

Emerging electrochemical processes for materials recovery from wastewater: Mechanisms and prospects

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HIGHLIGHTS

- Mechanisms for selective recovery of materials in electrochemical processes are discussed.
- Wastewaters that contain recoverable materials are reviewed.
- Application prospects are discussed from both technical and non-technical aspects.

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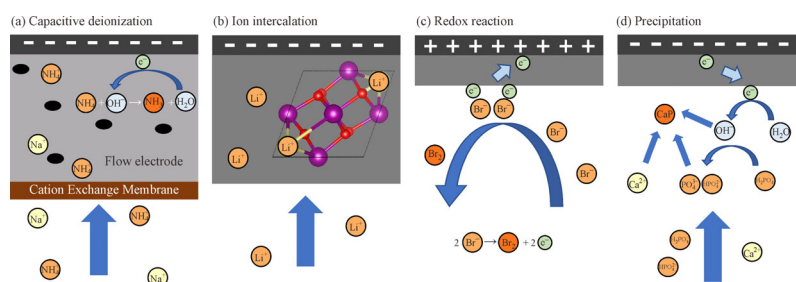
Electrosorption

Capacitive deionization

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Electrochemical precipitation

GRAPHIC ABSTRACT



ABSTRACT

Recovering valuable materials from waste streams is critical to the transition to a circular economy with reduced environmental damages caused by resource extraction activities. Municipal and industrial wastewaters contain a variety of materials, such as nutrients (nitrogen and phosphorus), lithium, and rare earth elements, which can be recovered as value-added products. Owing to their modularity, convenient operation and control, and the non-requirement of chemical dosage, electrochemical technologies offer a great promise for resource recovery in small-scale, decentralized systems. Here, we review three emerging electrochemical technologies for materials recovery applications: electrosorption based on carbonaceous and intercalation electrodes, electrochemical redox processes, and electrochemically induced precipitation. We highlight the mechanisms for achieving selective materials recovery in these processes. We also present an overview of the advantages and limitations of these technologies, as well as the key challenges that need to be overcome for their deployment in real-world systems to achieve cost-effective and sustainable materials recovery.

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1 Introduction

The treatment of municipal and industrial wastewaters has traditionally been motivated by the detrimental impacts of pathogens and chemical pollutants on human health and the natural environment (van Loosdrecht and Brdjanovic, 2014). While this wastewater treatment approach has achieved significant public health benefits over the past century, it falls short to achieve our society's sustainability

goals as we face a host of emerging environmental challenges including water stress, climate change, and resource scarcity (Puyol et al., 2016). As the societal production system transitions from a raw-material-to-waste paradigm to a cradle-to-cradle model, wastewater is increasingly being viewed as a collection of resources, notably, water, energy, and materials. The extraction of water and energy from wastewaters has been discussed in recent reviews (Shaffer et al., 2013; Gao et al., 2014). Municipal and industrial wastewaters also contain a variety of materials that can be recovered for beneficial use (Xu et al., 2003; Kehrein et al., 2020). Separation of valuable materials, such as phosphorus and metals, from wastewater provides an alternative to industrial production and mining processes which can cause substantial environmental

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damages. In the review, we will focus on the recovery of valuable materials from wastewaters.

Techniques for separating materials from wastewaters include biological, physical, and chemical approaches. Recently, several electrochemical technologies emerge and offer unique advantages in the recovery of materials from wastewater. In this review, we highlight three electrochemical processes that show great potential for recovering valuable materials from wastewater: capacitive deionization (CDI) or electrosorption, electrochemical redox reactions, and electrochemically induced precipitation (Fig. 1). We then discuss the advantages and limitations of these technologies and identify scenarios under which they are most promising for resource recovery applications. Finally, we make recommendations for future research that would allow for more efficient, durable, and economically viable electrochemical systems for materials recovery.

2 Capacitive deionization for materials recovery

CDI is an electrochemical technology to separate ions from water (Murphy and Caudle, 1967; Porada et al., 2013). Traditional CDI processes utilize carbonaceous electrodes. With an applied potential bias, ions transport to and are stored capacitively in the electrical double layers (EDLs) on the porous surface of the electrodes (Porada et al., 2013). Anions are adsorbed on the positive electrode and cations are adsorbed on the negative electrode during the charging step. During the discharging step, ions are released back to the bulk solution when the voltage is released or reversed.

CDI technology advances with the innovation of electrode materials and cell configurations. Inspired by rechargeable batteries, insertion compounds including sodium manganese oxide (NMO) (Pasta et al., 2012b),

lithium manganese oxide (LMO) (Ryu et al., 2015), and copper hexacyanoferrate (CuHCF) (Kim et al., 2017) have emerged as promising electrode materials for ion separation. Ion storage in these insertion electrodes involves the intercalation of ions into the crystalline lattices of bulk inorganic matrices and the concurrent redox reactions on metal cations in the matrices. Insertion electrodes offer high ion removal capacity, owing to the ion storage in bulk electrode, and intrinsic selectivity, enabled by the nano-sized channels within the crystalline lattice (Liu et al., 2019). With respect to cell configurations, a CDI cell consists of a pair of porous carbon electrodes placed in parallel with a separator in between; membrane capacitive deionization (MCDI) systems have ion-exchange membranes on the electrodes and have charge efficiency and ion adsorption capacity superior to CDI (Lee et al., 2006); and flow-electrode capacitive deionization (FCDI) systems enable continuous ion separation by regenerating carbon electrodes outside the operating cell (Rommerskirchen et al., 2018).

Due to its potential to achieve selective ion separation (Su and Hatton, 2017; Su et al., 2017; Kim et al., 2020; Srimuk et al., 2020; Zhang et al., 2020), CDI offers a means to separate and concentrate resources that are present in an ionic form in wastewaters. Here we only consider CDI as an ion separation process, in which the oxidation states of target ions are unchanged.

