Coordination Chemistry Reviews 548 (2026) 217186

Contents lists available at ScienceDirect

Coordination Chemistry Reviews

journal homepage: www.elsevier.com/locate/ccr

Recent advances in the recycling of precious metals using sustainable chemistry

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ARTICLE INFO

Keywords:
Dissolution
Precious metal recovery
Selective separation
Sustainable chemistry
Electronic waste recycling

ABSTRACT

Precious metals (PMs) such as silver, gold, palladium, platinum, and rhodium are used not just in traditional industries like jewelry, but also in modern electronics, medicine, catalysis and others. Their scarcity, as well as the environmental impact of current extraction procedures that frequently include harmful compounds such as cyanide and mercury, provide substantial global issues. With a growing interest in sustainable chemistry, researchers are developing eco-benign ways to extract PMs from secondary sources, like electronic waste, spent catalysts which frequently have greater PM concentrations. This review presents a contemporary analysis of PM recovery with focus on underexplored and emergent avenues, such as bio-based leaching, mechanochemistry, photocatalysis, ionic liquids and deep eutectic solvents, and computationally driven ligand design, in addition to reviewing conventional procedures. Sustainability criteria including toxicity, energy use, recyclability, and life-cycle assessment (LCA) are prioritized. Comparative tables and cross-cutting studies reveal which techniques are industrially scalable, which are still in proof-of-concept stage, and where knowledge gaps persist. This review gives a unique perspective on chemical innovation and sustainability evaluation, complementing existing surveys and providing actionable information for academics and industries seeking greener PM recovery.

1. Introduction

The increasing strain on earth's ecological systems has focused emphasis on how we manage finite natural resources, especially precious metals (PMs). These elements are critical to supporting both renewable energy technologies and the establishment of digital infrastructure, making them vital to a low-carbon economy and modern communication networks. However, their limited global supply, along with the environmental cost of extraction and unequal geographic distribution, puts at risk the viability of these developments. As we strive for a cleaner and more connected society, the capacity to protect PMs through sustainable recovery methods becomes increasingly important. Using secondary sources, such industrial by-products and end-of-life electronics, is a viable way to lessen reliance on primary mining and promote a circular economy while staying within the safe operating parameters of our planet.

PMs include gold (Au), silver (Ag), and the platinum group metals (PGMs - Pt, Pd, Rh, Ru, Ir, and Os). PMs not only have value in jewelry and investment but also have extensive applications in modern electronics, medicine, and chemical catalysis. As representative PMs, Au and Ag have long been important components of national monetary systems, and have served as symbols of wealth for thousands of years. Similarly, it is widely known that the catalytic effect of Pd is required to produce gasoline from petroleum during the cracking and processing. [1] Pt, Pd, and Rh catalysts are necessary for gasoline-burning vehicles to remove NOx gases from their exhaust emissions. [2] CO_2 emissions arising from the combustion of fossil fuel resources has a significant greenhouse effect that results in anthropogenic global warming. PM catalysts can be used to transform CO_2 into carbon raw materials with significant added value. [3]

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https://doi.org/10.1016/j.ccr.2025.217186
Received 3 July 2025; Accepted 11 September 2025
Available online 23 September 2025

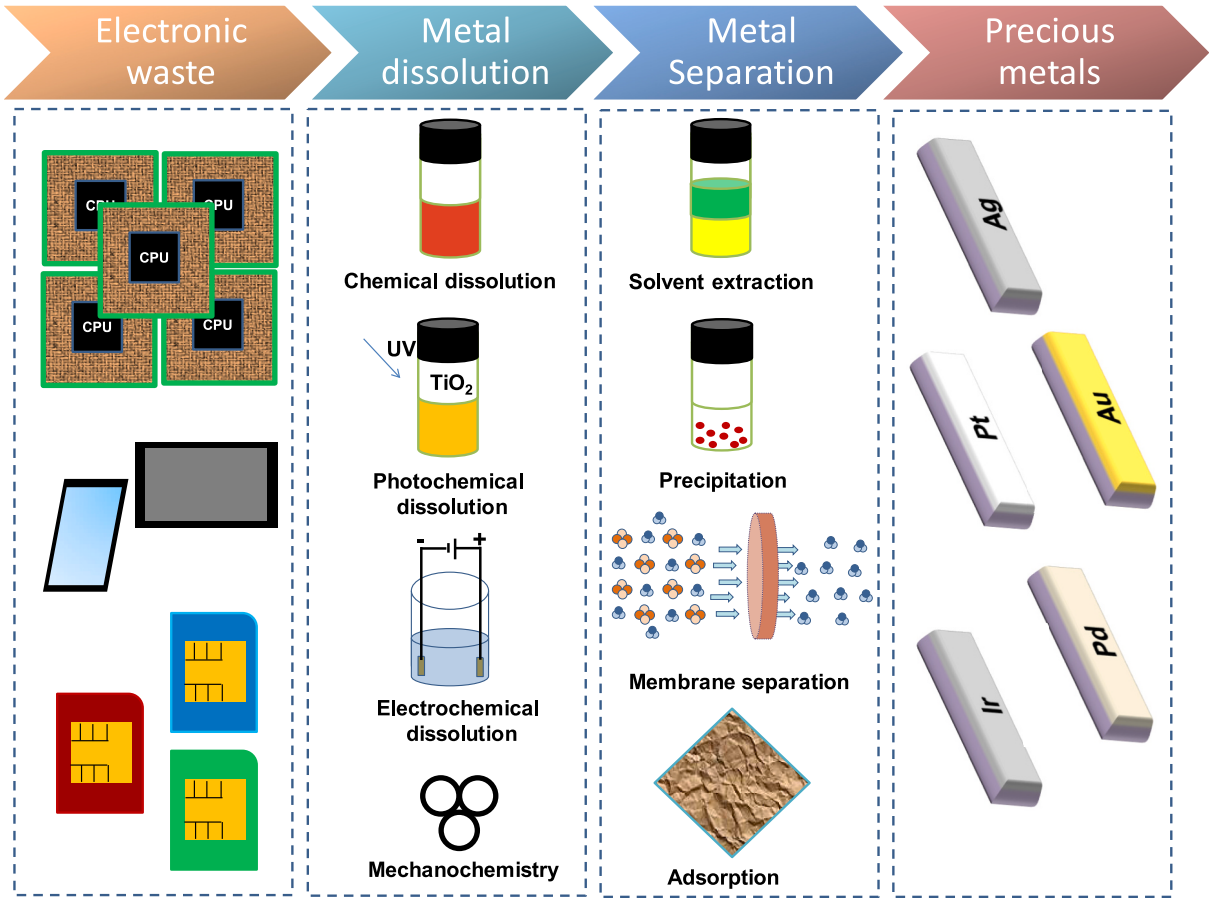
The monetary value of PMs also stems from their low abundance in their ores, although more recently secondary sources such as nanomaterials and electronic waste (e-waste) have attracted attention due to the higher concentrations found in these resources. [4–6] E-waste and spent catalysts are the most common secondary sources of PMs. The catalytic converter in an automobile is made of a porous ceramic material that is coated with PMs, such as Rh, Pd, and Pt. The PM content in used electrical equipment, car exhaust catalysts, electroplated objects, and industrial catalysts is high and, as a result, the strategy of recovering PMs from secondary resources has gained increased attention.

The markets for high-efficiency small storage devices, photovoltaics, medical diagnostics, imaging, and other gold-based nanotechnology applications are expected to grow dramatically. [7] According to estimates, the global market value of gold nanoparticles (AuNPs) was $1.34 billion in 2014. [8] By 2022, the market for gold-based nanotechnologies was expected to increase rapidly, with an estimated 20,000 kg/yr of gold used in the nanotechnology industry. [8] The World Gold Council estimates that about 190,000 tons of gold have been extracted from mines worldwide, with almost two-thirds of that amount having been extracted since 1950. [9] But, according to the distribution of known resources, worldwide gold reserves were only projected to be about 53,000 tons in 2020, despite the enormous amount that had previously been collected. [6] PGM minerals have a much lower global annual output than gold. COVID-19 had a significant impact on global demand for PGMs in 2020. [6] Furthermore, the increased adoption of alternative energy-powered vehicles is likely to drive up demand for PGMs even further in the coming years. According to the World Platinum Investment Council (WPIC), there will be a growing need for PGMs as a result of increased manufacturing of both heavy-duty and lightweight automobiles.

PMs can be extracted and recycled by leaching them from ore or secondary sources, separating the targeted PM ions from the multimetal leachate, and isolating or reducing the separated PM ions to their elemental form or metal compounds (Scheme 1). Each of these stages is associated with considerable energy use, global warming potential, and severe environmental pollution. [10] Current industrial gold extraction procedures (over 90 %) typically use highly toxic sodium cyanide to leach gold in the form of the soluble coordination complex, $NaAu(CN)_2$. [11] In more informal and artisanal practices, highly toxic mercury is used to alloy with gold and is the world's largest source of mercury pollution. [12] Alternative approaches to current procedures, which rely on selective precipitation, extraction, or adsorption of Au from leach solutions, are being actively investigated, but recovery of gold from ores, as well as e-waste, has both technological and environmental challenges. The discovery of environmentally friendly and economically feasible methods for recycling e-waste would give global circular economy aspirations a boost, and thus inspire increased research efforts. [5]

Over the last decade, various reviews have examined green leaching reagents, solvent extraction (SX), precipitation, and adsorption techniques for PM recovery. [5,6,13–16] However, the majority of these studies primarily catalogue existing chemistries rather than offering a unified framework for sustainability evaluation or covering emergent and underexplored methods. For example, recent advances in mechanochemistry, photocatalytic dissolution, microbial leaching, and bio-derived ligands have received little attention, despite their potential to minimize hazardous chemical inputs and energy demands. Similarly, computational chemistry and machine learning (ML) are increasingly directing the design of selective ligands, although their involvement in PM recovery is limited.

The present review fills these gaps by conducting a thorough and



Scheme 1. Schematic presentation of various PM recovery methods.

critical examination of both conventional and new recovery approaches within the context of sustainable chemistry. We also prioritize comparative study of toxicity, recyclability, energy consumption, and scalability across various techniques, which are supported by summary tables and LCA considerations. Unlike previous reviews, which primarily describe methods in isolation, our analysis emphasizes cross-cutting insights that inform practical adoption, as well as identifying future research directions required to translate laboratory discoveries into industrially viable, and environmentally responsible technologies.

2. Dissolution of PMs

In this part, we first describe the key techniques (old and recent) used to dissolve PMs, followed by a discussion of current breakthroughs, mechanism, problems, and prospects for developing greener and more selective dissolution processes.

2.1. Cyanide method

One of the most important steps in the recovery of PMs is leaching, which is underpinned by chemistry at the interface. The cyanide method is one of the main leaching technologies used for gold because of its cost-effectiveness, high recovery rate, and 100 years of technological maturity. [6] In this method, Au and Ag are treated with alkali metal cyanide in an aqueous solution. There are many theories to explain the mechanism of this process, including Bodlander's hydrogen peroxide theory, Elsner's oxygen theory, and Boonstra's corrosion theory. [17,18] At the initial stage, in order to form $[Au(CN)_2]^-$, Au is oxidized to Au^+, and forms a soluble complex with CN^- (eq. 1). Meanwhile, dissolved O_2 in the solution is reduced and reacts with H_2O to produce H_2O_2 and OH^-. The essential ingredient in this extraction process, cyanide, is toxic and its use in several cases resulted in environmental disasters. Cyanide combines with carbon dioxide to form hydrocyanic acid (HCN), a very poisonous chemical that, when inhaled, can paralyze the respiratory system and be lethal. Furthermore, traditional cyanidation is renowned for its low efficiency in leaching PGMs. However, pressure or high-temperature cyanidation can alleviate this constraint. [19]

$$4Au + 8NaCN + 2H_2O_2 \rightarrow 4NaAuCN_2 + 4NaOH \quad (1)$$

2.2. Cyanide-free dissolution

The use of aqua regia (1:3 mixture of concentrated HNO_3 and HCl) is another highly used method for the dissolution of PMs from e-waste. [6] Pd can be dissolved using HNO_3, H_2SO_4, or aqua regia. Au and Pt, on the other hand, can only be dissolved in aqua regia. Meanwhile, Os, Ru, Rh, and Ir are insoluble in aqua regia and other acids. Silver, on the other hand, does not dissolve in aqua regia because it forms insoluble silver chloride (AgCl). Dissolution of Au, Pt, and Pd in aqua regia results in the generation of chloridometalate complexes like $HAuCl_4$, H_2PtCl_6, and H_2PdCl_4, respectively (eqs. 2, 3, and 4). The major challenge with this dissolution method is the release the highly toxic gases NO and NO_2.

$$Au + 4HCl + HNO_3 \rightarrow HAuCl_4 + 2H_2O + NO\uparrow \quad (2)$$

$$3Pd + 12HCl + 2HNO_3 \rightarrow 3H_2PdCl_4 + 4H_2O + 2NO\uparrow \quad (3)$$

$$3Pt + 18HCl + 4HNO_3 \rightarrow 3H_2PtCl_6 + 8H_2O + 4NO\uparrow \quad (4)$$

More environmentally benign methods of dissolving PMs have been developed as awareness of the negative health and environmental effects of the cyanide leach and aqua regia methods mentioned above have become better appreciated. [6] Thiourea, thiosulfate, KI-I_2, and electrochemical methods have been developed to dissolve Au and Ag. Thiourea is a reductive ligand that can form stable complexes with a diverse variety of metal ions in solution. As a result, a small amount of oxidant is required to aid the dissolution of Au and Ag. [20] Thiourea possesses unbound electron pairs on its nitrogen and sulfur atoms, allowing it to adsorb on the gold surface. As a result, this interaction reduces the redox potential of gold, allowing for its dissolution under milder reaction conditions. Thiourea, however, is unstable in alkaline solutions and readily breaks down into cyanamide and sulfide. [13] Consequently, the thiourea leaching process has higher costs than cyanidation but with lower toxicity. [6] Thiosulfate can also dissolve Au under alkaline conditions, [21] forming a stable complex after the reaction with Au, to form $[Au(S_2O_3)_2]^-_3$. [22]

The stability of Au complexes generated with different anions varies, influencing the complexation process and, as a result, the leaching efficiency. [23] Au-anion complexes are stable in the following order: $CN^- > I^- > Br^- > Cl^- > NCS^- > NCO^-$. The gold-iodine complex is the second most stable, following the gold-cyanide complex. The electronegativity and oxidizing power of the halogen elements decreases down the periodic table grouping, making heavier halogens less effective as oxidants. Consequently, iodination (the process of generating the iodide ion by combining iodine (I_2) and potassium iodide) is a frequently used technique for Au leaching. [24] It has various benefits, such as being relatively non-toxic, having good leaching capabilities while remaining relatively stable. In addition to the classical methods of PMs dissolution, electrochemical dissolution techniques have received interest in recent applications. However, because of the complicated equipment requirements, they have not yet received much practical use. [25]

2.3. Recent developments in dissolution of PMs

2.3.1. Mild dissolution processes

Challenges of the above-mentioned extraction technologies typically include lengthy dissolution cycles, high reagent and energy consumption, complicated operational procedures, and significant environmental pollution. [6] In order to address these challenges and make PMs dissolution more practical, more environmental benign and economically feasible leaching techniques are currently receiving significant research interest.

