Metal recovery by microbial electro-metallurgy

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ABSTRACT

Raw metals are fundamental to the global economy as they are essential to maintain the quality of our life as well as industrial performance. A number of metal-bearing aqueous matrices are appealing as alternative supplies to conventional mining, like solid industrial and urban waste leachates, wastewaters and even some natural extreme environments (e.g. deep marine sediments, geothermal brines). Some of these sources are already managed for recovery, while others are not suitable either because they are too low in content of recoverable metals or they contain too many impurities that would interfere with classical recovery processes or would be cost-prohibitive. Microbial electro-metallurgy, which results from the interactions between microorganisms, metals and electrodes, in which the electron transfer chain associated with microbial respiration plays a key role, can contribute to overcome these challenges. This review provides the state of the art on this subject, and summarizes the general routes through which microbes can catalyse or support metal recovery, leading to nano- and macro-scale materials. Competing sorption and electrochemical technologies are briefly revisited. The relevant sources of metals are highlighted as well as the challenges and opportunities to turn microbial electro-metallurgy into a sustainable industrial technology in the near future. Finally, an outlook to pursue functional materials through microbial electrometallurgy is provided.

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1. Introduction

Metals are crucial in the global economy as they are key constituents of a vast number of products, crafts, and industrial processes. From conductors in mobile phones to alloys for strong but light cars, they enable core societal and industrial activities.

Each metal and its alloys have unique properties that make them interesting for particular applications. For instance, carbon-iron alloys produce high-strength steels, whereas aluminium is alloyed to manufacture airplane frames, beverage cans, engines and electrical cables due to the formation of highly stable passive films. A mobile phone can contain functional components with more than 40 elements including base metals such as copper and tin, special metals such as cobalt, indium and antimony, precious and platinum-group metals, silver, gold, tungsten as well as rare earth elements (REEs), including yttrium [1]. Fluorescent lamps also contain various materials and elements which include a range of REE and other non-critical metal resources like iron [2]. Strength, corrosion resistance, wear resistance, machinability and colour are examples of distinctive properties provided by metals and their alloys [3].

The manufacturing of these and other modern technologies depends today on the availability of freshly extracted metals. Typically, these are mined from their ores. Some countries have a monopoly on the beneficiation of some metals which may signify vulnerability for nations who are not primary suppliers [4,5], e.g., currently China produces 97% of the REEs whereas South Africa generates 79% of platinum [6,7] both of which have been highlighted as critical raw metals for application in low carbon technologies [8,9]. This provides impetus by nations who are not primary producers for alternative sources [10] and for developing technologies to scavenge these metals from end-of-life consumer products or solid waste [11], labelled as waste of electric–electronic equipment (WEEE) [12].

The art and science of metal beneficiation and recovery come under the field of extractive metallurgy [13], further branched into the sub-fields of: (1) pyrometallurgy, which uses dry thermal methods, (2) hydrometallurgy, which chemically extracts metals from their ores, and (3) electrometallurgy, which uses electrolytic or galvanic methods typically at late steps in the recovery chain [13]. In general, hydro/electrometallurgy involves two distinct steps: (a) selective dissolution (leaching) of the metal from the ore/WEEE and (b) selective recovery of the metal from solution.

Pyrometallurgical processing is the traditional method to recover non-ferrous metals as well as precious metals from electronic waste [12]. In the past two decades, the most active research areas on the recovery of highlighted critical metals from electronic scraps concern the hydro and electrometallurgical methods [12]. Compared to pyrometallurgical processing, hydro/electrometallurgical methods are more exact, more predictable, and more easily controlled [12]. Moreover, from the environmental and economic perspectives, hydrometallurgical methods are preferred to pyrometallurgical methods, as the latter usually require high temperatures ($\approx$1200 °C), produce harmful gases (such as SO_2) and dust, and require high capital costs [13].

Spent leachates and industrial wastewaters here represent an additional source [14,15]. Recovery from these aqueous sources, as opposed to recovery from solid waste, provides the advantage that the metals are already in solution. However, the grand challenges to extract metals from these matrices are: (1) their typically low concentration, (2) the presence of other metals, inorganics and organics, (3) high ionic strength of some matrices complicating extraction, (4) existing removal techniques are available but geared to meeting discharge limits, and (5) unavailability of technology targeting recovery, that can be integrated within existing processing chains. To meet these challenges, microbial technologies are up and growing [16].

The study of the interactions between microbes and metals is not new. A long trajectory exists on how microbes associate with metals in both natural and man-made environments, with the majority of scientific research concerned with the biogeochemical cycling of metals by microorganisms [17]. In the 1970s Beverage and Murray were forerunners in the investigation of the role of microbes in the binding and mineralisation of metal ions [18,19]. Later, Gadd and co-workers addressed the interactions between microbes and a variety of metals, as well as metal accumulation thereby [20]. The role of microbes in the generation of acidic, metal-rich mine waters has also been addressed extensively [21]. For instance, acidophiles accelerate the dissolution of pyrite and other sulphide minerals. The resulting acid mine drainage (AMD) is a major environmental pollutant [22]. Microbially-influenced corrosion (MIC) has also been investigated extensively and added much to our understanding of microbial redox interactions with metals [23].

From the engineering perspective, a paradigm shift has occurred over the last 35 years in the application of metal-microbial interactions. In the 1980s, applications majorly focused on the remediation of metals and radioactive elements from polluted aqueous systems [24,25]. Later, in light of the critical need for some metals and the potential of future supply risk interruptions, attention shifted to recovery, recycling and economic prospection alternatives by microbially-assisted mining [9,16]. More recently, the application of microorganisms as a green methodology for the synthesis of metallic nanoparticles (NPs) has also been reported [26]. Here, bacteria are used as "nano-factories" for the bottom-up synthesis of various metallic NPs from ionic precursors in aqueous systems under ambient conditions. Today, remediation, recovery, and synthesis converge [27]. The remediation of metal-containing waste streams can be combined with recovery and synthesis of novel (nano)materials [28]. Ultimately, trends in the production of functional materials are emerging.

Biosorption has been used extensively to remove metals and metalloids from aqueous streams using biologically-derived materials [24]. Although usually applied to the passive non-faradaic sorption (absorption and adsorption) mechanisms, using non-viable microbial biomass, the term has also been extended to living cells [29] and faradaic metal ion oxidation/reduction reactions [30]. Otherwise, most microorganisms can create a matrix in which metals adsorb by ion-exchange or chelation at the cell wall interface, leading in some cases to the subsequent transformation of metallic states. The works of Lovley and Macaskie have much developed such microbial transformations and their understanding [31,32]. More details about these purely-microbial approaches are briefly provided later in this review. For now, what is most relevant to highlight is that the study of microbial-metal interactions has predominantly focused on removal (i.e., depollution, remediation) and to a less
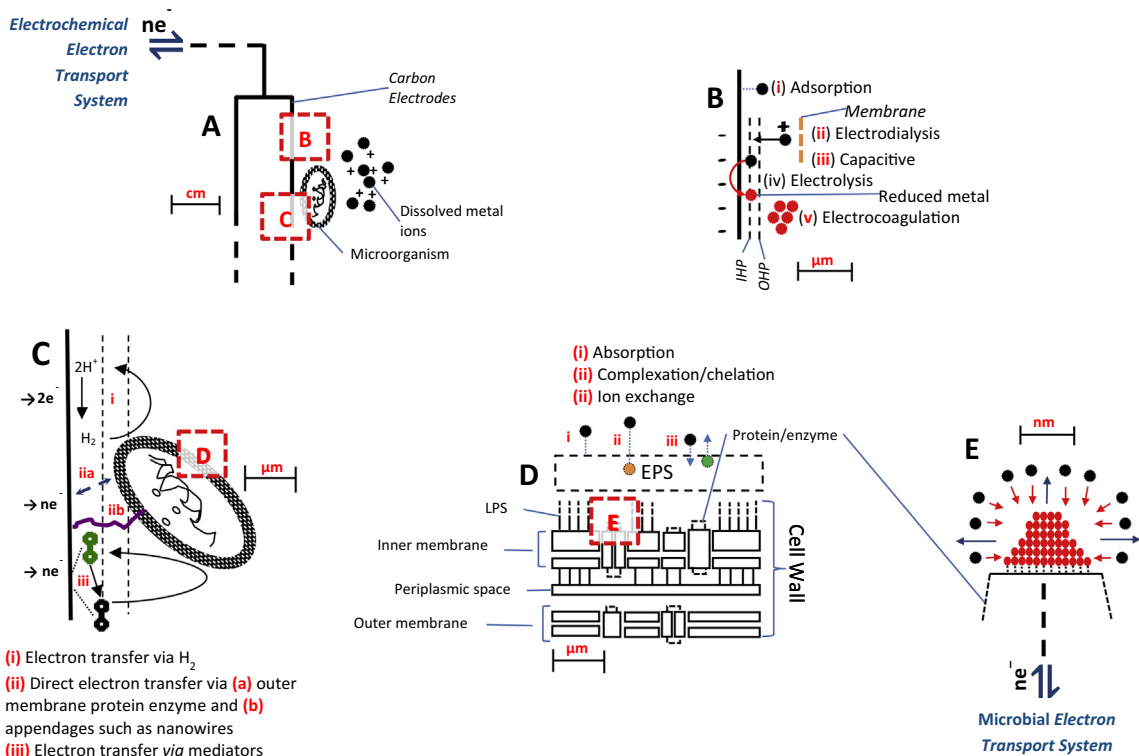
Fig. 1. Microbial electrochemical phenomena related to metal recovery discussed in this review, perceived from different hieratical levels of resolution. (A) "Macro" carbon electrodes involved in (B) sorption and electrochemical recovery of met ions. (IHP - inner Helmholtz plane, OHP - outer Helmholtz plane (C) Electron transfer to microorganisms immobilised as biofilms on the electrode or suspended in solution, applied for metal recovery. (D) "Micro" microbial metal ion biosorption and (E) "nano" microbial enzyme electrodes, reported to reduce and precipitate metallic nanocrystals, principally at the cell wall interface, e.g. outer membrane c-type cytochromes of *Shewanella oneidensis* [215]. Figure modified from Harnisch and Rabaey [216] and Varia et al. [158], Fig. 1D representative of gram-negative bacteria.

extent on recovery (i.e., to obtain marketable products). Second, most microbes carrying out metal transformations depend on specific electron donors or acceptors and most work under strict anaerobic conditions, making metal recovery slow and poorly manageable, especially for metals possessing multiple valence states. The recent resurgence of the use of solid-state electrodes as electron donors or acceptors for microbial growth [33] opened a wide range of new possibilities, giving birth to what we know today as microbial-electrochemical technologies (METs).

METs take advantage of the synergistic alliance of electrochemical and microbiological phenomena [34]. METs have emerged as a versatile technology for applications ranging from electricity generation [35] to synthesis of valuable chemicals [36]. Only recently METs have been applied to remove and recover metals from aqueous matrices. Metal recovery with METs results from the interactions between microorganisms, metals, and electrodes, where the electron transfer chain associated with microbial respiration often plays a key role. This poses significant advantages with respect to systems based on the microbiology alone, as the possibility to control the electric potential at which the separations or conversions take place adds a certain degree of selectivity and rate. Compared to the more classical electrochemical counterpart, METs are less energy-intensive due to both the effective electrode catalysis and microbial power generation; furthermore, the microbial metabolism can enable reactions that otherwise would not be thermodynamically or kinetically favourable [37]. Lastly, METs appear more sustainable due to the lack of expensive metal catalysts (such as Pt) and the ability to use relatively cheap carbon-based electrodes.

Fig. 1 illustrates possible pathways for metal removal and recovery in METs at different hierarchical levels of resolution. Macro-scale carbon electrodes, which are often used in METs, can remove metals by sorption and electrochemical reduction (Fig. 1A and B). Micro-scale microbial cells can remove metals through several different mechanisms such as sorption (electrostatic, ion chelation and ion exchange) and transformation (reduction, oxidation, chemical precipitation) (Fig. 1C–E).

In this review we provide insights into the METs research frontier, we outline the recent developments in the field with particular focus on the mechanisms that make recovery of metals possible with METs, as well as on the opportunities they bring to develop sustainable and energy-efficient recovery of metal products with ample functionality.

2. Overview on the recovery of metals from aqueous matrices

A number of metal-bearing aqueous matrices and leachates generated from solid waste are appealing from a metal recovery perspective. On the one hand, metals need to be removed as some are regulated as environmental pollutants, this especially holds for heavy metals. Wastewaters are a priority, due to their very large annual flows, metal waste content and environmental impact per mass unit [38]. The concentration of metals in wastewaters fluctuates significantly from one source to another ($\mu g \, L^{-1}$ to tens of $g \, L^{-1}$). The metal recovery process can already become profitable from the costs avoided by meeting the discharge limits enforced in most countries. In addition, many industrial wastewaters contain resources worth billions of euros today shed as lost product and lost opportunity. Given the large volumes in which these metals are contained, metal recovery from these matrices represents economic advantages from k€ to M€ per year for some individual companies [39]. On the other hand, some natural environments previously regarded as not prospective have become interesting sources for certain metals. The deep continental and marine environments as well as geothermal brines fall into this category for the several critical metals including Mn, Co, Li, and the REE [40,41].

As the economic value of some particular metals rises, new recovery technologies start to make sense even for concentrations in the parts-per-million range and below. Thus, efficient recovery of valuable and critical metals from aqueous environments has become of increasing importance for a local and stable supply along with the general desirability for resource and environmental sustainability [42].

High metal concentrations (e.g. $>1000 \, mg \, L^{-1}$) can be usually handled with conventional separation technologies [13]. Electrochemical processing, for instance, is used extensively in the primary extraction of metals (electrowinning), purification and recycling of metals (electrorefining), as well as for the formation of metal coats (electroplating) [43]. However, electrochemical processing is more effective in non-aqueous media and in molten salts [43], mainly as in aqueous medium there are kinetically-competing reactions, such as hydrogen evolution.

Anthropogenic and natural waste streams contain metal ions in low concentrations and require special methods for recovery. Dilute aqueous matrices containing metals are characterized by (1) the nature of the metals combined with other polluting inorganics (heavy metal ions, phosphates) and organics, (2) the concentration range of the chemical species present; mostly lower than $1 \, g \, L^{-1}$ for the metals concerned, (3) the nature and the concentration of supporting electrolyte mostly lower than $1 \, g \, L^{-1}$ (however, in some cases the concentration is one to two orders of magnitude higher), and (4) the conductivity of solution; mostly lower than $1 \, \Omega^{-1} \, m^{-1}$ ($1 \, S \, m^{-1}$), except for marine systems and most geothermal brines.