2.1 Nitrogen

The most predominant form of nitrogen, nitrogen gas, needs to be converted to reactive nitrogen, including ammonium, nitrite, and nitrate, to be used as a nutrient for plant growth. The Haber–Bosch process for fixing N_2 as NH_3 , despite its great success in feeding the world's population, is highly energy- and carbon-intensive: it consumes 1% of the global energy production and

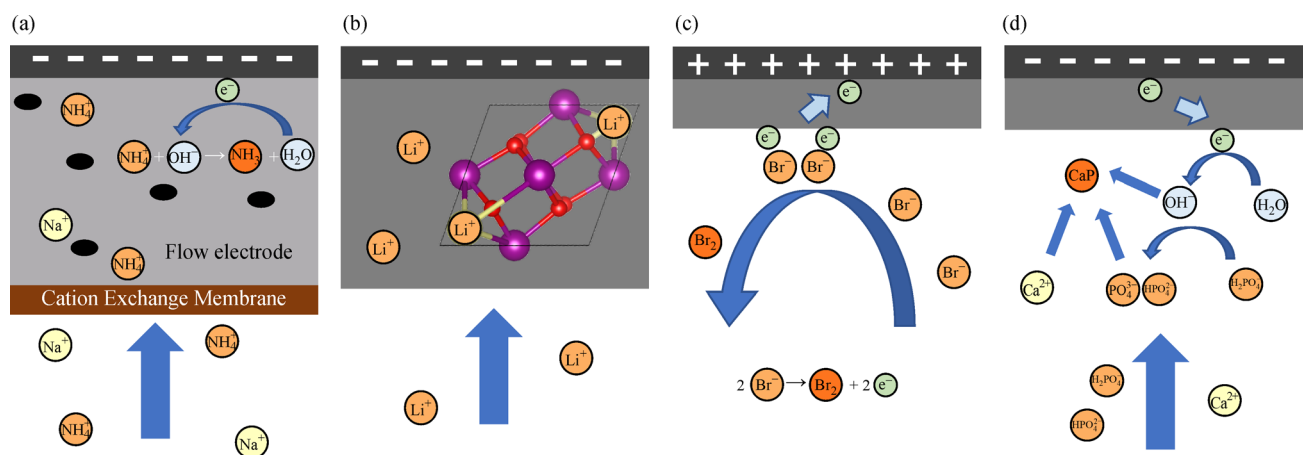


Fig. 1 Schematic of different materials recovery mechanisms: (a) ammonium recovery by flow-electrode CDI (FCDI), (b) lithium recovery by intercalation electrode lithium manganese oxide, (c) bromine recovery from bromide by redox reaction, and (d) phosphorus recovery by electrochemically induced precipitation of calcium phosphate.

contributes to 1.4% of global CO₂ emissions (Capdevila-Cortada, 2019). Additionally, the reactive nitrogen used in food production can be lost to the environment via municipal sewage and runoff of excess nitrogen fertilizers. Separating reactive forms of nitrogen from wastewater for beneficial agricultural use will not only offset the environmental damages from ammonia synthesis but also alleviate the eutrophication of natural water bodies caused by N pollution.

2.1.1 Ammonium

Ammonium-based fertilizers are used on a large scale to promote agricultural production. Municipal wastewater contains ammonia (NH₃) and ammonium (NH₄⁺), which are converted to N₂ by nitrification/denitrification or Anammox process in wastewater treatment plants. Recovering ammonium from municipal wastewater, or directly from urine (Larsen and Gujer, 1996), presents an opportunity to reuse the reactive nitrogen for agricultural production. CDI has been demonstrated as a promising technology to recover ammonium.

Carbonaceous materials, including carbon aerogel (Farmer et al., 1996), activated carbon (Broséus et al., 2009), and graphene laminates (Wimalasiri et al., 2015), have been applied in CDI systems for NH₄⁺ removal. An early study tests the removal of NH₄ClO₄ from water by a CDI system using carbon aerogel as the electrode (Farmer et al., 1996), which has high electrical conductivity owing to the covalently bonded carbon particles in the monolithic structure. In a mixture of NH₄⁺ and NaCl, an increase in NaCl concentration results in a decrease in the removal of NH₄⁺ by a CDI system of activated carbon electrodes, indicating the competition of electrode adsorption sites (Broséus et al., 2009). In an MCDI system with graphene laminates as the electrodes, a faster adsorption rate for NH₄⁺ than Na⁺ is observed based on a pseudo-first-order kinetic model, suggesting a separation selectivity of NH₄⁺ over Na⁺ (Wimalasiri et al., 2015). It is noted that, however, this kinetic model does not account for ion transport mechanisms.

In a membrane-free CDI system, unless the system reaches an adsorption equilibrium after extended charging at a constant voltage, the selective removal of two ions are controlled by their relative ion transport rates (Wang and Lin, 2019). Assuming equal concentrations of Cⁿ⁺ (e.g., NH₄⁺, Ca²⁺, or Mg²⁺) and Na⁺ in the spacer channel, and assuming a linearized potential profile and an absence of concentration gradient, the molar electromigration ion flux of Cⁿ⁺ relative to that of Na⁺ in the bulk solution is related to their diffusion coefficients and valence according to the Nernst–Planck equation (Bard and Faulkner, 2001):

$$\frac{J_{C^{n+}}}{J_{Na^+}} = \frac{nD_{C^{n+}}}{D_{Na^+}}, \quad (1)$$

where $J_{C^{n+}}$ and J_{Na^+} are the electromigration molar ion flux for Cⁿ⁺ and Na⁺, respectively; $D_{C^{n+}}$ and D_{Na^+} are the diffusion coefficients of Cⁿ⁺ and Na⁺ in the bulk solution, respectively, and n is the valence of Cⁿ⁺. This ratio $\frac{J_{C^{n+}}}{J_{Na^+}}$ is calculated as presented in Table 1. The transport selectivity of NH₄⁺ over Na⁺ in a CDI system is approximately 1.5.

This selectivity can be further enhanced in an MCDI system. The electromigration molar flux of Cⁿ⁺ relative to that of Na⁺ in a cation exchange membrane (CEM) is (Zuo et al., 2018; Wang and Lin, 2019):

$$\frac{J_{m,C^{n+}}}{J_{m,Na^+}} = \frac{nD_{m,C^{n+}}}{D_{m,Na^+}} \frac{K_{C^{n+}}}{K_{Na^+}} \quad (2)$$

where $D_{m,C^{n+}}$ and D_{m,Na^+} are the diffusion coefficients of Cⁿ⁺ and Na⁺ in the CEM, respectively; and $K_{m,C^{n+}}$ and K_{m,Na^+} are the partition coefficients between the CEM phase and aqueous phase for Cⁿ⁺ and Na⁺, respectively. The value of $\frac{K_{C^{n+}}}{K_{Na^+}}$ can be inferred from the separation factors for Cⁿ⁺ over Na⁺ in strong-acid cation exchange resins (Clifford, 1999). Assuming that $\frac{D_{NH_4^+}}{D_{Na^+}}$ is equal to $\frac{D_{m,NH_4^+}}{D_{m,Na^+}}$,

an MCDI system can, in theory, achieve selective removal of NH₄⁺ relative to Na⁺ with a molar ion flux ratio of roughly 2. However, other cations including Ca²⁺ and Mg²⁺ migrate faster than Na⁺ in both CDI and MCDI systems (Table 1). Additionally, in real wastewaters, target ions are typically present at lower concentrations than coexisting ions. For example, the ammonium concentration in domestic wastewater is typically below 60 mg/L of NH₄-N (Henze et al., 2008), while the sodium concentration in domestic wastewater frequently exceeds 150 mg/L (Harussi et al., 2001). Therefore, it would be difficult to selectively separate NH₄⁺ based solely on the difference in ion transport rates in the presence of a mixture of competing cations. This also indicates that nutrient-rich waste streams, such as urine and animal wastes (Larsen and Gujer, 1996; Ham and DeSutter, 1999), are better targets than domestic wastewater for the recovery of nitrogen.

