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Frontier review on metal removal in bioelectrochemical systems: mechanisms, performance, and perspectives

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ABSTRACT

Bioelectrochemical systems (BESs) have been investigated for metal removal and potential recovery from wastewaters. To better understand BES-based metal removal, in this paper we conducted a deeper literature analysis of BES-based metal removal, explored the removal mechanisms, and discussed the challenges of this approach. Four mechanisms are involved to achieve metal removal in BESs: direct redox reaction (DRO), indirect byproduct precipitation (IBP), ion migration, and biological removal. Most removals were via DRO or IBP mechanisms. IBP showed the highest median removal rate at 0.062 kg m^{-3} d^{-1} and biological removal had the lowest at 0.0034 kg m^{-3} d^{-1}. More than 60% of the studies could achieve >95% removal efficiency. Cathode efficiency is affected by the competition from co-existing electron acceptors. More energy consumption data should be reported to better understand the energy advantages of BESs in metal removal. Kinetic analysis demonstrates that IBP may lead to a higher removal rate when the metal concentration is low, while DRO would be more advantageous at a higher initial concentration. The future of metal removal is to recover the removed metal and the recovering methods must consider the minimal interruption of BES operation.

1. Introduction

Hazardous metals in waste streams from anthropogenic activities such as Cr (VI) and Cu (II) in electroplating wastewaters can threat human health (Li et al., 2008), cause decay of primary producers and aquatic lives (Singh and Kalamdhad, 2011), and negatively impact the aesthetic effects of a water body (Hogsden and Harding, 2012). Traditional methods for treating metal contaminants include chemical redox reactions, coagulation, precipitation, adsorption, membrane filtration, and biological accumulation (Fu and Wang, 2011). Those methods usually require intensive chemical inputs and produce a vast amount of metal sludge or concentrated brines (Djedidi et al., 2009; Pérez-González et al., 2012). As an emerging treatment concept, bioelectrochemical systems (BESs) have also been investigated for removing hazardous metals (Wang and Ren, 2014). Because the driving force for metal separation and removal is bioelectricity produced from the oxidation of organic substrates, the energy requirement for metal removal by BESs can be potentially low (Heijne et al., 2010).

Metals can be removed from a wastewater by BESs through four different mechanisms (Fig. 1): 1. direct redox reaction (DRO); 2. indirect byproduct precipitation (IBP); 3. ion migration; and 4. biological removal. DRO is the most widely reported removal mechanism in typical BESs like microbial fuel cells (MFCs) and microbial electrolysis cells (MECs). A wide range of metals including Cu (II), Pb (II), Hg (II), and Cd (II) can be reduced to elemental deposits or lower oxidation states (e.g. Cr (VI)) that have less solubility and thus are easier to precipitate (Huang et al., 2015; Nancharaiah et al., 2015; Wang and Ren, 2014). Metalloid in a reduced state such as AsO_2^- can also be utilized as an electron donor by the anode and detoxicated to As^{5+} via oxidation (Nguyen et al., 2016). IBP is to precipitate metals with the aid of byproducts from a cathodic reduction reaction such as OH^-, H_2O_2, and sulfide, or a sacrificial anode (Abourached et al., 2014; Song et al., 2019; Wang et al., 2020b; Wang et al., 2017b). Metal ion migration is driven by electron movement, for example in a three-chamber microbial desalination cell (MDC) that can have ions moved across ion exchange membranes (inset in Fig. 1). It was reported that >95% of Cu (II) and Cd (II) in a low-strength metal-laden wastewater could be separated via ion migration and subsequently removed in the cathode (Jiang et al., 2020b). Biological removal can occur in either an anode or a cathode, mainly via intracellular or extracellular biological reduction, bioaccumulation, and biosorption (Cao et al., 2020; Catal et al., 2009; Zhang et al., 2018b; Zhang et al., 2018c).