In the context of wastewater treatment, different technologies have been used for removal purposes, including biological treatments, membrane processes, advanced oxidations, chemical and electrochemical methods. The work of Crini (2005) refers to studies that comprehensively review several of these removal techniques [44]. Conventional methods targeting the recovery of metals from water and wastewater include ion exchange, reduction, oxidation, solvent extraction, precipitation, electro-driven separations, and adsorption. Adsorption processes are considered the most suitable option as sorbents can have some specificity, low cost, safety and high efficiency. Here we begin by first by overviewing classical materials such as activated carbon and complexing/chelating sorbents and methods such as ion exchange [45], following on with current practices and principles of individual microbially and electrochemically driven recovery. METs are extensively discussed

subsequently. Phenomena highlighted in classical systems all have multidisciplinary crossover (see Fig. 1) to mechanisms described here in METs for metal removal and transformation and thus provide a premise to METs metal recovery state of the art.

2.1. Metal ion sorption and ion exchange from aqueous matrixes

2.1.1. Activated carbon adsorption

Adsorption of metal ions on activated carbon from complex aqueous solutions has been studied since the 19th century, yet it did not receive significant attention until about 50 years ago. Activated carbons are organic materials which in essence have graphitic structure. They can be produced by a wide variety of methods, conferring them a wide range of physicochemical properties which lead to differing adsorption rates and metal-loading capacities. The most important properties of activated carbon for use in metal recovery are its adsorptive capacity, adsorption rate, high mechanical strength and wear resistance, its reactivation characteristics, and particle size distribution. As a function of the combination of these properties activated carbon allows the adsorption of metals by different mechanisms. Several previous works review such mechanisms, the properties of activated carbons and their influence on metal recovery processes [46–48]. The use of activated carbon for metal recovery from dilute aqueous solutions suffers some drawbacks which include slow rates of metal adsorption, poor performance in solutions containing organic material and non-selective recovery in mixed metal solutions. Activated carbon can be quite expensive; the higher the quality, the greater the cost. Besides, its regeneration can be costly and can also result in loss of the adsorbent [44]. Finally, activated carbons do not fully recover metals from dilute solutions, and an important residual metal content is typically found in the treated aqueous matrix [49].

Activated carbons and graphitic carbons, in general, are widely employed materials in electrodes built in METs. Therefore, metal recovery processes can also be related to adsorption in the carbon structure to some extent. Many studies using carbon electrodes in METs report some removal of metal ions under open circuit conditions as well as under electrically-polarized circumstances [50].

2.1.2. Adsorption by ion exchange

Ion exchange has been applied for metal sequestration since the 1940s. It basically consists of either a synthetic (inert) matrix or a natural material (e.g., chitosan) with anchored functional groups like amines and carboxylic acids, that exchange ions with other charged ionic species in solution. The most relevant parameters for metal adsorption by ion exchange are the properties of the functional groups, as well as the charge, size, polarizability and concentration of the ions in solution [51–53]. The functional groups can generally be classified with weak or strong acid/base properties, depending on their degree of ionization. The metal loading capacity mainly depends on the structure and concentration of the functional groups [54]. Some ion-exchange materials offer advantages over activated carbons, especially concerning metal recovery rates and loadings, regeneration by elution, operation at high concentrations of ion-exchanger without loss in efficiency and mechanical performance. Also, ion-exchangers are less prone to poisoning with organics and competing ions than activated carbon. Yet, ion exchangers are limited by the concentration of the ions (metal ions and impurities) to be recovered, with unfiltered solutions they are highly susceptible to fouling, and waste (e.g., saline waste, sludge) is produced during regeneration of the ion exchanger. Despite some selectivity being offered, ion-exchangers are often not selective or they are sensitive to adsorb unwanted cations. Many ion-exchange materials are also costly making their use prohibitive for the recovery of common metals [55,56].

Ion exchange phenomena are also inherent to microbial biofilms participating in METs not only due to the properties of the biofilm matrix but also to the structure and characteristics of microbial cell walls, which are reviewed further in this work.

2.1.3. Complexing/chelating sorbents

Compared to ion-exchange, chelating sorbents can provide higher selectivity and thus a concentration factor of targeted metal ions up to several hundred folds, better separation of interfering ions and higher efficiency. Chelating sorbents can be of organic or inorganic (silica gel, alumina) nature. The organic chelating sorbents can be of natural (cellulose, chitosan, dextran) or synthetic origin (foamed plastics, polymeric resins). Inorganic supports offer higher mechanical, thermal and chemical stability but they have a poor degree of functionalization and sorption capacity. Organic natural chelating polymers are better suited for the environment, as they are non-toxic, bio-compatible, biodegradable, poly-functional, and highly chemically reactive. Besides, they have high hydrophilicity, larger number and diversity of functional groups, and flexible structure of the polymeric chain [44]. Metal sorption by synthetic polymers has been widely investigated. Such polymers can be insoluble or soluble in aqueous solutions. Most polymers belong to the first category wherein adsorption takes place heterogeneously, resulting in low recovery and low adsorption rates [42]. Metal adsorption with water-soluble polymers has also been reported, however laborious downstream processes like ultrafiltration are typically required to isolate the recovered metals [57]. The combination of polymeric adsorption and extraction with organic solvents has also been addressed [42]. This latter approach is not sustainable as large amounts of hazardous and flammable organic solvents are typically required. Several works explain the recovery of metals by adsorption in polymers [44,58,59]. What is most relevant to highlight is that this approach most typically takes place *via* polymer-metal complexes, in which a coordinate bond is established between a ligand function (mainly based on N, O and S groups) anchored with a polymeric matrix and a metal ion [60]. In general, syn-

thetic chelating sorbents are disadvantageous due to synthesis difficulties [61]. Natural chelating sorbents are inconvenient as they cannot be used in highly acidic media and also often require some type of pre-treatment to work appropriately at large scale (e.g., in packed columns) [44]. Both synthetic and natural chelating sorbents exhibit low reversibility of adsorption-desorption of metals and irreversible adsorption of mixed organics, sensitivity towards many chemicals, easy loss of mechanical stability and swelling, and unsatisfactory kinetic rates [61,62]. The effect of synthetic or natural chelating agents in METs has not been investigated so far, yet this phenomenon is also likely to take place and participate in the metal recovery process.

2.2. Microbial cell wall and extracellular polymeric substances

Microbial extracellular polymeric substances (EPS) and cell walls are an interesting alternative to other natural or synthetic equivalents, discussed hitherto. Bacteria could be conceptualised as "living" activated carbon particles. Their particular structure, physicochemical characteristics, chemical stability, high reactivity and excellent selectivity towards certain metals suggest them as competitive candidates against other more conventional methods. Furthermore, the cell surfaces of dissimilative Fe^{3+} reducing bacteria such as *Shewanella putrefaciens* have a high level of electrochemical heterogeneity [63]. Cell surfaces, therefore can function as highly differentiated interfacial systems, capable of supporting multiple intermolecular interactions with both solutes and solids [63]. In addition, they are abundant, renewable and biodegradable [44]. Potential interactions between microbial EPS or cell wall and metals have been extensively reviewed [20]. In general, correlations are found between high anionic charge and metal complexing capacity although metal removal and recovery takes place by a combination of both adsorption by ion-exchange and complexation in cell-wall or polymeric metal-binding components [44].

Typically, Gram-positive bacteria are found to have high ability to accumulate metal ions in the cell-wall when exposed to unique metals, whereas actinobacteria have shown higher accumulation capacity without particular selectivity. Yet, some microbes do show selectivity [64].

EPS are also of particular importance for biofilm-mediated processes (METs included). In a bacterial biofilm the microbes typically only account for less than 10% of the dry mass, whereas the EPS matrix can account for over 90% [65]. Most bacterial strains produce EPS during their life cycle. The maximal EPS production generally occurs at the end of the log phase (or exponential phase) and during the stationary phase of growth [66]. The composition of EPS and hence their physicochemical properties vary from one bacterial strain to another. The typical composition of bacterial EPS described thus far is summarized in Fig. 2.

The variations in the composition of EPS are attributed to factors such as the type of microbe, culture media composition, growth phase, pH, temperature, bioreactor type, extraction method, and analytical tool used. EPS can be described as a continuum, ranging from gels to a fully dissolved state. These polymers also exist as capsules, sheaths, looser slimes and as dissolved organic carbon [67,68]. The EPS can actually comprise different classes of macromolecules and hydrolysates thereof, such as polysaccharides, proteins, nucleic acids, lipids and humic substances. Some neutral macromolecules (e.g., aromatic compounds) can be present as well, but the predominant molecules contain charged groups like $-OH^-$, $-COO^-$, $-SH^-$, $-SO_4^{2-}$, $-H_2PO_4^-$, and $-NH_4^+$ [67,69]. At neutral and slightly alkaline pH (e.g., seawater) the EPS contain mostly negatively charged groups [70–72]. In Gram-negative cells, the EPS are mainly composed of lipopolysaccharides, capsule polysaccharides, and proteins that are less firmly bound to the cell surface. Some EPS are neutral, whereas others are polyanionic due to the presence of uronic acids; phosphate or sulphate. Gram-positive cells often produce polycationic EPS, lipoteichoic acids, as well as polysaccharides and proteins, which are not attached to the cell wall. The produced EPS can be closely bound to microbial cells (tightly-bound EPS), or as soluble EPS which may be weakly bound to cells or dissolved into the solution (loosely-bound EPS) [67,73]. Many strains form more than one specific type of EPS, and the composition of the overall EPS matrix may change during the life cycle of such organisms, due to the growth conditions and environmental stresses [69]. EPS are also a key constituent of electrochemically-active biofilms, and although the use of electrochemically-tunable EPS has not yet been addressed as a strategy to achieve metal recovery, these may also play a significant role on MET metal-recovery processes.

Adhesion and cohesion of EPS are based on weak physicochemical interactions and not on covalent bonds; electrostatic, ion-attractive and repulsive forces, hydrogen bonding and van der Waals interactions are some of the forces that can be
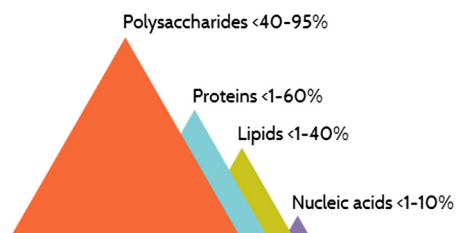

Fig. 2. Typical content of bacterial extracellular polymeric substances (EPS) from various natural and synthetic systems [65].

typically distinguished within the EPS matrix [65,74]. Through these forces, non-selective metal adsorption can take place. Conversely, exopolysaccharides and other biopolymers bind a wide variety of metals, such as Pb, Sr, Zn, Cd, Co, Cu, Mn, Mg, Fe, Ag, and Ni [66,73] with various degrees of specificity and affinity [75]. The binding affinity of the complex depends principally on the metal ion size/charge ratio, and other factors such as EPS composition, physical gel state, pH, ionic salinity, and carbohydrate/protein ratio [66,75]. It has also been reported that under natural conditions the EPS may also act as polyanions by forming salt bridges with carboxylic groups of acidic polymers such as uronic acids, or by forming electrostatic bonds with hydroxyl groups on polymers containing neutral carbohydrates [75]. Therefore the adsorptive affinity of certain metals has often been correlated with the content of uronic acids in the EPS [73].

The bacterial cell walls also have remarkable ability to fix metals ions [76]. The cell walls of Gram-negative bacteria differ significantly from those of Gram-positive species, especially regarding the outer cell membrane, the principal interface for metal ion sorption. The outer membrane of Gram-positive bacteria consists of a thick layer of peptidoglycan (PG) or murein, a biopolymer consisting of peptide-cross-linked N-acetylglucosamine and N-acetylmuramic acid [77]. The PG layer associated with proteins, teichoic, and lipoteichoic acid derivatives, presents a surface that is rich in acid functional groups [77]. The cell-wall of Gram-negative bacteria also consists of a PG layer, which is thinner. The PG layer is in turn surrounded by an overlying outer membrane, the outer leaf of which is largely composed of lipopolysaccharides (LPS). LPS also contain acid functional groups [78] ($-OH^-$, $-COO^-$, $-H_2PO_4^-$, and $-NH_4^+$) which play an important role in metal binding [79].

The isoelectric behaviour of bacteria can vary significantly although there is no significant difference between Gram-negative or positive species [80]. Haas et al. conducted [72] acid-base potentiometric titrations with the facultatively anaerobic bacterium *S. putrefaciens* for further insights into the thermodynamics of U^{4+} sorption. They reported pH-buffering properties of bacteria from the equilibrium ionization of three discrete populations of functional groups, i.e., $-COO^-$ (pK_a 5.16 ± 0.04), $-H_2PO_4^-$ pK_a (7.22 ± 0.15) and $-NH_4^+$ pK_a (10.04 ± 0.67). Similar pK_a values have been reported for Gram-positive bacteria such as *Bacillus subtilis*, i.e., pK_a values of 4.82 ± 0.14, 6.9 ± 0.5 corresponding to $-COO^-$ and $-H_2PO_4^-$ and 9.4 ± 0.6 for $-OH^-$ groups [81].

Therefore, functional groups of microbial cell surfaces may be either negatively or positively charged at near neutral pH values [82]. Metal anion and cation binding may vary considerably within the localized microenvironments in the biofilm due to the photosynthetic and respiratory activities of microorganisms [66,73]. Two general types of mechanisms may be involved in the EPS and cell wall metal-binding capacity: (1) ion exchange due to the high amount of negatively charged functional groups in EPS; and (2) complexation with charged groups mentioned above [66,70,75,83].

At low pH the availability of negatively-charged sites such as $-COO^-$ groups is strongly decreased in the presence of H^+ and, consequently, a small number of metallic cations can bind. At higher pH (i.e., above the pK_a), metal cation binding is enhanced by a proportional increase in the number of ionized acidic groups that are free to bind cations and therefore tend to favour their chelation. The maximum binding affinities occur near the pH of seawater, generally between 8.0 and 8.2. The reverse condition would also hold true for metallic anionic species such $AuCl_4^-$, with faster sorption for solutions of low pH [84].

