 239 (2012) 257–264.
[19] J.-T. Ren, L. Chen, H.-Y. Wang, W.-W. Tian, Z.-Y. Yuan, Water electrolysis for hydrogen production: from hybrid systems to self-powered/catalyzed devices, Energy Environ. Sci. 17 (2024) 49–113.
[20] A. Singh, A. Majumder, D. Saidulu, A. Bhattacharya, A. Bhatnagar, A.K. Gupta, Oxidative treatment of micropollutants present in wastewater: a special emphasis on transformation products, their toxicity, detection, and field-scale investigations, J. Environ. Manage. 354 (2024) 120339.
[21] D.A. Armstrong, R.E. Huie, W.H. Koppenol, S.V. Lymar, G. Merenyi, P. Neta, B. Ruscic, D.M. Stanbury, S. Steenken, P. Wardman, Standard electrode potentials involving radicals in aqueous solution: inorganic radicals (IUPAC Technical Report), Pure Appl. Chem. 87 (2015) 1139–1150.
[22] M.Z. Ren, S.H. Sun, Y.Q. Wu, Y.C. Shi, Z.J. Wang, H.B. Cao, Y.B. Xie, The structure-activity relationship of aromatic compounds in advanced oxidation processes: a review, Chemosphere 296 (2022) 134071.
[23] T.C. An, Y.P. Gao, G.Y. Li, P.V. Kamat, J. Peller, M.V. Joyce, Kinetics and mechanism of •OH mediated degradation of dimethyl phthalate in aqueous solution: experimental and theoretical studies, Environ. Sci. Technol. 48 (2014) 641–648.
[24] W.J. Tian, S. Chen, H.Y. Zhang, H. Wang, S.B. Wang, Sulfate radical-based advanced oxidation processes for water decontamination using biomass-derived carbon as catalysts, Curr. Opin. Chem. Eng. 37 (2022) 100838.
[25] M.B. Ahmed, J.L. Zhou, H.H. Ngo, W.S. Guo, N.S. Thomaidis, J. Xu, Progress in the biological and chemical treatment technologies for emerging contaminant removal from wastewater: a critical review, J. Hazard Mater. 323 (2017) 274–298.
[26] A. Sharma, J. Ahmad, S.J.S. Flora, Application of advanced oxidation processes and toxicity assessment of transformation products, Environ. Res. 167 (2018) 223–233.
[27] Y.F. Yang, Z.H. Xie, H. Wang, S.R. Yang, T.T. Wang, C.S. He, B. Lai, Ecological risk assessment methods for oxidative by-products in the oxidation degradation process of emerging pollutants: a review, Sci. Total Environ. 950 (2024) 175401.
[28] H. Park, C.D. Vecitis, J. Cheng, N.F. Dalleska, B.T. Mader, M.R. Hoffmann, Reductive degradation of perfluoroalkyl compounds with aquated electrons generated from iodide photolysis at 254 nm, Photochem. Photobiol. Sci. 10 (2011) 1945–1953.
[29] B.D. Fennell, S.P. Mezyk, G. McKay, Critical review of UV-advanced reduction processes for the treatment of chemical contaminants in water, ACS Environ. Au. 2 (2022) 178–205.
[30] O.S. Arvaniti, A.S. Stasinakis, Review on the occurrence, fate and removal of perfluorinated compounds during wastewater treatment, Sci. Total Environ. 524 (2015) 81–92.
[31] H.H. Huang, X.R. Liang, Q.S. Li, J. Deng, J. Zou, X. Li, X.Y. Ma, G.X. Li, G.Y. Chen, High-performance reductive decomposition of trichloroacetamide by the vacuum-ultraviolet/sulfite process: kinetics, mechanism and combined toxicity risk, Water Res. 225 (2022) 119122.
[32] Y. Cao, W. Qiu, J. Li, J. Jiang, S. Pang, Reviewon UV/sulfite process for water and wastewater treatments in the presence or absence of O_2, Sci. Total Environ. 765 (2021) 142762.
[33] S.J. Dong, Y.C. Ding, H.J. Feng, J.X. Xu, J.L. Han, W.L. Jiang, Y.J. Xia, A.J. Wang, Source preventing mechanism of florfenicol resistance risk in water by VUV/UV/sulfite advanced reduction pretreatment, Water Res. 235 (2023) 119876.
[34] X. Wang, F. Aulenta, S. Puig, A. Esteve-Núñez, Y. He, Y. Mu, K. Rabaey, Microbial electrochemistry for bioremediation, Environ. Eco. Technol. 1 (2020) 100013.
[35] X.B. Jiang, D. Chen, Y. Mu, D. Pant, H.Y. Cheng, J.Y. Shen, Electricity-stimulated anaerobic system (ESAS) for enhanced energy recovery and pollutant removal: a critical review, Chem. Eng. J. 411 (2021) 128548.
[36] D.R. Lovley, D.E. Holmes, Electromicrobiology: the ecophysiology of phylogenetically diverse electroactive microorganisms, Nat. Rev. Microbiol. 20 (2022) 5–19.
