# Enhancing the degradation of selected recalcitrant organic contaminants through integrated cathode and anode processes in microbial electrochemical systems: A frontier review

Kaichao Yang [a], Ibrahim M. Abu-Reesh [b], Zhen He [a,*]

[a] Department of Energy, Environmental and Chemical Engineering, Washington University in St. Louis, St. Louis, MO 63130, United States
[b] Department of Chemical Engineering, Qatar University, Doha, Qatar

ABSTRACT

Microbial electrochemical system (MES) technology has been widely investigated for organic degradation. However, the removal of recalcitrant organic contaminants containing halogen-, nitro-, or azo-groups remains a great challenge. Integrating the cathodic and anodic processes in an MES is able to improve or complete the mineralization of the target halogen-, nitro- and azo-organics via a sequential reductive and oxidative process. In this way, a cathode is used to reduce the toxic target organics, while an anode is to oxidize the residual organics from the reduction process and at the same time generate electrons to support the reduction process. This paper has provided a concise review about the sequential cathode-anode contaminant degradation in an MES and its specific mechanisms. Potential strategies to improve the MES degradation performance were discussed, mainly including the application and development of the biocatalyzed cathode as well as the optimization of the anodic operating condition and the improvement of anodic bacteria and electrode material. Perspectives on future directions were proposed and the key challenges were identified as the competitive or inhibitive influence of other compounds that could coexist in real wastewater on the target contaminants.

## 1. Introduction

Microbial electrochemical system (MES) technology has shown a great potential for organic contaminant degradation. By utilizing an anode electrode as an electron acceptor, organic compounds in a wastewater can be degraded via an oxidative pathway (Yang et al., 2020). Some organic contaminants containing halogen-, nitro-, and azo-groups (e.g. chlorophenol, nitrobenzene and azo dye) are resistant to the anodic degradation and can exert toxicity to anodic microbes (Yang et al., 2021a). However, these compounds may be degraded in a reductive pathway, in which by utilizing a cathode electrode as an electron donor, halogen-, nitro- and azo-groups receive electrons and are then reduced into less toxic hydrogen- and amino-groups (Wang et al., 2012; Wen et al., 2013). Incomplete degradation often occurs and the residual organics (e.g., phenol and aniline) can still be hazardous and need further treatment. Therefore, there is a need for exploring a more effective approach to maximize the degradation of these compounds in an MES.

The sequential reductive and oxidative degradation offers a promising approach for maximal degradation of these recalcitrant organics, where the toxic halogen-, nitro- and azo- groups can be firstly degraded by a reductive process and the residual compounds will be further mineralized by an oxidative process. In fact, an MES is capable of providing both reductive and oxidative environments through integrating the cathodic and anodic processes, in either a sequential anode-cathode mode or a sequential cathode-anode mode (Fig. 1). Although both modes could achieve organic degradation, their degradation mechanisms are different. In the sequential anode-cathode mode, the recalcitrant organic contaminants utilize the easily degraded substrates like glucose in the anode as an electron donor for reductive degradation and use $O_2$ supplied to the cathode as an electron acceptor for oxidative degradation (Fig. 1A). Such a degradation pathway does not involve either the anode or the cathode electrode directly as an electron acceptor or donor. Instead, it actually creates a competition between the organics and the electrodes (for electron donors or acceptors). Thus, this pathway is not an ideal process to fully use the potential of an MES.

The sequential cathode-anode mode allows the organics to use a cathode as an electron donor for reductive degradation and then an

* Corresponding author.
*E-mail address:* zhenhe@wustl.edu (Z. He).

anode as an electron acceptor for oxidative degradation (Fig. 1B). This pathway meets the need for degrading organic contaminants containing halogen-, nitro-, and azo- groups and directly involves electrodes in the degradation. This paper aims to provide a concise review focusing on the sequential cathode-anode degradation of halogen-, nitro- and azo-organic contaminants in the MES. The importance of applying bio-cathode to improve the selectivity and efficiency and the decisive roles of the bioanode in the MES were discussed. We also offered the perspectives on challenges and future research directions such as further improving the degradative abilities of the electrodes, understanding the effect of the coexistence of other organic and inorganic matters, as well as developing novel operational modes.