Electrodes in METs systems could be used to influence acid function groups by anodic or cathodic polarization. For instance, the EPS or cell wall could be cathodically deprotonated, for instance, by application of cathodic potentials. To date little attention has been given to the electrochemical influence of metal binding groups in EPS and cell wall, making the sorption of metal cations more favourable. Another factor that may influence metal chelation is the modification of bacterial surfaces by UV-irradiation. Laboratory studies have shown that there is an enhancement of available carboxylic groups after exposure to UV-irradiation, which may increase the potential for binding metallic ions in EPS [66].

Furthermore, functional groups which bind metal ions may act independently. The pH for the point of zero charge of *S. putrefaciens* has been reported to be 5.4 [63]. Hass et al. reported strong U^{6+} sorption at pH as low as 2 which goes against surface complexation theory [85], predicting that a net positive charged surface would repel cations electrostatically. A potential explanation they gave was that positive charges on the bacterial surface tend to be localized. A separation of >~1 nm would be greater than the thickness of the electrical double layer, allowing each point charge to interact quasi-independently with ions in the surrounding solution.

Bacterial communities are usually applied as biofilms in METs. The metal binding/sorption capacity of the biofilm matrix is important for microbial-electrochemical processes concerning metal recovery, although this has not been yet addressed within the context of METs. A certain type of bacterial surface could provide thermodynamic and kinetic conditions that otherwise would not be available [86]. For instance, the metal ion concentrations in the EPS may completely differ from those in the electrolyte, playing a key role in metal speciation. Furthermore, the metal ions trapped within the biofilm matrix become concentrated, forming complexes within a wide range of redox potentials. Under favourable conditions, these may participate in the electron-transfer processes, and affect the overall electrochemical characteristics of a given electrode-biofilm interface by increasing the kinetic rates or by providing additional cathodic or anodic reactions [87,88]. Reports and models of EPS-metal ions interactions highlight the role of anionic polysaccharides in metal binding but rarely consider the participation of proteins, nucleic acids or lipids [82,89].

Despite their benefits, metal adsorption and accumulation in microbial EPS or cell walls alone have the disadvantage that only low amounts are accumulated, typically in the range of µmol g^{-1} dry cells, making this approach discouraging for large-scale recovery. Thus, despite the numerous advances in this area there is consensus on a lack of commercial potential for this type of sorption [90]. Metal ion chelating properties of bacterial EPS may improve in the framework of METs, i.e., chelation or

complexation *via* electrochemically-tuneable EPS. Control of a particular electrochemical environment may improve ion-accumulation rate and capacities [91].

2.3. Microbial metal redox transformations

Following initial adsorption, a multiplicity of reactions may occur and account for removal and recovery of metals in purely microbial systems. Mechanisms directly dependent on microbial metabolism can lead to metal transformations. For instance, microbial precipitation as sulphides, oxidation, reduction, methylation, and dealkylation are some possibilities [25]. Microbes can even transform some metalloids by reduction of the cations to elemental forms and methylation to methylated derivatives which are volatile. Most of these mechanisms have been prospected for bioremediation, and some could be important for metal recovery and valorization [20].

A taxonomically-diverse group of bacteria can use a wide variety of metal cations as terminal electron acceptors under anaerobic conditions. Fe^{3+} and Mn^{4+} seem to be the most frequently utilized metals by microbes in natural environments like soils and water [92], yet this widely extended route is not of economic interest, as the commonly produced metal species, e.g., Fe^{2+} or Mn^{2+}, are more soluble than their oxidized counterparts and therefore not suitable for recovery [20]. Nonetheless, Zachara et al. achieved crystalline Fe^{3+} oxides [93] and Liu et al. [94] reported the reduction of Fe^{3+}-citrate complexes with evidence of crystalline Fe mineral formation within the bacterial cell wall. Iron oxide nanoparticles have been highlighted for application in biomedicine [95]. Yet, iron is not considered to be a critical raw material in terms of supply risk and economic importance. Mn can be precipitated by some bacteria in oxyhydroxides, however this is not always an energetically favourable process [96,97]. As a consequence of photosynthesis, cyanobacteria can induce pH rises and subsequent Mn precipitation [98]. Also, some enzymatic reactions involving EPS result in Mn oxidation [99]. Dissimilatory reduction of uranium U^{6+} leads to the formation of precipitated uraninite UO_2. This is due to the low solubility of the product [100]. In some cases, such processes are mediated by non-enzymatic activity whereas in others the enzymatic activity involving the electron transport chain may be involved, related or unrelated to the microbial conservation of energy (i.e., respiration) [101,102].

After these pioneering works, many other studies have followed. Dupraz et al. reviewed the role of microbial mats in the precipitation of carbonates *via* various mineralization processes in modern freshwater, marine and hypersaline environments. The physicochemical properties concerning the metal binding potential by acidity and chemical composition of functional groups in the EPS have been discussed as a necessary preceding step for the formation of metal precipitates by microbial transformation [103]. Rawlings et al. reviewed the biomineralization of metal-containing sulphide, iron-containing ores, and mineral concentrates. In this process, iron and sulphides are oxidized to produce soluble ferric iron and sulphuric acid which transform insoluble sulphides of metals like copper, nickel, and zinc which can be recovered from solution. Also, with this microbial activity, ores containing gold can be oxidized, which allows gold-solubilizing chemicals such as cyanide to penetrate the mineral. The most important mineral-degrading microbes are the Gram-negative iron- and sulphur-oxidizing chemolitotrophic bacteria which grow by fixing CO_2 under anaerobic conditions, although some grow better with air-enriched CO_2. The microbes achieving this process usually operate at low pH ($\sim$1.5) at which ferric iron is soluble [104]. The crystallisation and precipitation of nanoparticle REE phosphates on microbial cells has also been reported, for example, the formation of nanoprecipitates of $NdPO_4$ and $EuPO_4$ on *Serrati* sp. [32,105], or $CePO_4$ [106] and $YbPO_4$ [107] on cells of *Saccharomyces cerevisiae*. The REE are critical raw materials and REE phosphate NPs have been highlighted for their fluorescence in many biological applications [108].

Over the past years considerable effort has been undertaken to generate the so-called biogenic crystalline zero-valent NPs by microbial processes [109]. Much attention has been given to the myriad of applications of nanometer-scale metals in new products and devices [110]. Whereas most studies have yielded single metal NPs of precious and platinum group metals (PGMs), mixed NPs have also been synthesised; e.g., core/shell Au/Pd NPs [111] and Au/Pd bimetallic NPs [112,113]. Several studies demonstrated that sulphate-reducing bacteria (SRB) and Fe^{3+}-reducing bacteria reduce palladium (Pd), platinum (Pt) and gold (Au) to zero-valent metallic NPs [84,114–116]. This has also been applied to cadmium, strontium, and heavy metals, among others [32]. Of note, biogenic nanoparticles have been shown to have a protein/peptide capping (corona), attributing them a high colloidal stability (>months) [117]. This implies that enzymatically-mediated electron transport reactions lead to nanoscale crystalline nanoparticles on the surface of bacteria. For example, c-type cytochromes or hydrogenases of bacteria, like the Fe^{3+} reducing *Geobacter metallireducens*, *Geobacter ferrireducens*, *S. algae*, *Thermotoga maritime* and *Pyrobacter* sp., transfer electrons to soluble $AuCl_4^-$ [118,119] leading to zero-valent Au nucleation and crystallisation.

The fact that they are decorated on a microbial scaffold would allow in-situ application of biogenic NPs located in the bacterial cell wall or EPS. For example biogenic PdNPs synthesised by *S. algae* and immobilised predominately within the cell wall periplasmic space have been applied as an anodic catalyst in polymer electrolyte membrane fuel cells for power generation [120], showing comparable power generation to those containing a commercial palladium catalyst. De Corte et al. [113] demonstrated that cell-associated bimetallic biogenic Pd/Au could catalyse the dehalogenation of environmental contaminants. Essentially bacterial biomass can be treated as carbonaceous material which serves as site, agent and matrix for preparing heterogeneous NP catalysts [121]. Otherwise, microbial deposition of NPs within the cell wall (5 to >100 nm) provides a process with ease in their separation and removal by cell wall disruption methods such as sonication [122]. The generation of biogenic NPs of Au and PGM requires in most cases an electron donor which is where METs can also provide a controlled supply. For example, the microbiological reduction and deposition of zero-valent AuNPs and TcO_2NPs [123] from

ionic precursors have shown to require H_2 as a mediator [84,124–126], implicating the cell wall protein hydrogenase [127]. Electrodes here could provide a clean source of H_2, *in-situ*.

The motivation for the reduction of various metal ions as part of metabolic processes by living microorganisms would be twofold: as part of dissimilative processes where metal ions are used as electron acceptors for the conservation of energy, or as defence mechanisms caused by toxic stress of metals ions (e.g. Ag^+ and Hg^+) [128,129]. E.g., recently, Ramanathan et al. [130] reported the synthesis of zero-valent CuNPs using a silver resistant bacterium *Morganella morganii*. Interestingly, voltammetry analysis of bacterial cells at different exposure times to Cu^{2+} ions, indicated a strong correlation between the silver and copper resistance machinery of bacteria.

The overall reason for living microbial cells to reduce precious metals remains elusive. In light of the high standard reduction potential of $AuCl_4^-$ (1.002 *vs.* SHE/V), Pd^{2+} (0.915 *vs.* SHE/V) and $PtCl_6^-$ (0.744 *vs.* SHE/V) in acid solutions [131] and dependence in some cases of a specific electron donor (e.g. H_2), dissimilative mechanisms could be speculated.

Despite its numerous advantages such as tolerance to the presence of organics and economic competitiveness, metal recovery by microbial transformations has several disadvantages. For instance, many metal-containing aqueous matrices are too aggressive for living cells. Also, there are high variations between batches of the biological product, as well a lack of specificity and sensitivity to pH and temperature changes [132]. A major limitation of these solely-microbial processes is the necessity of an electron donor or acceptor. There is a large spectrum of compounds which can accomplish this function. Yet, it is a great challenge to select economically attractive types and concentrations [32]. The discovery of METs that can achieve metal recovery is a major step in overcoming this challenge. Soluble electron donors and acceptors can be replaced by more economically-attractive solid-state electrodes which can be well controlled at a certain applied potential, adding selectivity to the metal transformations.

2.4. Electrochemical or electro-driven processes

Electrochemical recovery of metals can be mainly obtained by direct electrolysis, electrodialysis, electrocoagulation and capacitive deionization. Electroless plating has also shown ample commercial application in the manufacturing of electronic devices [133], but little attention has been given to its application for metal recovery. The key parameters in electrochemical or electro-driven processes are the current density distribution, current efficiency, and mass transfer rates that determine the techno-economic feasibility for a certain level of removal and recovery [134].

If the concentration of the supporting electrolyte is ten times higher than the concentration of metals to be recuperated (e.g., 100 mg L^{-1} Mn^{2+} in seawater), transport of the metal by migration can be neglected. Oppositely, in the absence or at low concentrations of supporting electrolyte, it is both migration and diffusion that determine the transport of the metal ions to an electrified interface under influence of an applied potential. Migration can be controlled with the use of appropriate ion-exchange membranes and by the electrolyte ionic composition and strength. Mass transfer is also determined by convection caused by e.g., the use of spacers that enhance turbulent flow and force the aqueous matrices through the electrodes, or by gas-bubble evolution (e.g., H_2) on the electrode.

Electrode configurations have been extensively reviewed by Koene and Janssen [135]. Two- or three-dimensional porous electrodes are employed. In general, two-dimensional electrodes are preferred for metal removal and recovery, as in most three-dimensional electrodes the metal deposits are only formed at the outer layer of the counter electrode (thus behaving as two-dimensional electrodes). When the metals deposit inside the three-dimensional structure, the porosity is drastically reduced resulting in high-pressure drops. Current density distribution in two-dimensional electrodes is practically uniform when adequate cell geometry, positioning, and shape of electrodes are in place. The same will hold for ion-exchange membranes. Yet, in three-dimensional electrodes heterogeneous current density distribution should be regarded as an effect of the potential drop across the electrode. Highly-performing three-dimensional electrodes can be achieved when high geometric surface areas per unit volume are used.

Electrolytic recovery of metals from dilute solutions with three-dimensional electrodes has generally been asserted not to be feasible in practice. Although this process is advantageous due to its high mass transfer rate, high degree of conversion, simplicity, and cost-effectiveness of electrode materials, deposition of the solid metals is limited by the electrolyte conductivity and metal dendrite formation which can cause damages to electrodes, membranes or separators; also, only a small range of electrode materials can be employed and high volumetric flow rates will result in high-pressure drops over the reactor. Dendrite formation can be prevented by the frequent change of the electrodes. For these reasons, electrolytic recovery of metals in three-dimensional electrodes is mostly preferred for electrolytic reactions where soluble reactants or products are available (e.g., Fe^{3+}, O_2, CrO_4^{2-}). Electrolytic metal recovery in two-dimensional electrodes is advantageous due to the practically uniform current distributions, high mass transfer rates, small spacing between electrodes (thus reducing the ohmic drop) and the possibility of continuous removal of the deposited metal. Some disadvantages are low conversion rates, redissolution of the metal deposits and the limited geometries. Electrolytic metal recovery with two-dimensional electrodes is then preferred when the final product lays as a solid phase over the surface of the electrode (e.g., Cu electrodeposition). However, the success and economic feasibility of electrolytic metal recovery can be limited by its high power consumption [135]. Usually, above 80% of operational costs of electrolytic processes are related to electricity consumption alone.

In electrodialysis, as well as in the aforementioned electro-driven processes, the concentration of supporting electrolyte must be low—except in some cases like Cu and Ag electrodeposition where it can be high. That is, practically only the metal ions to be removed should be present. Ion exchange-assisted electrodialysis may enhance classical electrodialysis by using

ion-exchange particles placed in a central compartment for the purpose of increasing conductivity and achieving more efficient metal separation [136]. Such particles can also induce strongly non-uniform current distribution. For this reason, careful design is needed [137].