In this context, Lin et al. demonstrated that PMs like Au and Pd can be dissolved with high leaching rates under favorable conditions using straightforward mixtures of thionyl chloride ($SOCl_2$) and some organic solvents/reagents such as *N*,*N*-dimethylformamide (DMF), pyridine (Py), and imidazole (Fig. 1). [26] This mixture of organic solvents and reagents has been referred to as 'Organic Aqua Regia'. Modifying the content of organic solvents enabled the selective dissolution of certain PMs, including Au and Pd from a mixture of Pt, Au, and Pd, and Au from a mixture of Au and Pd; this latter example comprises dissolving Au in a $SOCl_2$/DMF solution, followed by the dissolution of Pd in a $SOCl_2$/Py mixture. Organic aqua regia represents a novel strategy to selectively dissolving PMs, with specific advantages over traditional inorganic procedures. However, $SOCl_2$ is a volatile liquid with a powerful, irritating odour, and pyridine has a distinctly unpleasant smell. Furthermore, the toxicity of these reagents raises significant health and environmental concerns, and the need for substantial post-reaction processing complicates and extends the procedure. Serpe et al. showed that the mixture of tetraethylthiuram disulfide (Et_4TDS) and I_2 in acetone has the ability to dissolve Au and form valuable metal complexes, with the stoichiometry of these complexes depending on the composition of the mixture. [27] Under mild conditions, these mixtures also uniformly and selectively removed the Au layer from thin-layered $Si/SiO_2/Ti/Au$ structures. In an alternative study, with the use of Py and N-bromosuccinimide (NBS), Yang et al. created a novel chemical process with mild reaction conditions and a significantly reduced environmental impact. With this process, Au from e-waste and ore can be directly dissolved into water to produce Au(III) complexes. [28] At ambient conditions and a neutral pH, the process yielded about 90 % Au dissolution using an NBS/Py etchant. According to the reaction mechanism (Fig. 1B), Au(0) is initially oxidized by NBS in step 1 resulting in the conversion of Au(0) to Au(III) as $AuBr_4^-$. In step 2, the Au(III) species

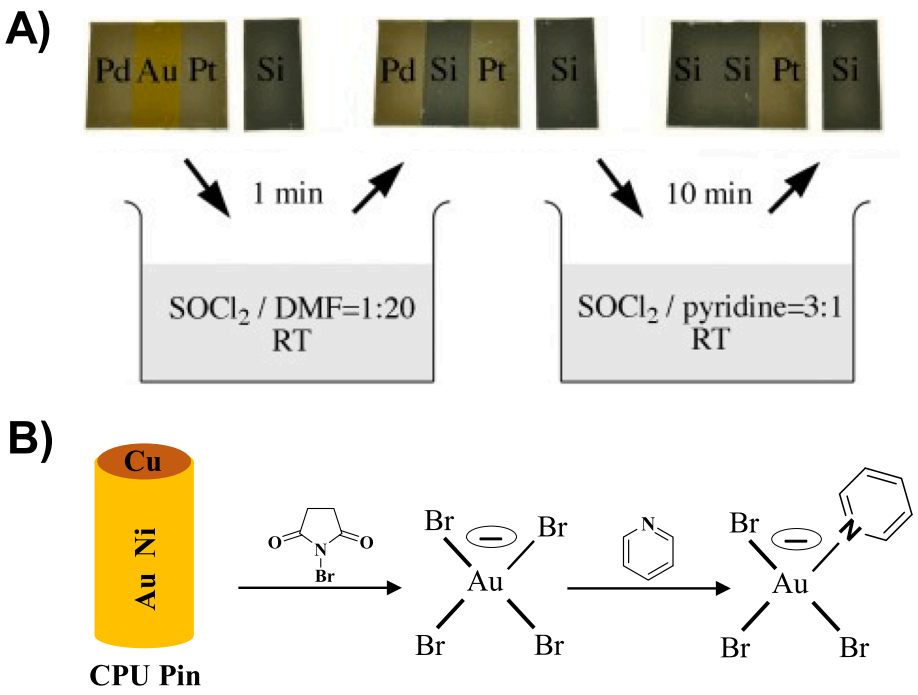


Fig. 1. A) A schematic representation of an effective and selective leaching of Pd, Au and Pt. Pd and Au were leached sequentially in $SOCl_2$/py and $SOCl_2$/DMF, respectively from a Si substrate. The photographs in the top row depict the Pd/Au/Pt layer on a Si substrate during the selective leaching method. (Adopted from ref. 26, Copyright 2010 Wiley.) **B)** Dissolution of Au from CPU pin using *N*-bromosuccinimide/pyridine mixture in water. (Reproduced from ref. 28, Copyright 2017 Wiley.)

($AuBr_4^-$) coordinates with pyridine (Py) ligands to produce the (Py) $AuBr_3$ complex with a binding constant ranging from 10^5 to 10^6 M. The dissolution of Au and PGMs was examined in highly concentrated solutions of hydrated $AlCl_3$ and $Al(NO_3)_3$ salts by Forte et al. [29] The research was motivated by a 1973 paper by Sare et al. in which it was noted that boiling aqua regia does not dissolve PMs as quickly as concentrated solutions of $AlCl_3 6H_2O$ and $Al(NO_3)_3 9H_2O$. [30] Using similar methods, 95 % of Pd was leached in 15 min at 80 °C from used automotive catalysts, whereas Pt required longer times, and 20 % Rh dissolution was achieved. The same procedure permitted the dissolution of Au from waste-electronic wiring in 24 h. While aluminium salt solutions are substantially less hazardous and safer to handle than aqua regia, they are not reusable or recyclable. The dissolution of various PMs using various reagents in different solvents and their toxicity is presented in Table 1.

Baksi et al. showed that Ag has a very strong chemical affinity for carbohydrates, allowing it to dissolve directly from the metallic state into an aqueous solution. [31] The inclusion of common ions considerably increased the method's efficiency, offering a new perspective on extractive metallurgy. An analysis of calorimetric data shows that the route is thermodynamically desirable. Continuous Ag extraction causes the surface to corrode, and as a result, microscopic roughness was seen (Fig. 2A). Studies have shown that the release of Ag occurs in two stages, with the formation of Ag ions at the metal surface followed by their binding with glucose. Using mass spectrometry, the resultant Ag-G complexes have been determined (Fig. 2B). The process was further extended with the use of glutathione in combination with glucose, which resulted in a 45 times enhancement in the dissolution process. [32]

Repo et al. described an effective approach for dissolving Au(0) that employed solutions of DMF containing pyridine-4-thiol (4-PSH) as a reactive ligand and hydrogen peroxide as an oxidizing agent (Fig. 3A). [33] The process of dissolving metallic Au involved a number of fundamental steps, including isomerizing the 4-PSH to pyridine-4-thione (4-PS), coordination with Au(0), and oxidizing the Au(0) thione species to Au(I). The final product from the dissolution is an Au(I) complex with

Table 1
Dissolution of PMs in various solvents with indicated toxicity.*

Entry	Solvent	Reagents	Targeted PM	Toxicity of the reagent & solvent	Ref.
1	Py, DMF, and imidazole	$SOCl_2$	Au and Pd	High	26
2	Acetone	Et_4TDS and I_2	Au	Low	27
3	Py	NBS	Au	Moderate	28
4	Water	$Al(NO_3)_3$ and $AlCl_3$	Au, Pt, Pd and Rh	Low	29
5	Water	Glucose	Ag	Low	31
6	DMF	4-PSH and H_2O_2	Au	Moderate	33
7	Ethanol	Catalytic amount of I_2, 2-MBI and H_2O_2	Au	Low	34
8	Acetonitrile and dichloromethane	TiO_2 photocatalyst	Au, Ag, Pt, Pd, Ru, Rh, and Ir	Moderate	41
9	Acetonitrile	Ph_3PCl_2 or $(COCl)_2$ and H_2O_2	Au, Pd, Pt and Cu	Moderate	10
10	Ethanol	CH_3COBr or CH_3COCl and H_2O_2	Au and Cu	Low	35
11	Tributyldecylphosphonium trihalide ionic liquids as solvent and reagent		Au, Cu and Pd	Low	49
12	Deep eutectic solvents		Au, Ag and Cu	Low	55

* Toxicity levels were assigned based on reported risks using PubChem and MSDS. We categorize chemicals as low (usually safe/biodegradable, e.g., water, ethanol), moderate (some dangers, managed with normal safety, e.g., thiourea, acetonitrile), and high (poisonous, carcinogenic, or persistent, e.g., cyanide, aqua regia, $SOCl_2$).

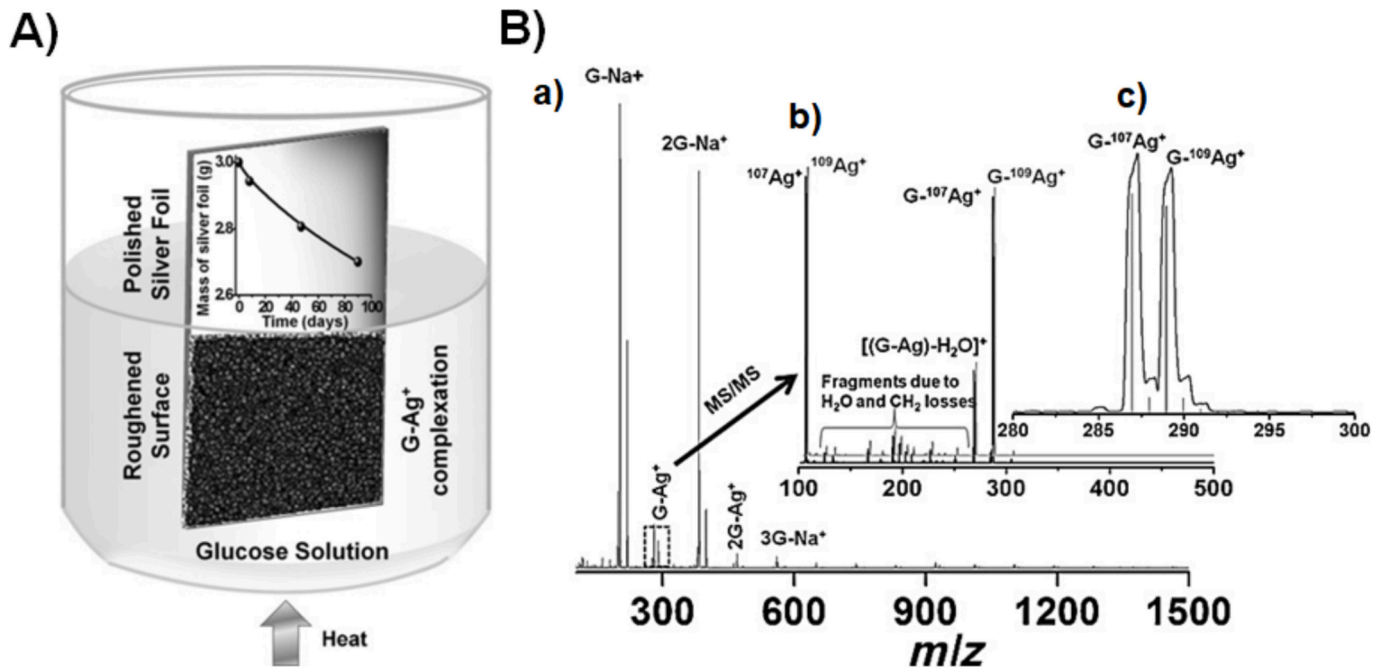


Fig. 2. A) Ag extraction by glucose (G) is depicted schematically (not to scale). After being partially immersed in a glucose solution at 70 °C, a silver foil piece gradually turned black in the immersed area. B) a) ESI MS analysis of G-Ag complexes. b) MS/MS of G-Ag^{+} indicating the loss of one G to yield Ag^{+}. c) Isotopic distribution of G-Ag^{+} complex. (Adopted from ref. 31, Copyright 2016 Wiley.)

