

Prospects of metal recovery from wastewater and brine

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Modern technology relies on an uninterrupted supply of metals, yet many metals have limited geological deposits. Recovering metals from wastewater and brine could augment metal stocks, but there is little guidance on which metals to prioritize for recovery or on the techno-economic viability of extraction processes. Here we critically assess the potential for recovering metals from wastewater and brine. We first look at which metals are critical for recovery on the basis of their supply risks and the impacts of those supply restrictions. We then assess the feasibility of recovering these metals from various water sources by estimating the required operational costs to match market prices. Next we discuss the limitations of established separation technologies that may inhibit the practicality and scalability of metal recovery from water. We conclude by highlighting materials and processes that could serve as more sustainable alternatives to metal recovery with further research and development.

Modern technology relies on the present and future availability of elements across the periodic table, especially metals and metalloids¹. The unique properties of each element impart distinct functionality to materials that allow them to perform effectively in a given technological application². For example, the path to global decarbonization is contingent on sustainably sourced lithium, nickel and cobalt to manufacture lithium-ion batteries with high energy density, as well as platinum to produce polymer electrolyte fuel cells with high catalytic performance. The perpetual supply of these critical metals and metalloids, however, is not guaranteed as supplies decrease and ore grades decline in the future^{3,4}.

A circular resource economy with routine recycling could increase the long-term supply of metals and metalloids, which we collectively refer to as ‘metals’ for convenience⁵. Some common metals are already recycled at rates near or exceeding 50% (for example, copper and lead), but are nevertheless projected to have supply deficits by 2050 (ref. ⁶). Specialty metals (such as rare-earth elements) largely cannot be recycled because they are used in small quantities in products with complex elemental compositions, such as computer chips, optoelectronic devices and high-strength magnets^{2,7}. Innovative recycling methods and improved reuse rates will be critical to meet

rising demand for both common and specialty metals over the next few decades^{6,7}.

Municipal and industrial wastewaters are increasingly regarded as potentially viable sources for recycling valuable elements⁸. Apart from augmenting metal supply, the valorization of ‘waste’ metals from these waters would potentially offset wastewater treatment costs. Naturally occurring brines, such as seawater, salt lakes and geothermal aquifers are even larger repositories of valuable metals, with some material stocks surpassing their availabilities on land⁹. A few metals are commercially extracted from these sources, including lithium from shallow brine beneath dry lakes and magnesium from seawater¹⁰, typically using one or more chemically intensive precipitation steps.

The prospect of extracting other valuable commodities has led to extensive research to develop chemical-free highly selective methods to recover dilute target metals from complex water matrices^{11,12}. There is no consensus, however, about which metals and water sources should be the focus of recovery efforts, nor is there much guidance about the techno-economic viability of metal recovery from these water sources. Accordingly, a diverse collection of metals from various water sources has been studied—ranging from lithium and uranium in seawater^{13,14} to mercury in groundwater¹⁵ and selenium in industrial

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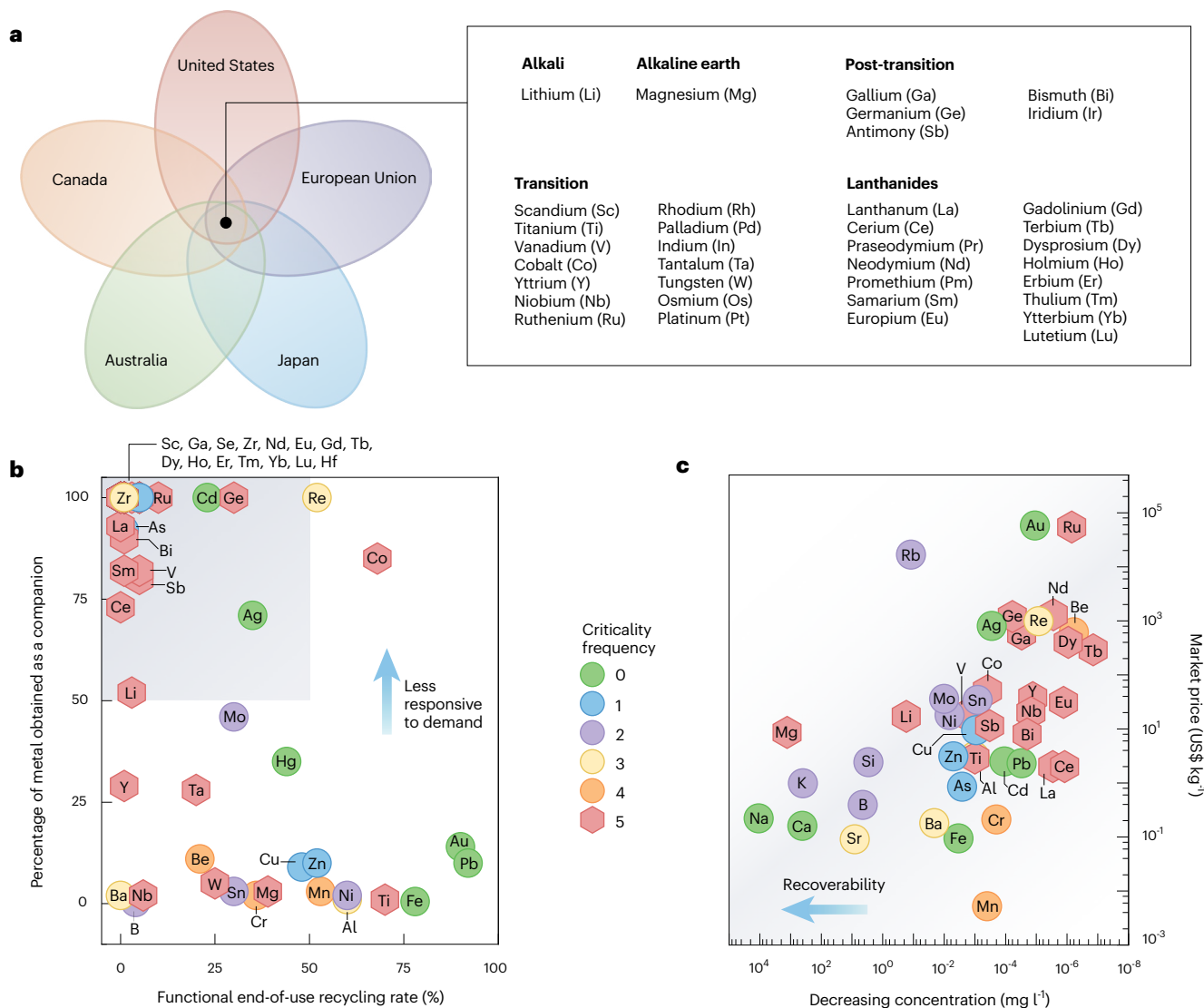