## 2. Sequential cathode-anode degradation

During the sequential cathode-anode degradation of the halogen-, nitro- and azo- organic contaminants, organic contaminants and electrons are moving in the opposite directions: organic contaminants are fed to a cathode chamber first and then moved to an anode chamber, while electrons that drive the degradation, are produced from the anode and then flow to the cathode. In theory, organic contaminants can provide electrons for their own degradation, assisted by electrochemistry (Fig. 1B): the cathodic reduction of the initial organic contaminants is performed by the electrons generated from the anodic oxidation of the intermediates that are produced from the former reduction process.

Several recalcitrant organic contaminants have been studied for their degradation via the sequential cathode-anode pathway in the MES, including azo-organics (azo dye and azobenzene (AB)), nitro-organics (nitrobenzene (NB) and *p*-nitrophenol (*p*-NP)), and halogenated phenolic and aliphatic organics (chlorophenol (CP) and chloroethylene (CE)) (Table 1). Because both azo- and nitro-organics are reduced into aromatic amines as intermediates that need to be further treated via an anodic oxidation, their mineralization efficiency is mainly affected by the cathodic reductive process. It was reported that the MES could achieve a high mineralization efficiency of >90 % in 27 h for treating both AB and azo dye reactive brilliant red X-3B (RBRX-3B), indicating that azo-bond is relatively easy to be reduced (Liu et al., 2015, 2017). The nitro-group (-$NO_2$) is more difficult to be transformed into the amino-group (-$NH_2$) due to the need for more electrons (6 electrons needed) and the existence of side reactions (e.g., nitro-group to nitroso-group (-NO)). It was found that NB and *p*-NP would need more than 96 h to achieve a cathodic reduction efficiency of >90 % with the production of less-toxic aniline (AN) and *p*-aminophenol (*p*-AP) as intermediates, which required 25 h in a subsequent anodic process to accomplish a mineralization efficiency of >90 %, much slower

compared to the degradation of azo-organics (Sun et al., 2012; Zhang et al., 2018).

The degradation performance of halogenated organics mainly depends on the number of the halogen-group and the structure of the organic carbon (aromatic or aliphatic). Monochlorophenols (MCPs) such as 4-chlorophenol (4-CP) and 2-chlorophenol (2-CP) could be converted into phenol with a cathodic reduction efficiency of about 80 % within 48 h, and 70 % of the generated phenol could be completely degraded in the subsequent anodic oxidation within another 48 h under an applied voltage of 0.5–0.8 V (Kong et al., 2014; Yang et al., 2021b). Cathodic dechlorination of poly-halogenated aliphatic organics including trichloroethylene (TCE) and perchloroethylene (PCE) was slower than the anodic oxidation of the residual aliphatic organic structure, because of the presence of more chloro-groups (Lai et al., 2017; Lohner et al., 2011; Lohner and Tiehm, 2009; Zeppilli et al., 2021).

Theoretically, the number of electrons required for the cathodic reduction of 1 mol of halogen-, azo-, or nitro-group will be 1, 4 or 6 mol, while the amount of electrons that can be generated from the anodic mineralization of 1 mol of benzene-ring or ethylene can be 30 or 12 mol. Thus, the sequential cathode-anode degradation could be self-sustained in terms of electron supply. Using 2-CP containing one benzene-ring and one chloro-group as an example, the ratio between the electrons produced from the benzene-ring in the anode and those consumed by the chloro-group in the cathode is theoretically 30–1. However, in practice it is challenging to achieve the self-sustained degradation of the target organic contaminants due to the low current efficiency of an MES, including both the cathodic and the anodic processes. The low efficiency of the cathodic process is mainly because that the electrons or $H_2$ generated in the cathode cannot efficiently and selectively react with the target organics (e.g., 2-CP and NB) without an appropriate biocatalyst (e.g., dechlorinator and nitro-reducer) or metal catalyst (e.g., palladium). In the anodic process, the intermediate organics (e.g., phenol and AN) can be still recalcitrant and thus hard to be directly and fully utilized as an anodic fuel by the electroactive bacteria; that will require an additional step to convert those intermediates into small molecule organics. Therefore, the abilities of organic transformation and electron utilization of the electrodes need to be improved.