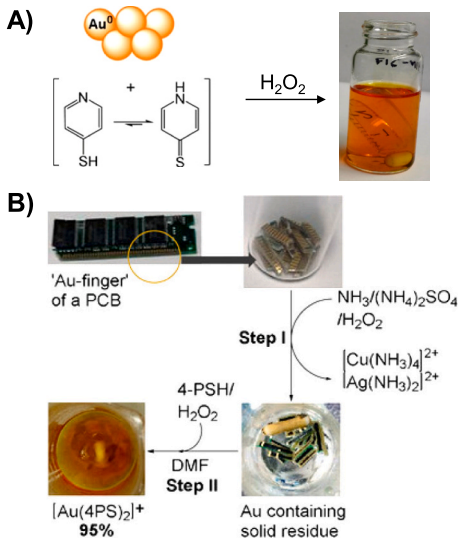


Fig. 3. A) A schematic representation of an efficient and selective dissolution of Au using 4-PSH and H_2O_2. **B)** Au dissolution in PCB samples Step I: Cu and Ag extraction with $NH_3/(NH4)_2SO_4/H_2O_2$. Step II: Quantitative Au dissolution in 30 min using the 4-PSH/H_2O_2 method. (Adopted from ref. 33, Copyright 2018 Wiley.)

two 4-PS ligands and a SO_4^{2-} counterion. The ligand was essential because it promoted oxidation and formed a stable complex with enhanced solubility. The authors were able to recover Au from printed circuit boards (PCBs) (Fig. 3B). PCBs only have 0.25 wt% of Au (and 0.008 wt% of Ag) compared with 23.4 wt% of Cu. Due to the higher Cu content than Au in this case, direct 4-PSH leaching of Au is not practical. To dissolve Cu and Ag and not gold, the authors therefore first treated the sample with $NH_3/(NH_4)_2SO_4$ and H_2O_2. Following filtration and immersion of the residue in a DMF solution of 4-PSH/H_2O_2, a significant 95 % yield of dissolved Au was recorded in 30 min. In another study from the same group, gold was dissolved quantitatively in ethanol using a catalytic amount of iodine and 2-mercaptobenzimidazole (2-MBI) as a ligand. [34] In terms of its mechanism, Au dissolved when I_2 oxidized Au (0) to create a $[AuI_2]^-$ species. This species then went through a series of ligand-exchange reactions to create a stable bis-MBI Au(I) complex. Free iodide was oxidized by H_2O_2 and then regenerated I_2 for the catalytic cycle. A reductant ($NaBH_4$) was added to the reaction mixture to quantitatively precipitate Au and partially regenerate the ligand (41 %).

Love et al. developed a new process for the dissolution of PMs in organic solvents rapidly by combining triphenylphosphine dichloride or oxalyl chloride with hydrogen peroxide, resulting in metal chloride salts. [10] At room temperature, almost complete dissolution of metallic Au, Cu and Pd occurred in minutes. Dissolution of Pt was achieved, though at a slower rate, with the chlorinating oxidant alone, but was slowed by the addition of hydrogen peroxide. Fig. 4A shows the CPU images before and after the leaching process. The leachate solution (Fig. 4B) extracted from electronic CPUs, the retaining of Au(III) chloride salt in the organic phase made it easier for it to be selectively separated from Ni and Cu. About 95 % pure gold was achieved by this process from CPUs (Fig. 4C and D).

Following this work, the same group discovered that the rapid dissolution of Au was possible using the mixtures of acetyl halides and hydrogen peroxide at room temperature in environmentally benign alcohols like ethanol, 1-butanol and 1-octanol. [35] Through the in-situ generation of halogens, both procedures quantitatively dissolve Au to create Au(III) halometalates. Compared with acetyl chloride, the dissolution rate with acetyl bromide is faster (within minutes). Significantly, following the recycling of the alcohol, this dissolution technique can be connected to a selective precipitation approach for the full extraction of Au from mixed-metal solutions. Based on these findings, this leaching process may be used in the future to purify gold from ores, used catalysts and electronic and nano waste.

2.3.2. *Photocatalytic dissolution*

Photocatalytic technology is an environmentally friendly solution that has enormous potential in the energy and environmental sectors, since light is a chemical-free reagent, that is becoming cheaper to employ due to the greatly improved efficiency of light-generating

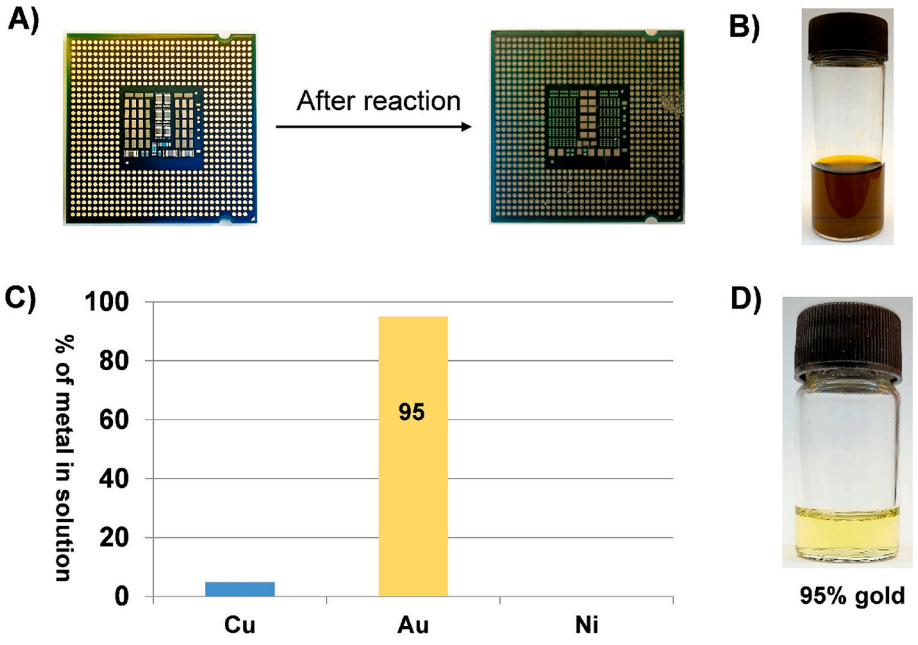


Fig. 4. **A)** Photographs of CPU before and after the leaching process. **B)** Leachate solution obtained from the CPU. **C)** ICP-OES data of Au solution after the separation process. **D)** 95 % pure Au solution after separation. (Adopted from ref. 10, Copyright 2022 Wiley.)

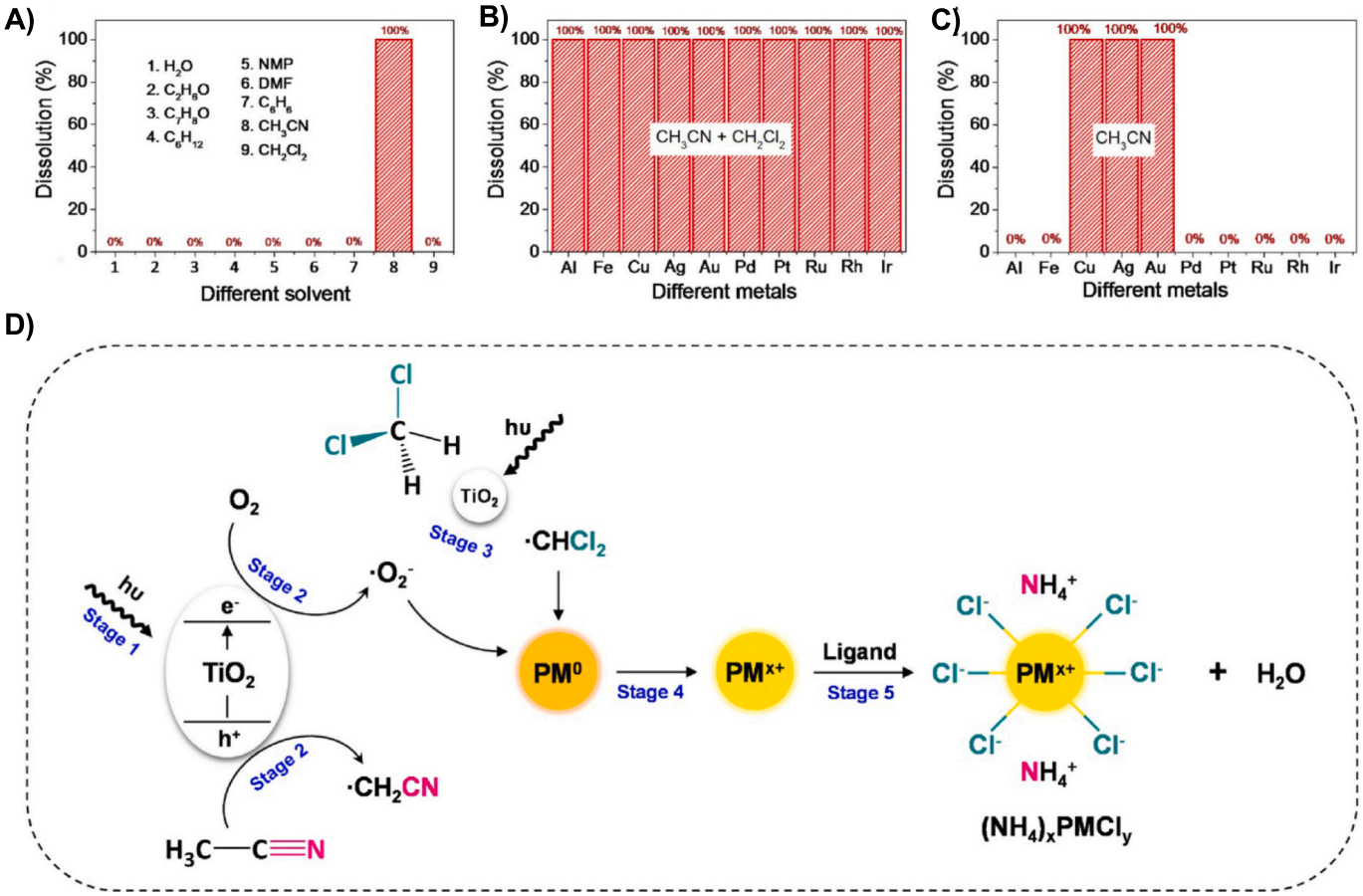


Fig. 5. **A)** The leaching of Au in different organic solvents in percentage. **B)** The leaching of Fe, Al, Ag, Cu, Au, Pt, Pd, Rh, Ru, and Ir in the mixture of DCM and MeCN using a photocatalyst. **C)** The leaching rate of Fe, Al, Ag, Cu, Au, Pt, Pd, Rh, Ru, and Ir in MeCN using a photocatalyst. **D)** A presentation of the mechanism of dissolution procedure using a photocatalyst. (Adopted from ref. 6, Copyright 2021 Elsevier Publishing Group.)

devices. Examples include light emitting diodes (LEDs), with white LEDs displaying a power-to-light conversion efficiency of around 40 %, which is significantly higher than the 2–5 % efficiency of traditional incandescent light bulbs. [36] Light stimulation of catalysts produces photogenerated electrons and vacancies, resulting in active species that include hydroxyl and superoxide radicals. These reactive entities can undergo oxidation-reduction processes with PMs, providing a novel technique for their dissolution. [37–40]

Bian et al. described a photocatalytic process for the selective leaching of seven PMs, including Ag, Pt, Au, Pd, Ru, Ir, and Rh from ternary automotive catalysts, ores, and scrap circuit boards (Fig. 5A, B and C). [41] Strong acids, bases, or toxic cyanide were not used for the entire process; instead, ultraviolet (UV) light and photocatalysts like titanium dioxide were employed for the dissolution of these PMs. Over 99 % of the necessary elements from waste sources could be dissolved, allowing for the recovery of PMs with purity (≥98 %) through a simple reduction procedure. Unfortunately, the breakdown of organic solvents is required for the dissolving process. Acetonitrile (MeCN) and dichloromethane (DCM) were converted into highly reactive organic radicals via photocatalysis, which facilitated in the dissolution of PMs as their corresponding chloridometalate complexes. Selective recovery of Au from e-waste was achieved using this method. The mechanism of the overall process is shown in Fig. 5D. Stage 1 of the process begins with UV light excitation of TiO_2, which produces holes and electrons. The photogenerated holes interact with MeCN in mixed solution to produce $CHCN^{\bullet}$ radicals, while the photogenerated electrons interact with O_2 to generate $O_2^{\bullet-}$ (stage 2). DCM breaks down into oxidizing $CH_2Cl^{\bullet}$ (stage 3), while the oxidation of PM(0) to PM^{x+} (stage 4) and the formation of $(NH4)_xPMCl_y$ were accomplished by these active species in tandem (stage 5).

The successful photocatalytic dissolution of Pd and Au was also achieved in water by the same group. [42] In order to create intermediate active substances to oxidize and dissolve Pd and Au by photocatalysis, bromine and iodine ions were utilized as reactants. Electron paramagnetic resonance (EPR) spectroscopy was utilized to exemplify the crucial role that the intermediate radical active substances play.