Despite the promise of BES-based metal removal, there is still much to explore to move this technology towards practical applications. To the best of our knowledge, pilot-scale BESs for real-world metal-laden wastewater treatment have not been reported (Wang and He, 2020). There is a need for better understanding of the mechanisms involved in the BES-based metal removal processes. The key issues such as kinetics of

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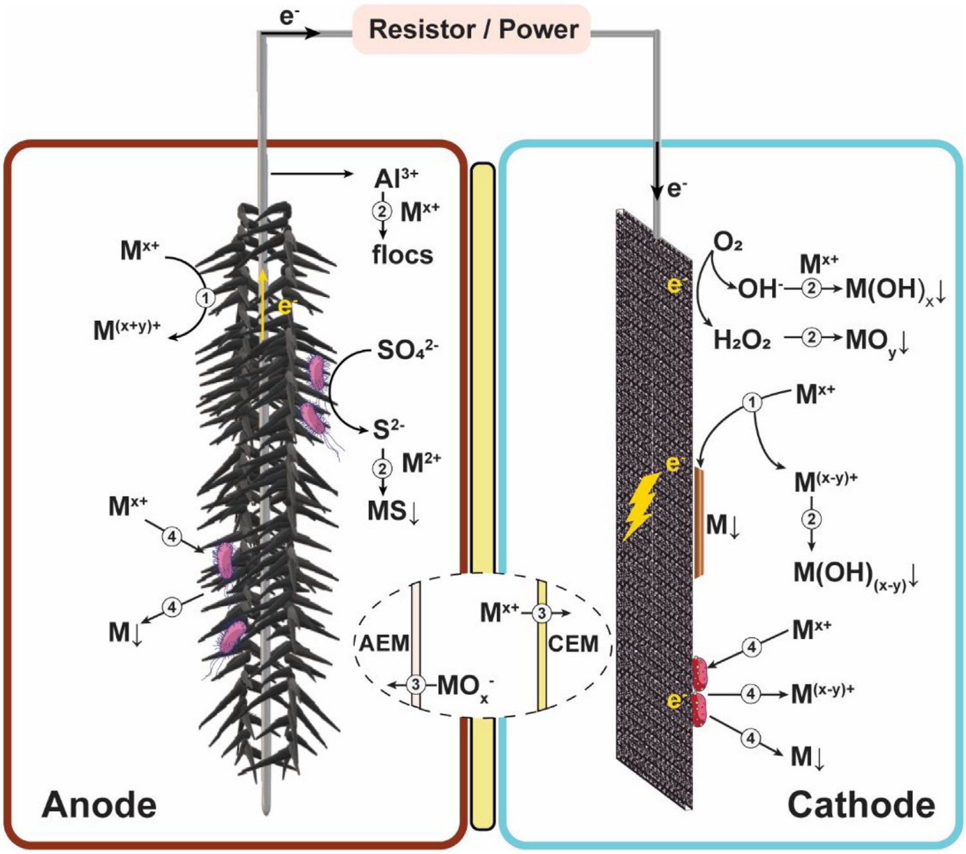

Fig. 1. Schematic of a bioelectrochemical system and major metal removal mechanisms: (1) direct redox reaction (DRO), (2) indirect byproduct precipitation (IBP), (3) ion migration, and (4) biological removal. M represents metals. AEM – anion exchange membrane; CEM – cation exchange membrane.

metal removal should be further analyzed to guide the selection of an optimal removal method. This paper aims to provide a concise analysis and discussion on BES-based metal removal and give perspectives to further this technology for sustainable treatment of metal wastewaters.