## 3. Enhancing cathodic reduction by functional bacteria

In the sequential cathode-anode degradation, the cathode performs an important pretreatment step to convert the target organics to simpler compounds with possibly lower toxicity via reductive reactions. Abiotic cathodes (e.g., graphite electrodes) have showed the ability of reduction, yet with limited efficiency and selectivity in the absence of a proper
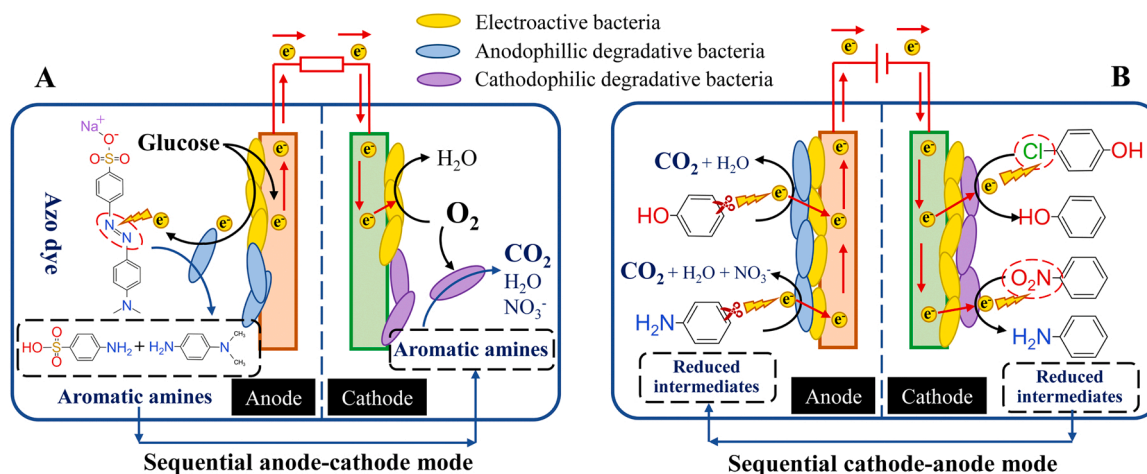


**Fig. 1.** MES degradation of selected recalcitrant organic contaminants in (A) a sequential anode-cathode mode; and (B) a sequential cathode-anode mode (using azo dye, 4-CP, and NB as examples).

**Table 1**

Summary of the degradation of selected recalcitrant organic contaminants in sequential anode-cathode mode and sequential cathode-anode mode MES.

| Organic pollutant | Operating mode | Electron donors/acceptors utilized | Major intermediate organic | References |
|---|---|---|---|---|
| Azo dye: Congo red | Sequential anode-cathode | Glucose in anode/$O_2$ in cathode | Aromatic amines (Anode effluent) | Li et al. (2010) |
| Azo dye: Methyl orange | Sequential anode-cathode | Glucose in anode/$O_2$ in cathode | Aromatic amines (Anode effluent) | Mittal et al. (2022) |
| Azo dye: Victoria blue R | Sequential anode-cathode | Acetate in anode/$O_2$ in cathode | – | Wu et al. (2020) |
| Real textile wastewater: Azo dyes | Sequential anode-cathode | Domestic wastewater in anode/$O_2$ in cathode | Aromatic amines (Anode effluent) | Pushkar and Mungray (2016) |
| Azo dye: RBRX-3B | Sequential cathode-anode | Cathode/Anode | Aromatic amines (Cathode effluent) | Liu et al., (2017) |
| Azobenzene | Sequential cathode-anode | Cathode/Anode | Aniline (Cathode effluent) | Liu et al. (2015) |
| 4-Chlorophenol | Sequential cathode-anode | Cathode/Anode | Phenol (Cathode effluent) | Kong et al. (2014) |
| 2-Chlorophenol | Sequential cathode-anode | Cathode/Anode | Phenol (Cathode effluent) | Yang et al. (2021b) |
| 4-Bromophenol | Sequential cathode-anode | Cathode/Anode | Phenol (Cathode effluent) | Chen et al. (2019) |
| Trichloroethylene | Sequential cathode-anode | Cathode/Anode | Vinyl chloride and ethylene (Cathode effluent) | Lai et al. (2017) |
| Perchloroethylene | Sequential cathode-anode | Cathode/Anode | Vinyl chloride and ethylene (Cathode effluent) | Dell'Armi et al. (2021), Lohner et al. (2009, 2011), Zeppilli et al. (2019, 2021) |
| p-Nitrophenol | Sequential cathode-anode | Cathode/Anode | p-Aminophenol (Cathode effluent) | Zhang et al. (2018) |
| Nitrobenzene | Sequential cathode-anode | Cathode/Anode | Aniline (Cathode effluent) | Sun et al. (2012) |