Fig. 1 | Determination of which metals are critical for recovery from water. **a**, Venn diagram showing the common critical metals designated by five governing bodies (Australia, Canada, the European Union, Japan and the United States). **b**, Scatter plot of the functional end-of-use recycling rate versus the percentage of the global primary production where the metal was obtained as a companion (data from ref. ²²). The supply of metals with higher companionship is less influenced by changes in demand. The upper left quadrant shaded in grey highlights elements with low recycling rates and high companionship as high-priority elements for recovery. **c**, Scatter plot of the average market price in

the last reported year (typically 2021) versus metal concentrations in seawater. Metals at lower concentrations typically require higher costs of separation than metals at higher concentrations (the background shading highlights this relationship). Metal concentrations in seawater were obtained from ref. ²⁹ and metal price values are based on 2022 US Geological Survey Mineral Commodity Summaries²⁷. In **b** and **c**, the colours of the data points indicate the number of the five governing bodies (listed above) designating the specified metal as critical; the criticality frequency of 5 is also denoted with a distinct hexagon shape.

wastewater¹⁶—using innovative separation methods with little consideration for practical, large-scale feasibility.

In this Perspective we critically evaluate the prospects of scalable metal recovery from wastewaters and brines. We first synthesize the literature to provide broad guidance on which metals should be prioritized for recovery and to assess the techno-economic viability of separating these metal species from various water sources. We then emphasize the barriers to implementing conventional physicochemical separation methods for metal recovery at scale. We conclude by highlighting two classes of emerging materials as potentially promising options for developing metal recovery technologies.

Which metals are worth recovering?

Most metals in the periodic table are present in wastewaters and brines to some degree, but only a subset of these metals may warrant extensive

research, development and investment to bring about commercial realization. In recent years, some metals have been designated as ‘critical’ elements by the European Union and other countries (Australia, Canada, Japan and the United States)^{17–21}. These governing bodies based their assessments primarily on supply risk and the impact of supply restriction, although each governing body employed slightly different methods and arrived at different conclusions.

In Fig. 1a, we provide a Venn diagram showing the metals considered critical by all five governing bodies. Most elements classified in this list are not main group elements (that is, groups I–II and XIII–XVIII in the periodic table), with the exception of lithium, magnesium, gallium, germanium and antimony—a listing that suggests that main group elements are generally less attractive targets for recovery. Beyond this principle, criticality designations offer limited guidance in choosing recovery targets from wastewater and brine, as the number of critical

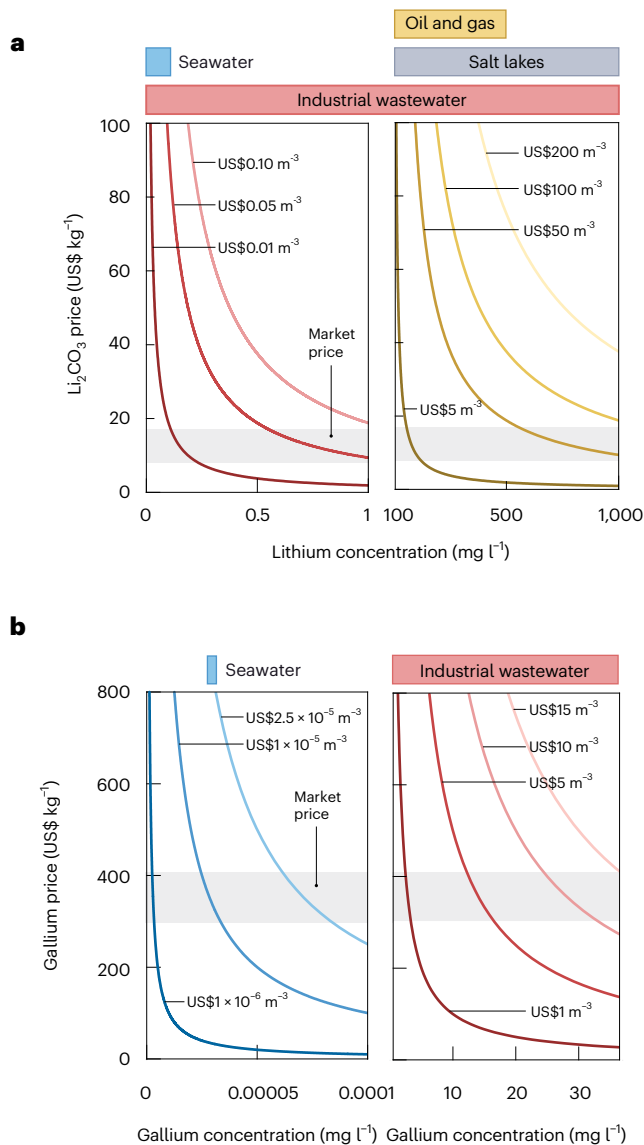


Fig. 2 | Economic assessment of metal recovery from water. **a, b.** Contour plots illustrating the maximum LCOWP that would allow economically viable recovery of lithium (**a**) and gallium (**b**) at a specific concentration and market price. Each contour represents the maximum LCOWP, which is an average cost that includes capital, operating, and transportation costs. This analysis assumes 100% recovery, conversion and purity of the salable metal, which is most commonly lithium carbonate (Li_2CO_3) and metallic gallium. The typical metal concentration ranges associated with water sources of interest, including seawater, industrial wastewater, oil and gas produced water and salt lakes, are indicated by coloured bars above each graph. Concentration estimates from refs. ^{29,30,32,34,77}. The grey shaded region indicates the range of end-of-year market prices over the past five years.

metals remains large. All metals have been designated as critical by one or more government agencies except iron, silver, cadmium, gold, mercury and lead, thereby rendering ‘criticality’ a label with little discriminatory value²².