2. A deeper look into removal performance

The treatment capacity of a BES-based metal removal process can be presented in “removal rate (kg m^{-3} d^{-1})”. We have summarized the literature information about removal rates of different metals via four mechanisms (Fig. 2A). The mean values of those with IBP, ion migration, and biological mechanisms are biased due to the small sample sizes and major outliers. Therefore, median values are used to compare different mechanisms. DRO has the most reported studies among four mechanisms and exhibits a median removal rate of 0.046 kg m^{-3} d^{-1}. The highest removal rate of 0.864 kg m^{-3} d^{-1} was obtained with Cd^{2+} reduction in an MEC that might have benefited from the externally applied voltage and the optimized cathode material (Zhou et al., 2020). Most of the metals with a high reduction potential (e.g., Au^{2+}/Au, Ag^{+}/Ag, Hg^{2+}/Hg) can be removed at a rate higher than the upper quantile (0.14 kg m^{-3} d^{-1}) (Choi and Hu, 2013; Tao et al., 2012; Wang et al., 2011). Several other factors have also been investigated for their effects on metal removal via DRO. For example, increasing the initial Cu^{2+} concentration from 0.25 g L^{-1} to 1 g L^{-1} could enhance the removal rate from 0.12 g L^{-1} d^{-1} to 0.37 g L^{-1} d^{-1} (Luo et al., 2015), use of Fe^{3+} as an electron mediator promoted electricity generation and thus the Cr^{6+} reduction rate from 0.16 to 0.26 g L^{-1} d^{-1} (Wang et al., 2017a), and an effective cathode material such as stainless-steel woven mesh could ensure fast and continuous copper deposition (Wu et al., 2016). IBP had the highest median value of 0.062 kg m^{-3} d^{-1} and the highest upper quantile of 0.245 kg m^{-3} d^{-1} (more explanation in section 4). One outlier showed a removal rate of 5.07 kg m^{-3} d^{-1} (normalized to the cathodic volume) that might be related to the high initial Cu (II) concentration and high salinity and caustics in the catholyte (Dong et al., 2017). In that study, the precipitation of Cu (II) with hydroxide occurred in a different chamber from the cathode and this could avoid the interruption of OH^{-} generation by metal precipitation in the cathode. The fast byproduct generation, low metal hydroxide solubility, and external power supply would contribute to a high metal removal rate via IBP (Huang et al., 2018; Pozo et al., 2017; Wang et al., 2017b). The median value of the removal rate via ion migration is 0.049 kg m^{-3} d^{-1}. Competition for electricity-drive migration between target ions and other ions in a wastewater can greatly affect the removal in this approach. For example, when a real wastewater from steel and electroplating industries was treated, the removal rates of Ni (II) and Pb (II) were 0.20 and 1.68 $\times$ 10^{-4} kg m^{-3} d^{-1}, respectively, much lower than 0.89 and 0.90 kg m^{-3} d^{-1} in a synthetic wastewater (Mirzaienia et al., 2017). Biological removal has a significantly lower removal rate (0.0034 kg m^{-3} d^{-1}) than that of the other three mechanisms, indicating that metal removal in BESs is mainly via abiotic pathways (although powered by biological oxidation of organic compounds in an anode). Under some specific conditions, biological removal can have a good performance, for example one study of the biological reduction of Se (IV) to Se (0) in a single-chamber MFC reported a removal rate of 0.0396 kg m^{-3} d^{-1}, likely benefited from Se-reducing enzymes by certain anodic microorganisms (e.g. *Thauera* sp.) (Debieux et al., 2011).

The metal loading rate in BESs ranges from 10^{-3} to 10 kg m^{-3} d^{-1} (Fig. 2B). Regardless of the removal mechanism, there is a linear relationship between the metal removal rate and its loading rate. Over 60% of studies reported a removal efficiency of >95% and the rest could mostly achieve the removal of > 50%. More than half of the studies had metal concentrations in the range of 0.01–0.1 g L^{-1} (Fig. 2B inset), which are within the typical range of metals in actual wastewaters (Wang and