Despite all this extensive advancement, the separation and recovery of valuable metals from natural primary aqueous sources and secondary aqueous sources like wastewaters and leachates still requires more efficient, less energy intensive and more environmentally friendly technologies, which can cope with the challenges of a highly complex aqueous matrix and a low metal concentration. METs have emerged as a promising route. Relatively pure metals can be recovered at low energy intensity, at satisfactory kinetic rates and efficiencies as described subsequently. The general principles, advantages, and disadvantages of the technologies described in the precedent sections should be remembered, given that in one way or another, they relate to the functioning of METs targeting metal recovery.

3. Microbial-electrochemical technologies

3.1. Principles of microbial-electrochemical technologies

Over the past decade, research on METs has boomed across the globe. In 2001, the generation of electric current from sediments was achieved in the so-called microbial fuel cells (MFCs) [138]. A somewhat higher value application for electrochemically-mediated microbial systems has been hydrogen generation in microbial electrolysis cells (MECs) [139]. More recently, in 2010 electricity-driven synthesis for the production of organic chemicals was first described in Microbial Electrosynthesis Cells (MESCs) [140]. Microbial Desalination Cells (MDCs) already demonstrated the possibility to reduce the salinity of an aqueous solution, while generating electrical power from electrolysis of organic matter [141].

In the slipstream of these discoveries, removal and recovery of an assortment of metals with METs appeared. For pragmatism here we term these processes as microbial electro-metallurgy (MEM). MEM works under the overall principles of METs but, within the process, metal removal and recovery are achieved.

Uranium recovery was first described in the work of Gregory and Lovley (2005) [50]. Silver recovery through cathodic reduction [142,143], chromium reduction [144], ferric iron reduction and ferrous iron oxidation [145,146], mercury removal [147] and copper removal and recovery [148], among others, followed using MFCs. MET recovery by electrodeposition of copper, lead, cadmium, and zinc from mixed dilute solutions was revealed as a promising approach [149].

Succinctly, MEM can (1) use complex solid waste or wastewaters as electron donors/acceptors, (2) reduce energy consumption compared to traditional processing, and (3) recover and generate metallic commodities with lower greenhouse emissions.

The working principle of MEM for metal recovery is reasonably straightforward. Microorganisms may colonize the anode (where oxidation occurs), the cathode (where reduction occurs) or both. For example, a cathode can be driven by a power supply to directly or indirectly (typically *via* H_2) provide reducing power to the microorganisms. The latter can use the energy gained for growth while simultaneously reducing the metallic contaminants as the electron acceptor. By fine-tuning the potential at which reduction (or oxidation) occurs, it should according to thermodynamic considerations be feasible to selectively separate metals.
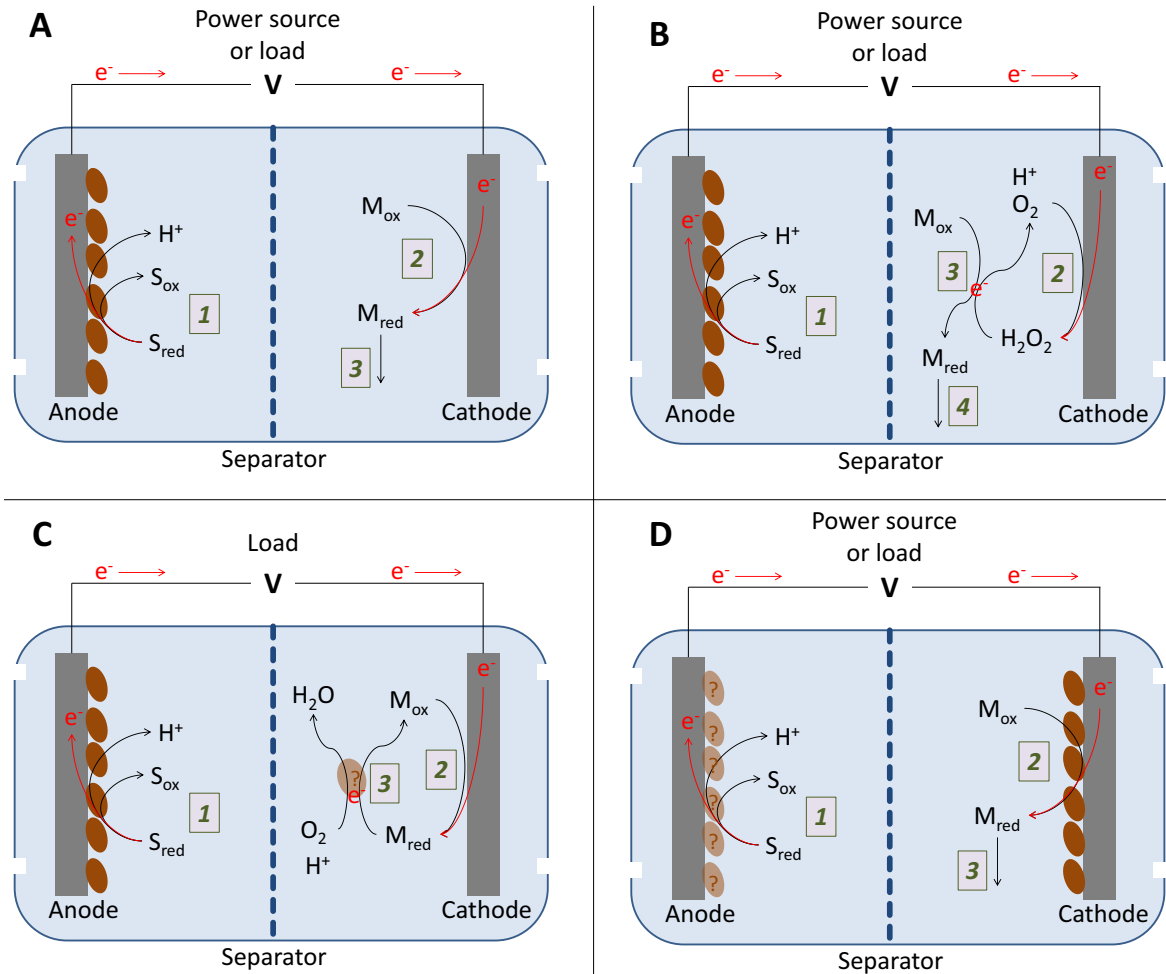
3.2. Microbial electro-metallurgy: mechanistic overview

Several strategies have been employed to achieve desirable metal transformations in MEM systems. Electrochemically active microorganisms have been used either at the anode to lower the overall energy consumption of the process by oxidizing organic compounds present in e.g., wastewater (Fig. 3A–C) or at the cathode to catalyse the reduction of oxidized metals and microbial reduction or precipitation of metal ions (Fig. 3C and D).

Based on the mechanisms used to transform and recover the metals, MEM systems can be divided into four general categories. Category A (Fig. 3A) includes systems with a microbiological (biotic) anode and an abiotic cathode. Metals are directly reduced by electrons from the cathode and the reduced form of the metal is recovered. If the metal has a high reduction potential relative to the biological anode, the system can be operated as a MFC. This is the case for e.g., Cu and Ag [143,148]. If the metal has a lower reduction potential, the system must be operated as a microbial electrolysis cell, i.e., with an external power supply. This is the case for e.g., Cd and Zn [149]. In most cases the reduced metal can be recovered as a precipitate or deposit on the cathode surface. However, other reactions are possible, like for cobalt the cathodic reduction process can be used to leach Co^{2+} from solid lithium-cobalt (Co^{3+}) oxide [150].

In category B systems (Fig. 3B), the electrochemical reduction at the cathode is used to generate a chemical reductant, which reacts with the oxidized metals in the solution. This process has been used to reduce O_2 to H_2O_2, which reacted with toxic Cr^{6+} to form less toxic Cr^{3+} and O_2 [151]. In the study by Liu et al. (2011), Cr^{3+} was formed both by reaction with in-situ produced H_2O_2 and by direct electrochemical reduction on the cathode.

In category C systems (Fig. 3C), the electrochemical reduction on the cathode surface is followed by a chemical or biochemical re-oxidation (or further reduction) of the metal. The purpose of reducing and then re-oxidizing the metal may be to enhance the power output of an MFC. By adding a redox couple with high reduction potential and fast reaction kinetics, the cathode can be operated at a higher potential compared to a conventional MFC. Examples include Mn^{2+}/Mn^{4+} [152] and

Fig. 3. A division of microbial electro-metallurgical systems into categories based on mechanisms for metal transformation and recovery. Category (A) A biological anode coupled to direct electrochemical metal reduction on an abiotic cathode. 1: An organic substrate (S_{red}) serves as electron donor for electrochemically active microorganisms using the anode as electron acceptor. 2: The cathode serves as electron donor for metal reduction (M_{ox}/M_{red}). 3: (i) The reduced metal is recovered e.g. as a precipitate or as a deposit on the cathode surface (e.g. the electrodeposition of Cu^{2+} to Cu^0 [217]) or leached out into the liquid followed by subsequent recovery (e.g. the reduction of Co^{3+} to Co^{2+} [150]. Category (B) A biological anode coupled to electrochemical generation of reductants at the cathode. 1: An organic substrate serves as electron donor for electrochemically active microorganisms using the anode as electron acceptor. 2: The cathode serves as electron donor for electrochemical generation of a reductant (e.g.·H_2O_2). 3: The metal is reduced by a chemical reaction between the reductant and the oxidized form of the metal. 4: The reduced metal is recovered as a precipitate, e.g. reduction Cr^{6+} to Cr^{3+} [151]. Category (C) A biological anode coupled to a cathode compartment with electrochemical metal reduction and (bio)chemical re-oxidation. 1: An organic substrate serves as electron donor for electrochemically active microorganisms using the anode as electron acceptor. 2: An oxidized metal serves as electron acceptor at the cathode. 3: The reduced form of the metal is re-oxidized either biologically or abiotically. An example is use of the Fe^{3+}/Fe^{2+} redox couple as catholyte in a microbial fuel cell [145]. Category (D) Systems with a biological cathode. 1: An oxidation reaction takes place at the anode. The reaction may or may not be biologically catalyzed. 2: Electrochemically active microorganisms use the cathode as electron donor to reduce an oxidized metal to its reduced form. 3: The reduced metal is precipitated and removed from the solution. An example is reduction of U^{6+} to U^{4+} [50] and reduction of SeO_3^{2-} to Se^0 [188].

Fe^{2+}/Fe^{3+} [145], which can be electrochemically reduced on the cathode surface and biologically re-oxidized by bacteria in the catholyte solution. This type of process can also be used to remove Fe from a solution. For example, Fe^{3+} was precipitated [153] by a pH increase that typically takes place at the cathode of a microbial fuel cell [154].

In category D systems (Fig. 3D), the electrochemically active microorganisms can be attached to the cathode or suspended in the catholyte. The principle was first applied for the remediation of perchlorate [155] and nitrate [156] from ground waters. Two strategies can be summarised here for metal recovery. Firstly, microorganisms can function as bioelectrocatalysts [157] of electrochemical reactions at the cathode [158], facilitating the reduction of metals for which abiotic electrochemical reduction would be difficult or require a large overpotential. Secondly, microbial metabolism can be stimulated by the *in-situ* electrochemical production of electron donors (e.g., H_2) or direct or indirect (mediated) electron transfer to microbial cells [33]. Microorganisms here sorb, reduce or precipitate metals within the cell wall or EPS matrix. Examples

Fig. 4. Reported metals recovered using MEM and examined in this study.

include reduction of U^{6+} to U^{4+} [50] and Cr^{6+} to Cr^{3+} [159]. Systems with biological cathodes may also contain biological anodes to allow operation as MFCs or to reduce the overall energy consumption of the system.

4. Current achievements in microbial electro-metallurgy

In the majority of MEM systems, bioanodes have been implemented. Usually mixed cultures of exoelectrogenic bacteria, inoculated from activated sludge, form biofilms on carbon anodes. These biofilms catalyse the oxidation of organic substrates and the transfer of electrons to the anodes. Most studies reported here have used acetate as the electron donor to drive or complement the respective cathodic reaction. Acetate oxidation can be described as shown in Reaction (1) [160].
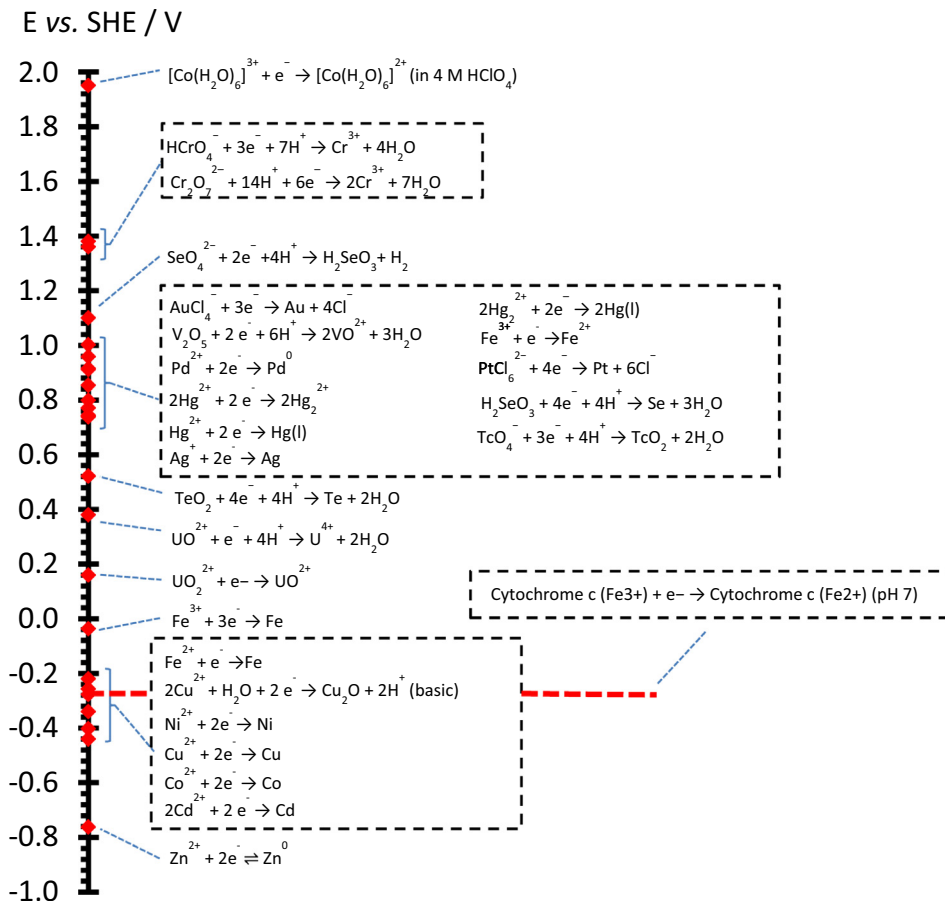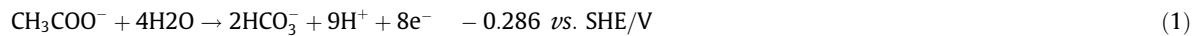

Fig. 5. Redox tower of metal ion standard reduction potentials in acidic solutions [218], and cytochrome-*c* [219] reported *vs.* standard hydrogen electrode (SHE).