Other characteristics of metals not comprehensively considered by the criticality assessments help to narrow the number of targets to some extent. Some metals have few or no viable mineral deposits of their own and are generally recovered only as by-products of the processing of their host metals; they are thus known as companions and the degree to which each is recovered as a by-product is its companionship (Fig. 1b; ref. ⁷). As companion metals from ores seldom generate more than a small fraction of the total financial return of

a mine, the availability of companion metals is only responsive to changes in demand for the host metal⁷. These companion metals are therefore particularly susceptible to supply restrictions and may be worthy targets to investigate for harvesting from water.

Many companion metals are also used in small amounts in products with complex elemental compositions. This design approach presents separation challenges to functional recycling. Functional recycling refers to the recovery of a metal with its inherent properties intact, which allows the metal to be employed many times, rather than recycling the metal with other elements where those properties are lost²³. The low functional recycling rate of many companion metals suggests they are often used only a single time and are then lost or discarded.

Metals with high companionship and low functional end-of-use recycling rates, which are located in the top-left quadrant of the plot in Fig. 1b, may be good candidates that justify extensive recovery efforts from wastewaters and brines. These metals have a particularly high risk for supply shortages because they are less responsive to demand and unlikely to be functionally recycled from discarded products. We specifically highlight the metals within the top-left quadrant that are also considered critical by all five governing bodies (shown as red hexagons) as ideal targets, such as gallium, germanium, ruthenium, neodymium, terbium and dysprosium (Fig. 1b).

Along with these select elements, particular attention may be given to scarce metals for which land mining and processing have considerable emissions of carbon dioxide per unit of material, in effort to reduce climate change impacts. The global warming potentials for most of the elements used in modern technology are available, and those with the highest global warming potentials are (in rank order) rhodium, gold, platinum, iridium, osmium, palladium, ruthenium and rhenium²⁴. Similarly, a few metals are particularly important for the expansion of non-fossil-fuel energy technologies: lithium, cobalt and nickel for batteries and cadmium, tellurium, praseodymium, neodymium, terbium and dysprosium for solar and wind power.

Given that the investigation of recovery efforts from wastewaters and brines seems to be justified for many metals, it is sensible to prioritize elements that are the most technologically and economically viable for recovery. The processing difficulty or recoverability of a metal from a feed stream can be approximated from the concentration of that metal, as originally proposed by T. K. Sherwood in 1959 for virgin ore feed streams²⁵. More specifically, metals at lower concentrations are typically more challenging to recover and have higher costs of separation, which is reflected in the higher market prices of those minerals. We also observe this (albeit modest) relationship between metal seawater concentrations and market prices (Fig. 1c). Metal concentrations in seawater, like those in ore, depend on their abundance in Earth’s crust²⁶, which explains this relationship when market prices are largely determined by land mining. The scarcest metals on land (for example, those designated as critical by all five governing bodies and shown as red hexagons in Fig. 1c) are thus typically most dilute in naturally occurring water sources such as seawater. Industrial waste streams, on the other hand, may provide higher concentrations of metals than those in the natural environment. In the following section, we further analyse the techno-economic viability of recovering critical metals from seawater, as well as from more highly concentrated sources.

Economic viability of metal recovery

The economic viability of recovering a specific metal from a water source can be estimated by comparing the metal market price to the total cost of its recovery. To be economically viable, the metal market price (P_m) must be greater than or equal to the cost of processing a unit volume of water, or the levelized cost of water processing per unit volume of water (LCOWP), divided by the given metal concentration (C_m) according to:

$$P_m \geq \frac{\text{LCOWP}}{C_m} \tag{1}$$

Note that this analysis assumes 100% recovery, conversion and purity of the salable commodity. Although complete recovery and perfect purity are likely to be impractical, we use this conservative assumption to calculate an absolute maximum LCOWP that would be economically acceptable for recovering a metal at a specified concentration and market price.

Given that the list of attractive metals for recovery is extensive, we can determine the LCOWP for the recovery of lithium and gallium as representatives of broader classes of critical metals: abundant and scarce metals. Lithium represents abundant metals that have relatively high concentrations in natural waters, low market prices, and widespread use. Lithium, for example, is essential for manufacturing the lithium-ion batteries used in electronics and electric vehicles²⁷, and its relative abundance has brought interest in recovering lithium from seawater²⁸. Gallium, in contrast, represents scarce metals which typically have lower concentrations in natural waters and are used in smaller quantities for specialized applications (for example, optoelectronic devices²⁷).

Using equation (1), we estimate that lithium recovery is only economically viable at present if the LCOWP approaches around US\$0.01 m⁻³ for seawater and US\$0.10 m⁻³ for industrial wastewaters with less than 1 mg l⁻¹ (refs. 29,30) (Fig. 2a). If, however, lithium is recovered from more highly concentrated waters such as oil and gas produced water or lithium-rich brines (for example, 50–1,000 mg l⁻¹; refs. 31,32), the LCOWP could be in the range of US\$5–100 m⁻³ for the process to be profitable. For comparison, direct lithium extraction from the Salton Sea in California, United States, which has a lithium concentration of about 200 mg l⁻¹, has been estimated to cost on the order of US\$4 m⁻³ of brine using lithium-selective sorbents³³.