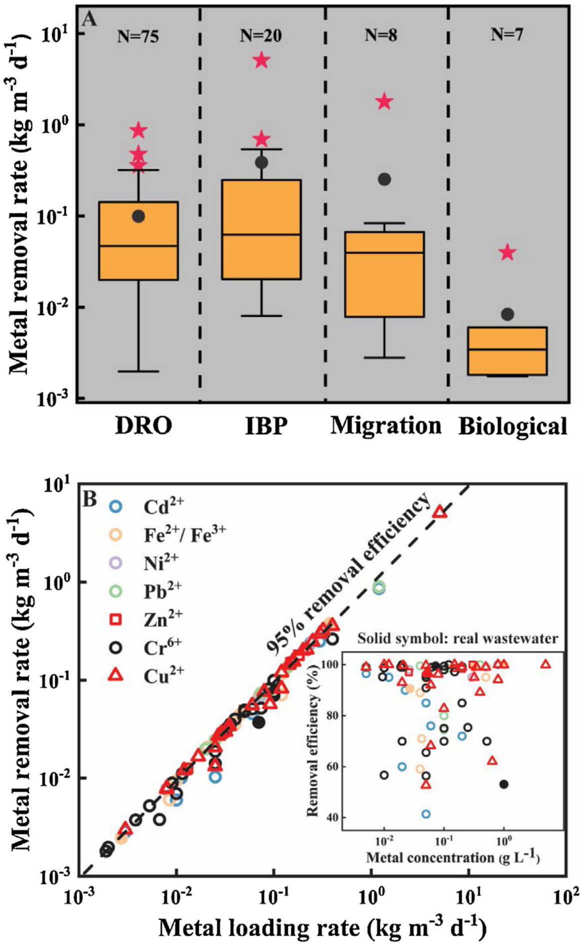

Fig. 2. Performance of BES-based metal removal: (A) metal removal rates of four removal mechanisms (black dots indicate mean value and red stars indicate outliers); and (B) metal removal rate as a function of the initial metal loading rates. Inset: removal efficiencies and metal concentrations. The dashed line corresponds to metal removal efficiency at 95%. Solid symbols indicate the cases of real metal-laden wastewaters.

Ren, 2014). Only 7% of the studies used actual metal-laden wastewaters such as acid mine drainage (Peiravi et al., 2017), electroplating wastewater (Li et al., 2008) and hydraulic fracturing flowback water (Zhang et al., 2018a).

3. It's all about "electricity"

The unique features of BES-based metal removal are bioelectricity generation and electron transfer processes that either directly or indirectly contribute to metal removal. Thus, electron transfer efficiency (ETE) is an important parameter. ETE includes two parts: Coulombic efficiency (CE) in the anode (from organic substrates to electrons/ charges) and cathode efficiency (from electrons to a final product, e.g., reduced metals). The methods for calculating those efficiencies can be found in Eq. S1-S3 (Supplementary Materials). It was found that 55% of the studies reported CE $>$ 30% and some could reach 95% (Heijne et al., 2010). The ETE from 19 studies centered around 24% (Fig. 3A, inset). We plotted the organic loading rate verses metal loading rate and compared the data with theoretical organic loading requirement as a function of metal loading rate (using Cu (II) as an example) at ETE of 1% (25 kg COD/ kg Cu) and 24% (1.04 kg COD/ kg Cu) (Fig. 3A). One can see that in most studies organic substrates were supplied at an ETE lower than 24% and some even lower than 1%, suggesting an oversupply of organic substrates to ensure enough electrons for metal removal. When a real wastewater was used (in about 6% of the studies that were analyzed here), a relatively lower metal loading rate was reported, likely related to the limited electron supply by complex organic compounds that could also decrease the ETE compared to that of simpler substrates (e.g., acetate was used in more than 90% of the studies) (Ai et al., 2020).