To further improve the selectivity of N recovery, the transition of NH₄⁺ to NH₃(g) at high pH can be leveraged (Fig. 2(a)) (Zhang et al., 2017). During the charging step, NH₄⁺ and other cations cross the CEM and accumulate in the cathode chamber. The Faradaic reactions in the cathode chamber result in a rise in the local pH, leading to the conversion of NH₄⁺ to uncharged NH₃ (Fig. 2(b)). When discharging step starts, co-existing cations migrate back into the flow channel, while NH₃ can be selectively recovered using a gas-permeable membrane module (Zhang et al., 2019). This system offers a great promise in selectively recovering N from the municipal wastewater.

Table 1 Estimated theoretical ratio of cation electromigration rates in CDI and MCDI systems (calculations are based on equal concentration of ions)

Ions	Diffusion coefficient (m^2/s) ^a	$\frac{J_{\text{C}^{n+}}}{J_{\text{Na}^+}}$	Approximate separation factor in strong acid cation exchange resin (relative to Na^+) ^b	$\frac{J_{m,\text{C}^{n+}}}{J_{m,\text{Na}^+}}$
NH_4^+	1.95×10^{-9}	1.5	1.3	2.0
Ca^{2+}	7.92×10^{-10}	1.2	1.9	2.3
Mg^{2+}	7.06×10^{-10}	1.1	1.7	1.8
Na^+	1.33×10^{-9}	1.0	1.0	1.0

Notes: a) Diffusion coefficients taken from (Newman and Thomas-Alyea, 2004); b) Separation factors taken from (Clifford, 1999); strong acid cation exchange resin is polystyrene divinylbenzene matrix with sulfonate functional groups.

Intercalation electrodes with intrinsic ion selectivity offer another means of selective separation of NH_4^+ over Na^+ . The intercalation potential to copper hexacyanoferrate (CuHCF) electrodes is more positive for NH_4^+ than Na^+ , allowing for selective recovery of NH_4^+ by modulating the potential window (Kim et al., 2018b) (Fig. 2(c)). The difference in their intercalation potential is attributed to their different Stokes radii: NH_4^+ has a Stokes radius of 1.2 Å smaller than that of the interstitial channels in the crystal structure of CuHCF (1.6 Å), whereas Na^+ has a larger Stokes radius of 1.8 Å (Wessells et al., 2011). A key challenge to employ intercalation electrodes in practical materials recovery lies in the uncertainty associated with the cycling stability of electrodes in complex environmental waters. For example, the charge capacity of CuHCF electrodes decreases by 30% after 50 charge-discharge cycles in a pure NaCl solution (Kim et al., 2017). Domestic wastewaters contain effluent organic matter, which may further deteriorate the cycling stability of intercalation electrodes by accelerating electrode dissolution and interfering with interfacial ion transport (Liu et al., 2018). Future studies that focus on enhancing the longevity of intercalation electrodes will facilitate their application in recovering resources from wastewaters.

2.1.2 Nitrate

Although nitrate (NO_3^-) is present in negligible quantities

in raw domestic wastewater, it can become the dominant form of nitrogen in secondary effluent with reported concentration up to 40 mg/L (Pastushok et al., 2019). Nitrate can be recovered as a nutrient for biomass production through the cultivation of microalgae and cyanobacteria (Kim et al., 2016). Studies on the removal of nitrate using CDI systems are mostly motivated by nitrate as a contaminant, and the insights can be leveraged for recovering nitrate as a potential resource.

Similar to the competitive adsorption between NH_4^+ and other cations, the removal of nitrate by CDI is influenced by the competitive electrosorption of chloride (Tang et al., 2015). To improve nitrate removal, an asymmetric CDI system is developed with the cathode coated by negatively charged SiO_2 and anode coated by positively charged Al_2O_3 (Lado et al., 2017). The coated electrodes remove more nitrate than uncoated electrodes because the metal oxides render the carbon electrodes less hydrophobic and created additional adsorption sites.

The above mentioning CDI systems exhibit a negligible preference for the removal of nitrate over other anions. The diffusion coefficient of nitrate ($1.9 \times 10^{-9} \text{ m}^2/\text{s}$) is similar to that of chloride ($2.0 \times 10^{-9} \text{ m}^2/\text{s}$) (Newman and Thomas-Alyea, 2004); therefore, CDI cannot achieve selective removal of nitrate over chloride kinetically. One strategy to separate nitrate from an anion mixture is to place nitrate-selective coatings, such as anion exchange resin, on carbon electrodes to leverage the preferential

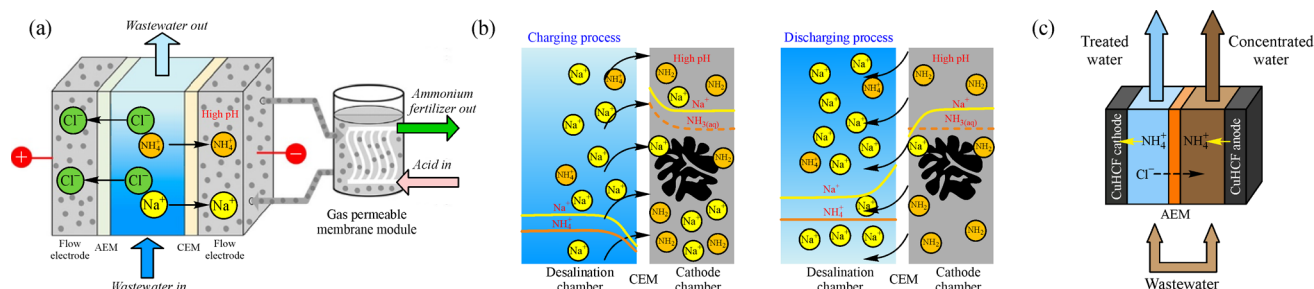


Fig. 2 (a) Schematic of ammonia recovery in the CapAmm system assisted by hollow-fiber gas-permeable membrane. Reprinted with permission from (Zhang et al., 2017). Copyright 2017 American Chemical Society. (b) Mechanisms of the selective ammonia recovery. Reprinted with permission from (Zhang et al., 2019). Copyright 2019 American Chemical Society. (c) Selective ammonium removal using two copper hexacyanoferrate (CuHCF) battery electrodes. Reprinted with permission from (Kim et al., 2018b). Copyright 2018 American Chemical Society.