[37] B. Liang, H.Y. Cheng, D.Y. Kong, S.H. Gao, F. Sun, D. Cui, F.Y. Kong, A.J. Zhou, W.Z. Liu, N.Q. Ren, W.M. Wu, A.J. Wang, D.J. Lee, Accelerated reduction of chlorinated nitroaromatic antibiotic chloramphenicol by biocathode, Environ. Sci. Technol. 47 (2013) 5353–5361.
[38] Y. Mu, R.A. Rozendal, K. Rabaey, J. Keller, Nitrobenzene removal in bioelectrochemical systems, Environ. Sci. Technol. 43 (2009) 8690–8695.
[39] H. Yun, B. Liang, D.-Y. Kong, H.-Y. Cheng, Z.-L. Li, Y.-B. Gu, H.-Q. Yin, A.-J. Wang, Polarity inversion of bioanode for biocathodic reduction of aromatic pollutants, J. Hazard Mater. 331 (2017) 280–288.
[40] B. Virdis, R.D. Hoelzle, A. Marchetti, S.T. Boto, M.A. Rosenbaum, R. Blasco-Gomez, S. Puig, S. Freguia, M. Villano, Electro-fermentation: sustainable bioproductions steered by electricity, Biotechol. Adv. 59 (2022) 107950.
[41] A.J. Wang, B. Liang, Z.L. Li, H.Y. Cheng, Bioelectrodegradation of Hazardous Organic Contaminants from Industrial Wastewater, Elsevier, 2019.
[42] C. Annabi, F. Fourcade, I. Soutrel, F. Geneste, D. Floner, N. Bellakhal, A. Amrane, Degradation of enoxacin antibiotic by the electro-Fenton process: optimization, biodegradability improvement and degradation mechanism, J. Environ. Manage. 165 (2016) 96–105.
[43] N.A. Salles, F. Fourcade, F. Geneste, D. Floner, A. Amrane, Relevance of an electrochemical process prior to a biological treatment for the removal of an organophosphorous pesticide, phosmet, J. Hazard Mater. 181 (2010) 617–623.
[44] A.B. Ponnusami, S. Sinha, H. Ashokan, M. Paul, S.P. Hariharan, J. Arun, K.P. Gopinath, Q.H. Le, A. Pugazhendhi, Advanced oxidation process (AOP) combined biological process for wastewater treatment: a review on advancements, feasibility and practicability of combined techniques, Environ. Res. 237 (2023) 116944.
[45] J. García-Montaño, X. Domènech, J.A. García-Hortal, F. Torrades, J. Peral, The testing of several biological and chemical coupled treatments for cibacron red FN-R azo dye removal, J. Hazard Mater. 154 (2008) 484–490.
[46] M. El Kateb, C. Trellu, A. Darwich, M. Rivallin, M. Bechelany, S. Nagarajan, S. Lacour, N. Bellakhal, G. Lesage, M. Heran, M. Cretin, Electrochemical advanced oxidation processes using novel electrode materials for mineralization and biodegradability enhancement of nanofiltration concentrate of landfill leachates, Water Res. 162 (2019) 446–455.
[47] Y.Y. Chu, L.J. Xu, L. Gan, W.C.A. Qiao, J.G. Han, X. Mei, H. Guo, W. Li, C. Pei, H. Gong, X.W. Guo, Efficient destruction of emerging contaminants in water by UV/S(IV) process with natural reoxygenation: effect of pH on reactive species, Water Res. 198 (2021) 117143.
[48] H. Milh, X.Y. Yu, D. Cabooter, R. Dewil, Degradation of ciprofloxacin using UV-based advanced removal processes: comparison of persulfate-based advanced oxidation and sulfite-based advanced reduction processes, Sci. Total Environ. 764 (2021) 144510.
[49] D. Mansour, F. Fourcade, S. Huguet, I. Soutrel, N. Bellakhal, M. Dachraoui, D. Hauchard, A. Amrane, Improvement of the activated sludge treatment by its combination with electro Fenton for the mineralization of sulfamethazine, Int. Biodeterior. Biodegrad. 88 (2014) 29–36.
[50] G. Moussavi, A. Khavanin, R. Alizadeh, The integration of ozonation catalyzed with MgO nanocrystals and the biodegradation for the removal of phenol from saline wastewater, Appl. Catal. B Environ. 97 (2010) 160–167.
[51] A. Sheikhmohammadi, A. Yazdanbakhsh, G. Moussavi, A. Eslami, M. Rafiee, M. Sardar, M. Almasian, Degradation and COD removal of trichlorophenol from wastewater using sulfite anion radicals in a photochemical process combined with a biological reactor: mechanisms, degradation pathway,

optimization and energy consumption, Process Saf. Environ. Prot. 123 (2019) 263–271.
[52] Y.C. Ding, J.L. Han, H.J. Feng, Y.X. Liang, W.L. Jiang, S.H. Liu, B. Liang, M.Z. Wang, Z.L. Li, A.J. Wang, N.Q. Ren, Source prevention of halogenated antibiotic resistance genes proliferation: UV/sulfite advanced reduction process achieved accurate and efficient elimination of florfenicol antibacterial activity, Sci. Total Environ. 849 (2022) 157844.