Table 1

Summary of MEM technologies defined by category A-MFC system as described by Fig. 3A. Category C-MFC iron systems are also included here as reactions mechanisms occurring in the cathode are relational.

Category	Metal	Anode	Cathode	Reaction	Ref
A-MFC	Cr	Biotic	Abiotic	Electrochemical $Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$ **R1**	[144,165]
				Chemical $2Cr^{3+} + 3H_2O \rightarrow Cr_2O_3 + 6H^+$ **R2**	
	V			Electrochemical $VO_2^+ + 2H^+ + e^- \rightarrow VO^{2+} + H_2O$ **R3**	[166,167]
	Cu			Electrochemical $Cu^{2+} + 2e^- \rightarrow Cu^0$ **R4**	[217,169]
				Electrochemical $2Cu^{2+} + H_2O + 2e^- \rightarrow Cu_2O + 2H^+$ **R5**	[171,172]
C-MFC	Fe		Biotic	Electrochemical $Fe^{3+} + e^- \rightarrow Fe^{2+}$ **R6**	[145,175,146,176]
				Microbiological $8Fe^{2+} + 8H^+ + 2O_2 \rightarrow 8Fe^{3+} + 4H_2O$ **R7**	
A-MFC	Fe		Abiotic	Electrochemical $Fe^{3+} + e^- \rightarrow Fe^{2+}$ **R8**	[153]
				Chemical oxidation $Fe(OH)^{2+} + e^- \rightarrow Fe(OH)^+$ **R9**	
				Chemical oxidation $Fe(OH)^+ + e^- \rightarrow Fe(OH)_2$ **R10**	
				Chemical precipitation $Fe^{3+} + 3H_2O \rightleftharpoons Fe(OH)_3 + 3H^+$ **R11**	
	Co			Electrochemical $LiCoO_2(s) + 4H^+ + e^- \rightarrow Li^+ + Co^{2+} + H_2O$ **R12**	[150,177]
	Hg			Electrochemical $2Hg^{2+} + 2e^- \rightarrow Hg_2^{2+}$ **R13**	[147]
				Electrochemical $Hg_2^{2+} + 2e^- \rightarrow 2Hg^0(l)$ **R14**	
				Electrochemical $Hg^{2+} + 2e^- \rightarrow Hg^0(l)$ **R15**	
				Chemical $2Hg^{2+} + 2Cl^- \rightarrow Hg_2Cl_2(s)$ **R16**	
	Ag			Electrochemical $Ag^+ + e^- \rightarrow Ag^0$ **R17**	[143]
				Electrochemical $[AgS_2O_3]^- + e^- \rightarrow Ag^0 + S_2O_3^-$ **R18**	[142]
				Electrochemical $Ag(NH_3)_2^+ + e^- \rightarrow Ag^0 + 2NH_3$ **R19**	[178]
	Au			Electrochemical $AuCl_4^- + 3e^- \rightarrow Au^0 + 4Cl^-$ **R20**	[179]
A-MFC–SLM	Zn		Abiotic	Chemical stripping: Zn^{2+} transport	[220]

$$CH_3COO^- + 4H2O \rightarrow 2HCO_3^- + 9H^+ + 8e^- \quad -0.286 \ vs. \ SHE/V \tag{1}$$

In classical MFC systems, oxygen has been applied as the electron acceptor at the cathode [131] (Reaction (2)). However, in MEM metal ions often replace oxygen as the cathodic electron acceptor.

$$O_2 + 4e^- + 4H^+ \rightarrow 2H_2O \quad 1.23 \ vs. \ SHE/V \tag{2}$$

Fig. 4 summarizes metals studied to date using MEM technology and highlights those which are highly profitable for recovery. Especially for critical metals such as PGM and lanthanides [9]. Noteworthy reports of microbial transformation and precipitation of nanoscale crystalline transitional metals ions, include Tc^{7+} [123], PGMs such as Pd^{2+} [161] and Pt^{4+} [162], chalcogens such as Te^{4+} [126] and lanthanides [32].

Fig. 5 shows some standard reduction potentials of MEM metal recovery. Cytochrome-c oxidase, an exemplar bacterial outer membrane protein enzyme previously implicated in electron transfer to metal ions [163], with a standard potential of 0.26 vs. SHE/V (pH 7), is also shown [164]. Cytochrome-c or other relational cell wall protein enzymes with similar redox potentials would be involved in the reduction of metal ions discussed. Therefore this potential provides an approximate thermodynamic limit for metal reduction. I.e., only metals with redox potentials above 0.26 vs. SHE/V can be reduced by bacterial cells with these characteristics. Discussed subsequently, on the whole, metal ions with standard potential below this value have found application in MECs systems while those higher in MFCs, predominantly with abiotic cathodes. Furthermore, metals with standard potentials higher than that of Cytochrome-c oxidase have shown the greatest promise for application in biocathodes as described by Fig. 3D. Current achievements are discussed subsequently based on categories A–D, illustrated in Fig. 3.

4.1. Category A MFC systems

Category A systems (Fig. 3A) operated as MFCs have been the most investigated MEM technology, applied for both the recovery of various metal ions and energy generation, as summarized in Table 1. In some cases, metal ions are electrodeposited as zero-valent metals on the cathode surface or precipitated as oxide species in solution or on the cathode. Organic oxidation by bioanodes provides electrons which drive the electrochemical reduction of metals.

TRANSITIONAL ELEMENTS - The reduction of hexavalent chromium Cr^{6+} to the less toxic, insoluble trivalent chromium dioxide Cr_2O_3, with the simultaneous production of energy, has been well demonstrated. The formation of insoluble oxides takes place via the respective electrochemical reduction and chemical precipitation (Table 1, R1-2). From the standard redox potentials of such reactions, it can be directly deduced that dichromate $Cr_2O_7^{2-}$ (1.36 vs. SHE/V) is theoretically more favourable as an electron acceptor than O_2 (1.23 vs. SHE/V) for reduction in MFCs. For instance, Li et al. reported 99.5% removal of hexavalent chromium Cr^{6+} from real electroplating wastewater, through electrochemical reduction to the less toxic trivalent chromium Cr^{3+} [144]. In a different study, Wang et al. reported the complete reduction of 100 mg L^{-1} Cr^{6+} during 150 h operation (pH 2) and a maximum power density of 150 mW m^{-2} generated with 200 mg L^{-1} Cr^{6+} as the electron acceptor using a flat graphite plate cathode [165].

Vanadium V^{5+} has been employed as an effective electron acceptor at the cathode compartment of MFCs [166,167]. Zhang et al. (2009) demonstrated vanadium recovery by reduction and solubilisation of vanadium oxides in the cathode chamber. A change of colour at the catholyte was noticed from yellow-brown to sky-blue, indicating the transformation of V^{5+} into V^{4+} (Table 1, R3). V^{5+} has a minimum solubility at pH 6; when the exhaust catholyte pH was raised to this pH with $NH_3 \cdot H_2O$, the colour of the solution further changed from sky-blue to dark grey, with exiguous particles suspended in the solution. After filtration of the brown precipitates, XPS analysis was used to confirm that microstructured amorphous $NaVO_4$ and V_2O_5 were the main constituents. Sulphide and total organics removal reached about 85% and 21%, respectively, whereas the V reduction efficiency was about 25%. Electricity generation also took place, reaching a maximum power density of approximately $\sim 0.57 \text{ W m}^{-2}$ [167].

Cu recovery was achieved in an MFC, coining the concept of "metallurgical microbial fuel cell," which is a type of MEM. Cu was recovered at the sandpapered graphite plate cathode in the form of pure crystals by reduction of Cu^{2+} from solution to Cu^0 on the electrode (Table 1, R4). Removal efficiencies from the aqueous solution reached over 99% via this approach [168,169]. In the presence as well as in the absence of oxygen, a similar layer of pure copper was found. Moreover, in the presence of oxygen, a faster reduction (i.e., higher current at the same overpotential) was observed compared to anaerobic conditions; this being the result of combined copper and oxygen reduction and a possible catalytic effect of copper for oxygen reduction. Furthermore, Cu^0 can be easily released from the cathode using an acid bath (e.g. nitric acid), or inexpensive carbon felt electrodes can be burned to recover the metal. Otherwise, Cu^0 can simply remain as a stable deposit over a supporting electrically-conductive material. Furthermore, copper deposited under aerobic conditions displays a microstructure with more octahedral features, compared to cauliflower-like features for copper precipitated under anaerobic conditions. Cu^{2+} reduction and precipitation on cathodes were also demonstrated in an MFC system at pilot-scale [170].

Besides metallic Cu, partially-reduced Cu compounds like Cu_2O have also found on the cathode as reported by Tao et al., in a membrane-free baffled MFC [171] and dual-chamber MFC [172]. Also of note, the higher initial concentration of Cu^{2+} (>500 mg L^{-1}) resulted in the formation of $Cu_4(OH)_6SO_4$. Two electrons are required to reduce Cu^{2+} to Cu^0 completely (Table 1 R4), while only one electron was needed for the reduction of Cu^{2+} to Cu^+ (Table 1 R5). A removal efficiency of 95.6% was reached for an initial concentration of 50.3 mg L^{-1} $CuSO_4$, whereas 48% was reached when the initial concentration was 1008 mg L^{-1}, at current efficiencies of 61.9% and 46.0%, respectively. The Cu removal efficiency was found to depend on the initial average Cu^{2+} concentration, while the mass of Cu metal crystals and Cu^+ compounds deposited on each cathode was dependent on current intensity [171,172].

It is indeed unexpected, from a purely electrochemical point of view, that higher removal takes place at lower concentrations. A few possibilities are suggested in the present review to explain this occurrence. Firstly, it is possible that at higher concentrations more precipitation takes place. Secondly, when a cation exchange membrane is in place, part of the copper could be lost to the anode or end up bound to the membrane. This phenomenon is usually more prominent at higher copper concentrations. However, it should be noted that the initial concentrations of copper used in the study by Tao et al. are low, i.e., 0.9 mM and 15.7 mM [172]. Thirdly, transport phenomena can play a part. If mass transfer is limiting, which is most likely, transport (before reduction) takes place by both diffusion and migration. From a system where diffusion alone is limiting, a higher percentage of removal can be expected at higher initial concentrations. However, if diffusional limitations are negligible and migration prevails the outcome is different. Migration is driven by the charge of the ions and the magnitude of the electrical gradient applied. For the purpose of illustrating the outcome, consider two independent identical electrochemical cells containing an aqueous solution with the same kind of ions (i) which have the same charge, e.g., i^+, where the said solutions differ only in concentration (C_i^+). It is assumed that faradaic processes are negligible and only electro-driven transport is induced when the said cells are polarized at a fixed current (j). The fixed amount of j can only be carried by a fixed amount of ions i. If there would be the possibility to exhaust the fixed j available and the resulting amount of ions transported by migration is counted, the latter would be equal for both the diluted and the concentrated electrolytes. However, regarding the percentage of removal, this translates into a higher value for the dilute case. In a typical microbial-electrochemical system, as in almost any other electrochemical system, a mixture of the aforementioned limiting transport phenomena is typical [173]. It is unfeasible to deduct the specific limiting type of transfer from the study of Tao et al. [172] with the data provided alone, but this third possible cause seems most likely to describe higher removal at lower concentrations for highly dilute electrolytes.

Although there are some reports dealing with copper recovery by deposition from dilute aqueous solutions, it is typically difficult to achieve it. The charge transfer coefficient for hydrogen evolution (e.g., about 0.45) is larger than that for copper deposition (e.g., in the range of 0.1–0.38) [174]. High removal efficiencies were reached by Tao et al. [172] and ter Heijne et al. [168]; because copper reduction was carried out on carbon-based electrodes, current efficiencies were significant as well. The use of graphite as supporting electrode for cathodic Cu deposition was key for such achievements, as this material minimizes the overpotential for copper reduction whereas it maximizes the overpotential for hydrogen evolution, which are paramount phenomena for industrial prospection [168,171]. Other materials could provide similar features.

The dissimilative reduction of Fe^{3+} to Fe^{2+} has been extensively applied in the cathodic compartment of MFCs as shown in Fig. 3C, category C. Such systems do not lead to metal recovery per se but are included, as they are relevant to the phenomena elaborated on in this study. The principal objective of the academic community here was to find an alternative cathode system for O_2 reduction, which would lead to higher power production. As described by the studies of ter Heijne et al. [145,146,175,176], Fe^{3+} reduction at the cathode was combined with biological Fe^{2+} re-oxidation to Fe^{3+} to achieve improvements in reduction reaction kinetics (Table 1 R6-7).

Following on from these studies, Fe^{3+} reduction was studied by Lefebvre et al. [153] with the objective to remove concentrated iron from AMD. In this case, re-oxidation of Fe^{2+} was explained to occur through several abiotic reactions (Table 1 R8-10) in the presence of O_2. Re-oxidation of ferrous hydroxides was followed by precipitation of Fe^{3+} in the cathode solution (Table 1 R11). Part of the electrons supplied *via* acetate oxidation resulted in iron reduction (or ferrous oxide formation) and part was used to support oxygen reduction at the cathode. This caused an overall pH rise due to the transport of cations through the membrane. Indeed, ferrous iron oxidation will occur rapidly (chemically) at high pH and it is almost impossible at low pH (2–3), unless iron-oxidizing microorganisms are present.