2.3.3. *Mild dissolution in ionic liquids and deep eutectic solvents*

Unfortunately, the use of organic solvents presents many environmental concerns related to toxicity, volatility and global warming, and impacts on the overall LCA of the dissolution process. [43,44] In an attempt to overcome these challenges, ionic liquids (ILs) have been explored as alternatives to conventional organic solvents. [45–47] The applicability of ILs in oxidative metal dissolution have mainly focused on alkyl phosphonium, alkylammonium, and alkyl methylimidazolium cations combined with halogen or sulfur-based anions. [45] An IL can act as oxidizing agents without the need for an added oxidant when the anionic component is a trihalogen ion. For example, the phosphonium trichloride room-temperature IL [P444,14][Cl_3] was utilized in the dissolution of the noble metals Au and Pt, base metals Fe, Cu, In, Zn, Ga, Sb, Ge, and Ta, the rare-earth metals Sm and Dy, and the alloys GaAs and InAs. [48] Another representative trihalide IL, [P444,10][Br_3] was tested for the oxidative dissolution of the noble metals Au, Pd, Pt, and Rh as well as the base metals Fe, Cu, Sb, Co, Zn, In, Ga, Bi, Ge, and Sn. [49] In this latter case, all metals were successfully dissolved except Pt and Rh which were described as being “more noble” than Au and Pd. The polyhalide IL [Hmim][Br_2I] was found to leach Cu, Au, and Ag foils at 40°-50 °C, although dissolution yields were below 50 %. [50] Room temperature ILs with polypseudohalide anions were formed on mixing BrCN with [$NBuEt_2Me$][Br] IL. [51] The resulting IL was found to dissolve Au overnight at 60 °C to form Au(I) and Au(III) cyanido as well as bromidocyanido species. Alternatively, ILs can be exploited solely as solvents in metal dissolution with the addition of an oxidizing agent and additional ligands. Several studies were undertaken to investigate the leaching of Au from ores, primarily using imidazolium cation ILs with varying anions. [52–54] Using [Bmim][HSO_4] with thiourea as the complexing agent and $Fe_2(SO_4)_3$ as the oxidizing agent, [52] highly selective leaching for Au (86 %) and Ag (60 %) as thiourea complexes were achieved. The efficacy of dissolution on variation of the anion, such as $CH_3SO_3^-$, BF_4^-, $N(CN)_2^-$, Cl^- and $[HSO_4]^-$, was studied with the outcome being that ILs with the $[HSO_4]^-$ anion performed best. This suggested that the solubility of the resulting complexes and the capacity of the IL to ion-pair with the metal cation are important factors. [53]. The poor performance of the IL [Bmim][Cl] was thought to be due to the insolubility of the Fe-based oxidant in the IL, while H_2O_2 was deemed unsuitable as it would oxidize the thiourea, requiring the need for alternative oxidants to be explored. [54] In this case, the optimum system was found to be [Bmim][Cl]/NaI/$[HSO_5]^-$ which leached up to 85 % Au from gold ore. More recently, a novel method for providing greater selectivity of dissolution was discovered utilizing biomass-derived ionic liquids and the green oxidant H_2O_2 to dissolve single metals from Cu, Ag, and Au combinations. [55] Magdalena et al. studied the leaching of Cu from e-waste with hydrogen sulfate ionic liquids in presence of H_2O_2. [56]

Deep eutectic solvents [13,57,58] (DESs), consisting of hydrogen bond (HB) donors (such as amides and organic acids) and acceptors (such as organic alcohols and choline chloride), have emerged as sustainable substitutes for conventional solvents. These solvents enable extraction of PMs through their unique coordination properties, proton transfer mechanisms, and oxidative potentials. Acidic DESs possess strong proton activity, and can efficiently break metallic bonds to forming metal-ligand complexes, thereby enhancing metal dissolution. The protonation process releases protons which diffuse into the solvent, further facilitating metal extraction. In contrast, non-acidic DESs exhibit lower proton activity, thereby limiting their dissolution efficiency, resulting in metal extraction being primarily reliant on coordination interactions. Enhancing the oxidative strength and coordination capacity of DESs remain crucial for optimizing their ability to dissolve PMs effectively. DESs have been found to be successful at dissolving and extracting metals, such as Au oxidation, sulfide processing, rare earth carbonates, and treating electric arc furnace and flue dusts. [59–65] Rivera et al. developed a DES with $CaCl_2{\cdot}6H_2O$ as the HB acceptor and ethylene glycol as the donor. [66] $FeCl_3$ and $CuCl_2$ acted as redox catalysts, allowing for selective Cu extraction from PCBs. Au and Ni were retrieved using simple filtration. The low-viscosity solvent system (40 mPa·s) greatly increased the Cu dissolution rate. $FeCl_3$ and $CuCl_2$ enhanced the leaching process due to their high solubility and rapid electron exchange. Rivera et al. used this DES system to investigate the effect of ultrasound-assisted catalytic dissolution of metals from PCBs. [67] Ultrasonic-induced density fluctuations (UIDF) assisted cavity formation by improving mass transfer efficiency and facilitating metal dissolution through random reaction zones. The results showed that high-power ultrasound greatly boosted the dissolution rate for Cu, by ca. 10,000 times compared with standard approaches. [66] Ultrasound triggers both physical and chemical processes, including loss of protective surface layers, resulting in better mass transfer, exposure of new reactive sites, and the formation of free radicals, all of which boosted the recovery of Au from PCBs. Furthermore, localized UIDF aided in the creation of cavities, boosting mass transfer efficiency and aiding the flow of reactants and dissolved compounds, with cavities varying in size and position. Recently, Repo et al. revealed a new method for sequentially dissolving single metals from Cu, Ag, and Au combinations with biomass-derived ionic solvents and green oxidants. [55] Cu was dissolved selectively in the presence of Ag and Au using a mixture of choline chloride, urea, and H_2O_2, followed by Ag dissolution in lactic acid/H_2O_2. Finally, the metallic Au, which is not soluble in either of the preceding solutions, is dissolved in choline chloride/urea/oxone. The metals were then collected from dissolutions in a simple and quantitative manner, while the solvents were recycled and re-used. The feasibility of this method was displayed by recovering metals from PCBs, Au fingers, and solar panels.

2.3.4. Dissolution using mechanochemistry

Mechanochemistry is an excellent complement to typical liquid-phase reactions and has proven to be important in enabling various kinds of chemistry by fully eliminating the need for expensive, toxic, and combustible solvents, so reducing the environmental burden. [68] In order to create complex molecules and nanostructured materials, mechanochemistry uses mechanical energy to promote chemical and physical transformations. It also promotes the dispersion and recombination of multiphase components and uses highly reactive surfaces to speed up reaction rates and efficiencies. Mechanochemistry generally involves solid-solid interfacial reactions. Tomislav et al. used mechanochemistry to convert PMs into water-soluble halide complexes or metal-organic catalysts at room temperature without the use of solvents (Fig. 6a). [68] With a focus on Pd and Au, this study showed that the mild oxidant oxone and halide salts ($(NH_4Cl$, KCl) worked together to activate PMs pellets, powder, or wire without the use of any harsh reagents or solvents (Fig. 6b-e). The method is much easier, cleaner, and safer than traditional methods for transforming metals into complexes. In an alternative study, a novel method for extracting Au from anode slime was developed by Shufeng et al. using in situ oxidative chlorine generated by a mechanochemistry approach. [69] Au in anode slime was efficiently converted into water-soluble $AuCl_3$ by dry ball milling the mixed anode slime with $KMnO_4$ and NH_4Cl, and then separated from solids by simple water leaching.

2.3.5. Electrochemical dissolution

Electrochemical dissolution is significantly advancing PM leaching. This technique uses electric currents to oxidize PMs at the anode, allowing them to shift into an ionic form in solution. PMs dissolve by cyclic potential shifts between oxidation and reduction. However, increasing the surface free energy in PM nano particles promotes Ostwald ripening, substantially lowering the efficiency of dissolution. [70] Surface-modifying agents can successfully address these issues, by e.g. preventing dissolved Pt from recrystallizing under reducing conditions while still allowing for improved dissolution during oxidation. The results showed that PMs that used this process dissolved at twice the rate of those without it. This dynamic surface regulation provides a viable technique for electrochemical PM leaching.

Song et al. established a novel method for dissolving PMs using the oxidation potential differences between Cu^{2+} halides and PMs. [71] Electrochemical dissolution tests showed that substituting sulfate with bromide ions increased the Cu^{2+}/Cu^{+} redox potential from 0.4 V to 0.75 V. This study found that altering ligand types and concentrations enabled Cu^{2+} and Fe^{3+} to selectively dissolve metals. Gold corroded efficiently in Cu^{2+}/Fe^{3+}-Br^{-}, while Pd dissolved quickly in Cu^{2+}/Fe^{3+}-Cl^{-}. Dissolution rates improved with optimum oxidant and halide levels. Electrodeposition resulted in nearly full PM recovery at the cathode and regenerated Cu^{2+}/Fe^{3+} at the anode.

2.3.6. Bio-based dissolution

In addition to conventional chemical processes, bio-based strategies have gained popularity as ecologically friendly and sustainable alternatives to PM recovery. One well-known example is bio-cyanidation, in which cyanogenic bacteria, such as *Bacillus megaterium*, generate cyanide in situ to leach gold, achieving recovery levels of over 87 % from certain low-grade sources, which is comparable to typical chemical cyanidation. [72] Reviews of biogenic lixiviants emphasize the use of cyanogenic bacteria such as *Chromobacterium violaceum*, *Pseudomonas aeruginosa*, and Micrococcus spp., as well as microbial synthesis of iodine species and amino acids, in gold extraction. [73]

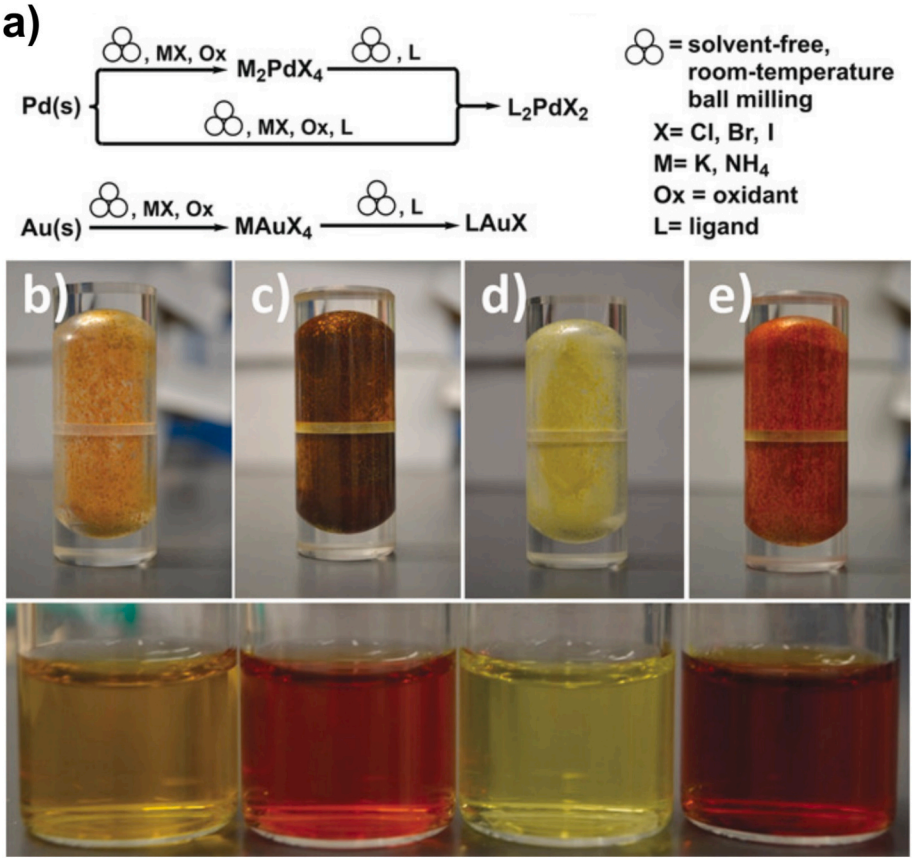


Fig. 6. a) A schematic representation of the formation of Pd and Au complexes using a mechanochemistry approach. Formation of Pd and Au complexes a using mechanochemistry approach presented in milling jars and dissolved in H_2O: **b)** $(NH_4)_2PdCl_4$, **c)** $(NH_4)_2PdBr_4$, **d)** NH_4AuCl_4 and **e)** NH_4AuBr_4. (Adopted from ref. 68, Copyright 2018 Wiley.)

Another environmentally benign option is through fungal and heterotrophic microbial leaching, in which species like Aspergillus niger and Penicillium spp. release organic acids such as citric, oxalic, and gluconic acids that act as natural chelating agents. These acids effectively dissolve metals, sometimes mobilizing more than 90 % of the target elements. [74] Bioleaching electronic waste with fungi yielded high concentrations of citric (up to ~152 mM), tartaric, oxalic, and gluconic acids, as well as significant yields of metals such as Zn, Cu, and Ni. [75] Broader studies have also shown the importance of fungal-produced citric acid in selectively dissolving PGMs and rare earth metals from residues and industrial waste. [76]

These microbial and biogenic ligand-based approaches adhere to green chemistry principles by reducing hazardous chemical input, and waste creation, and allowing for selective and potentially scalable recovery procedures. While these approaches are still in their early stages when compared with known hydrometallurgical procedures, they offer a fascinating and developing frontier in PM recovery, and so ought to be included alongside traditional techniques in any comprehensive consideration of green PM recovery.

Sustainable dissolution strategies for PMs can be generally classified based on their current level of maturity. Thiourea- and thiosulfate-based systems are among the most established and effective techniques and, while not without obstacles, they have consistently performed as greener alternatives to cyanide. Biogenic ligand-assisted leaching, mechanochemistry-assisted dissolution, mild dissolution and DESs systems, on the other hand, are intriguing but still emerging technologies that need to be validated under practical circumstances. Enhancing selectivity, increasing reaction kinetics, and demonstrating scalability remain critical issues for these techniques, as does the need for complete LCA to determine their genuine sustainability credentials. Section 6 of this review provides a more in-depth analysis of these strategies and their future possibilities.

3. Integration of computational approaches in metal extraction

Recent breakthroughs in computational chemistry are increasingly being used to predict metal-ligand interactions and lead the development of selective, environmentally benign extraction technology. For example, density functional theory (DFT) and related quantum-chemical methods have been used to design ligand extractants, calculate stability constants and elucidate bonding characteristics in chlorido complexes of Au(III), Pd(II), and Pt(II) in aqueous media, providing quantitative thermodynamic insights that guide leachant selection and optimization. [77] Furthermore, DFT has been utilized to study ligand interactions in gold leaching systems by looking at orbital interactions, electron back-donation, and energy decomposition in distinct Au-ligand complexes. [78]

Beyond static quantum-chemical modeling, molecular simulations such as enhanced-sampling molecular dynamics (e.g., metadynamics) are being used to characterize the conformational free-energy landscapes of extractants in solution. These methods illustrate how ligand flexibility and solvation effects affect the capacity of extractants to adopt metal-binding conformations, a key but often neglected aspect of ligand performance. [79]

Furthermore, ML models are gaining popularity for predicting metal-ligand stability constants. Notably, techniques that combine ML with ligand design tools (e.g., LOGKPREDICT coupled with HostDesigner) allow for rapid screening and ranking of ligands based on projected binding affinity and selectivity, which speeds up discovery procedures in hydrometallurgical applications. [80]

Taken together, computational tools such as DFT, molecular dynamics, and ML-assisted prediction provide a valuable supplement to experimental investigations by allowing for rational design of selective ligands and green solvents with less reliance on trial-and-error. Even this brief mention highlights the potential for modeling studies to facilitate the transition towards more sustainable PM recovery.

4. Separation methods

This section outlines the key strategies employed for separating PMs after dissolution, including precipitation, adsorption, and solvent extraction, with a focus on their mechanism, efficiency, selectivity, and environmental impact. Various separation methods are summarised in Table 2.