For gallium, which is much less abundant than lithium, recovery from seawater is only economically viable if the LCOWP approaches US\$10⁻⁵ m⁻³ (Fig. 2b). This LCOWP is far below a reasonably attainable value, and the LCOWP would be even lower if the gallium recovery was less than 100%. Instead, gallium could be potentially recovered profitably from more highly concentrated industrial wastewaters (1–25 mg l⁻¹; refs. 34,35) with LCOWP on the order of US\$1–10 m⁻³. Altogether, these conservative estimates for lithium and gallium suggest that highly concentrated sources—such as oil and gas produced water, salt lakes and some industrial wastewaters—are potentially viable sources to target with emerging technologies, whereas economically recovering metals from sources containing less than 25 mg l⁻¹ (for example, seawater) is a formidable and unpromising challenge. Further research that determines reasonable LCOWP ranges for various technologies and water sources could offer more precise guidance on which metals are economically worth recovering.

Another consideration in determining the viability of large-scale metal recovery is the amount of water processed to harvest a meaningful amount of metal. For instance, to replace all conventionally sourced lithium that the United States consumes each year²⁷ would require processing approximately 12 billion m³ of seawater, which is about three times the annual desalination capacity in the United States (3.9 billion m³; ref. 36). For gallium an even greater extreme, about 500 billion m³ of seawater, would need to be processed annually to meet US consumption, or over 125 times the US desalination capacity. Conveying this amount of water to a processing facility, not to mention the processing itself, would be very energy intensive unless the extraction technology was integrated into an existing process train.

It is possible that smaller volumes of water would need to be processed for industrial wastewaters, which can have higher concentrations of a target metal than natural sources. Nevertheless, the practical feasibility of metal recovery from industrial wastewaters is more complex and case dependent than natural sources because they are diverse in composition and difficult to process (Box 1). To recover metal from these complex source waters will probably require an efficient process train that incorporates pretreatment steps and one or more selective

BOX 1

Identifying industrial wastewaters for metal recovery

Although we refer to industrial wastewaters as a unified category, industry produces wastewaters of different compositions. Previous reports suggest that the effluent of a semiconductor fabrication plant, for example, can reach up to around 35 mg l⁻¹ of gallium, depending on the process and plant generating the waste³⁵. Lithium concentrations in wastewater effluents from battery manufacturing and recycling facilities can rise to over 1 g l⁻¹ and nearly 2 g l⁻¹, respectively^{83,84}. Other industrial facilities may generate very little gallium or lithium waste. The viability of metal recovery from any given wastewater is heavily dependent on its composition, so broad conclusions should not be drawn for industrial wastewaters when treating them as a monolithic group.

The recovery of a specific metal will necessitate the highly concentrated wastewaters containing that element to be identified and the recovery process to be tailored to the composition of that wastewater. One source of highly concentrated wastewater for many elements is waste residues from mining ore. Metals are typically extracted from solid ore using acidic aqueous solutions that then undergo extensive processing to recover a high-purity metal⁸⁵. After the metal is recovered, there are residual slurries called tailings that contain high concentrations of dissolved metals that leach from the ore but cannot be extracted. It may be feasible to recover valuable metals from tailings with the development of highly metal-selective technologies^{86,87}. The recovery of these metals would maximize the extraction potential of the metal from the mined ore, which would in turn reduce the need to locate and mine new mineral deposits. More complete utilization of the mined ore would also reduce the volume of mining tailings, which are typically contained in environmentally hazardous ponds that can contaminate nearby water supplies.

separation methods. Established separation technologies, however, have limitations that may prevent effective and scalable recovery of a range of metals from water, as discussed in the next section.

Separation mechanisms for metal recovery

Differences in metal solubility, size, charge and reduction potential can be exploited to separate target metals from wastewaters and brines. Arguably the most widely used separation mechanism in industrial metal recovery processes leverages solubility differences to selectively separate metals. In chemical precipitation, for instance, a chemical reagent (typically a hydroxide, sulfate or carbonate) is added to a feed stream to form a new, less soluble metallic salt that can be recovered as a precipitate, either in the reaction basin or a downstream clarifier (Fig. 3a; ref. 37). This separation relies on the concentrations of constituent salts exceeding their solubility product. Alternatively, a target species can be selectively extracted using an alternative solvent (for example, an organic solvent) in which the target species is more soluble than the interfering species, known as solvent extraction (Fig. 3b; ref. 38). Although chemical precipitation and solvent extraction are effective technologies for recovering elements from water, solubility-based separation methods also share disadvantages, such as excessive chemical use and waste production.

Separating metals on the basis of their size and charge is another recognized mechanism for metal recovery. Size, charge and their interdependent properties (such as polarizability) determine whether a