[53] J.P. Scott, D.F. Ollis, Integration of chemical and biological oxidation processes for water treatment: review and recommendations, Environ. Prog. 14 (1995) 88–103.
[54] J.L. Wang, L.J. Xu, Advanced oxidation processes for wastewater treatment: formation of hydroxyl radical and application, Crit. Rev. Environ. Sci. Technol. 42 (2012) 251–325.
[55] T. Mandal, S. Maity, D. Dasgupta, S. Datta, Advanced oxidation process and biotreatment: their roles in combined industrial wastewater treatment, Desalination 250 (2010) 87–94.
[56] H.L. Feng, W.L. Mao, Y.N. Li, X.J. Wang, S.H. Chen, Characterization of dissolved organic matter during the O_3-based advanced oxidation of mature landfill leachate with and without biological pre-treatment and operating cost analysis, Chemosphere 271 (2021) 129810.
[57] Y. He, Z. Tian, Q. Yi, Y. Zhang, M. Yang, Impact of oxytetracycline on anaerobic wastewater treatment and mitigation using enhanced hydrolysis pretreatment, Water Res. 187 (2020) 116408.
[58] A.-J. Wang, H.-C. Wang, H.-Y. Cheng, B. Liang, W.-Z. Liu, J.-L. Han, B. Zhang, S.-S. Wang, Electrochemistry-stimulated environmental bioremediation: development of applicable modular electrode and system scale-up, Environmental Science and Ecotechnology 3 (2020) 100050.
[59] D. Cui, Y.Q. Guo, H.S. Lee, W.M. Wu, B. Liang, A.J. Wang, H.Y. Cheng, Enhanced decolorization of azo dye in a small pilot-scale anaerobic baffled reactor coupled with biocatalyzed electrolysis system (ABR-BES): a design suitable for scaling-up, Bioresour. Technol. 163 (2014) 254–261.
[60] X.B. Jiang, J.Y. Shen, K.C. Xu, D. Chen, Y. Mu, X.Y. Sun, W.Q. Han, J.S. Li, L.J. Wang, Substantial enhancement of anaerobic pyridine bio-mineralization by electrical stimulation, Water Res. 130 (2018) 291–299.
[61] A.J. Wang, K. Shi, D.L. Ning, H.Y. Cheng, H.C. Wang, W.Z. Liu, S.H. Gao, Z.L. Li, J.L. Han, B. Liang, J.Z. Zhou, Electrical selection for planktonic sludge microbial community function and assembly, Water Res. 206 (2021) 117744.
[62] H.C. Wang, H.Y. Cheng, D. Cui, B. Zhang, S.S. Wang, J.L. Han, S.G. Su, R. Chen, A.J. Wang, Corrugated stainless-steel mesh as a simple engineerable electrode module in bio-electrochemical system: hydrodynamics and the effects on decolorization performance, J. Hazard Mater. 338 (2017) 287–295.
[63] J.C. Thrash, J.D. Coates, Review: direct and indirect electrical stimulation of microbial metabolism, Environ. Sci. Technol. 42 (2008) 3921–3931.
[64] K. Guo, A. Prevoteau, S.A. Patil, K. Rabaey, Engineering electrodes for microbial electrocatalysis, Curr. Opin. Biotechnol. 33 (2015) 149–156.
[65] D.-C. Xu, S.-Y. Zhai, H.-Y. Cheng, A. Guadie, H.-C. Wang, J.-L. Han, C.-Y. Liu, A.-J. Wang, Wire-drawing process with graphite lubricant as an industrializable approach to prepare graphite coated stainless-steel anode for bio-electrochemical systems, Environ. Res. 191 (2020) 110093.
[66] M. Zhong, K. Tran, Y. Min, C. Wang, Z. Wang, C.-T. Dinh, P. De Luna, Z. Yu, A.S. Rasouli, P. Brodersen, S. Sun, O. Voznyy, C.-S. Tan, M. Askerka, F. Che, M. Liu, A. Seifitokaldani, Y. Pang, S.-C. Lo, A. Ip, Z. Ulissi, E.H. Sargent, Accelerated discovery of CO_2 electrocatalysts using active machine learning, Nature 581 (2020) 178–183.
[67] Z.N. Gu, Z.Y. Zhang, N. Ni, C.Z. Hu, J.H. Qu, Simultaneous phenol removal and resource recovery from phenolic wastewater by electrocatalytic hydrogenation, Environ. Sci. Technol. 56 (2022) 4356–4366.
[68] M. Zheng, Z.T. Hu, T. Liu, M. Sperandio, E.I.P. Volcke, Z.Y. Wang, X.D. Hao, H.R. Duan, S.E. Vlaeminck, K.N. Xu, Z.Q. Zuo, J.H. Guo, X. Huang, G.T. Daigger, W. Verstraete, M.C.M. van Loosdrecht, Z.G. Yuan, Pathways to advanced resource recovery from sewage, Nat. Sustain. 7 (2024) 1395–1404.