4.1. Precipitation and encapsulation

Precipitation is a crucial technique for recovering PMs due to its selective recovery, high purity control, efficiency, scalability, environmental considerations, and versatility. It allows for the selective removal of specific metals from a solution, ensuring purity and efficiency. Precipitation methods can be tailored to produce high-purity solids, making them essential for industries with exacting standards. These methods are also scalable, suitable for both small-scale refining operations and large-scale industrial applications. As precipitation methods often negate, or at least minimize, the need for organic solvents, they are more environmentally benign than the traditional biphasic solvent extraction approaches.

Stoddart et al. identified that $KAuBr_4$ and α-cyclodextrin (α-CD) form a host-guest complex $\{[K(H_2O)_6][AuBr_4](\alpha\text{-CD})_2\}_n$ in solution. This complex precipitated as needle-like crystals, generating a superstructure in which the α-CD nanochannels were filled alternately by $[K(H_2O)_6]^+$ and $[AuBr_4]^-$ ion pairs. These ion pairs were kept in place within the channels by a series of preorganised HBs (Fig. 7 Aa). [81] The formation and co-precipitation of $\{[K(H_2O)_6][AuBr_4](\alpha\text{-CD})_2\}_n$ indicated that the self-assembly process was governed by an optimal structural match between the stereoelectronic characteristics of $[K(H_2O)_6]^+$, $[AuBr_4]^-$, and α-CD, enabling their precise interaction and organization within the superstructure (Fig. 7A b-d). The axial [Au − Br···H − O] and equatorial [Au − Br···H − C] HBs induced second-sphere coordination, directing the formation of {[K(H2O)6][AuBr4](α-CD)2}n and its rapid precipitation. These interactions were critical to the structural assembly and stability of the complex. Starting with Au-bearing materials and mixtures of square planar anions ($[PtX_4]^{2-}$, $[AuX_4]^-$, and $[PdX_4]^{2-}$, X = Cl, Br), this particular precipitation method recognized a theme for the selective isolation of Au in the form of $KAuBr_4$. According to life-cycle analysis, this approach has the potential to significantly mitigate the environmental risks connected with Au nanoparticle production. [8] After this initial finding, more research showed that mixing β-cyclodextrin (β-CD) with small molecule additives, such as dibutylcarbitol (DBC), produced almost complete precipitation of the metalate, surpassing 99 % [Fig. 7B]. [82] The same group achieved another Au recovery protocol based on rapid complexation of $[AuX_4]^-$ (X = Cl/Br) and cucurbit [6]uril (CB [6]) (Fig. 7 Ca). [83] Mixing CB [6] with $MAuX_4$ (X = Br/Cl, M = H/K) in aqueous solution resulted in the formation of yellow or brown precipitates. The presence of weak [O=C···X-Au] ion-dipole interactions and [C-H···X-Au] HBs contributed to this outcome (Fig. 7C(b)). Under optimal conditions, the efficiency of the precipitation process reached 99.2 %. The same group reported on the simultaneous co-crystallization and co-precipitation of $[PtCl_6]^{2-}$ dianions and CB [6], which was based on the selective recognition of these dianions via non-covalent bonding interactions on the outer surface of CB [6]. [84] Weak [C-H···Cl-Pt] and [O=C···Cl-Pt] interactions drove the selective $[PtCl_6]^{2-}$ dianion recognition. CB [6] was found to selectively isolate $[PtCl_6]^{2-}$ dianions from a mixture containing $[PdCl_4]^{2-}$, $[PtCl_6]^{2-}$, and $[RhCl_6]^{3-}$. In a separate study, two macrocyclic tetralactam receptors have been demonstrated by Smith et al. to be capable of selectively encapsulating anionic, square-planar bromide and chloride complexes of Pd (II), Pt (II), and Au (III). [85] The prearranged structure of both receptors was intended to complement their PM guests. The receptors offered a variety of arene-electron donors that interacted with the electropositive metal and HB donors that interacted with the surrounding electronegative ligands, rather than coordinating directly with

Table 2
Separation of PMs using various mechanisms with toxicity.*

Entry	Reagents	Targeted PMs	Mechanism	Toxicity of the reagent	Ref.
1	α-cyclodextrin	Au	Supramolecular recognition	Low	69
2	Cucurbit[6]uril	Au	Supramolecular recognition	Low	71
3	Cucurbit[6]uril	Pt	Supramolecular recognition	Low	72
4	Tetralactam receptors	Au, Pd, and Pt	Supramolecular recognition	Low	73
5	Niacin	Au	Electrostatic attraction and supramolecular interactions	Low	74
6	Simple tertiary diamide	Au, and Pt	Electrostatic attraction and supramolecular interactions	Low	75
7	Triamidoarene	La	Electrostatic attraction and supramolecular interactions	Low	76
8	Triphenylphosphine oxide	Au	Electrostatic attraction and supramolecular interactions	Low	77
9	Fe-BTC/PpPDA MOF	Au	Adsorption	Low	86
10	3D bio-MOF of L-methionine	Au	Adsorption	Low	87
11	COP-180	Au	Adsorption	Low	88
12	Porphyrin-phenazine-based polymers	Au	Adsorption	Low	89
13	rGO	Au	Adsorption	Low	91
14	Polymeric membranes comprised of the UiO-66 series	Pd and Pt	Adsorption	Low	92
15	Peralkylated pillar[5]arenes	Ag	Adsorption	Low	94
16	Pyridine-based porous organic polymers	Pd	Adsorption	Low	95

* Toxicity levels were assigned based on reported risks using PubChem and MSDS. We categorize chemicals as low (usually safe/biodegradable, e.g., water, ethanol), moderate (some dangers, managed with normal safety, e.g., thiourea, acetonitrile), and high (poisonous, carcinogenic, or persistent, e.g., cyanide, aqua regia, $SOCl_2$).

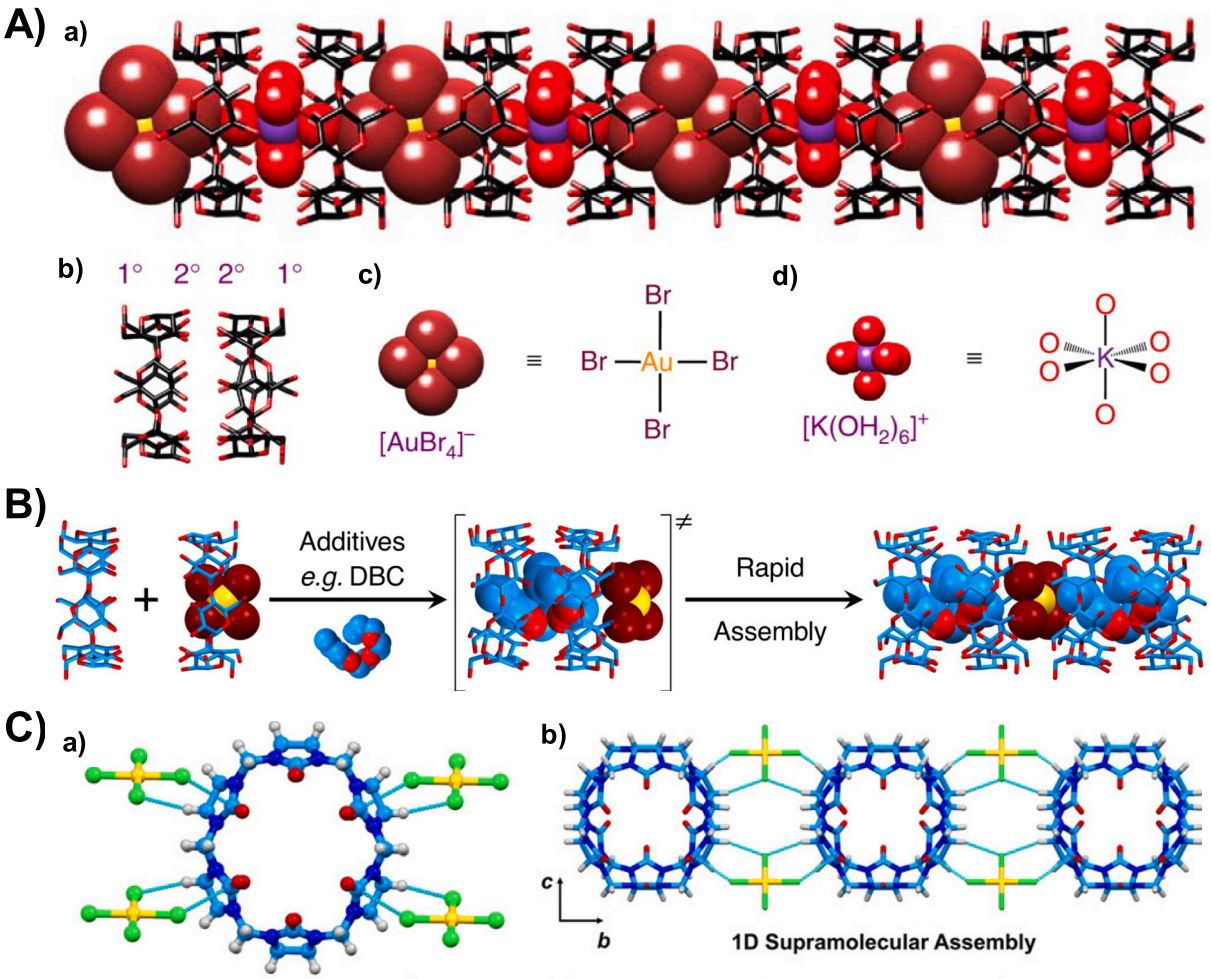


Fig. 7. A) a) A schematic presentation of a 1D structure extending along the c-axis in which the α-CD (**b**) tori form a continuous channel occupied by alternating $[AuBr_4]^-$ (**c**) and $[K(H_2O)_6]^+$ (**d**) ions. C, O, Br, Au, and K stand for black, red, brown, yellow, and purple, respectively (Adopted from ref. 81, Copyright 2013 Nature Publishing Group.) B) Graphical representation of the process of additive-induced precipitation of $[AuBr_4]^-$ anion using DBC additives to the β-CD. (Adopted from ref. 82, Copyright 2023 Nature Publishing Group.) **C)a)** The single crystal XRD structure of $HAuCl_4$ and CB [6] adduct. Interactions of CB [6] with four $[AuCl_4]^-$ anions via ion-dipole interactions and [C-H···Cl-Au] HB interactions. **b)** Assembly of a 1-D structure extending along the b axis, with two parallelly aligned $[AuCl_4]^-$ anions connecting adjacent CB [6] molecules. Cl, H, N, C, O, and Au stand for green, grey, blue, pale blue, red, and yellow, respectively. (Adopted from ref. 83, Copyright 2020 American Chemical Society.) (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

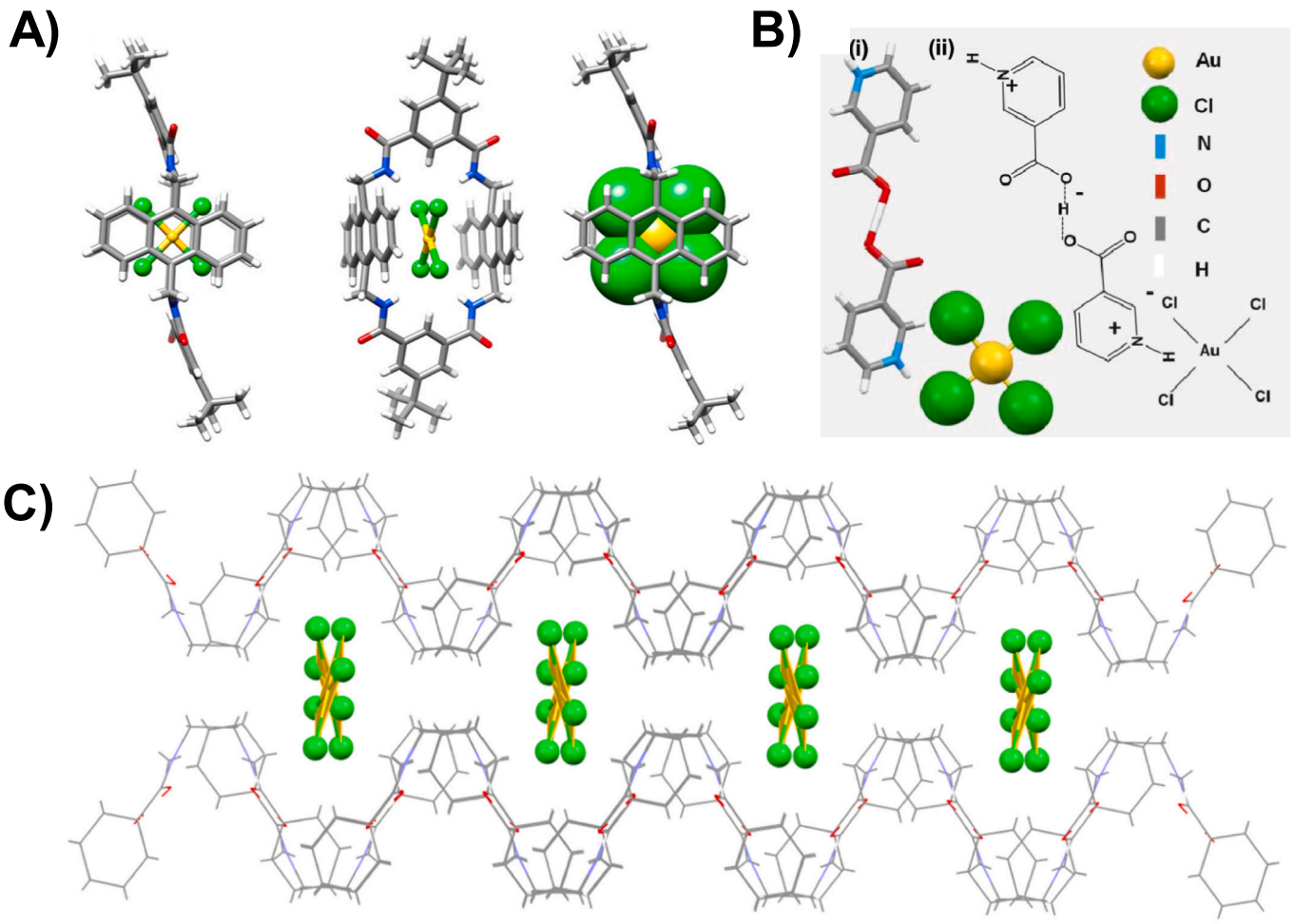


Fig. 8. A) Single crystal XRD structure of macrocyclic tetralactam receptors and $[AuCl_4]^-$. H, C, O, Cl, and Au stand for white, grey, red, green, and yellow, respectively. (Adopted from ref. 85, Copyright 2018 American Chemical Society.) **B) i)** Single crystal XRD and **ii)** ChemDraw structure of niacin and $[AuCl_4]^-$. (Reproduced from ref. 86, Copyright 2021 American Chemical Society.) **C)** Single crystal XRD structure of simple diamide and $[AuCl_4]^-$. H, C, O, Cl, and Au stand for white, grey, red, green, and yellow, respectively. (Adopted from ref. 87, Copyright 2021 Nature Publishing Group.) (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

the metal centre. The encapsulation of $[AuCl_4]^-$ within the ligand was validated by single crystal X-ray diffraction (SCXRD), demonstrating a unique method of supramolecular recognition (Fig. 8A).