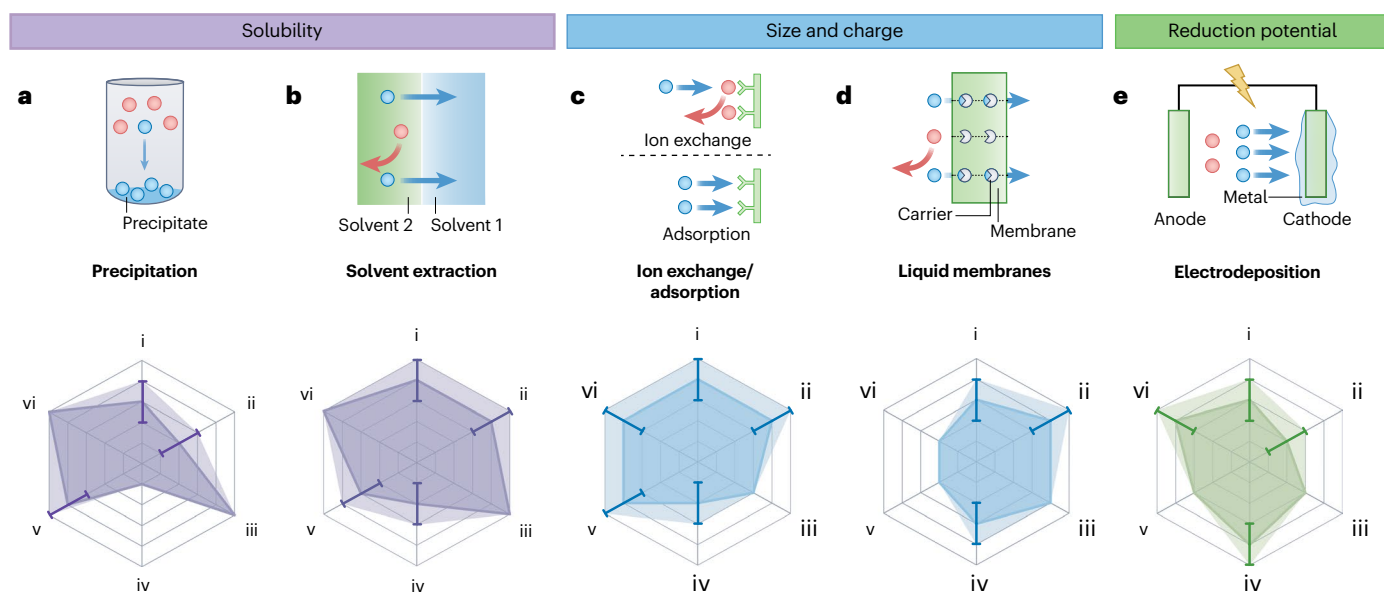


Fig. 3 | Established separation methods for metal recovery. **a, b**, A target metal is precipitated by adding a chemical to the solution (**a**) or selectively extracted using a more soluble solvent (**b**). **c, d**, A metal selectively interacts with an ion exchange resin or adsorbent (**c**) or selectively associates with a carrier molecule that carries the metal across a liquid membrane (**d**). **e**, A metal is electrochemically reduced and deposited onto a cathode. Metals are separated using differences in solubility (**a, b**), size and charge (**c, d**) and reduction potential (**e**). The blue and red spheres represent the target metal for recovery and the

non-target metals, respectively. Under each separation mechanism, radar plots qualitatively compare key metrics of metal recovery technologies (i, recovery; ii, customizability; iii, process continuity; iv, environmental friendliness; v, technology affordability; vi, commercial maturity) on a scale of 1 to 5, where 1 is low and 5 is high. Thick coloured lines indicate best estimates and the error bars reflect the variability for that technology and the uncertainty in the estimate. The results are from the authors' perspective and informed by a literature survey.

metal interacts with or diffuses through a material³⁹ and thus provide selectivity in ion exchange, adsorption and liquid membrane technologies. Ion exchange and adsorption are similar processes by which target metals are removed from solution via adsorption to a solid material (Fig. 3c; ref. ⁴⁰). Both technologies are commercially mature, but they require periodic regeneration to release the target metal from the material, involving considerable energy or chemical demands. In contrast, liquid membranes can be operated continuously without the need for regeneration^{41,42}. Dissolved carriers within the membrane selectively extract the target metal from the source water and then co-diffuse with the metal to the other side of the membrane, where the metal is released (Fig. 3d; ref. ⁴³). This continuous operation presents an advantage over other recovery techniques, but the application of liquid membranes is distinctively hampered by their poor stability, as carriers and solvent gradually leach from the membrane⁴³.

As an alternative, metals may be separated on the basis of their reduction potentials via electrochemically reducing and depositing a metal onto the surface of a cathode (Fig. 3e). In this process, which is known as electrodeposition or electrowinning, an electric potential is applied between electrodes so that metals migrate towards the cathode, where they are reduced in accordance with their reduction potentials⁴⁴. After the deposited metal reaches a specified thickness, the metal product is physically scraped off the flat-plate cathode. This process is well established for some metals, such as copper and aluminium, but its applicability for recovering a broader range of metals is limited. Metals with highly negative reduction potentials may require high voltages (that is, high energy consumption) and co-deposition of metals with greater (more positive) reduction potentials onto the electrode will reduce product purity⁴⁵.

Although many of these technologies have been applied to recover metals from ore leachate, wastewater or brine, they each present challenges that make them less likely to be sustainable solutions for recovering a range of metals from wastewaters and brines at scale (Fig. 3a–e).

Precipitation, solvent extraction and ion exchange generally require at least 1 mol of input chemical to produce 1 mol of recovered metal. To replace traditional mining practices with these methods, chemical requirements would at best equal the amount of target compounds, and additional measures would be needed to recycle or dispose of those chemicals. Potentially more environmentally friendly alternatives also seem to be impractical because they are unstable (liquid membranes) or unsuitable for many metals (electrodeposition), despite decades of research. In the following section, we discuss two emerging material platforms that, with further development, may be more compatible with large-scale, sustainable metal recovery.

Emerging materials for metal recovery

Carbonaceous and intercalation electrodes

Capacitive electrodes have demonstrated promise for overcoming challenges with established metal separation methods, including chemical demand and regenerability (Fig. 4a). Unlike typical charge-transfer electrodes, capacitive electrodes primarily sustain a current through the progressive storage of ions⁴⁶. In capacitive electrode processes applied to metal recovery in aqueous systems, a small electrical potential (generally less than 1.4 V to avoid water splitting and minimize energy consumption) is applied across a pair of electrodes. The potential difference generates an electric field that drives metal ions in solution between the electrodes towards the oppositely charged electrode, where they are immobilized. The build-up of charge at the electrode–solution interface is balanced by the flow of electrons between the electrodes, in turn converting ionic current to electrical current.