catalyst (Fig. 2A) (Mu et al., 2009; Sun et al., 2012). For example, in an abiotic cathode, dechlorination process needs to happen at a low potential (−800 to −1000 mV) (Aulenta et al., 2007; Shimomura and Sanford, 2005), which would trigger side reductive reactions of other redox-active components (e.g. nitrate and sulfate) (Strycharz et al., 2008), leading to a lower current efficiency of the reductive process and a waste of electric energy. Furthermore, a noncatalytic electrochemical nitro-reduction process generated the intermediates containing the nitroso-group that had more toxic effects and was more recalcitrant (Fig. 2A) (Mu et al., 2009; Sun et al., 2012; Wang et al., 2011). Therefore, despite some success in the reduction of halogen-, nitro- and azo-groups by an abiotic cathode, the noncatalytic reductive process is less efficient and selective.

To improve the efficiency and selectivity of the cathodic reduction, functional cathodophilic bacteria were studied to serve as an effective biocatalyst (Fig. 2). Electroactive bacteria were found to be able to accept electrons directly from the cathode electrode and use them to reduce the target organics (Fig. 2B). For example, a cathode electrode acted as an electron donor for the biocatalytic reactions by several electroactive dechlorinators (e.g., *Geobacter lovleyi* and *Anaeromyxobacter dehalogenans*), to achieve an enhanced dechlorination performance of chlorinated organics (TCE, PCE and 2-CP) (Aulenta et al., 2007; Jiang et al., 2022; Strycharz et al., 2010, 2008). Electroactive *Enterococcus* species exhibited an ability to catalyze the cathodic reductive reaction of NB, in which NB was selectively transformed into AN in a one-step process without the generation of more toxic intermediate nitrosobenzene (NSB) (Fig. 2B). The transformation efficiency was increased by about 10 times, compared to the abiotic reductive process that required many steps (Wang et al., 2011). In addition, electroactive nitroaromatic reducers such as *Paracoccus* and *Variovorax* have demonstrated the ability to biologically catalyze the nitro-reduction process (Liang et al., 2014). The cathodic reductive process of azo-bond could be enhanced from 77.8 % with an abiotic cathode to 95.8 % with the introduction of electroactive species such as *Shewanella oneidensis* MR-1 (Gao et al., 2016).

The discovery and enrichment of cathodophilic hydrogenotrophic bacteria provide another way to enhance the cathodic reductive process, where electrons can be indirectly utilized via the formation of the electrochemically-generated $H_2$ (Fig. 2C) (Lohner et al., 2014). For example, when hydrogenotrophic dechlorinating bacteria (*Dehalococcoides* and *Desulfitobacterium* species) were introduced into a cathode chamber, an improved transformation of PCE to vinyl chloride and ethylene was accomplished while most PCE would be converted into *cis*-dichloroethylene in an abiotic electrochemical dechlorination process (Lohner et al., 2011; Lohner and Tiehm, 2009) (Fig. 2C). The cathodic reduction efficiency of azo dye RBRX-3B as well as the reduction selectivity of NB were enhanced by enriching anaerobic hydrogenotrophic reducers in the cathode in the presence of the electrochemically-generated $H_2$ (Liu et al., 2017; Wang et al., 2012). Because $H_2$ can be easily produced in an MES through applying an external potential, both direct and indirect electron transfer activities could co-exist in the biocathode, jointly contributing to the cathodic reduction.

These functional cathodophilic bacteria have exhibited a relatively good ability to tolerate the toxic organic contaminants at an environmentally relevant concentration. For example, a biocathode maintained a reduction efficiency of >95 % of 50–200 mg/L NB for 80 days (Wang et al., 2012), and a stable dechlorination efficiency of around 90 % of 100 mg/L 4-CP was obtained for more than 5 cycles (each cycle of 168 h) (Kong et al., 2014).

## 4. The decisive role of bioanodes

The residues (or intermediates) from the cathodic degradation include compounds such as phenol (from halogenated phenols), aromatic amines (from azo dyes, NB and NP), and vinyl chloride (from CE), which still need further treatment in the anode where an electroactive bioanode can assist and play a decisive role in complete organic mineralization. The bioanode will not only affect the degradation of residue compounds in the anode, but also influence the cathode process via current generation (to deliver electrons).