By creating compounds with the biomolecule niacin, Pradeep et al. were able to precipitate aqueous $HAuCl_4$, resulting in the overall formula [2Niacin + H][$AuCl_4$], which was a very economical and environmentally benign approach for recovering gold (Fig. 8B). [86] This precipitation is selective for Au^{3+} in the presence of Ni^{2+}, Cu^{2+}, and Zn^{2+}, as well as alkaline earth (Mg^{2+}/Ca^{2+}) and alkali (Na^+/K^+) ions that are commonly found in metal waste streams. With further support from spectroscopic analysis, SCXRD investigations demonstrated that supramolecular interactions and electrostatic attraction were the driving forces behind the co-precipitation. This method made it possible to recover roughly 97 % of gold from e-waste that contained Au, Cu, and Ni in just two minutes. A simple tertiary diamide was shown by Love et al. to precipitate Au selectively from an acidic aqueous solution comprising 29 metals. [87] SCXRD showed the precipitate comprised an infinite chain of diamide cations interspersed with $[AuCl_4]^-$ (Fig. 8C). For [HL][$AuCl_4$] (L = diamide ligand), the methyl and phenyl substituents within the ribbon-like structure of the protonated diamides provide rhombohedral clefts that hosted the $AuCl_4^-$ guest through noncovalent interactions. When exposed to water, the precipitate released gold, allowing the ligand to be reused. At 2 M HCl, the diamide displayed excellent selectivity for gold, whereas gold, iron, tin, and platinum were completely precipitated at 6 M HCl, suggesting that this single variable could be used to regulate the selectivity of metal precipitation.

Recently, Love et al. reported a novel technique for the selective recycling of copper and gold which mitigated the need for organic solvents commonly used in solvent extraction procedures (Fig. 9 A and C). [88] The compound $[(TPPO)_4(H_5O_2)][AuCl_4]$ (9Bi) (designated **1**, where TPPO = triphenylphosphine oxide), was used to selectively extract gold from a multi-metal solution (containing Fe(III), Cu(II), Zn (II), Ni(II), Pd(II) and Pt(IV)) in HCl. Iron, zinc, and gold could be precipitated under controlled conditions by adjusting the acid concentration. Susequently, 2,3-pyrazinedicarboxylic acid (2,3-PDCA) was used to preferentially precipitate copper as the polymeric coordination compound $[Cu(2,3\text{-}PDCA\text{-}H)_2]n \cdot 2n(H_2O)$ (9Bii). Combining these two precipitation techniques allowed for the extraction of 99.5 % Au and 98.5 % Cu from an end-of-life computer processing unit. These precipitation methods show promise for future industrial applications in purifying Au and Cu from e-waste due to their high selectivity, convenience of use, and ability to recycle and reuse the precipitants.

4.2. Adsorption

Adsorption is a crucial method for recovering PMs due to its high selectivity, efficiency, economic viability, and environmental benefits. [89–94] It can capture target metals from complex mixtures or low-

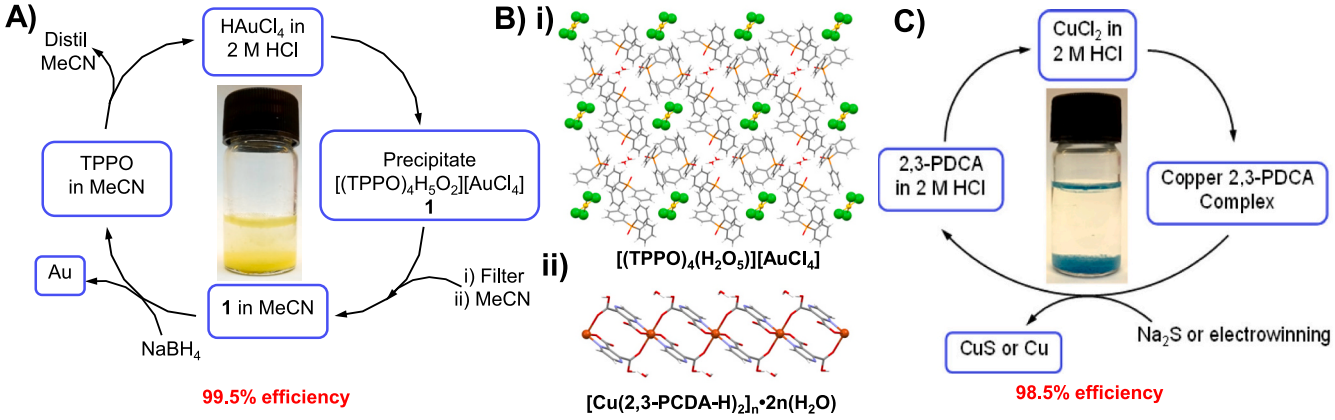


Fig. 9. A) Gold recycling using TPPO in 2 M HCl, followed by reduction of the Au(III) complex with $NaBH_4$ to generate Au(0) and recycling TPPO. **B) i)** SCXRD of **1** showing two pockets in which $H_5O_2^+$ and $AuCl_4^-$ reside, colour codes: P, Cl, green; orange; O, red; C, grey; Au, yellow; and H, white. **ii)** Crystal structure of [Cu(2,3-PCDA-H)$_2$]n•2n(H_2O). **C)** Recycling of Cu from 2 M HCl using 2,3-PDCA. (Reproduced from ref. 88, Copyright 2023 Wiley.) (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

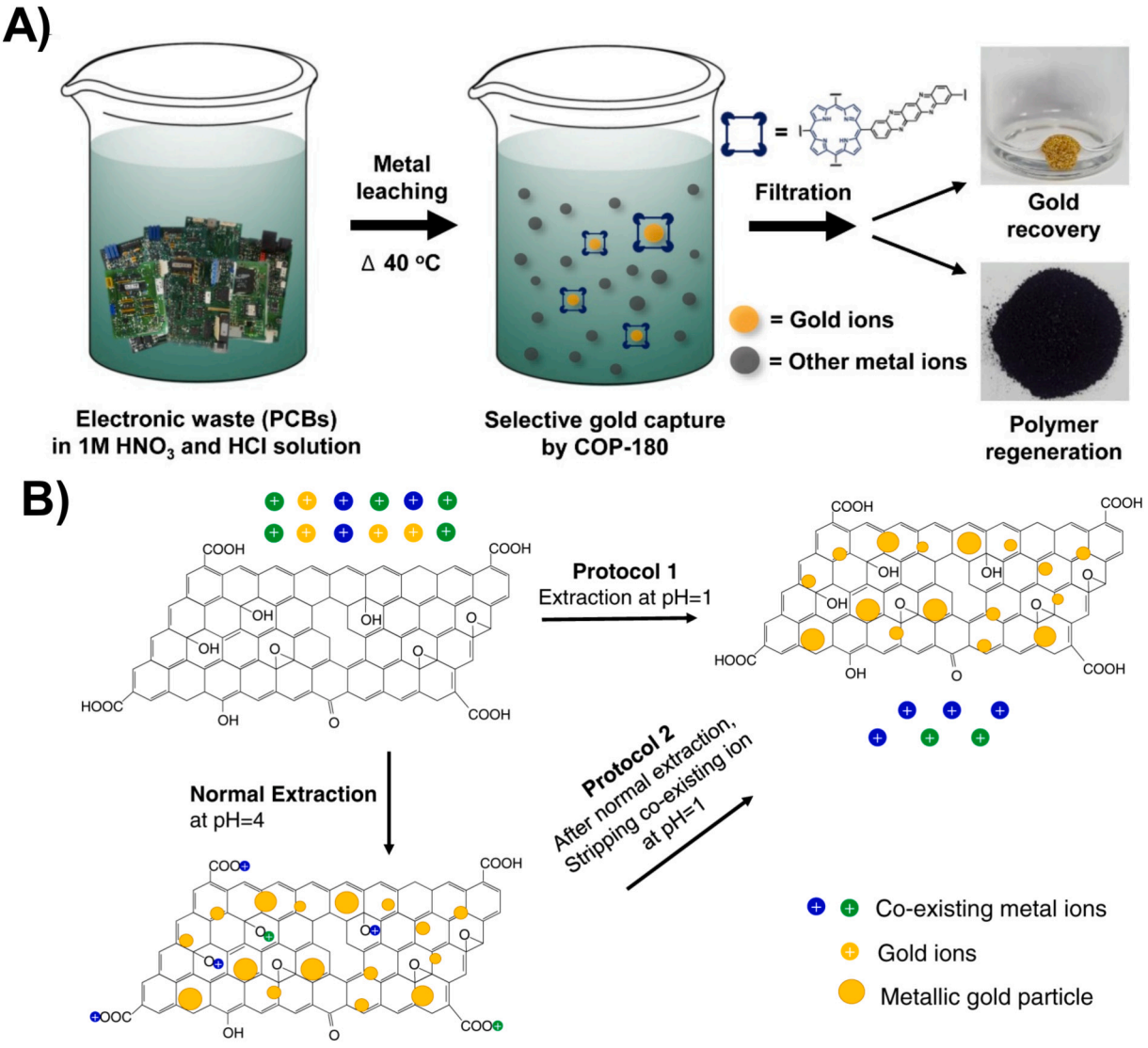


Fig. 10. A) Recovery of gold using COP-180 from PCBs. The gold was >99.6 % pure. (Adopted from ref. 99, Copyright 2020 National Academy of Sciences.) **B)** A schematic representation showing two additional protocols to enhance selectivity by modifying pH conditions. Co-existing ions are either prevented from adsorption (protocol 1) or removed later after Au reductive adsorption (protocol 2). (Adopted from ref. 102, Copyright 2022 Nature Publishing Group.) (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

concentration solutions, making it ideal for diluted sources like mine tailings or industrial wastewater. Many adsorption technologies can operate at ambient temperatures and pressures, so reducing operational costs. They are also more environmentally benign than traditional extraction methods, reducing the need for harsh chemicals. Adsorption techniques can be adapted to various scales and applications, making it suitable for various scenarios. Adsorption is the most common technology used in processes involving solid-liquid interfaces. [95]

Adsorption of $[Au(CN)_2]^-$ on activated carbon is a simple and cost-effective approach The technique benefits from the use of large activated carbon particles, which can be easily separated from the leach liquor via screening or filtration. [96]. Queen et al. reported a design blueprint for several highly porous composites comprising a metal-organic framework (MOF) template and redox-active polymeric building block. Fe-BTC/PpPDA [(BTC = 1,3,5-benzenetricarboxylate), (PpPDA = poly(para-phenylenediamine))] is one such MOF composite that has been shown to rapidly extract trace amounts of gold from a variety of complex water mixtures, including fresh water, wastewater, and seawater, as well as solutions used to leach gold from e-waste and sewage sludge ash. [97] The material had a remarkable removal capacity of 934 mg Au/g of composite, and it extracted Au at rates as little as 2 min from these complex mixtures. The composite efficiently concentrated Au to 23.9 K purity, and is highly cyclable. In another study, a new chiral 3D bio-MOF with functional channels derived from L-methionine was sensibly synthesized by Marta et al. [98] Au exhibits a strong attraction to sulfur-containing compounds, and the flexible thioether groups present in the channels enable the selective recovery of Au (III) and Au(I) species. This high selectivity continues even in the presence of other metal ions commonly present in e-waste, confirming efficient Au recovery. Alternatively, Hong et al. presented a porous polymer containing porphyrins (COP-180) that selectively captured PMs from e-waste leached solution (Fig. 10A). [99] The nanoporous polymer was produced in two steps using low-cost monomers and without the need of expensive catalysts, making it suitable for scalable production without compromising functionality. This reductive capture method recovered Au at ten times the theoretical maximum, with a record of 1.62 g/g. The adsorbed PMs on the porous polymer can be quickly desorbed and recycled for repeated batches because 99 % of the uptake occurred in the first 30 min. According to DFT calculations, energetically advantageous multinuclear-Au binding improved adsorption as clusters, resulting in rapid capture, while Pt capture still primarily occurred at single porphyrin sites. The same group reported Au and other PM recovery using a family of porphyrin-phenazine-based polymers from e-waste. [100] The performance of these adsorbents was shown to be affected by the pH of the solution and the illumination conditions, with the maximum capacity of 1.354 g/g being attained under nonstop UV exposure at acidic pH. Similarly, a 2D acridine-based COF was developed to detect and trap gold selectively and efficiently. [101] Li et al. recently devised a technique using reduced graphene oxide (rGO) to enable the selective extraction of Au ions at ultrahigh capacity, extracting more than 1000 mg of Au per gram of rGO at a concentration of 1 ppm. [102] The excellent gold extraction performance of rGO is due to its graphene domains and oxidized areas. The graphene domains actively reduce Au ions to metallic Au, whilst the oxidized regions boost rGO dispersibility, allowing for more effective adsorption and reduction of Au ions at graphene domains. Au can be selectively recovered by controlling the protonation of the oxidized portions of rGO, preventing contamination from the 14 other elements commonly found in e-waste. These findings were used to establish the scalability and cost-effectiveness of recycling Au from real-world e-waste via rGO membranes in a continuous flow-through process. A schematic representation is shown in Fig. 10B where two additional protocols were used to enhance selectivity by modifying pH conditions.