partition of nitrate in the coating (Kim and Choi, 2012) for selective nitrate separation (see Table 2 for estimation of transport selectivity). Another strategy is to impart ion-selectivity to the carbon electrodes by tuning the pore size. Ultramicroporous hierarchical carbon aerogel monolith (μ HCM) electrodes that are prepared through moderate activation contain exclusively narrow (< 1 nm) pores and offer high selectivity for nitrate adsorption ($S_{\text{NO}_3^-/X} > 5$, X is Cl^- or SO_4^{2-}) (Hawks et al., 2019). The selective removal of nitrate over sulfate is because sulfate ions are too large to adsorb in the small micropores; in comparison, the selectivity of nitrate over chloride is attributed to the lower hydration energy of nitrate (Marcus, 1991) and thus a weak binding of water to the axial direction of the nitrate ion. This selective separation mechanism is akin to the selective transport of solutes in reverse osmosis (RO) membrane: the magnitude of solute-water pair interaction energy, or the difficulty for the solutes to shed their water solvation shells, determines their rate of transport through the smallest open space between the entangled polymer chains in the RO membrane (Shen et al., 2016).

2.2 Phosphorus

Phosphorus, as an essential element for plant growth, plays an important role in promoting agricultural productivity. Since phosphorus is a non-renewable resource (Van Vuuren et al., 2010), even a partial depletion of phosphorus resources may disrupt the sustainability of agriculture. The most common forms of phosphorus on Earth are apatite, igneous rocks, and sedimentary deposits, and these “easy-to-mine” phosphorus sources have been projected to be depleted in the next 50–100 years at current rates of extraction and consumption (Cordell and White, 2011). The ineffective use of phosphorus fertilizer results in phosphorus loss to natural water systems, deteriorating water quality. Recovering phosphorus from wastewaters is crucial for conserving phosphorus as a valuable, non-renewable resource as well as for protecting the aquatic environment. It is worth noting that human excreta (e.g. source-separated urine) (Larsen and Gujer, 1996), some industrial wastewaters (e.g., cheese whey effluent) (Comeau et al., 1996), and livestock wastewaters (Kishida

et al., 2009) contain higher concentrations of phosphorus than domestic wastewater, and therefore are potentially more amenable to efficient recovery of phosphorus.

Phosphate ions are the main target of P recovery from wastewater. The separation of P in CDI systems is influenced by pH due to the pH-dependent speciation of phosphate (Huang et al., 2017). Both H_2PO_4^- and HPO_4^{2-} have lower diffusion rates and migrate slower than Cl^- (Table 2). Upon prolonged charging, divalent HPO_4^{2-} ion has an energetic advantage over Cl^- and can be stored in the EDL preferentially (Hou et al., 2008). A promising strategy to achieve selective P recovery is to employ phosphate-selective anion exchange membrane (AEM) (Paltrinieri et al., 2019) in an MCDI system. However, the presence of sulfate in wastewater will likely interfere with the selective separation of phosphate in both CDI and MCDI systems (Table 2).

In addition to recovering N and P separately, CDI systems can also achieve concurrent recovery of these two resources. In an FCDI system (Fig. 3(a)) (Bian et al., 2019), the efficiency of phosphate recovery is sensitive to the electrode loading because phosphate removal is based on both physical adsorption and electro-sorption. For wastewaters that contain heavy metals other than nutrients, treatment systems combining adsorption and CDI can achieve simultaneous decontamination and nutrient recovery. A demonstrated system consists of functional hydrogel adsorbents to remove metal ions and a following CDI system to enrich P and N (Yuan et al., 2020). Plants using recovered liquid fertilizers recovered from Pb-contaminated wastewater show similar heights, root lengths, and chlorophyll contents compared with those using actual fertilizer (Fig. 3(b)) (Yuan et al., 2020). This study offers a strategy for direct agricultural reuse of the recovered nutrients in the form of liquid fertilizers.

2.3 Lithium

Lithium and lithium compounds have found broad application, particularly lithium-ion batteries for energy storage (Swain, 2017). Recovering lithium from wastes will help meet the increasing global demand for lithium and mitigate environmental pollution caused by the wastes.

Table 2 Estimated theoretical ratio of anion electromigration rates in CDI and MCDI systems (calculations are based on equal concentration of ions)

Ions	Diffusion coefficient (m^2/s) ^a	$\frac{J_{A^{n-}}}{J_{\text{Cl}^-}}$	Approximate separation factor in strong base anion exchange resin (relative to Cl^-) ^b	$\frac{J_{m,A^{n-}}}{J_{m,\text{Cl}^-}}$
NO_3^-	1.90×10^{-9}	0.9	3.2	2.9
H_2PO_4^-	8.79×10^{-10}	0.4	NA ^c	NA
HPO_4^{2-}	4.39×10^{-10}	0.4	NA	NA
SO_4^{2-}	1.06×10^{-9}	1.0	9.1	9.1
Cl^-	2.03×10^{-9}	1.0	1.0	1.0

Notes: a) Diffusion coefficients taken from (Newman and Thomas-Alyea, 2004; Huang et al., 2017); b) Separation factors taken from (Clifford, 1999); strong basic anion exchange resin is polystyrene divinylbenzene matrix with $-\text{N}^+(\text{CH}_3)_3$ functional groups; c) NA: not available for the same type of resin under similar conditions.

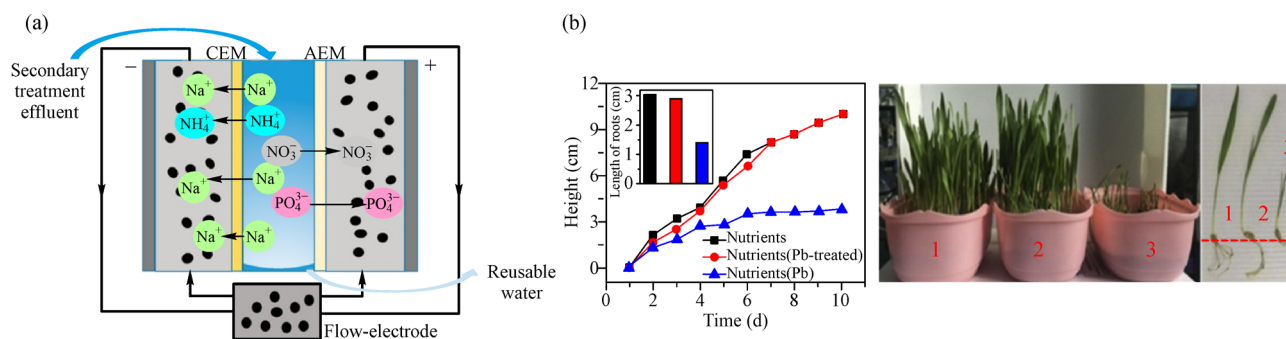
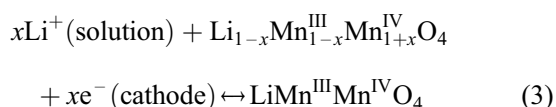


Fig. 3 (a) Schematic of concurrent removal of N and P using FCDI. Reprinted with permission from (Bian et al., 2019). Copyright 2019 American Chemical Society. (b) Height and root length of the plants (left) and images of the plants and their roots (right) using actual fertilizer (1), recovered liquid fertilizers, (2) and Pb-contaminated wastewater (3). Reprinted with permission from (Yuan et al., 2020). Copyright 2020 Elsevier.