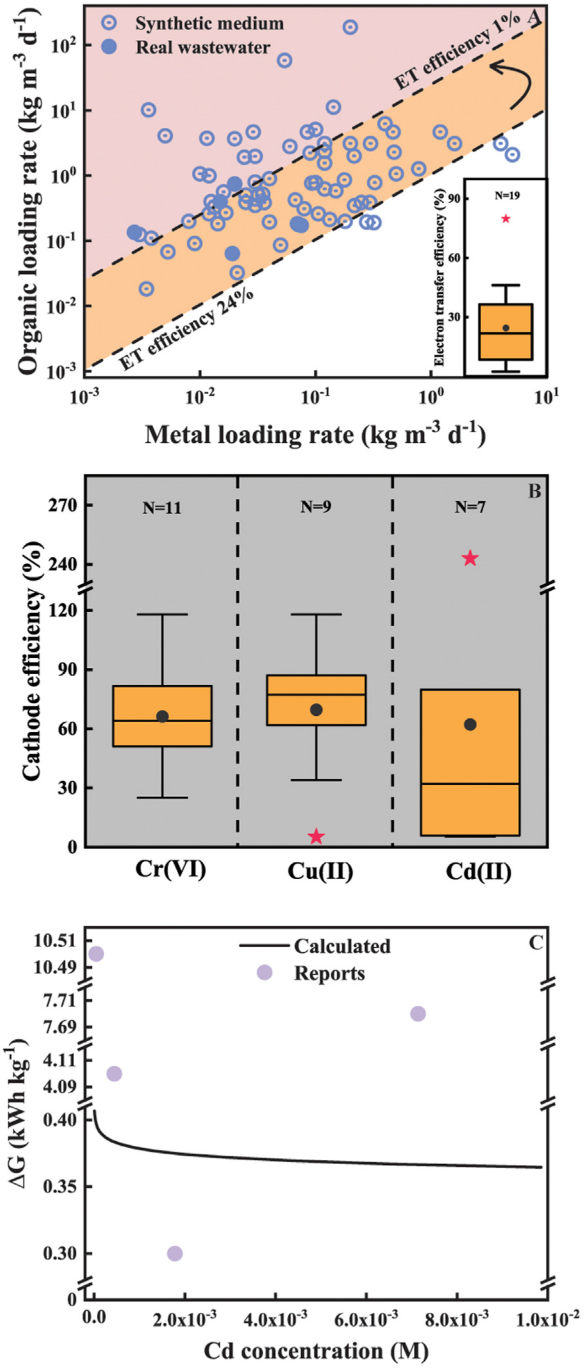

Fig. 3. Efficiency of electricity: (A) The metal loading rate and organic loading rate reported in literatures. Dashed lines are required organic loading rate as a function of Cu (II) loading rate at 1% and 24% electron transfer efficiency. Inset, electron transfer efficiency boxplot. Black dots indicate mean value, red stars indicate outliers; (B) cathode efficiency box plots of three metals; and (C) energy consumption of Cd (II) removal. The solid line indicates the theoretical Gibbs free energy required for Cd (II) reduction at 0.3 V cathodic potential (vs. NHE).

Among the studies that reported cathode efficiency, 38 were based on DRO and only 1 was about IBP. The cathode efficiency (all via DRO) of three widely studied metals, Cr (VI), Cu (II), and Cd (II), spans 25-118%, 34-117.9%, 5.3-243% with median values at 64%, 76%, and 32%, respectively (Fig. 3B). Other electron acceptors present in a wastewater can compete with metal ions for electrons and lead to a low cathode efficiency. For example, in an MEC, H^+ is reduced to generate H_2 by accepting electrons from a cathodic electrode, decreasing the cathode efficiency of Cd(II) reduction to 5.3% (Modin et al., 2012). When including the generated H_2 as a final product, the cathode efficiency can reach 49-89% (Huang et al., 2015; Luo et al., 2014). Theoretically, the maximum cathode efficiency is 100%. However, some reported values are as high as 243%; this is because that metals can be removed by other mechanisms that do not directly involve electron transfer such as precipitation and adsorption (Colantonio and Kim, 2016; Wang et al., 2020a). Cathode efficiency is also affected by electrode material, cathodic potential, and the type of metals to be treated (Zhang et al., 2015; Zhou et al., 2020). To improve the cathode efficiency for metal removal, the presence of other competing electron acceptors (e.g. O_2, H^+ under an MEC mode) should be minimized.

Energy consumption is another key parameter to evaluate metal removal in BESs but very few studies have reported it. Cd (II) is the only metal for which we can find energy data in several BES studies (all via DRO). The theoretical Gibbs free energy of Cd (II) reduction at a 0.3 V cathodic potential (vs. normal hydrogen electrode (NHE)) is estimated as 0.37 kW h kg^{-1} (Eq. S4). As shown in Fig. 3C, there is a wide range of the reported energy consumption between 0.3 and 10.5 kW h kg^{-1} Cd (Huang et al., 2015; Modin et al., 2012; Wang et al., 2016; Zhou et al., 2020). Most studies have a relatively low initial Cd (II) concentration (<50 mg L^{-1}) and strong H_2 evolution competition, both of which could cause a higher energy consumption than the theoretical value (Huang et al., 2015; Wang et al., 2016). However, such a consumption is still lower than that of electrocoagulation (12.1–73.6 kW h kg^{-1}) at a similar removal rate range (0.2~1.1 kg m^{-3} d^{-1}) (Vasudevan et al., 2011), owing to the bioenergy generated from the anode reactions. The energy advantage of BES-based metal removal benefits from electricity generation from low-grade substrates such as organics in a wastewater. To better understand this advantage, energy performance should be reported in more studies of metal removal.