As the electrodes are charged, their finite capacitance is approached over time, eventually requiring the regeneration of storage sites for continued metal recovery. Following short-circuiting or reversing the polarity of the electrodes (that is, discharging), the ions are released back into the solution to create a metal-enriched stream⁴⁷. Thus, the charging step in a capacitive electrode process consists of

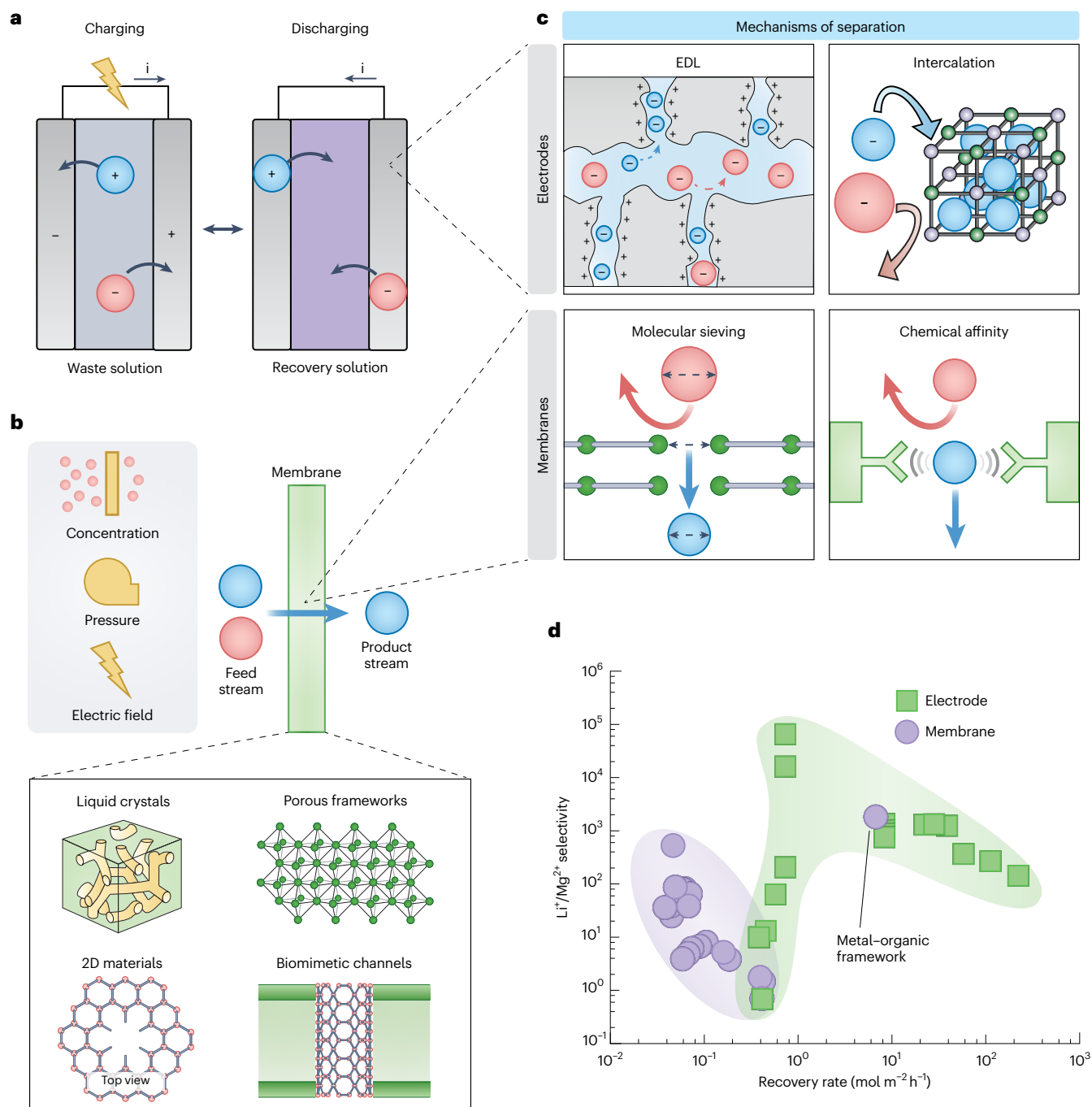


Fig. 4 | Strategies to engineer technologies and processes for metal recovery. **a**, A schematic of capacitive-based metal recovery processes. Capacitive electrode processes consist of a charging (left) and discharging (right) step. In the charging stage, an external voltage is applied across the electrodes, causing ions in solution to migrate towards the oppositely charged electrode, generating a diluted waste stream. Redox reactions at the electrodes convert ionic current into electrical current (i). After discharging (either by short-circuiting or the application of a reverse voltage), the ions stored in the electrodes are released back into a separate recovery solution, regenerating the electrodes and producing a concentrated solution of the desired species. **b**, A schematic of membrane-based metal recovery processes. In membrane processes, a concentration, pressure or electrical potential difference promotes ion transport from a feed stream across a semipermeable membrane to a product stream. To perform membrane separations between similar metals, materials with molecular-level design (such as liquid crystals, porous frameworks, two-dimensional (2D) materials or biomimetic channels) may be required.

c, A schematic of mechanisms for precise separation of metals with electrodes (top) and membranes (bottom). The mechanism of selective ion storage in the electrodes can be based on adsorption into the EDL (left) or intercalation (right). The mechanism of ion separation in membranes can be based on molecular sieving (left) or chemical affinity (right). **d**, Literature data on $\text{Li}^+/\text{Mg}^{2+}$ selectivity and Li^+ recovery rate for capacitive electrodes and synthetic membranes under varying solution conditions. The green and purple shaded areas are to guide the eye to the typical performances of electrodes and membranes, respectively. The labelled outlier is a poly(styrene sulfonate)-threaded metal-organic framework membrane⁷², which demonstrates that defect-free advanced materials may provide high separation performance. No data are available for electrodes with EDL-based capacitors because these materials are expected to favour electrosorption of Mg^{2+} over Li^+ . Data from refs.^{57-60,64,72,79-82}. Panel **b** adapted with permission from: liquid crystals, ref.⁷⁸, Springer Nature Limited; porous frameworks, ref.¹², Wiley.

the selective accumulation of metal ions in the electrodes, with the generation of a metal-depleted effluent stream. When switched to discharging, a separate recovery solution is introduced between the electrodes into which the metal ions are released, generating a readily harnessable metal-rich brine (Fig. 4a).