Post transitional elements - Huang et al. [150] demonstrated the recovery of Co^{2+} from spent lithium-ion batteries. Co^{3+} ions were leached and reduced from lithium cobalt particles, loaded on the surface of a carbon cathode (Table 1 R12). The catholyte pH was a significant factor in cobalt leaching and power generation, changing the pH from 1 to 3, lead to cobalt leaching of 71%, 63% and 9% respectively; while power generation decreased from 258 mV m^{-3} at pH 1 to 33 mV m^{-3}, pH 3, after 48 h operation. Catalysis of Co^{2+} leaching from $LiCoO_2$ with the addition of Cu^{2+} has also been demonstrated [177]. A dosage of 10 mg L^{-1} Cu^{2+} improved cobalt leaching up to 308% compared to Cu^{2+} absent controls.

Removal of Hg^{2+} in the presence of Cl^- ions was successfully demonstrated with MFCs [147], with a maximum power density of 433 mW m^{-2}, achieved at pH 2 and with 100 mg L^{-1} Hg^{2+}. Higher removal efficiencies of 98–99.5% for initial concentrations of 25–100 mg L^{-1} Hg^{2+} were reported. Products of the reduction of Hg^{2+} were verified as round microscale Hg deposits on the cathode surface and as Hg_2Cl_2 precipitates at the bottom of the cathode chamber. The electrochemical reactions concerned for Hg^{2+} reduction at the abiotic cathode are described in Table 1 (R13-15). While in the presence of Cl^-, Hg_2Cl_2 precipitation observed in the cathodic chamber would be described by Table 1 R16.

Precious metals - MFC technology was applied to recover silver from organic-based wastewater while producing electrical energy. Ag^+ in the catholyte was introduced in the form of $AgNO_3$, which in aqueous solutions is fully dissociated into Ag^+ and NO_3^-. Solid metallic silver was found to be deposited (Table 1 R17) at the cathode surface [143]. In a similar study Tao et al. [142] report the reduction of Ag^+ and $[AgS_2O_3]^-$ to Ag^0 (Table 1 R18). Power densities of 109 and 35 mW m^{-3} for Ag^+ and $[AgS_2O_3]^-$ were reported for 1 mM initial metal concentration. Removal efficiencies of >89% were achieved with Ag^+ solutions after 5.5 h operation. For a better representation of silver wastewater, Wang et al. [178] studied Ag recovery from ammonia-chelated silver in alkaline solutions using an MFC system. As in the above studies, bioanodes where used to generate electricity and drive the reduction of silver ions at the cathode (Table 1 R19).

The recovery of gold metal coupled with power generation using $AuCl_3^-$ has been demonstrated by Choi and Hu [179]. Power densities of up to 6.58 W m^{-2} were achieved with 2 g L^{-1} Au^{3+} (pH 2), in the cathode chamber, while recovery efficiencies as high as 99.89% were achieved with 200 mg L^{-1} Au^{3+}. At low pH in chloride solutions, Au^{3+} co-ordinates as $AuCl_4^-$ and is reduced at the cathode and deposited as elemental gold Au^0 (Table 1 R20).

The synthetic alliance of MFC integrated with a supported liquid membrane (SLM) has been investigated by Fradler et al. [180], for zinc recovery and power generation. The SLM comprised a liquid cationic exchanger D$_2$EHPA (di-2-ethylhexyl phosphoric acid), dissolved in an organic liquid and impregnated into a porous membrane exchange. This arrangement included an anodic-, a cathodic-, and a stripping-chamber, with biocatalysts for acetate oxidation in the anode chamber. The anodic/cathodic and cathodic/stripping chambers were separated by a bipolar membrane and an SLM, respectively. The cathode chamber, containing 400 mg L^{-1} Zn^{2+} was the feed stream to the SLM. Zn^{2+} was extracted by the SLM from the feed phase, stripped at the SLM/stripping phase and released into the stripping chamber. The stripping chamber contained 400 mg L^{-1} H_2SO_4. D$_2$EHPA was simultaneously regenerated by exchanging Zn^{2+} with two protons to achieve charge balance. Zn^{2+} concentrations were reduced from 400 mg L^{-1} to 26 mg L^{-1} and 16 mg L^{-1} in the MFC/SLM and SLM, respectively. The Zn^{2+} recovered in the stripping phase was 157 mg L^{-1} and 227 mg L^{-1} for the MFC/SLM and SLM systems. Significant improvements in the power generation were discovered, with a difference of 0.233 mW and 0.094 mW for MFC/SLM and MFC systems.

4.2. Category A MEC systems

The recovery of pure cobalt metal and H_2 production from a Co^{2+} electrolyte was reported by Jiang et al. [181] using mixed cultures consisting mainly of delta- and beta-proteobacteria biofilms on bioanode MEC. SEM and XPS analysis revealed initially sporadic Co metallic crystals, subsequently leading to micro to nano scale flake blooms growing away from the cathode surface, which would have potential application in electrochemical capacitors [182]. Optimally-applied cell potentials were 0.3–0.5 V for Co recovery and H_2 production (Table 2 R1). In a similar study, Qin et al. [183] demonstrated the recovery of nickel in a MEC system. Ni was deposited on the cathode (Table 2, R2) at an applied cell potential of 0.9 V. With an initial Ni^{2+}

Table 2
Summary of MEM technologies defined by category A-MEC system as described by Fig. 3A.

Category	Metal	Anode	Cathode	Reaction	Ref
A-MEC	Co	Biotic	Abiotic	Electrochemical $Co^{2+} + 2e^- \rightarrow Co^0$ **R1**	[181]
	Ni			Electrochemical $Ni^{2+} + 2e^- \rightarrow Ni^0$ **R2**	[183]
A-Stacked 2MFC–MEC	Cd			Electrochemical $Cd^{2+} + 2e^- \rightarrow Cd^0$ **R3**	[184]

Table 3
Summary of MEM technologies defined by category B system as described by Fig. 3B.

Category	Metal	Anode	Cathode	Reaction	Ref
B-MFC	Co	Biotic	Biotic	Bioelectrochemical $O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$ **R1**	[185]
				Chemical $Co^{2+} + OH^- \rightarrow Co(OH)_2$ **R2**	
	Cr		Abiotic	Electrochemical $O_2 + 2H^+ + 2e^- \rightarrow H_2O_2$ **R3**	[221]
B-MFC-PEC	Cr			Chemical $2HCrO_4^- + H_2O_2 + 8H^+ + 2e^- \rightarrow 2Cr^{3+} + 3O_2 + 8H_2O$ **R4**	[187]
				Chemical $2Cr^{3+} + 3H_2O \rightarrow Cr_2O_3 + 6H^+$ **R5**	

concentration of 1 g L^{-1} (pH 5), the removal efficiency for experiments carried out in duplicate was 33% and 10%, in a reactor operated with the abiotic cathode. Furthermore, with initial Ni^{2+} concentrations of 50 mg L^{-1} and 1 g L^{-1}, the removal efficiency decreased from 99 to 33%, while the current density increased from 51 to 166 A m^{-2}, respectively. Perhaps, in the latter case, the system was under mass transport control and not enough time was provided to remove all the Ni^{2+} available.

Choi et al. reported cadmium recovery using a combination of MFC and MEC [184]. In this study, two MFCs with chromium as electron acceptor in the cathode (Cr-MFC) were connected in series to a MEC with Cd^{2+} in the cathode chamber. Here the Cr-MFCs were used to complement insufficient electrical potential needed to drive Cd^{2+} reduction in the MEC. High removal efficiencies of 93.4, 93.3 and 89.7% were observed for concentrations of 50, 100 and 200 mg L^{-1}, respectively, after 60 h of operation. Cadmium was recovered as metal, as described in R3, Table 2.

4.3. Category B

Table 3 summarizes MEM technology on this category, applied to date as described in Fig. 3B.

Huang et al. [185] demonstrated the recovery of Co^{2+} using an oxygen-reducing biocathode in an MFC. Biofilm biocathodes were established using mixed cultures inoculated from aerobic and anaerobic sludge, sediments and metalworking wastewaters. The in-situ production of OH$^-$ by O$_2$ reduction at the biocathode lead to the precipitation of amorphous microscale Co(OH)$_2$ (Table 3 R1-2), with simultaneous energy production. Maximum power densities of 1.5 W m^{-3} were achieved under optimal conditions of 31 M O$_2$, pH 5.6 and a Co^{2+} concentration of 508 M. Also of note, SEM analysis revealed that the majority of Co(OH)$_2$ precipitates occurred on the microbial cell surface.

In another study, the reduction of Cr^{6+} (Table 3 R4-5) was completed in strong association with electrochemically-generated H$_2O_2$ (Table 3 R3) at an air-bubbling cathode [151]. This was driven by pure cultures of the iron-reducing bacteria *S. decolorationis* and *Klebsiella pneumonia* or anaerobic activated sludge collected from a wastewater plant inoculated on the surface of the anode. Higher concentrations of H$_2O_2$ were produced with activated sludge in the anode chamber and the addition of the electron mediator ADQS to the anode. Cr^{3+} reduction could occur *via* direct electrochemical reduction or *via* electrochemically-produced H$_2O_2$ [186]. H$_2O_2$ was shown to be a superior reducer because when H$_2O_2$ was not formed (i.e., when the chamber was gassed with N$_2$), Cr^{6+} was reduced at lower rates and lower removal efficiencies (42.5% with nitrogen after 12 h *vs.* about 100% with air after 4 h). This study showcases a novel system with the combination of microbial bioelectrocatalysis, which drives the electrochemical reduction and *in-situ* production of chemical reducing species, leading to the removal of Cr^{6+} in the abiotic cathode.

In an original study, Li et al. [187] demonstrated the integration of MFC and a photoelectrochemical cell (PEC), for simultaneous power generation and chromium recovery. In this system, a biotic anode was coupled to an abiotic semiconductor photovoltaic (rutile-coated) cathode. Under light irradiation, 97% of Cr^{6+} (initial concentration 26 mg L^{-1}) was reduced and precipitated within 26 h (Table 3 R4-5), which was 1.6 times faster than in a non-photocatalytic process. Their finding demonstrated that microorganisms can indirectly use the photogenerated holes as an intermediate electron acceptor at the cathode. Oxidized species such as Cr^{6+} with energy levels lower than the conduction band of the semiconductor would serve as the terminal electron acceptors in the cathode chamber of an MFC. Photoelectrons produced may also react with H$_2O$, OH$^-$, and O$_2$ to produce other redox -active species such as hydroxyl radicals ($^\cdot$OH), superoxide radicals (O$_2^-$) and H$_2O_2$ [186], which might also have contributed to the higher Cr^{6+} reduction rates.

4.4. Category D

Reports of metals recovered in biocathodes (Fig. 3D) are summarised in Table 4.

Table 4
Summary of MEM technologies defined by category B system as described by Fig. 3D.

Category	Metal	Anode	Cathode	Reaction	Ref
D-MFC	U	Biotic	Biotic	Biological $UO_2^{2+} + 2e^- \rightarrow UO_2^+$ **R1**	[50]
	Se			Biological $SeO_3^{2-} + 4e^- + 6H^+ \rightarrow Se^0 + 3H_2O$ **R2**	[188]
	Cr			Biological $Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$ **R3**	[159,190,191]
				Chemical $2Cr^{3+} + 3H_2O \rightarrow Cr_2O_3 + 6H^+$ **R4**	
D-MEC	Co	Biotic		Microbial-electrochemical $Co^{2+} + 2e^- \rightarrow Co^0$ **R5**	[192]
	Au	Abiotic		Microbial-electrochemical $AuCl_4^- + 3e^- \rightarrow Au^0 + 4Cl^-$ **R6**	[193,158]

In a pioneering investigation, which opened the gate to extensive research now dedicated to unravel the principles and applications of biocathodic MEM, Gregory and Lovley used *Geobacter sulfurreducens* for U^{6+} reduction on a biocathode. Uranium removal was effectively achieved by reducing soluble hexavalent uranium U^{6+} to the relatively insoluble tetravalent uranium U^{4+} oxide precipitate (Table 4 R1) [50]. With an applied cathode potential of -600 *vs.* Ag/AgCl/V, the cathode served as electron donor to *Geobacter sulfurreducens*. U^{4+} remained as a stable precipitate on the electrode in the absence of O_2. In the absence of microbes, uranium could not be reduced. However, it remained adsorbed onto the electrode surface. The process of adsorption was found to be non-faradaic but still accompanied by the flow of current, which would be related to electro-driven transport and capacitive deionization of U^{6+}. Without current flow (i.e., no applied potential) U removal by reduction did not take place. Furthermore, when the cathodic polarization was interrupted, adsorbed U^{6+} desorbed rapidly. The process was demonstrated in flow-through columns of uranium-contaminated subsurface sediments. 89 μmol of uranium were recovered from the electrochemical conversion and extraction, which represented 87% of the total U^{6+} removed in the column over the duration of the experiment. The process was achieved at 97% current efficiency.

In an original study, bioanodes/cathodes were applied for selenium recovery using MFCs. Simultaneous electricity generation and selenium recovery were evaluated in a single chamber air-MFC [188], leading to elemental selenium on the electrode surface and in the electrolyte, indicated by red deposits and colloids, respectively. Carbon cloth was used for both the anode and cathode. Electrodes were placed 1.7 cm apart, with the air-facing side of cathode coated with carbon and the liquid facing side coated with platinum. Electrodes were enriched with mixed cultures from domestic wastewater. Acetate and glucose were applied as electron donors in the solution between anode and cathode electrodes. With a medium free from SeO_3^{2-}, power densities up to 2.9 W m^{-2} and 0.38 W m^{-2} were achieved with acetate and glucose, respectively. Further increases of SeO_3^{2-} concentrations lead to a decrease in power generation. High removal efficiencies of selenite were demonstrated, with up to 99% and 88% using glucose and acetate, respectively, as anode electron donors. Selenite concentrations higher than 100/200 mg L^{-1} for acetate/glucose media, lead to reduced power generation and removal efficiencies. Presumably, this would be due to toxic stress to exoelectrogenic microorganisms on the cathode. When the MFC was placed in an anaerobic chamber no electricity was generated, indicating that oxygen and not SeO_3^{2-} was used as the electron acceptor by the biocathode. Based on previous reports [189], one could propose that SeO_3^{2-} was used by bacterial cultures immobilised on bioanodes, as an electron acceptor, for dissimilative respiration (Table 4 R2).