A collection of polymeric fibrous membranes comprising the UiO-66 series was synthesized, and the compatibilities between MOF and polymer were examined by Liu et al. [103] These membranes were tested for their abilities to adsorb and desorb Pt(IV) and Pd(II) from a strongly acidic medium. Strong π–π interactions between MOF NP and polyurethane (PU) with a high configuration of energy were responsible for the high chemical stability and strong acid resistance of polyurethane (PU)/UiO-66-NH_2. The effectiveness of these MOF membranes was established in both gravity-driven and continuous-flow systems, with outstanding recycling selectivity and performance. The membranes showed excellent adsorption/desorption performance, with no nanofiber breakage or aggregation, as well as no MOF NP leakage. The use of zero-valent iron nanoparticles on a large scale for gold enrichment and recovery from industrial wastewater was achieved by Zhang et al. [104] In these materials, a metallic iron core is surrounded by a thin layer of iron oxides/hydroxides in the core-shell structure of iron nanoparticles. The two nanocomponents work synergistically to separate, enrich, and stabilize metal ions such as Au, Ag, Ni, and Cu. Only a small amount of iron nanoparticles were required for the recovery of metals due to their advantages of small size, large surface area, and high reactivity.

Hua et al. were the first to present the metal ion-pair recognition using a pillarene. [105] Three peralkylated pillar[5]arenes (Fig. 11A) formed complexes with CF_3COOAg. X-ray crystallography of single crystals revealed that CF_3COOAg generated a unique dinuclear silver motif that intruded into the pillar[5]arene cavity within these structures (Fig. 11B). Multiple O···H–C and F···H–C HBs arise between the counterion and the pillar[5]arene host, in addition to π…Ag interactions, which were crucial in stabilizing and preserving the integrity of the host-guest complexes. Furthermore, through Ag ion-pair recognition, perethylated pillar[5]arene (EtP_5) acts as a solid absorbent capable of efficiently absorbing CF_3COOAg from solution (Fig. 11C), indicating its potential utility in precious metal recycling. Ma et al. demonstrated the adsorption of Pd using pyridine-based porous organic polymers (POPs). [106] POPs were created strategically; with the nitrogen site in the pyridine monomer acting as a Lewis base to enable coordination with Pd. This study investigated the effects of introducing an amino group and how positional variation affects the entire system for Pd capturing. Incorporating the amino group enhanced the nucleophilicity of the pyridine binding site, resulting in improved kinetics, excellent selectivity, optimal absorption capacity, and better chemical stability. Furthermore, placing the amino group at the ortho site aided in the formation of a more robust Pd complex, as evidenced by X-ray photoelectron spectroscopy and SCXRD. A schematic representation is shown in Fig. 11D where selective recovery of Pd was shown using pyridine-based POPs.

Researchers are motivated to develop biosorption technology because of its high repeatability and low sludge production, which helps to prevent the release of secondary pollutants. Various studies showed that PM ions can be selectively adsorbed by a variety of proteins. [107] Histidine-containing proteins, for example, interact specifically with Pd^{2+} and Au^{3+}. Consequently, Au^{3+} and Pd^{2+} can be successfully extracted from PM refining solutions using protein-rich biomass. According to Dodson's review, the selective extraction of PMs can be enhanced by surface and biochelate modification, or the choice of particular parent biomass. [108] A recent study investigated protein amyloid nanofibrils (AF) generated from whey, a by-product of the dairy industry, as a new adsorbent for gold recovery from e-waste. [109]

4.3. Solvent extraction

SX is an important method for recovering precious metals because of its selectivity, efficiency, adaptability, scalability, and environmental benefits. It can successfully separate metals such as Au, Ag, Pd, and Pt from complicated mixes or low-concentration solutions, increasing recovery yields while reducing losses. SX can withstand a variety of conditions, temperatures, and pressures, making it appropriate for both small-scale and large-scale mining projects. It also enables the selective removal of metals from loaded organic phases, improving recovery efficiency and lowering reagent use. SX can be environmentally benign,

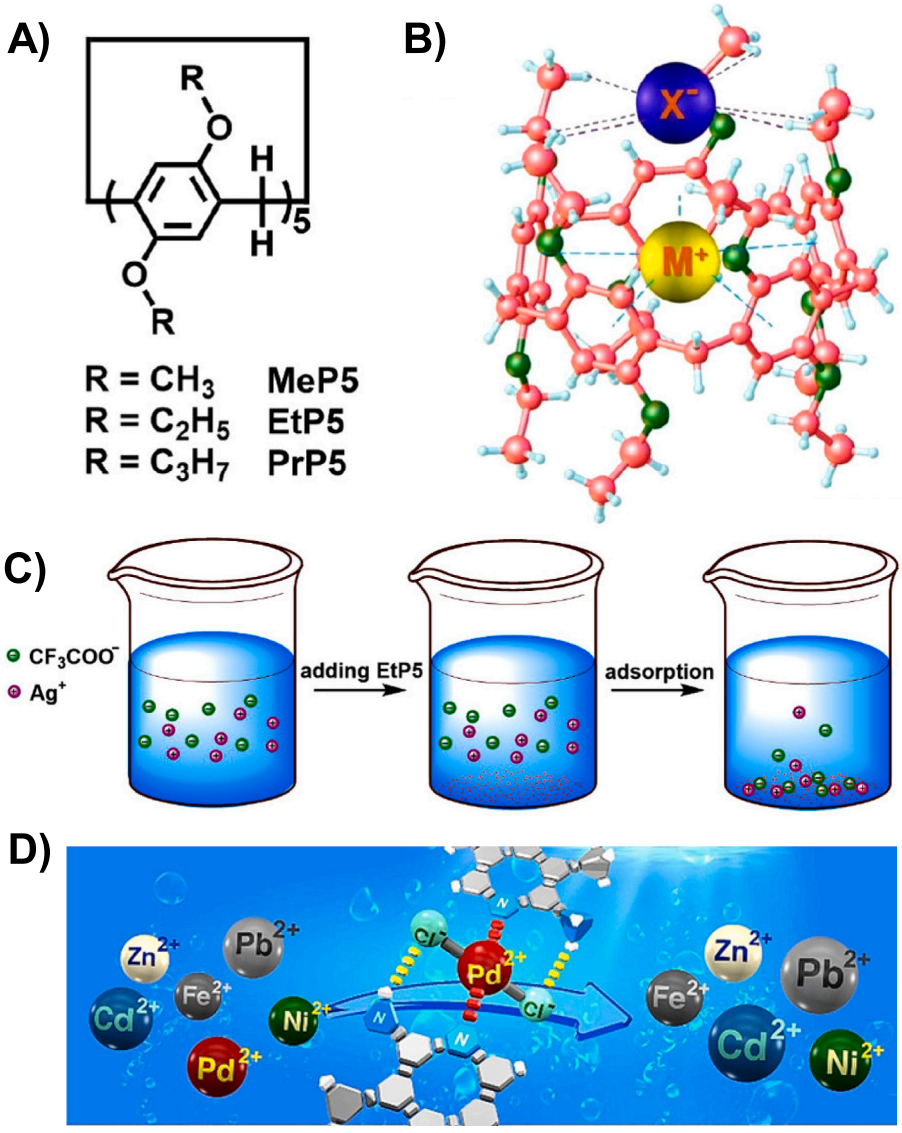


Fig. 11. A) Molecular formula of various peralkylated pillar[5]arenes used. **B)** The proposed structure of metal ion-pair recognition based on EtP_5. **C)** A schematic representation of adsorption of CF_3COOAg using treated EtP_5 powders in methanol by ion-pair recognition. (Reproduced from ref. 105, Copyright 2019 American Chemical Society.) **D)** A schematic representation of Pd^{2+} selectivity over other common ions using pyridine-based POPs. (Reproduced from ref. 106, Copyright 2020 Wiley.)

using fewer chemicals and producing less waste than other techniques. It works particularly well for digesting complicated ores and residues.

The effectiveness of the SX process is dependent on the efficiency and selectivity of the extracting ligand, and on achieving complete phase separation. Selectivity is engineered by utilizing coordination and supramolecular chemistry concepts, with customized ligands designed to bind selectively to target metal ions based on their charge, size, shape, and solvent interactions. [110–113] In commercial applications, solvents like dibutyl carbitol (DBC), methyl isobutyl ketone (MIBK), and 2-ethyl hexanol (2-EH) are routinely used to extract the halometalate $[AuCl_4]^-$ from gold ore halide leach solutions. Organic amides have been studied extensively as reagents for gold recovery by SX. Tertiary amides like DOAA (*N*,*N*-di-*n*-octylacetamide) and DOLA (*N*,*N*-di-*n*-octyllauramide) exhibit good selectivity for gold compared with base metals like Fe, Cu, Ni, and Zn and other PMs like Pt, Pd, and Rh. [114] In these instances, thiourea is required for the back extraction of gold, which could affect mass balance by forming some precipitation. The selective separation of gold as $[AuCl_4]^-$ from a mixed-metal solution obtained from HCl-leached PCBs was presented more recently using the simple primary amide 3,5,5-trimethylhexanamide (L1). [115] Protonation of L1 is crucial for selective gold extraction because it produces the neutral, hydrophobic complex assembly $[H(L1)_2][AuCl_4]$ that is stabilised via HBs and electrostatic interactions (Fig. 12A).

At 2.0 M HCl, this method extracted around 80 % of the gold from a complex mixture of metals, whereas the extraction of other metals such as Fe, Cu, and Zn, which are frequently found in PCBs, was low. One of the primary benefits of this approach is that the extractant concentration is low (0.1 M), and $[AuCl_4]^-$ can be transported into a pure aqueous solution using only water, which varies greatly from standard Au extractants like DBC and MIBK. According to further research, the analogous secondary (N-3,5,5-tetramethylhexanamide) and tertiary (N, N-3,5,5-pentamethylhexanamide) amides display better gold extraction capabilities when applied to single-metal solutions (Fig. 12B). [116] However, when used on mixed-metal solutions made from e-waste, these techniques showed low extraction efficiency, forming viscous third phases comprising Fe, Cu, and Sn. that did. More polar organic solvents inhibited the formation of third phases but lowered the selectivity for gold,. This study further underlined the significance of the

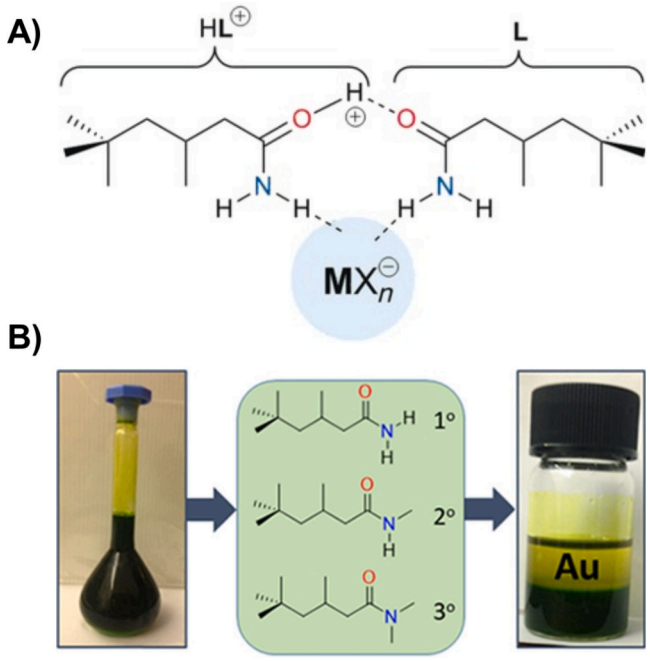


Fig. 12. A) Structure of the $[AuCl_4]^-$ and L1 for gold extraction. The presence of HBs and electrostatic interactions are shown between $H(L1)_2^+$ and $[AuCl_4]^-$ from MD calculations. (Adopted from ref. 115, Copyright 2016 Wiley.) **B)** Separating $[AuCl_4]^-$ using a primary, secondary, and tertiary amide. (Adopted from ref. 116, Copyright 2019 American Chemical Society.) (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

ability of the amide group to transfer a stabilize the proton in the organic phase as $H(L)_2^+$ (where L = amide) and showed that water plays an insignificant role in the formation organic phase assembly.