Oilfield brines, which are wastes in oil production, contain enriched lithium resulting from seawater evaporation (Chan et al., 2002). Additionally, wastewater from lithium battery recycling plants contains elevated concentrations of lithium (~1900 mg/L) (Kim et al., 2018a).

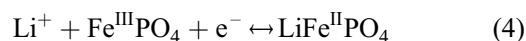
Lithium manganese oxide (LiMn₂O₄, LMO), the electrode material used in some lithium-ion batteries, can achieve selective separation of lithium ions from wastewater. The lithium recovery mechanism of LMO can be explained from crystallography fundamentals. LMO has a spinel structure shown in Fig. 4(a) (Zhang et al., 2013): oxygen is cubic close-packed with manganese occupying half of the octahedral sites and lithium occupying one-eighth of the tetrahedral sites. Lithium recovery is achieved by Li⁺ insertion in λ-MnO₂ cubic phase in the charging step and Li⁺ release from LiMn₂O₄ in the discharging step. The cathode half-cell reaction can be expressed by Reaction 3 (Missoni et al., 2016).



A modified MCDI system is reported for lithium recovery (Ryu et al., 2013); this system contains a graphite sheet as a current collector, selective lithium adsorbent electrode, AEM, and activated carbon electrode (Fig. 4(b)). Lithium ions are first adsorbed, without an electrical field, to the lithium selective adsorbent layer while other cations are flushed away with effluent water. When a positive potential is applied, lithium ions are released from the adsorbent layer. This electro-assisted desorption avoids the use of hydrochloric acids in desorption and is more environmentally friendly. Their following work (Ryu et al., 2015) leverages electrostatic field assistance to accelerate lithium adsorption into the LMO electrode, and the mechanisms are similar to water desalination using intercalation electrodes.

Besides lithium manganese oxide, lithium iron phosphate (LiFePO₄) is another intercalation electrode material

that can be used for lithium recovery. Lithium inserts into octahedral sites of the olivine structure according to Reaction 4:



A battery system with LiFePO₄ as the lithium-capturing electrode and Ag as the chloride-accepting electrode has been reported for selective lithium recovery. This system is able to convert a brine rich in sodium (lithium/sodium = 1/100) to a solution rich in lithium (lithium/sodium = 5/1) (Pasta et al., 2012a).

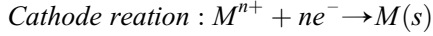
3 Electrochemical redox processes

Converting target ions to a different oxidation state via redox reactions is another way to selectively separate ionic resources. Electrochemical redox processes are advantageous when the difference in redox potential between different ions can be leveraged to achieve selective separation. Additionally, some resources, such as metals, can be of higher value in the form of simple substances (e.g., zero-valent metal) than in the ionic form which is dominant in wastewater.

3.1 Heavy metals

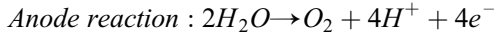
Electroplating wastewaters contain toxic but reusable heavy metals such as copper, zinc, cadmium, and gold. The use of CDI systems with functionalized electrodes for heavy metal removal and recovery has been recently reviewed (Chen et al., 2020). Electrowinning is used in the electroplating industry to recover these metal ions as pure metals which can be recycled. During the electrowinning process, dissolved metal ions migrate to the cathodes, where the metal ions are reduced and deposited as pure metal (Reaction 5). Simultaneously, water or other dissolved species are oxidized on the anode (Reaction 6). Due to the difference in reduction potentials, selective

heavy metal recovery can be achieved (Tran et al., 2017). Since the redox potential for Cu^{2+} is more positive than that of Ni^{2+} , Cu^{2+} will be reduced and separated from the solution before Ni^{2+} .



$$E^0 = +0.34V \text{ for } \text{Cu}^{2+}; E^0 = -0.257V \text{ for } \text{Ni}^{2+} \quad (5)$$

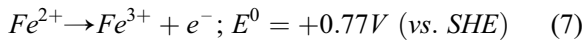
vs standard hydrogen electrode (SHE) (Haynes, 2014)



$$E_{eq} = 1.1V \text{ at pH2 vs. SHE} \quad (6)$$

In industrial wastewaters, however, impurities frequently co-exist with target heavy metal ions. Chelating agents, such as citrate and ethylenediaminetetracetic acid (EDTA), bind to heavy metal to form ligand-metal complexes which are difficult to recover via electrodeposition. In this case, advanced oxidation can be used to break down the complexes to release free heavy metal ions that are amenable to recovery via electrodeposition. A reported process integrates the decomplexation of Cu^{II} -EDTA via photoelectrocatalysis and the simultaneous recovery of copper via electrodeposition (Zhao et al., 2013).

Some other impurities in wastewater may be beneficial to the recovery of target metals. For example, the presence of Fe^{II} in wastewater lowers the cell voltage for copper recovery by providing an alternative anodic reaction (Reaction 7) with a lower potential compared to the water oxidation reaction (Hannula et al., 2019). As a result, the specific energy consumption for copper recovery is significantly lower in the presence of Fe^{II} ions.



Due to its low reduction potential (Cr^{3+}/Cr , $E^0 = -0.74V$ vs. SHE), chromium is not recoverable via electrowinning. A poly(vinyl)ferrocene-carbon nanotube

electrode is designed to selectively capture CrO_4^{2-} in the presence of co-existing anions (Su et al., 2018). During the adsorption step, hexavalent chromate is captured by the anode through the selective binding between chromate and ferrocenium as an ion pair; during the release step, the reduction of ferrocenium to ferrocene and Cr(VI) to Cr(III) takes place simultaneously (Fig. 5(a)). Similar concepts have been applied in the selective separation of charged pesticides and arsenic in asymmetric faradaic systems (Su et al., 2017). For example, poly(vinyl)ferrocene (PVF) and poly-TEMPO-methacrylate (PTMA) are used to selectively remove As(III) . PVF captures As(III) and PTMA achieves synergistic electrocatalytic oxidation of As(III) to As(V) (Kim et al., 2020). It is worth noting that although these systems are designed to achieve water decontamination, the concepts can be further explored to achieve selective recovery of ionic resources that are present at low concentrations in wastewaters.