Because the residual organics could still be resistant, they cannot be easily degraded by a conventional bioanode. As a result, proper improvement strategies such as the optimization of the bioanode condition are required. Adding easily degraded co-substrate (e.g., acetate) into the bioanode can promote the growth of the functional anodic bacteria, thus improving the organic degradation process (Fig. 3A) (Chen et al., 2019; Hedbavna et al., 2016). However, acetate will compete with the target organic contaminant for the electron acceptor (i.e., anode). Previous studies found that phenol could have a maximum
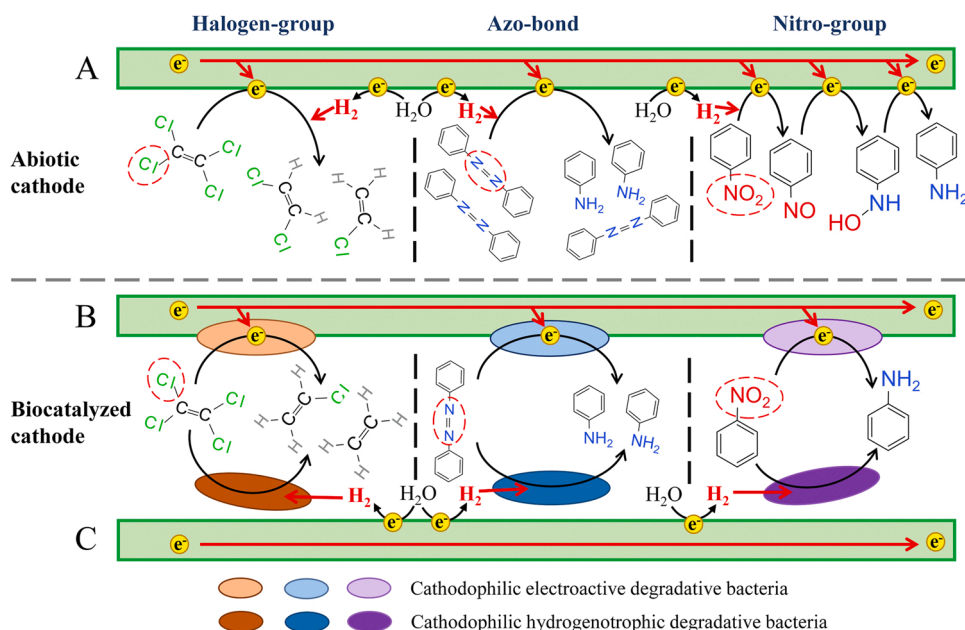
**Fig. 2.** Reductive degradation of halogen-, azo-, and nitro- organic contaminants via (A) abiotic cathode, as well as via (B) biocatalyzed cathode in direct pathway and (C) indirect pathway (using PCE, AB and NB as examples).
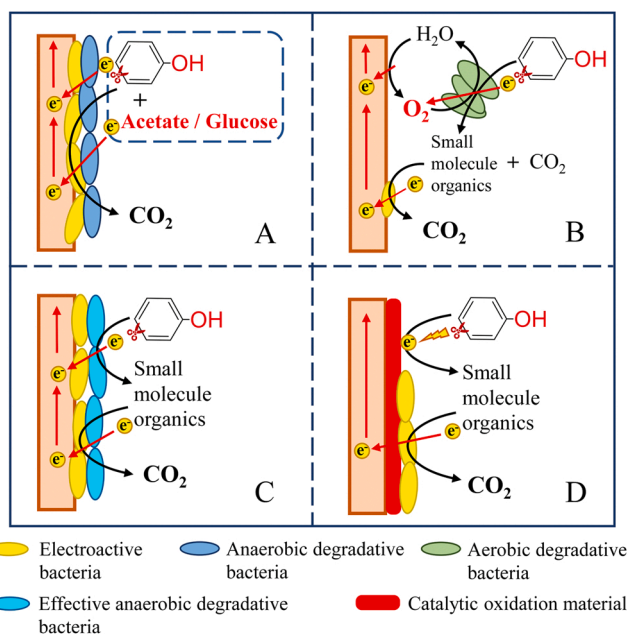


**Fig. 3.** Strategies to improve the bioanode oxidative degradation ability by (A) supplying easily degraded carbon source and (B) generating $O_2$ via applying a higher voltage as well as by (C) enriching effective anaerobic degradative bacteria and (D) introducing catalytic oxidation material (using phenol as an example).

degradation efficiency (80–98 %) when adding acetate to phenol at a molar ratio of 3–6 (Chen et al., 2019; Yang et al., 2021b). Another method is to increase the applied voltage to generate a small amount of $O_2$, which serves as a more powerful electron acceptor for degradative bacteria to degrade the residual recalcitrant organics (Fig. 3B) (Del-l'Armi et al., 2021; Lai et al., 2017; Liu et al., 2017; Lohner et al., 2011; Lohner and Tiehm, 2009). However, such an aerobic degradation is actually separated from the anode process; furthermore, $O_2$ will inhibit the electroactive bacteria and thus the current generation.