Recently, ILs are becoming promising candidates for the extraction of PMs from e-waste using a SX process. The hydrophobic ILs [Bmim][PF_6], [Bmim][Tf_2N], and Cyphos 101 were used as alternative extractants for Ag and Au from an aqua regia e-waste leach solution and were highly effective, with Au extraction efficiency exceeding 90 %. [117] Recovery of Ag in [Bmim][PF_6] and Cyphos 101 was greater than 93 %, whereas no recovery was seen in [Bmim][Tf_2N]. Recovery of Cu ranged between 60 % in [Bmim][PF_6] and 99 % in Cyphos 101. Unfortunately, the mechanism of the process was not explored in detail. Several ILs containing bis(trifluoromethanesulfonyl)imide (Tf_2N^-) or halide anions and cations 1-octylpyridinium, 1-methyl-1-octylpyrrolidinium or 1-octyl-3-methylimidazolium, were used to extract tetrachloroaurate or tetrabromoaurate anions from acidic media. By combining Au complexes in aqueous solutions with water-soluble halide ILs, the extraction f Au anionic species from aqueous solutions was first investigated. A liquid phase or a solid precipitate, similar to a hydrophobic IL with tetrahaloaurate anions, was produced as a result of this process. [118] The liquid-liquid extraction of anionic Au complexes with hydrophobic ILs was further investigated. Gold was successfully recovered from aqueous solutions regardless of pH or type of IL used. The extraction procedure involved an anion exchange, with Tf_2N^- (Y) anions replacing the Au complex (eq. 5). The IL is written as Cat^+Y^-.

$$Cat^+Y^- + KAuX_4 + HNO_3 \rightarrow [Cat][AuX_4] + K^+Y^- \quad (5)$$

Various reports by the same group described IL-based methods for separating PM complexes. [119–122] In the first step, Au was extracted from water using the hydrophobic IL 1,2-dimethyl-3-octylimidazolium bis(trifluoromethylsulfonyl)imide. Pt was subsequently extracted from a solution in KSCN by employing 1-methyl-3-octylimidazolium bis(trifluoromethylsulfonyl)imide. [123]

4.4. Other methods

Electrochemical recovery transports metal ions to electrodes, where they deposit without the need for additional redox agents. [124] Electrodeposition, electrodialysis, electrocoagulation, and electrosorption are the four most used electrochemical recovery procedures. [125–127]

Liu et al. established a sustainable electrodeposition technique for selectively recovering Ag—Pd alloy from polymetallic e-waste leachates containing Cu, Ni, Ag, Bi, and Pd. [128] The viability of this strategy was determined using linear sweep voltammetry. Controlling the applied voltage resulted in a high-purity Ag—Pd alloy with recovery of both metals over 97 after 5 h from 0.5 mol/L HNO_3 at 0.35 V. A chronoamperometry study demonstrated that Ag—Pd electrodeposition occurred in a 3D instantaneous nucleation and growth model, consistent with Scharifker-Hills theory, and resulted in a solid solution. Halli et al. used electrochemical principles to extract metals from complex solutions on pyrolyzed carbon using the electrodeposition-redox replacement technique. [129] The Pt/Ni deposition ratio on the pyrolyzed carbon electrode reached around 900 in the improved synthetic Ni electrolyte with 60 g L^{-1} Ni and 20 ppm Pt. This novel approach produced outstanding recovery results. According to Korolev et al., this method for selective PM extraction involved electrodepositing nonferrous metal ions with a steady current, which then interacted with PM ions in solution, reducing them to their elemental state under open-circuit conditions. [130] The redox replacement step between electrodeposition cycles allowed for the effective recovery of PMs in this procedure. Cotty et al. developed an electrochemical redox-based approach that used a polyvinylferrocene (PVF) electrode to selectively extract and concentrate Au from simulated mining ores and e-waste. [131] The PVF electrosorbent was highly selective for $[Au(CN)_2]^-$, with a 20:1 selectivity ratio over other ions such as Ag, Cu, Ni, and Fe. The $[Au(CN)_2]^-$ ion transferred charge to the ferrocene binding site, resulting in selective binding and oxidation. The electrochemical properties of the ferrocene sites enabled the recovery of approximately 99 % of the Au in just five minutes, yielding a product purity of 88.4 %. The PVF recovery technique was evaluated for cost-efficiency and performance, using just 15 kJ g^{-1} Au, which is less than 1/75 of the energy required by standard activated carbon-in-pulp methods. An asymmetric electrochemical method was developed to recover Au and Cu from CPU leached solutions. [131] Polyaniline (PANI) was electropolymerized on carbon cloth (CC), resulting in electrostatic interaction, complexation, and reduction characteristics. Even when competing metal ions were present, the CC/PANI anode selectively removed Au. In this case, $[AuCl_4]^-$ dissolved in acid was attracted to the anode and spontaneously reduced to Au. Cu was simultaneously deposited on the CC electrode in the cathode chamber. This unique technique recovers both Au and Cu, offering vital insights into the simultaneous extraction of numerous precious metals.

A recent study demonstrated the effective use of a polymer inclusion membrane (PIM) incorporating aminocarbonylmethylglycine as an extractant to efficiently isolate Au from an e-waste leached solution. [132] Here, gold is transported from the leach solution to an aqueous strip solution containing thiourea via the extractant-embedded PIM, avoiding the need for an organic solvent in the traditional SX method.

In terms of development, precipitation and adsorption technologies are among the most established and effective approaches, providing great selectivity while having a low environmental impact. SX is still important and flexible in the industrial sector, but its reliance on organic solvents and phase separation issues necessitates the use of greener solvents such as ILs and PIM. Newer techniques, such as supramolecular host-guest encapsulation, bio-inspired adsorption, and electrochemical separation, show great promise in terms of selectivity and energy efficiency, but they need to be tested on bigger scales. Additional research should focus on fine-tuning selectivity in complex leachates, enhancing the long-term stability of adsorbents and membranes, assuring scalability, and conducting LCA to validate sustainability claims. Section 6 provides a broader comparative examination of various strategies.

5. LCA study for PM recovery

Despite being advertised as sustainable and selective, precipitation-based PM recovery technologies are rarely analysed by systematic LCA. Where such assessments exist, they clearly indicate the environmental benefits of recycling secondary sources over primary mining. Conventional gold mining emits 16 t CO_2 eq per kg due to low ore grade and cyanide leaching. [133] Recovery from high-value waste by hydrometallurgical techniques like aqua regia results in significantly lower emissions of only 0.058 t CO_2 eq per kg of Au. [133] Pt manufacturing produces 13,500 kg CO_2 eq per kg, whereas recycling reduces this to 694 kg CO_2 eq per kg, a reduction of more than 95 %. [134] LCA studies for Pd estimate that mining and refining emit around 3880 kg CO_2 eq per kg of Pd, [135] but recovery from spent catalysts reduces this burden from 9670 to 1962 kg CO_2 eq per kg Pd, resulting in an 80 % reduction. [136]

Recycling, despite its high chemical and energy requirements, can cut CO_2 emissions by one to two orders of magnitude compared with mining. However, most studies using recovery methods such as precipitation, SX, and adsorption solely report on recovery efficiency and selectivity, without taking into account broader environmental factors. To make these methods a truly sustainable separation approach, future research should include LCA that determines CO_2-equivalent emissions, cumulative energy demand, waste generation, and reagent biodegradability. These assessments will enable the methods to be benchmarked against mining and alternative recycling technologies, as well as giving strong proof of their environmental benefits. In recycling, the process must not generate waste that itself becomes unmanageable (new metrics are proposed in this context). [137]

6. Discussions on comparative assessment of PM recovery technologies

The trade-offs between scalability, sustainability, and efficiency are highlighted by the comparative study of PM recovery systems (Table 3). Because of their high selectivity and throughput, respectively, traditional methods like pyrometallurgy and conventional hydrometallurgy are still used extensively. However, they are less desirable in the context of sustainable chemistry because to their high energy consumption, toxic reagents (such as cyanide and aqua regia), and the production of hazardous by-products.

Mechanochemistry and biometallurgy, on the other hand, appear to be more environmentally benign alternatives with low energy requirements and emissions. While promising technologies, their slow kinetics, restricted scalability, and lack of industrial adoption currently limit their widespread application. Similarly, adsorption and precipitation are environmentally acceptable, low-energy options with good metal selectivity, but also have potential scalability issues when applied to complex waste streams.

Thiosulfate and thiourea leaching are greener alternatives to cyanide-based hydrometallurgy, with lower toxicity and controlled effluents. However, reagent instability and low economic success prevent broad adoption. Mild solvents such as DES and ILs, are gaining popularity due to their versatility, recyclability, and low environmental effect. However, high costs and difficulties in synthesis/recycling remain important barriers.

Emerging approaches like photochemical and electrochemical leaching provide selective recovery pathways. Photochemical approaches have low reagent toxicity but are limited by solvent volatility, whereas electrochemical processes enable direct electrodeposition of

Table 3
Comparative assessment of PM recovery technologies.

Method	Applicability / Feedstock	Targeted Metals	Energy Requirement	Reagent Toxicity	Waste / By-products	Remarks	Key References
Pyrometallurgy	Broad (ores, e-waste, catalysts)	Au, Ag, Pt, Pd, Rh	Very high (furnaces, smelting)	High (risk of dioxins & halides from plastics)	Slag with residual metals & flue gases	High throughput, not sustainable	[138,139]
Mechanochemistry	Composites, powders	Au, Pd, etc.	Low-moderate	Low	Minimal emissions	Slow, Not scalable, emerging, sustainable	[68,69]
Conventional hydrometallurgy (cyanide, aqua regia, halogens)	Ores, e-waste, jewelry scrap	Au, Ag, Pt, Pd, Rh	Moderate-high	High (CN^-, HNO_3, Cl_2)	Wastewater, toxic residues	High selectivity & yield, not sustainable	[6]
Thiosulfate & thiourea leaching	Gold & silver-rich feeds	Au, Ag	Moderate	Low	Less toxic effluents	Greener cyanide alternatives, limited adoption	[6]
Mild solvents dissolution (DES, ILs, etc.)	Catalysts, e-waste, mixed wastes	Ag, Au, Pd, Pt	Moderate	Low	Mostly recyclable, low gaseous emissions	Eco-friendly, tunable, costly, synthesis & recycling issues	[48,49 and 55]
Photochemical leaching	*E*-waste, catalysts	Au, Pt, Pd	Low-moderate (UV/visible source)	Low	Catalyst residues	Selective but issue with the organic solvent volatility	[41]
Electrochemical leaching	E-waste, catalysts	Au, Pt, Pd, Rh	Moderate (electricity-driven)	Low	Spent electrolytes (recyclable)	Enables direct electrodeposition	[71]
Biometallurgy (microbial, biosorbents, plants)	Low-grade ores, wastewaters	Au, Ag, Pt, Pd	Low-moderate	Low	Biodegradable residues	Cheap, sustainable, slow kinetics	[72–75]
Precipitation	E-waste, catalysts	Au, Ag, Pt, Pd	Low	Low	Ligand recyclable	Cheap, eco-friendly, not scalable for all methods	[82–88]
Adsorption (Carbon, Resins, MOFs, Biomass)	Leachates, dilute waste streams	Au, Ag, Pt, Pd	Very low	Low	Adsorbent regeneration waste	High selectivity, renewable adsorbents emerging	[100–106]
Membrane & ion exchange	Dilute leachates, wastewater	Au, Pt, Pd	Low-moderate	Low	Concentrated brines; fouling	Good separation, but fouling issues	[132]
Solvent extraction	E-waste, catalysts	Au, Ag, Pt, Pd	Low-moderate	Moderate (organic solvent)	Recyclable	High selectivity, less greener	[114–116]

*Energy requirements are grouped according to reported process demands: Low for near-ambient conditions (<150 °C, atmospheric pressure). Moderate for moderate heating/pressurization (150–400 °C); High for energy-intensive operations (> 400 °C or high-pressure procedures). [140] Toxicity levels were assigned based on reported risks using PubChem and MSDS. We categorize chemicals as low (usually safe/biodegradable, e.g., water, ethanol), moderate (some dangers, managed with normal safety, e.g., thiourea, acetonitrile), and high (poisonous, carcinogenic, or persistent, e.g., cyanide, aqua regia, $SOCl_2$). [141,142]

PMs, although energy consumption and electrolyte management must be tuned.

Membrane and ion exchange techniques can effectively separate PMs from dilute leachates with low toxicity and moderate energy needs. However, membrane fouling and concentrated brine production present operational issues. Similarly, solvent extraction remains a strong technology with great selectivity, but its reliance on hazardous organic solvents undermines its sustainability.

Overall, the Table 3 demonstrates a paradigm shift from traditional, high-impact methods to sustainable, low-toxicity solutions. While no single method emerges as universally desirable, future research should prioritize hybrid approaches that consider efficiency, selectivity, and the environment, as well as the ability to scale up promising sustainable technologies like mechanochemistry, biometallurgy, precipitation and mild solvent systems.

7. Conclusion and future perspectives

PM recovery is transitioning from old hydrometallurgical techniques to more sustainable chemistries. Established techniques, such as oxidative leaching, pyrometallurgy and conventional hydrometallurgy and SX, continue to be prevalent in the industry, but their reliance on hazardous reagents and large energy inputs restricts their sustainability. Emerging techniques, such as bio-based dissolution, DESs and mild dissolution, mechanochemistry, photocatalysis, supramolecular separations and precipitations, provide more environmentally benign options, although challenges with kinetics, selectivity, and scale-up remain.

A thorough evaluation of these techniques finds that IL-based separation, supramolecular recognition, and adsorption materials have good selectivity, while bioleaching and mechanochemistry have low chemical inputs and energy needs; however, none of these approaches meet all of the conditions for industrial feasibility. This emphasizes the importance of hybrid process designs that integrate the benefits of many methods.

Future progress will be determined by three factors: (i) the systematic integration of LCA, eco-toxicity, and energy metrics into method evaluation, (ii) the use of computational chemistry and machine learning to design selective ligands and predict process viability, and (iii) the advancement of techno-economic analysis and pilot-scale demonstrations to connect laboratory advances with industrial adoption.

Unlike previous surveys, this review offers a unique perspective by combining current and new ideas within a sustainability framework. It focuses not only on chemical advances, but also on the metrics and strategy required to transform PM recovery into scalable, ecologically acceptable solutions that correspond with circular economy and net zero objectives.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Kasper Moth-Poulsen reports financial support was provided by European Research Council. Kasper Moth-Poulsen reports a relationship with European Research Council that includes: funding grants. Abhijit Nag reports a relationship with European Commission Marie Sklodowska-Curie Actions that includes: funding grants. If there are other authors, they declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

A.N. and K.M.P. acknowledges the Marie Skłodowska-Curie Actions–European Commission post-doctoral grant (REWCHEM, Grant agreement ID: 101152892) and Sustain-a-Print project (Grant agreement ID: 101070556) from European Commission for research funding. K.M.P. acknowledges funding from the European Research Council (ERC) and the Catalan Institution for Research and Advanced Studies (ICREA). A.N. and A.Q. would like to express their gratitude for the support received from AMCC and chemistry department at Khalifa University of Science and Technology. A.N., C.A.M., and J.B.L would like to acknowledge the support received from the EPSRC-GCRF (grant number EP/T020504/1) and the University of Edinburgh. T.P. acknowledges funding from the Centre of Excellence (CoE) on Molecular Materials and Functions under the Institution of Eminence scheme of IIT Madras.

Data availability

Data will be made available on request.

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