3.2 Bromine

Bromine and bromine compounds are key components in agricultural chemicals, pharmaceuticals, and flame retardants (Wisniak, 2002). Brines generated from oil and gas production, including flow back water and produced water, contain high concentrations of bromide ions ($\sim 1 \text{ g/L}$) (Sun et al., 2013), which not only constitute a health concern associated with the generation of brominated disinfection byproducts but also provide an opportunity for bromine recovery.

Since chloride can be present in the brines at concentrations as high as 200 g/L , selective separation of bromide over chloride is needed. This can be achieved by leveraging the difference in the reduction potential of bromine and chlorine: $\text{Br}_2(\text{aq})/\text{Br}^{-}$, $+1.09 \text{ V}$; $\text{Cl}_2(\text{aq})/\text{Cl}^{-}$, $+1.36 \text{ V}$ (vs. SHE) (Haynes, 2014). In a system designed by Sun et al., graphite electrodes are used in an electrolyzer with the anode and cathode chambers separated by a CEM to achieve selective recovery of bromide from brines

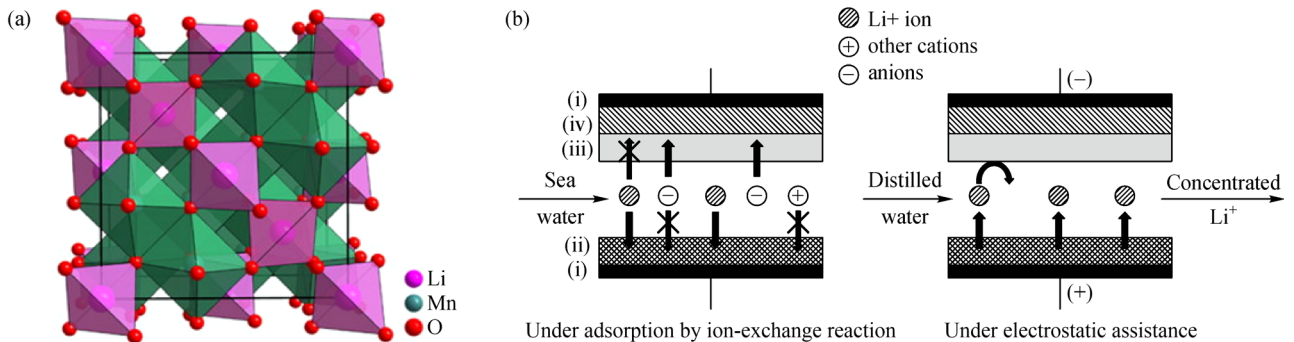


Fig. 4 (a) Crystalline structure of spinel LiMn_2O_4 . Reprinted with permission from (Zhang et al., 2013). Copyright 2013 Elsevier. (b) Schematic of the electrostatic-assisted recovery of lithium ions. (i) graphite current collector, (ii) selective lithium adsorbent electrode, (iii) anion exchange membrane, and (iv) activated carbon electrode. Reprinted with permission from (Ryu et al., 2013). Copyright 2013 American Chemical Society.

(Fig. 5(b)) (Sun et al., 2013). Bromide is oxidized to bromine at the anode in the presence of chloride at significantly higher concentration (15 mmol/L Br^- vs. 2.1 mol/L Cl^-), and the produced bromine can be stripped out of the electrolyte with air (Sun et al., 2013). The graphite electrodes play an important role in selective recovery since they exhibit a greater overpotential for chloride oxidation than bromide oxidation (Sun et al., 2013). Inspired by the strong interaction between activated carbon and bromine, a hybrid physical adsorption/CDI system is designed for selective bromide recovery (Cohen et al., 2018). Bromide ions are electro-oxidized during the charging step and the bromine molecules are physically adsorbed onto the electrode surface (Cohen et al., 2018). In this process, the anode potential is higher than bromide oxidation potential but lower than chloride oxidation potential so that selective removal of bromide is achieved (Cohen et al., 2018).

4 Electrochemically induced precipitation

With an applied potential bias, some dissolved species in solution can undergo reactions to form insoluble precipitates which can be easily separated from the wastewater. One important mechanism involves water splitting

near the cathode surface and the generation of hydroxide ions, which facilitate the precipitation reaction.

4.1 Rare earth elements (REEs)

REEs are crucial components in permanent magnets, modern electronics, and catalysis (Reisman, 2012). The mining of REEs generates large amounts of wastes and has significant environmental impacts. Recovering REEs from industrial wastes and used consumer products may reduce the need to explore new REE mineral resources. Industrial waste effluents, including acid mine drainage and coal-mine discharge, contain REE contents of up to 80 nmol/L (Ayora et al., 2016) and offer an opportunity for REE recovery. It is noted that such concentration is still low compared with other metal ions (e.g., Cu^{2+} and Ni^{2+}) existing in the industrial wastewater.

Carbon nanotube (CNT)-enabled filters, due to their high surface area and high electrical conductivity, have shown the potential to recover low-concentration REEs selectively from wastewater (O'Connor et al., 2018). The CNT filter has been demonstrated to recover Eu, Nd, Ga, and Sc at precipitates in their trivalent oxide form (O'Connor et al., 2018). The OH^- ions generated from water splitting and oxygen reduction reactions capture the metal species by forming metal hydroxide intermediates