Capacitive electrode processes can broadly be categorized according to the underlying mechanism of ion storage—either electrosorption in electrical double layers (EDL) or intercalation into a host lattice (Fig. 4c; ref. 46). Electrical double layer storage processes typically use highly porous carbon materials to maximize active surface area and achieve appreciable adsorption capacity, with the majority of electrosorption occurring within the micropores of the electrodes⁴⁷. Intercalation materials, in contrast, are lattice or layered structures that facilitate the insertion of particular ions, accompanied by a redox transformation of either the host material or the intercalating species⁴⁸. These two storage mechanisms vary in their ability to provide selectivity between metallic species, which is a critical property for effective application of capacitive electrodes to metal recovery.

In EDL-based processes, selectivity between species is primarily controlled by sieving, electrostatic effects and interaction with surface functional groups^{49,50}. The structure of most porous carbon materials primarily consists of molecular-scale micropores (<2 nm)⁴⁷, which results in size-based selectivity between metals, as illustrated in Fig. 4c. Pristine porous carbon materials have not demonstrated practically relevant selectivity factors without modification⁴⁹, although controlled tuning of electrode pore structure has proved to be an effective approach for enhancing size-based selectivity. For example, ultramicroporous carbon aerogels, which were synthesized to predominantly consist of narrow pores (<1 nm), have shown selectivity factors >15 for nitrate over sulfate electrosorption⁵¹. Such an approach could also be extended for the selective electrosorption of small metal ions over larger competing ions. Another method that has demonstrated a marked improvement in electrosorption selectivity is surface functionalization of the electrode, whereby the affinity of the target ion to the electrode is strengthened. For instance, carbon aerogels were modified with phosphate-containing groups, which resulted in selectivity factors >50 for the electrosorption of uranium (VI) over competing metal species⁵².

Although selective electrosorption has successfully been demonstrated, the application of this technique to metal recovery may remain practically challenging. A major shortcoming of electrosorption is the short lifespan of the carbonaceous electrodes. Specifically, activated carbon electrodes typically show significant capacity loss within hundreds of cycles, which severely limits the economic feasibility of EDL-based processes^{53,54}. It should also be noted that selective electrosorption techniques have thus far culminated in relatively modest selectivity values. Consequently, the specific energy consumption (that is, energy consumed per unit of metal recovered) is likely to remain high, particularly when compared with much more selective intercalation electrodes.

Selectivity in intercalation processes, in contrast to EDL-based capacitors, is primarily governed by ion size and valency, where ions that form the most thermodynamically stable host–guest complexes have the highest propensity for insertion⁴⁸. In lattice structures, such as Prussian blue analogues, the insertion of a cation is accompanied by the reduction of a lattice atom to maintain electroneutrality. Accordingly, only ions with valences that facilitate a viable reduction transformation of the host material may be effectively intercalated⁵⁵. Intercalation materials are also inherently size selective, preferring to host ions of smaller size than the interstitial site or van der Waals gap (in the case of two-dimensional layered materials), while sieving out larger-sized ions^{48,56}.

With the vast majority of work on intercalation processes motivated by energy storage applications, materials that accommodate the intercalation of light alkali metals (that is, lithium, potassium, sodium) are the most established^{48,55,56}. Several recent works have investigated the use of intercalation electrodes for the recovery of lithium from

aqueous solutions in the presence of common competing species^{28,56–59}. Selectivity factors >1,000 have been reported between lithium and magnesium, which are metal ions of nearly identical ionic size (Fig. 4d; refs. 58–60). Intercalation electrodes have also been applied for lithium to sodium separations—relevant for recovery from brines—and have demonstrated impressive selectivity ratios of >10,000 in the highly unfavourable conditions of seawater²⁸. Similarly, a Berlin green battery electrode has been applied to seawater for the recovery of potassium, with reported potassium to sodium selectivity ratios >100 (ref. 61).

Although intercalation materials exhibit exceptional selectivity, their application to broader metal recovery is limited by poor long-term stability (that is, capacity loss within less than 100 cycles) and a lack of diversity of host materials for non-alkali metal ions^{48,55,56}. Furthermore, many intercalation materials show poor electrical conductivity, limiting the recovery rates of metal ions and increasing the energy consumption of the process⁶². The development of alternative intercalation materials with high electronic and ionic conductivity, selectivity and stability is therefore essential.

Synthetic membranes

As with capacitive electrodes, synthetic membrane technologies provide several key advantages over other separation methods, including high energy efficiency, low chemical consumption, stability and modularity. Membrane materials are generally designed to allow semi-selective passage of one species with respect to another, where the valuable product crosses the membrane into a product stream and the unwanted product is retained by the membrane (Fig. 4b). Transport of the valuable target species for recovery can be driven by a concentration, pressure or electrical potential difference across the membrane. Membrane technologies under these operating conditions are applied in many industrial sectors (for example, water purification, chemical production and medical applications⁶³) and offer the potential to be applied for continuous metal recovery from water.