The application of biocathodes with power generation for Cr^{6+} removal as $Cr(OH)_3$ (Table 4 R3-4) was first demonstrated by Tandukar et al. [159]. In this study, electrodes enriched with mixed bacterial cultures were from an anaerobic digester. The contribution of biomass decay and abiotic processes for the reduction of Cr^{6+} were minimal, which would confirm that Cr^{6+} reduction was assisted by the microbial activity on the cathode. For the initial Cr^{6+} concentration, of less than 80 mg L^{-1}, Cr^{3+} reduction was fast (<5 h), with Cr^{3+} precipitated as $Cr(OH)_3$ on the bacterial biomass or cathode.

Following this initial investigation, Huang et al. [190] studied Cr^{6+} recovery by setting cathode potentials in a similar system to that described by Tandukar et al. [159]. In this case, cathode potentials were set in individual runs from −0.45 to +0.20 *vs.* SHE/V. A set potential of −0.300 *vs.* SHE/V was found to give the fastest reactor start-up time and potentials of −0.30 and −0.15 *vs.* SHE/V achieved higher Cr^{6+} reduction, with a $Cr(OH)_3$ precipitate observed on the bacterial biomass and not the cathode. Also of note, SEM revealed putative pili for cathodic potentials of −0.30 and −0.15 *vs.* SHE/V, which would suggest their necessity for optimal performance. The application of various materials such as graphite fibres, graphite felt, and graphite granules as biocathodes have also been studied using a tubular or two-cylinder shape MFC [191]. Graphite fibre was found to be a superior biocathode substratum, out of those investigated.

The application of biocathodes in MECs for cobalt recovery was first reported by Huang et al. [192], with simultaneous production of methane and acetate. With an applied cell potential of 200 mV, 88% Co^{2+} was reduced to Co^0 (Table 4 R5) mainly on the bacterial surface with 0.113 mol CH_4 per mol COD and 0.103 acetate per mol COD, produced after 6 h operation. Furthermore, under open circuit conditions up to 30% of Co^{2+} was removed, which could be attributed to pseudo-capacitive deionization of Co^{2+} on the graphite cathode, similar to the phenomena described by Gregory and Lovley [50]. Biocathodes in this system were inoculated with mixed cultures. It is therefore unclear which microorganisms were involved in Co^{2+} deposition or what their role was. Furthermore, biofilms at different applied potentials were greatly different, indicating that the electron transfer components in the biofilms EPS could be altered by the use of different applied cathode potential.

Recently Varia et al. investigated the application of biocathodes for metal remediation and recovery [158,193]. Initially live *S. putrefaciens* were suspended in a cathode chamber containing 200 mg L^{-1} Au^{3+} (pH 2) and a G-10 graphite electrode. Of note, *S. putrefaciens* has previously shown to reduce and precipitate biogenic AuNPs in the presence of H_2 [194]. Interestingly, in the presence of bacteria, gold electrodeposition thermodynamics was influenced, as revealed by positive shifts in the reverse potentials of $AuCl_4^-/Au^0$ (Table 4 R6) [193]. Further investigation of bacterial influence on electrochemical gold nucleation and deposition was also studied [158]. Although bacteria were shown to lag deposition kinetics, as determined by a decrease in exchange current density (j_o) [86], this study provided a systematic approach for future investigations of bacterial catalysis of other electrodeposition reactions using biocathodes.

4.5. Mixed/ simultaneous metal recovery

All reports of MEM systems studied up to 2012 focused on the recovery of a single type of metal in solution. However, in wastewaters and leachates, different metals often exist in mixtures. One example is wastewater from vanadium mining and

manufacturing processes, which contains a mixture of V^{5+} and Cr^{6+} ions [195]. Zhang et al. (2012) investigated the simultaneous reduction of these two ions at the cathode of an MFC. Cr^{6+} was reduced to Cr^{3+} which deposited as an oxide on the cathode surface. V^{5+} was reduced to V^{4+}, which remained in solution. By raising the pH from 2 to 6 at the end of the experiment, V^{4+} could be precipitated. During a 240 h run, metal removal efficiencies of 60.9% for V and 71.4% for Cr could be obtained from a solution initially containing 250 mg L^{-1} of each metal.

Another example of wastewater containing a mixture of several metals is the leachate from solid waste incineration fly ash, which can contain high concentrations of Cu, Pb, Cd, and Zn. Modin et al. (2012) varied the control of a microbial-electrochemical system to sequentially recover these metals individually from a mixture [149]. The system consisted of a biological anode oxidizing acetate and a titanium cathode for reduction of metals. First, the cell potential was controlled at zero, which allowed recovery of Cu from the solution without an electrical energy input. Second, the cathode potential was controlled at −0.51 vs. SHE/V to recover Pb, which required an applied cell potential of about +0.34 V. Third, the cathode potential was controlled at -0.66 vs. SHE / V to recover Cd, which required an applied cell potential of +0.51 vs. SHE/V. Finally, Zn was the only metal remaining in solution and was recovered by controlling the anode at +0.2 vs. SHE/V to maximize the current generated by the electrochemically-active microbes (as per observations in the corresponding polarization curve). This required an applied cell potential of about 1.8 V. The initial concentration of the metals was in the range of 381–811 mg L^{-1} and the time intervals used to sequentially recover the individual metals ranged from 45 to 126 h. At the end of the experiment, no metal ions could be detected in the catholyte [149]. Tao et al. (2014) used an MFC connected to a conventional electrolysis system to recover Cu, Pb, and Zn from a real fly ash leachate. In the MFC, 97.1% of the Cu could be removed in 36 h from an initial concentration of 52.1 mg L^{-1}. The effluent from the MFC was fed to the electrolytic system operated at an applied cell potential of 6 V where Pb^{2+} and Zn^{2+} were reduced simultaneously. In 10 h, 98% of Pb and 95% of Zn were removed from initial concentrations of 100 mg L^{-1} and 180 mg L^{-1}, respectively [196].

Acid mine drainage from metal mining can contain high concentrations of metals, e.g., Cu, Ni, and Fe. Luo et al. [197] investigated the use of a MEC for simultaneous reduction of these three metals in a mixed solution. When applying a cell potential of 1 V, hydrogen gas was produced in combination with metal reduction. Deposits of discrete crystalline branch-like structures of Cu^0, a smooth microscale thin layer of Ni^0 and flaky Fe^0 crystals, were observed on the cathode surface. The results suggested that the energy content of produced H_2 gas could offset the energy requirements for running the reactor. Also, the deposits of Cu^0 on the cathode surface during electrolysis improved the H_2 generation rate by increasing the cathode surface area [197].

Recently, Zhang et al. [198] reported the combination of MFC and MEC systems for recovery of Cr, Cu, and Cd. In this study, MFCs using Cr^{4+} and Cu^{2+} as electron acceptors were stacked in parallel or series to drive a MEC using Cd^{2+} as the final electron acceptor. SEM and XRD confirmed the precipitation of $Cr(OH)_3$ and pure copper spherule-shaped crystals and a smooth cadmium deposit on respective cathodes. As discussed by Zhang et al., this certainly represents a new sustainable approach but a number of challenges will have to be overcome in MFCs and MECs as the complexity of coupled systems is significantly increased. For example, the performance of each cell is interrelated, leading to potential reversal and thereby the increase of internal energy loss. Furthermore, although 40–57% of metals were simultaneously recovered in the system containing initial concentrations of 500 mg L^{-1}, process optimization or further processing would be further required to meet discharge release standards.

## 4.6. Electrochemical equilibria of metals in aqueous solutions

Reduction potentials in aqueous solutions at equilibrium are derived from thermodynamic data and thus function reversibly. The pH and potential, play a fundamental role at equilibrium. These determine the various conditions in which it is possible or impossible to form certain ions, oxides, hydroxides and stable solid metals from their interaction with water and other present reagents. Out of equilibrium, being definitely the majority of cases, reduction potentials remain unchanged as long as the composition of the system, temperature, and pressure also remain unchanged. Therefore, knowledge of the pH-potential electrochemical equilibria can provide valuable guidelines to characterize the regions of practical predominance of the species at given concentrations. The effects of overpotential and the ohmic drop should be carefully regarded.

Table 5
Ions and concentrations at the cathodic compartment of MEM system studied by Modin et al. [222], for the recovery of metals.

Ions in solution	Concentration (mM)
Cl^-	2079.9
NO_3^-	9.7
Cu^{2+}	15.7
Pb^{2+}	4.8
Cd^{2+}	8.9
Zn^{2+}	15.3
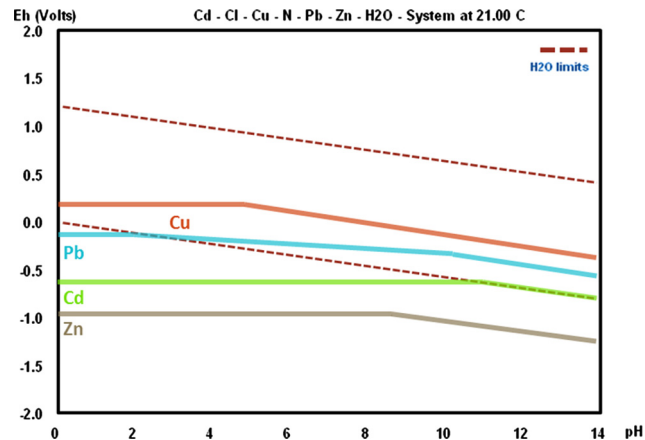
Fig. 6. Extract from the thermodynamic equilibria for the mixture of Cu^{2+}, Pb^{2+}, Cd^{2+} and Zn^{2+} in aqueous solution, constructed to approximate the system described by Modin et al. [149]. The concentration of the individual elements is taken as per Table 1. The regions of stability for the zero-valent metal species are shown below their respective highlighted lines. At low pH (0–5) a well-defined region is observed, where the individual metals can be thermodynamically recovered at differentiated potentials. Still needs further workout. Supplementary info will be provided on the premises to construct this diagram. Below the coloured lines: regions of stability of solids: **orange**: **Cu**, **navy**: **Pb**, **Green**: **Cd**, **Olive**: **Zn**.
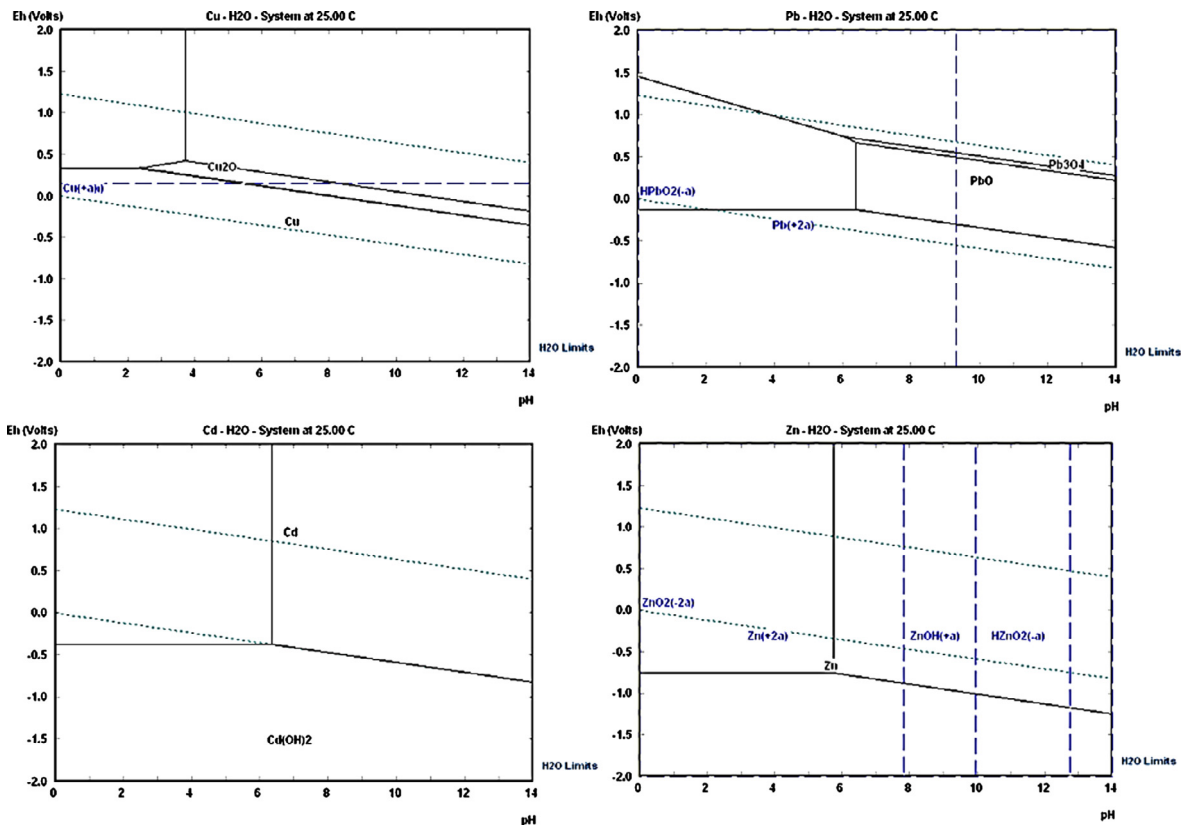
Fig. 7. Thermodynamic equilibria for the individual metal ions Cu^{2+}, Pb^{2+}, Cd^{2+} and Zn^{2+} in a solution with the same characteristics as those exposed for Fig. 1, except for the presence of secondary metals in each case. The concentration of the individual ions is taken as per Table 5. The regions of stability for the zero-valent metal species differ from those obtained for the mixed metal system. Still needs further work. Make it at 21 °C, higher quality images, colour line stability of solids.

The work of Pourbaix [199] provided a panoramic examination of thermodynamic predictions of metal states. The domains of relative predominance of the dissolved species and the domains of thermodynamic stability of solids were given for pure metals and non-metals at 298.1 K (25 °C), hydrogen or oxygen pressure of 1 atm and M practically equal to one,

where M here represents the fugacity or corrected partial pressure of gaseous substances or the activity or corrected concentration of dissolved substances [199].

All the same, one must take into account that Pourbaix diagrams do not provide information about the behaviour of alloys or mixed metal systems. Nor do such diagrams reveal either kinetic information or mechanisms through which irreversible redox processes take place. It is wrong to assume that the classical Pourbaix diagrams are applicable for any practical or concrete problems. However, they do provide for a clear understanding of the limits of thermodynamic equilibria of metal ions, in aqueous solutions. Such cases as that for mixed metal ion systems require a rational construction within the boundaries of the specific case of study.