To avoid the addition of carbon compounds (Fig. 3A) or oxygen

inhibition (Fig. 3B), it is desired to minimize the toxic effect of the organic compounds on the anodophilic bacteria and utilize the residual organic compounds as a sole carbon source. This can be achieved by the inoculation and enrichment of effective anaerobic degradative species (Fig. 3C). For example, the anaerobic bacterial culture containing both aniline-degrading and electroactive species could be acclimated in a bioanode to complete a 90 % mineralization efficiency of AN (Liu et al., 2015). Several degradative species (e.g., *Geobacter metallireducens*) were found to be capable of degrading aromatic contaminants (e.g., phenol) under an anaerobic Fe(III)-reducing condition (Jiang et al., 2020; Zhang et al., 2013), a similar condition to an anode environment, and thus may be introduced to promote the bioanode oxidative process. In addition to anodic microbes, the anode electrode materials may be designed to have a stronger oxidation ability (Fig. 3D). Carbon-based anodes coated with catalytic materials (e.g. N-doped $TiO_2$ and mpg-$C_3N_4$) (Long et al., 2020; Wang et al., 2019; Zhou et al., 2017) or modified with transitional metal oxides $MnO_2$ (Chen et al., 2017; Zhang and Liu, 2020) can serve as bioanode electrodes and assist with oxidizing the residual toxic organics. By coupling the catalytic and biological oxidative processes, AN and phenol can be completely oxidized in an anode of an MES (which did not involve the cathodic reduction) (Chen et al., 2017; Long et al., 2020). However, this approach is yet to be demonstrated in a sequential cathode-anode degradation process.

## 5. Conclusions and perspectives

Maximum degradation of the selected halogen-, nitro-, and azo-organic contaminants can be accomplished in an MES through the integration of the cathode and anode processes. In theory, a target compound can provide sufficient electrons from the oxidation of its reducing products to support its reduction, but in practice this will be challenging due to low current efficiency. Enriching functional electroactive bacteria may improve the cathodic reduction and the optimization of the anodic operating conditions or electrode materials may enhance the anodic oxidation. Despite some success, this sequential cathode-anode degradation requires further investigation towards possible applications of MES technology. First, in a real wastewater, multiple recalcitrant organic contaminants may exist together (e.g. NP and CP) (Tseng and Lin, 1994) and compete for electron

donors/acceptors. They may involve direct competition for electron donors/acceptors or indirect competition in which there is the influence of the degradation intermediates from one target compound (e.g., nitrate from NP or phenol from CP) on the degradation of another target. In addition to the competitive effects, the toxic effects of multiple organic contaminants, for example NP could have significant toxic effect on dechlorinators, are worth further consideration. Second, the target compound may coexist with some easily degraded carbon sources, especially in a municipal wastewater that receives industrial wastewater (Zou et al., 2020). The easily degraded carbon compounds could serve as an electron donor in the cathode and/or a co-substrate in the anode to promote the degradation of target compounds. However, they may also inhibit the cathodic $H_2$ evolution process and compete with the target compounds for the anode electrode (electron acceptor), thereby inhibiting the anodic degradation of the target compounds. Third, inorganic compounds (e.g., nitrate and sulfate) can be present with the target compounds, for example in groundwater near the industrial sites (Roy and Bickerton, 2012). The denitrification process will significantly inhibit the dechlorination process due to the competition for electron donors and the generation of byproduct $N_2O$ (which can strongly inhibit the reductive dehalogenases in dechlorinators) in the biocathode (Yin et al., 2019); after the complete removal of nitrate, dechlorination can recover (Zhang et al., 2022). With proper catalysts or microbes (biocatalysts), nitrate can serve as an electron acceptor to promote the degradation of the target organics.

## 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.

## Acknowledgements

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