4. Direct redox reaction or indirect byproduct precipitation?

The BES-based metal removal is essentially to convert soluble metals into their less soluble forms to precipitate as solids and this principle is shared by three out of four removal mechanisms (DRO, IBP, and biological removal). The method of ion migration may eventually need to precipitate metals after ion-moving separation. Thus, DRO and IBP are considered the dominant removal mechanisms, and this is also reflected by the number of studies involving those mechanisms (Fig. 2A). Some metals can be removed via either DRO or IBP, raising a question on which mechanism should be employed. We attempted to find some answers to this question by using Cu removal as a case study and performing a kinetics analysis. In DRO, Cu (II) is reduced to Cu by accepting electrons from a cathodic electrode, while in IBP O_2 reduction on the cathode generates hydroxide to precipitate Cu (II). The rate constant of the electrochemical reduction reaction can be estimated using the Butler-Volmer kinetics (Eq.1)

$$k = k_f - k_b = k^0 \exp\left[\frac{-\alpha nF(E-E^{0'})}{RT}\right] - k^0 \exp\left[\frac{(1-\alpha)nF(E-E^{0'})}{RT}\right] \qquad (1)$$

where k° is standard rate constant (m s^{-1}), α is transfer coefficient, n is the number of transferred electrons, R is gas constant (8.314 J mol^{-1} K^{-1}), T is temperature (293.15 K), $E^{0'}$ is equilibrium potential (V), and E is actual cathodic potential (V). The transfer coefficients α and standard rate constants k° were adopted from the previous studies (Cifuentes and Simpson, 2005; Freguia et al., 2007; Fu et al., 2011; Heijne et al., 2010; Renslow et al., 2011). The backward kinetics k_b can be neglected when the cathodic potential (assumed at 0.15 V vs. NHE) is 88 mV or 44 mV more negative than the reduction potential of Cu (II) or O_2 (0.24 V or 0.83 V at 20 mg-L^{-1} Cu (II) and neutral pH) (Renslow et al., 2011). The assumptions include first-order reaction, 10% OH- utilization, saturated atmospheric O_2 concentration, and oxygen reduction potential loss of 0.4 V (Renslow et al., 2011). The transient reaction rates were calculated and plotted as a function of Cu (II) concentration as shown in Fig. 4. It is observed that the rate of DRO increases with the Cu (II) concentration, due to the increased $E^{0'}$ (i.e. k increases) according to Nernst equation and the assumed first-order kinetics. The reported Cu (II) removal rates (Fig. 4) exhibit a similar positive relationship with the initial concentration. The use of catalysts can lead to more hydroxide production and thus promote metal precipitation via IBP, for example the removal rate of Cu was enhanced from 0.09 to 1.08 kg Cu m^{-3} d^{-1} by catalyzed oxygen reduction reaction (Fu et al., 2011). Our analysis shows that IBP can have a faster removal rate than that of DRO at a low Cu concentration (<0.5 g L^{-1} with catalyzed oxygen reduction or 0.1 g L^{-1} when a catalyst is not included). Nearly 80% of Cu-removal studies had an initial Cu (II) concentration < 0.5 g L^{-1}, which may favor the use of the IBP removal method. However, very few of those studies adopted IBP (Fig. 4). When an initial Cu (II) concentration is higher than 0.5 g L^{-1}, DRO would have an advantage of achieving higher removal rates.

In addition to removal rate, there are also other differences between DRO and IBP. For example, in DRO, a metal deposits mostly on the cathodic electrode, and the precipitates in IBP can occur on the electrode, ion exchange membrane, and other parts of the cathode chamber (Abourached et al., 2014; Dong et al., 2017; Lefebvre et al., 2012). DRO results in pure metallic solids while IBP produces the precipitates of metal chemicals (e.g., metal hydroxide). Metal hydroxides may also be formed during DRO when hydroxide ions are generated and can cause cathode deactivation by reducing electron transfer to electron acceptors (Huang et al., 2018). For examples, Cr (VI) reduction was strongly inhibited by the formation of $Cr(OH)_3$ on the cathode (Xafenias et al., 2013). When iron hydroxide precipitated on anion exchange membrane of an MFC, the system performance was deteriorated (Foudhaili et al., 2019). Furthermore, the precipitates can also build up in the pipes and cause severe blockage in a long-term operation. DRO is expected to have less effect of precipitates than IBP. To minimize such a problem with IBP, the precipitation may occur outside BESs; that is, BESs provide hydroxide ions to an external unit where a metal wastewater is treated, and this may also facilitate metal recovery as described in the followings.