For instance, the study of Modin et al. [149] presented the MET recovery (Category A, Fig. 3A) of 4 individual metals in the cathodic chamber containing an aqueous solution with high amounts of Cl^- and relevant concentrations of NO_3^- (Table 5). Given such concentrations, the thermodynamic equilibria in aqueous solution were here constructed for the mixed solution. The potentials are relative to the standard hydrogen electrode (SHE), unless stated otherwise. The thermodynamic pH-potential regions in which the solid zero-valent metal species (M^0) are stable can be appreciated in the equilibrium diagram of Fig. 6. Modin et al. used a highly acidic catholyte. At low pH (0–5), it is clear from Fig. 6 that all metals studied in their system can be reduced to the M^0 as a function of potential alone. Cu^{2+} can be reduced to Cu^0 below E = ∼0.2 vs. SHE/V, Pb^{2+} can be reduced to Pb^0 below E = ∼0.1 vs. SHE/V, Cd^{2+} can be reduced to Cd^0 below E = ∼-0.65 vs. SHE/V, and Zn^{2+} can be reduced to Zn^0 below E = ∼0.9 vs. SHE/V.

Experimentally, Modin et al. [149] recovered the four metals in the same sequence of decreasing applied cathode potentials (E_{app}): Cu E_{app} = −0.18 vs. SHE/V, Pb E_{app} = −0.51 vs. SHE/V, Cd E_{app} = −0.66 vs. SHE/V, and Zn E_{app} = −1.12 vs. SHE/V. The differences in potential between the thermodynamic and the practical cases presumably arise from overpotentials and the ohmic drop.

Furthermore, the thermodynamic E-pH equilibrium diagrams for the mixed metal solution are here compared against the thermodynamic E-pH equilibrium diagrams of the individual metals (Fig. 7), all constructed at comparable amounts of Cl^- and NO_3^- (Table 5). It is clear that the equilibrium behaviour differs in both cases (pure individual metals vs. mixed metal solution). In the mixed solution, the conditions to separate Pb from Cd are clear whereas from the diagrams of the individual metals alone a rather narrow region is derived. From the original Pourbaix diagrams [199] the possibility to deposit pure Pb, Cd, and Zn in aqueous solutions by establishing selectivity on potentials alone, without detectable contamination of the other metals, would not seem feasible right away. An appropriate calculation of the equilibria that match the conditions of study justifies this type of recovery.

It should be noted though, that in the mechanisms of Fig. 3A–C, the presence of microbial substrates and metabolites is negligible for the cathode when an appropriate membrane is employed. However, for cases as illustrated in Fig. 3D or membrane-less setups, their presence plays an important role on thermodynamic equilibria. This is also the case of complex streams where a mixture of organics and inorganics coexists, wherein some could act as chelating agents for the targeted metal species.

4.7. Membranes in MEM technology

Numerous metal-containing waste streams have an acidic pH, e.g., between 1 and 5. This poses challenges to their treatment in MEM systems because when coupled to a bioanode that oxidizes organics such as acetate, the anolyte pH should be near neutral. Most studies on metal recovery make use of cation exchange membranes [153]. At a catholyte pH lower than the anolyte pH, proton transport from the anode to the cathode becomes unlikely. For example, when a MEM with anolyte pH 7 and catholyte pH 3 is operated, protons need to be transported against their concentration gradient, which is a factor 10^4 lower in the anolyte compared to the catholyte. Because wastewaters have other cations at concentrations several orders of magnitude higher than protons; proton transport due to migration is also unlikely to occur [154,200]. As a result, the protons produced during oxidation of acetate will remain in the anolyte, leading to acidification and a decrease in acetate oxidation activity. At the same time, the cathode pH will increase, dependent on the proton dependency of the cathode reaction. Unfortunately, in most studies aimed at metal recovery limited information is given on membrane performance and pH changes. In cases where a cation exchange membrane is used, not only the pH changes but also the transport of cations from the cathode to the anode as a result of diffusion should be considered. Most metal species in the catholyte are positively charged; thus, a cation exchange membrane will allow the metals to be transported from cathode to anode due to their concentration gradient.

Alternatively, several studies focusing on metal recovery have used anion exchange membranes to separate anolyte from catholyte. Although ion transport across this membrane in MEM has not been analysed until now, anion exchange membranes are likely to transport mainly anions from catholyte to anolyte. Metal-bearing waste streams often contain anions mostly in the form of sulphates, and to a lesser extent chlorides, so these are the most likely candidates to be transported [201]. Similarly, this transport will lead to acidification of the anolyte, and increase in pH in the catholyte.

For both types of ion exchange membranes, it should be noted that the pH changes are dependent on the operation mode, e.g., in continuous flow mode the effects might be marginal when the solutions are refreshed at a sufficiently high rate.

The third type of membrane that has been tested in METs with metal ions is the bipolar membrane [146,168,202]. A bipolar membrane is conventionally used for the production of acid and base and might, therefore, provide an option to maintain a pH difference between anolyte and cathode. A bipolar membrane consists of an anion exchange membrane and a cation

exchange membrane linked together. When a potential is applied across the membrane, water is split into protons and hydroxides. It has been shown that this type of membrane is indeed able to partly maintain a pH difference between anolyte and cathode, however, part of the charge is carried by other cations, mainly K$^+$ [146]. It was argued by Harnisch et al. that bipolar membranes are not a good alternative as too much energy is required to start water splitting [203]. Indeed, the theoretical required cell potential for the production of 1 M acid and 1 M base is 1.2 V; however, if the pH difference is lower, a lower potential may be required [145]. These bipolar membranes have, to our knowledge, not been characterized under conditions prevalent in METs, like near neutral pH and with low conductivity solutions with different types of cations and anions. Depending on the behaviour of the bipolar membrane under these conditions, its use may still provide considerable advantages compared to cation and anion exchange membranes, if sufficient proton/hydroxide selectivity can be achieved, even at a certain energy cost.

A final aspect to take into account regarding membranes is that the cation exchange membrane will attract the positively charged metals and they may occupy the active sites of the membrane. This effect was studied for a bipolar membrane, for which the cation exchange side was facing an iron sulphate solution [146]. Iron was found in the outer layer of the membrane but could be removed thereof by HCl. Metal retention inside the cation exchange membrane and its effect on selectivity, resistance, and transport across the membrane has not been studied yet in detail and needs to be addressed to come to an applicable design.

4.8. Applicability and limitations of MEM in metal recovery

MEM technology, as pointed out here, has the potential for metal recovery from diverse aqueous waste streams. Advantages of MEM include low-cost microbial catalysts instead of expensive noble metals, potential selectivity for targeted metals, low cell potential or even simultaneous power generation, the combination of conversion and adsorption, and pH correction in cathode and anode, which can make a stream more treatable. However various hurdles will have to be overcome such as instability of microbial catalysts with e.g., cold temperature, low concentration of metals limiting transport to the electrode surface, low pH metals streams rendering problematic, toxicity of metals towards catalysts, limited experience, and the need for organic electron donors or different electron sources, besides small quantities of recovered products that make market logistics difficult.

Furthermore, metals are not always present in soluble form, even in aqueous systems. In wastewater, there can be sludges or solids from which first the metals may need to be leached with pH changes to enable recovery. Therefore, pre-treatment is of great importance in most industrial cases. Studies so far have only focused on demonstrating concepts, not optimizing reactor configuration and operational parameters. Thus, there is ample room for improvements in performance. However, it is promising that high removal/recovery efficiency can be obtained with solutions containing quite low concentrations of metals.

Several waste streams such as fly ash leachate and AMD would contain a metal mix such as Cu (which can be reduced in an MFC) and metals such as Pb, Cd, Zn which cannot be spontaneously reduced under typical MEC conditions. This makes the MFC a good technology to selectively extract relatively clean Cu from complex metal mixtures. If Fe^{3+} occurs in the mix, it could also be a reduced in an MFC, but it could potentially be reduced as nano to macro scale precipitates of Fe(OH)$_2$ rather than deposited on the cathode.

Varying the control of a reactor is one way to selectively extract individual metals from a mix (i.e. [149]). Utilizing the fact that different metals change phase at different pH is another way. For example, Fe^{3+} and Fe^{2+} precipitate at higher pH (which could be accomplished with an MFC, e.g., [153]). Similarly, V^{5+} could be reduced to V^{4+} followed by precipitation at higher pH (i.e. [195]). This makes it possible to extract those metals by precipitation and recover other metals directly on the cathode by reduction.

One of the main advantages of using MEM for metal removal/recovery is that less energy is required compared to conventional technologies. Therefore, the choice of electron donor at the anode is crucial. Until now, most of the studies on metal recovery have used bioanodes that oxidize acetate. This requires an organic waste stream to be available at the same location as the metal stream, which makes application of the technology limited to specific locations. On the other hand, compared to precipitation of metals with sulphides, the carbon efficiency for some MEM is several times higher [168]. For metal recovery *via* sulphide precipitation, where the sulphide is produced from sulphate reduction, eight moles of electrons, originating from organic components, are required to reduce one mole of copper. For MEM, the use of organics can be up to four times as efficient, because only two moles of electrons are required to recover one mole of copper.

Besides the use of organics, other electron donors can be considered. Sulphur-based components may provide an interesting alternative, as they are abundantly present in mining and metallurgical waste streams. Possible reactions would be the oxidation of sulphides, or elemental sulphur, to produce sulphates [167,204].

Despite the wide variety of microbes that have been reported to carry out metal transformations in purely microbial systems, the same diversity has not been yet extended to MEM. Only *Geobacter, Shewanella* and *Acidithiobacillus* have been studied for direct participation in metal reduction processes. Further investigation of extremophiles for the recovery and prospection of metals from extreme environments, such as the deep sea [10] is warranted. For example, Reimers et al. [138] demonstrated the application of MFCs in a simulated sediment-seawater environment, with an a sediment/anode and seawater/cathode configuration. Other extreme environments such as geothermal brine [39], and hydrothermal vents [205] could indeed be a lucrative metal-mining direction. Especially if MEM technology can be applied to supplement the

supply of those metals highlighted recently by the European Commission [206] as critical to foster environmental sustainability, with a shift to a low carbon economy.

5. Functional materials produced by microbial electro-metallurgy

The shift in attention from metals regarded as residues that need to be removed (remediated) to metal recovery, entails not only economic benefits but the possibility to focus on the production of materials whose properties can be targeted in a controlled manner. In the case of MEM, such remediation and recovery can converge with the tailored synthesis of functional materials, which can be achieved by manipulating the type of microbe, the electrochemical interface and even other operational parameters such as the applied temperature, metal concentration, redox mediators and pH. So far, there are not many instances on this direction but it is the path we encourage to take.

For example, Ramos-Ruiz et al. showed the feasibility to convert toxic tellurite Te^{4+} to non-toxic insoluble elemental tellurium Te^0 NPs using an anaerobic granular sludge bed reactor [207]. The effect of four redox mediators was also tested with the same biofilm [208]. The redox mediators increased the rate of Te^{4+} reduction. They also tuned the morphologies and localization of Te^0 NPs. Utilizing a developed MFC architecture, spherical NPs of iron oxide (120–700 nm) can be produced with sizes that could be controlled by changing the conditions in the fuel cell [209]. These authors demonstrated that the most efficient production of goethite α-FeO(OH) occurred at a pH of 6.3 and Fe^{2+} concentrations above 200 mg L^{-1}. Other studies also showed that a progressive increase of metal concentration enable microbial adaptation in MEM as the cases of Cr^{+4}, Cu^{2+}, and Cd^{2+} [210].

The recovery of PGMs have also been reported by immobilised cells of *Desulfovibrio desulfuricans* using a novel MEM process. The system was fed with a precious metal processing wastewater where the continuous removal of Pd, Pt, and Rh was up to 88%, 99% and 75%, respectively at an input pH of 2.5 and a total metals concentration of 5 mM [211].

This year, a continuous MEM treatment also demonstrated the recovery of REEs together with yttrium from AMD of a mining site in Australia [212]. This study showed recovery rates up to 498 ± 70 µg Y, 166 ± 27 µg Nd, 155 ± 14 µg Gd per gram of solid, among other high-value metals. The high-REY precipitates could be used to offset the treatment costs. To determine the effects of electrode polarization, Van Khanh et al. compared the heterotrophic selenite reduction, using organic compounds as electron donors under microaerobic condition *vs.* and electrode-driven selenite reduction process, using an electrode polarized at −0.3 V *vs.* SHE as the sole electron donor under anoxic conditions [213].

This study demonstrated that a pure culture of a new strain of the genus *Cronobacter* THL1 could take up electrons from a cathode to perform selenite reduction. SEM of the electrode materials showed the attachment of bacterial cells on the cathode surface and elemental selenium NPs produced by cathodic growth of the strain THL1.

Also of note, the application of conventional biological processes, to produce functional nanomaterials use high value feedstock's as an electron donor for microbial growth and require highly controlled conditions.

Producing such materials under electrode-driven control such as a MEM system therefore, is an attractive proposition, since it could be used to manufacture a high value product using electricity as a driving force without the need of chemical electron donors for metal reduction [214].

6. Conclusions

The current state of the art of MEM, reviewed here, shows much promise for metal recovery, especially from diverse dilute metal-rich aqueous streams. However, one must emphasize that further investigation and optimization, especially for mixed metal ion systems, will be required to go beyond lab and pilot scale studies. Most studies on MEM technology have used bioanodes, which do not actually interact directly with the metal. A number of studies have also demonstrated hybrid systems, such as the integration of SLM or photoelectrocatalyic electrodes in MEM technology. As highlighted in this review, some studies apply microbes in the cathodic chamber or on biocathodes, which do participate and enhance metal recovery, yet this is only limited to a few individual metals. In light of numerous reports of microbial sorption and transformation phenomena scanning the width and breath of the periodic table, therefore further investigations of microbial interactions with metals in biocathode chambers are imperative. Novel insights in microbial-electrochemical metabolism and its implications could provide new routes towards metal recovery and functional material synthesis. Furthermore, electrochemically-tunable EPS would be a promising aspect to explore for further improvement. The use of undiscovered exerogenic extremophiles as biocatalysts or nano-factories in MEM could enable metal recovery from environments such as deep marine and continental waters, as well as geothermal brines.

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