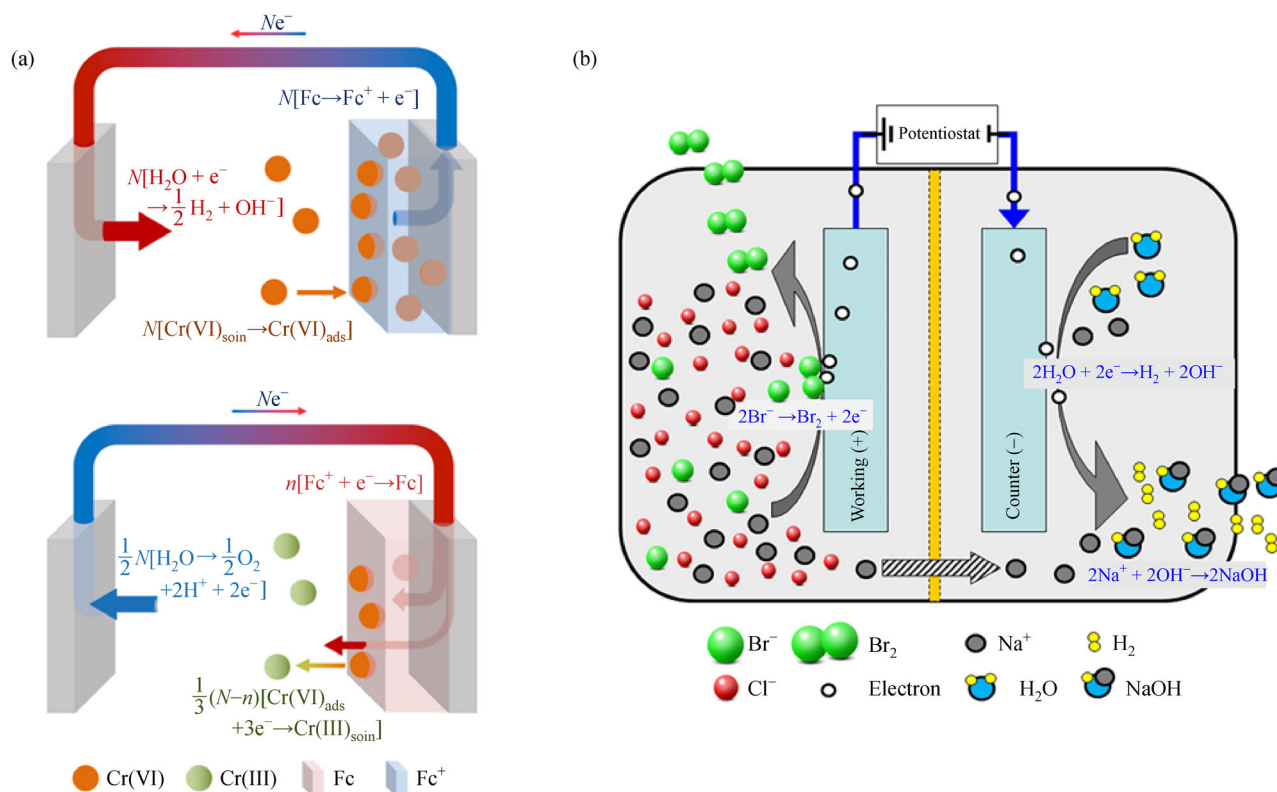


Fig. 5 (a) The Faradaic reactions occurring at the surface of the electrodes for Cr(VI) removal. Reprinted with permission from (Su et al., 2018). Copyright 2018 Springer Nature. (b) Schematic of the redox reaction for bromine recovery by selective electrolysis from brines. Reprinted with permission from (Sun et al., 2013). Copyright 2013 from Elsevier.

which dehydrate to form metal oxides (O'Connor et al., 2018) (Fig. 6(a)). Zero-valent metals of REEs are not formed on the CNT electrode due to their low reduction potentials (Eu^{3+}/Eu : -1.99 V; Nd^{3+}/Nd : -2.32 V; Ga^{3+}/Ga : -0.55 V; Sc^{3+}/Sc : -2.08 V, vs. SHE) (O'Connor et al., 2018). Selective separation of Eu and Cu is achieved in a two-stage filter system, with a lower voltage to recover Cu and higher voltage for Eu (O'Connor et al., 2018).

4.2 Phosphorus

Electrochemically induced precipitation is particularly promising for phosphorus recovery. Struvite ($\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$) precipitation is a well-established method to recover phosphorus from wastewater. Because of the low concentration of Mg^{2+} in municipal wastewater, magnesium salts like MgCl_2 need to be added to induce struvite precipitation. The chemical dosage system involves high automation which can be challenging to achieve in small systems. In an electrochemically induced struvite precipitation system, a sacrificial Mg electrode can provide dissolved Mg ions, and the dosage can be easily controlled by changing the current (Fig. 6(b)) (Hug and Udert, 2013). Mg electrode undergoes fast anodic dissolution, resulting in a high precipitation rate, and the non-galvanic corrosion of the Mg electrode reduces the energy consumption of the process (Hug and Udert, 2013).

Despite the potential of struvite as a slow-release fertilizer, the need to supply an Mg source presents a challenge to achieving economical struvite recovery. An alternative approach is to recover P via the precipitation of calcium phosphate (CaP). CaP precipitates in supersaturated solutions at high pH. Due to the buffering capacity in wastewater, large amounts of caustic soda need to be added to increase the pH. This chemical precipitation method generates sludge waste which needs to be further treated. To circumvent this challenge, electrochemical systems can be used for CaP precipitation (Lei et al., 2017).

A high local pH environment is created through water electrolysis near the cathode surface (Fig. 6(c)), and CaP precipitates on the cathode surface as an amorphous phase which then transforms to crystalline hydroxyapatite (Lei et al., 2017). In the electrochemical recovery of CaP from real municipal wastewater, calcite (CaCO_3) and brucite ($\text{Mg}(\text{OH})_2$) are formed as byproducts (Lei et al., 2018a). Both the abundance of P in the wastewater and operating conditions impact the sequence of precipitation (Lei et al., 2018a). Amorphous calcium phosphate can be selectively precipitated at high P content, or by using a relatively low current density to reduce the electromigration rate of Ca^{2+} and Mg^{2+} (Lei et al., 2018a).

5 Prospects of electrochemical processes for materials recovery

The global rise of water reuse and zero liquid discharge provides a solution to freshwater scarcity (Durham and Mierzejewski, 2003). Simultaneously, the recovery of materials from municipal and industrial wastewaters as value-added products will not only offset the cost of advanced water treatment but also reduce the environmental damages associated with resource extraction from nature. Electrochemical processes offer unique advantages in materials recovery applications, but also face crucial challenges.

5.1 Rational for decentralized materials recovery

Recovering materials from highly concentrated waste streams is expected to be more cost-effective than from dilute wastewaters. For example, human urine contains high concentrations of N and P (9 g/L and 1 g/L, respectively) (Larsen and Gujer, 1996). Livestock manures in liquid storage systems contain elevated contents of water-extractable P with a typical concentration of 5 g/kg