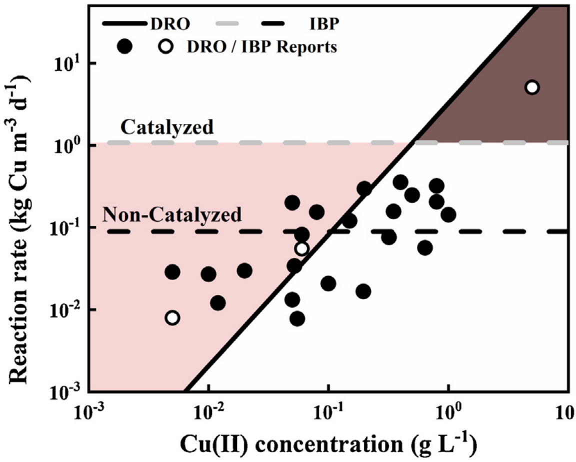

Fig. 4. Transient kinetics estimation of Cu (II) removal via direct redox reaction (DRO) and indirect byproduct precipitation (IBP) at 0.15 V cathodic potential (vs. NHE). Assuming cathode electrode surface area 20 cm^2, cathode effective volume 40 mL, and pH = 9.

5. Recovery, one step beyond removal

The concept of sustainability has been embedded into many treatment technologies and is reflected by recovering useful resources from wastes. The removed metals in BESs, if valuable, are available for being recovered, one step beyond their removal. There have been some attempts to recover metals, for example 83% of Ag was removed via DRO from the $AgNO_3$ solution in an MFC and then 67.8% was scraped from its cathode and subsequently used as an anti-biofouling agent (Ali et al., 2019). The method for recovering a metal in BESs is strongly related to the removal mechanism. Metals removed via DRO depositing on a cathodic electrode are mostly recovered by manual scraping or acid dissolution (Ali et al., 2019; Sravan et al., 2020; Tao et al., 2011). The reported metal recovery efficiency ranges from 10.2 to 79.3%, affected by the incomplete manual collection and the loss to other removal pathways (Colantonio, 2016). The solids products on the cathodic electrode are mostly elemental metals, with some impurities such as metal oxides (Rikame et al., 2018). The scrapping or dissolution method would require disassembling a BES reactor and could interrupt its operation. The metal precipitates via IBP can be readily collected, as most are settled by gravity and then collected (Huang et al., 2018). It was reported that the metal sludge produced by BESs was 9-fold more settable than chemically dosed sludge and could be easily dewatered by centrifugation (Pozo et al., 2017). Ion migration creates a metal brine solution that requires further metal reduction or precipitation to recover metal solids (Jiang et al., 2020a; Jiang et al., 2020b). The recovery of metal via biological removal involves energy-intensive cell lysis and physical separation (Zhang et al., 2018c).

Metals can also be recovered outside a BES reactor, or *ex situ* recovery. This approach is usually linked with IBP removal method. For example, a BES supplied a caustic catholyte effluent to a tank containing a copper waste stream for $Cu(OH)_2$ precipitation (Dong et al., 2017). The catholyte can also be recirculated between the cathode chamber and a precipitation tank with heterogeneous precipitation of metal hydroxides in the tank (Pozo et al., 2017). The heterogeneous precipitation benefited from the conical design of the tank and a stable pH at 7.3 manipulated by an internal pH controller. Such *ex situ* recovery is also feasible to recover metals from the brine solution produced with ion migration.

6. Conclusions

BESs have been demonstrated to be an effective technology for metal removal with four major mechanisms involved. Most studies provided surplus organic compounds that might result in a relatively low Columbic efficiency. The cathode efficiency of BES-based metal removal can be strongly affected by the presence of competing electron acceptors. Because of bioenergy production, the energy consumption of BES-based metal removal can be potentially lower than that of other removal technologies but the understanding of such an advantage would need more reports of energy performance data. The kinetic analysis reveals that at a low concentration, indirect byproduct precipitation may lead to a higher removal rate than that of direct redox reaction. Collection of the removed metals, which may be available for recovery and reuse, must consider the removal method and minimize the perturbation on BES operation.

Declaration of Competing Interest

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

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.hazl.2020.100002.

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