Conventional membranes, which are typically polymeric, have a porous structure in which the sizes of the pores control transport rates through the material. Smaller ions can occupy a larger proportion of the porous area of the material, which allows them to move through the membrane more quickly than larger ions. Differences in ion valency also invariably alter the membrane selectivity via attractive or repulsive interactions (for example, Donnan effects) with the functional groups of the membrane³⁹. Consequently, polymeric membranes have demonstrated modest selectivity factors (<100) between nearly identically sized ions of different valency, such as Li⁺ and Mg²⁺ (Fig. 4d; ref. 64), but little to no selectivity (-1) for ions of similar size and charge, such as Li⁺ and Na⁺ (ref. 65).

Substantial research efforts have been made recently to develop membranes with selectivity between nearly identical metallic species, primarily using differences in metal size (that is, molecular sieving) or chemical affinity to the membrane (Fig. 4c). These mechanisms are partly inspired by biological ion channels, such as potassium ion channels, which are known to have ultrahigh selectivity because of constricted regions called selectivity filters that are lined with amino acid residues⁶⁶. In potassium ion channels, for instance, precise separation is attributable to the size and chemistry of the selectivity filter, which performs sieving and provides preferential binding for potassium⁶⁷. If synthetic membranes are to be developed with similar separation mechanisms, it will probably require pore structure and chemistry to be fine-tuned at the molecular level, which is challenging for conventional polymeric materials^{12,68}.

Advanced materials, such as liquid crystal mesophases, porous frameworks, two-dimensional materials and biomimetic channels, possess more molecular-level tunability and thus offer the potential for developing membranes with precise selectivity (Fig. 4b; refs. 12,69). Experimental studies have demonstrated the promising transport properties of these materials as single channels or in

nanofluidic devices^{70,71}. For example, membranes made from porous metal–organic frameworks have been applied to separate lithium and magnesium with reported selectivity ratios >1,800 (Fig. 4d; ref. 72). Covalent organic framework membranes, which are generally more stable in water than metal–organic frameworks, have also demonstrated impressive selectivity factors between lithium and magnesium of nearly 500 (ref. 73).

Despite the promise of these advanced materials, only a few studies have translated these materials into high-performance and defect-free membranes. Considerable improvements in material design and membrane fabrication are needed for these high-performing membranes to be reliably produced at the laboratory scale¹². In addition, strategies to overcome the deleterious effects of defects on membrane performance should be developed, such as patching defect areas. Effective fabrication and manufacturing techniques for advanced materials will be essential to developing membranes for metal recovery from wastewater and brine.

Outlook

Ensuring long-term supplies of metals will require improved metal recycling or mining of new, unconventional sources. Recycling from scrap materials is particularly challenging for many specialty metals because they typically only comprise a small fraction of a discarded product. For instance, less than 1% of rare-earth elements are recovered from discarded products owing to the inability to separate them from other more abundant metals in recycling processes². Mining metals from waste streams and brines is an alternative method to augmenting metal supplies, but, as with recycling scrap materials, there are no separation methods to efficiently recover them from complex mixtures. Maintaining supplies of metals is therefore a separation problem, not an availability problem⁷⁴.

Established separation processes may limit the large-scale viability of metal recovery from water because they require regular regeneration, produce large volumes of waste or lack customizability. More resource-efficient and versatile technologies, such as those based on capacitive electrodes and membranes, could be more sustainable solutions to apply at scale. Nevertheless, these technologies may be unable to selectively recover a broad range of metals from complex wastewaters and brines unless they are constructed from advanced materials, which come with their own set of challenges. The performance of advanced materials is considerably hampered in capacitive electrodes by inadequate stability and in membranes by the presence of defects. Overcoming these material limitations, or engineering around them, will determine the usefulness of capacitive electrodes and membranes for metal recovery moving forward.

Innovation in process design will also be important in improving metal recovery and purity, such as asymmetric cascades in diafiltration to improve metal recovery and purity⁷⁵ or alternating current in electrosorption to avoid the adsorption of unwanted species¹⁴. These innovations should be integrated into processes that produce a desired form of a metal product, such as a metal hydroxide in bipolar membrane electrodialysis or a zero-valency metal in electrodeposition. In some cases, multiple units or processes can be integrated into a process train to recover one metal more effectively or multiple metals from the same source.

Reaching broad consensus as a scientific community about which metals should be prioritized for recovery may be impractical, considering that geopolitical factors incentivize efforts to recover specific metals at a regional or national level. Nevertheless, guidelines will be useful and necessary to expedite the development of technologies that can recover metals of practical importance. We advise that metals that are geologically scarce, vital to essential industries (for example, renewable energy), available primarily as companion metals, rarely recycled or energy intensive to produce are designated as priority metals. Notable examples include rare-earth metals, battery materials (for example, lithium and cobalt), gallium and vanadium.

Recovery efforts should also be directed towards metals that are more technologically and economically viable for recovery, such as those with high concentrations in less complex water matrices. Concentrations in seawater, for example, are generally too low for scalable recovery of most metals (except sodium, potassium, magnesium and calcium) because of the very large volume of water that needs to be processed. More highly concentrated brines, such as salt lakes, are more appropriate sources to target, and industrial wastewaters, although complex in composition, may be the most sustainable, long-term source of some metals. Recycling metals from industrial wastewaters would potentially allow metals to be reused onsite, which would appreciably reduce reliance on traditional mining practices.

Mining metals from water may well be an attractive solution to minimize or avoid resource shortages that are projected within the coming years. Future research should systematically assess the characteristics of specific wastewaters and brines to evaluate their potential for the recovery of particular metals⁷⁶. Research is also needed to continue developing highly efficient metal recovery technologies that can separate similar metals from these complex waters. As these technologies become more effective and metal market prices change, techno-economic and life-cycle assessments will aid in evaluating the costs and benefits of metal recovery. We anticipate that some metals could be economically recovered from select wastewaters and brines, especially as demand for those metals continues to increase.

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Competing interests

The authors declare no competing interests.

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