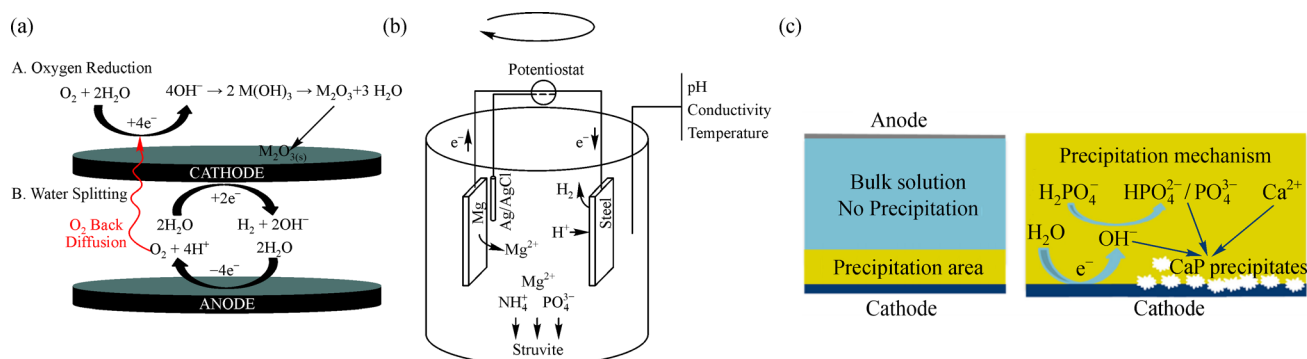


Fig. 6 (a) Electrochemical deposition of REE oxides via formation of metal hydroxide intermediates, Reprinted with permission from (O'Connor et al., 2018). Copyright 2018 The Royal Society of Chemistry. (b) Magnesium as a sacrificial electrode for struvite precipitation, Reprinted with permission from (Hug and Udert, 2013). Copyright 2013 Elsevier. (c) Electrochemically induced calcium phosphate precipitation. Reprinted with permission from (Lei et al., 2017). Copyright 2017 American Chemical Society.

(Kleinman et al., 2005). Wastewaters from mining industries contain heavy metals and REEs that can be recovered.

Considering the geographical dispersion of waste-generating activities, decentralized technologies that allow the *on-site* recovery of resources provide an attractive alternative to centralized recovery. First, combining waste streams containing different resources, or dilution of concentrated wastes, will result in unnecessary energy to be consumed for future separation. Second, although decentralized systems may not have the economy of scale, they can avoid the costs and aesthetic concerns associated with piping or trucking concentrated waste streams required for centralized treatment and recovery (Larsen et al., 2009).

5.2 Advantages of electrochemical processes for materials recovery

Electrochemical technologies have unique advantages that render them well-suited for decentralized materials recovery systems. First, the use of electricity to drive separation minimizes the dosage of chemical reagents, thereby mitigating the costs and risks associated with the transport and storage of chemicals. Using electricity generated from renewable energy sources, such as solar and wind, will help decarbonize wastewater treatment processes. Second, electrochemical separations are highly modular and are well suited for resource recovery at places of waste generation. Third, electrochemical resource recovery devices can be easily arranged and operated to adapt to the fluctuations of wastewater composition by simply adjusting the number of modular units or adjusting the operating current. Finally, electrochemical technologies provide a variety of mechanisms for achieving selective separation, which is crucial for producing high-purity products for reuse or sale.

Recently, an onsite electrochemical toilet wastewater treatment system has been designed and implemented in regions with limited sanitation (Cid et al., 2018). The system achieved disinfection of pathogens, reduction of chemical oxygen demand, and recycling of treated wastewater for toilet flushing, with energy consumption < 0.2 kWh per user per day (Cid et al., 2018). It is anticipated that, with proper integration with source separation technologies (such as the NoMix toilet) (Larsen et al., 2009), similar electrochemical systems may be further developed for recovering nutrients onsite.

5.3 Challenges for implementing decentralized electrochemical materials recovery systems

5.3.1 Achieving selective recovery in complex wastewaters

As discussed above, the ability to achieve selective

separation is an intrinsic virtue of electrochemical technologies. In CDI systems, selective separation can be achieved via leveraging the difference in ion transport rates, size exclusion by ultramicropores, the difference in ion binding energetics, and the use of intercalation materials with ion-selective nanochannels (Zhang et al., 2020). In electrochemical redox processes, selective separation is typically attained by the differentiation in the reduction potential of various species. Electrochemical precipitation achieves selective separation based chiefly on the stoichiometry and saturation index of precipitate-forming species.

Given the promise of these electrochemical systems in selective separation, it remains to be investigated to what extent selective recovery can be attained in complex wastewaters which frequently contain high concentrations of solids, dissolved organic matter, and a variety of ions. In some cases, the presence of impurities in recovered products can be detrimental to their value; examples include the incorporation of heavy metal impurities in recovered REEs. Under certain scenarios, impurities can have a beneficial effect on the recovered products. For example, the incorporation of natural organic matter in CaP can improve the bioavailability of P for plants (Lei et al., 2018b). As such, the necessity to achieve selective recovery needs to be evaluated on a case-by-case basis.

5.3.2 Robustness of electrochemical systems

The complexity of wastewater composition also has a major impact on the robustness of electrochemical systems, particularly with respect to the durability of electrodes (Liu et al., 2019). The ion storage capacity of intercalation electrodes can be impaired by the presence of humic substances and multivalent ions in water (Liu et al., 2018; Shanbhag et al., 2017). Since electrode and module replacement contribute appreciably to the system operating cost (Hand et al., 2019), pretreatment can be an essential component of a decentralized electrochemical facility to maintain system robustness. Pretreatment processes, such as ultrafiltration, remove organic foulants from the feedwater (Maartens et al., 1999) so that the lifespan of electrochemical systems can be prolonged (Liu et al., 2019). Identifying operating conditions as well as system design and adequate pretreatment that allow for maximum electrode lifespan is crucial for lowering the cost of electrochemical materials recovery systems.

5.3.3 Where is the market? From laboratory studies to real-world applications

While most laboratory studies of materials recovery focus on technological feasibility and process optimization, there is an urgent need to explore the potential market for the recovered valued-added products. Under a decentralized

resource recovery framework, the logistics of collecting and transporting recovered products for reuse needs to be established. In particular, if nutrients are recovered as liquid fertilizers, the resource recovery systems would ideally be located near farmland to avoid costly transportation of liquids. For agricultural reuse of recovered nutrients, there is also a need to align the chemistry of the recovered products with soil characteristics (Trimmer et al., 2019). Future studies that establish the connection between technology development and market adoption will enable a holistic assessment of the feasibility of electrochemical resource recovery technologies.

6 Outlook

Recent research has highlighted the potential of electro-sorption, electrochemical redox process, and electrochemical precipitation in recovering materials as value-added products from wastewaters. Despite the progress, several critical questions remain. First, we lack an understanding of the effectiveness of selective materials recovery in complex wastewater matrices. While systems have demonstrated selective recovery in simple mixtures of constituents, the presence of high concentrations of organic matter and/or salts in wastewaters will likely diminish the separation performance and product quality. Second, the stability of electrodes and system modules need to be evaluated in complex wastewaters over realistic durations. Techno-economic assessments that account for both system cost and the value of recovered products will help quantify the benefits of resource recovery systems. Third, there is a need to establish the connection between laboratory-scale experiments to real-world systems which require not only materials recovery devices but also source separation, electronic control systems, and product processing and transport. Pilot-scale demonstrations will accelerate the acceptance of electrochemical technologies for decentralized materials recovery as a solution to dwindling natural resources.

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