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Advances and Challenges in Metal Separation

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Abstract

Technologies for selective metal separation from water and wastewater are currently attracting strong research interest as a pathway to greater sustainability. The chemistry of metal separation processes is critical for understanding the mechanisms of selectivity and making the technologies viable. This paper discusses current advances and challenges in metal separation technologies from chemical point of view and proposes how they should be approached in the future.

Keywords:

Introduction

Contaminant removal and resource recovery from water and wastewater are now attracting attention from researchers and industries with the aim of achieving economic and environmental sustainability¹. Target contaminants and resources include water, gases, salts, metals, and organic compounds, which are separated from the aqueous phase to reduce environmental impacts or to be recycled and used as valuable resources. Since these materials are completely dissolved in water, research on separation technologies such as precipitation, adsorption, filtration, and electrochemical separation are critical. By using these technologies, recent studies have been moving toward selective separation of a target material for both contaminants that are difficult to remove and pure resources for industrial use^{2,3}. This Perspective focuses on metal separation technologies for contaminant removal such as mercury and chromium, and resource recovery such as lithium.

Metal contaminants are severe problems for human and environmental health. They mainly originate from industrial plants and mining sites where wastewater treatment is not appropriately implemented. Metal cations such as Hg^{2+} and metal oxyanions such as CrO_4^{2-} and AsO_4^{2-} are highly mobile in the aqueous phase and toxic to humans⁴. To immobilize and separate them from wastewater, the most efficient methods include precipitating them by neutralization, attaching them onto adsorbents by simple adsorption or electrochemical means, or excluding them by size or charge with filtration. Metal separation is also important because metals in water and wastewater can be recycled for industrial use instead of exploiting mined ores. For example, technologies for lithium extraction from brine have been rapidly developed in recent years in response to increasing demand for electric vehicle batteries⁵. To be recovered for industrial use, metals should be selectively separated from water and purified to satisfy an industrial standard. In this case, unlike contaminant removal, various combinations of separation technologies must be considered, and the process must be designed toward a marketable end-product.

What kind of technologies can we use to achieve these goals? Chemical precipitation is a conventional method of separating metals from water; however, it is not very selective compared to other technologies, and it produces a large amount of sludge as solid waste⁶. Filtration via membrane technologies is widely used, and enables the removal of even small metal cations such as Na^+ , K^+ and Li^+ ⁷, with partial selectivity in some realizations. Another conventional but robust technology is adsorption. It includes ion exchange resins⁸, metal-organic frameworks (MOFs)⁹, covalent organic frameworks (COFs)¹⁰⁻¹³, and porous organic polymers (POPs)¹⁴⁻¹⁶. Easy, inexpensive operation makes adsorption attractive for wide application at many sites. Careful investigation of chemical reactions taking place and chemical structural features of the materials used in these technologies is necessary to develop technologies for economic and environmental sustainability. Therefore, in this work, we discuss chemical phenomena and mechanisms in metal separation from the aqueous phase, and we outline advances and challenges from the chemical point of view.

Technologies for metal recovery: science and application

Here we describe major research directions that have effectively addressed metal recovery from water and wastewater and are widely used both in academic and industrial work. These include chemical precipitation, membrane filtration, adsorption, and electrochemical methods. Table 1

summarizes advantages and challenges of each method, as well as the general metals which can be extracted by the methods.

Chemical precipitation

Chemical precipitation is by far the most widely used process in industry. Precipitation can remove various kinds of heavy metals (Cu^{2+} , Zn^{2+} , Cr^{3+} , Pb^{2+} , Hg^{2+} , and Cd^{2+}) depending on design and preparation of chelating materials, due to its simple operation and low cost^{17–21}. During precipitation processes, chemicals react with metal ions to form insoluble precipitates, then to be separated from the water by sedimentation or filtration. The precipitation method is particularly effective for highly concentrated contaminants (> 1000 mg/L). Sulfide and hydroxide reagents are often used for conventional precipitation processes^{21,22}. However, this method often generates large volumes of low-density sludge; and fouling by precipitates on the surface of filtration membranes inhibits efficient operation of the plant. When water contains high salinity, the situation gets worse. The buffering effect of seawater²³ is problematic for chemical precipitation. To precipitate low concentrations of metal cations in seawater, a high concentration of hydroxide is required to surpass the solubility product of a target precipitate. Unfortunately, the equilibrium between carbonate and bicarbonate ions in seawater brine offsets the addition of hydroxide reagents, which significantly increases the amounts of chemical reagents to be added. Even if metals are precipitated by adding large amounts of reagents, it is difficult to separate each element because heavy metals usually precipitate simultaneously after addition of chemical reagents. Light metals such as calcium and magnesium in seawater also consume chemical reagents by forming precipitates such as calcium carbonate and magnesium hydroxide, and precipitate with heavy metals, which makes chemical precipitation from seawater more challenging. The high salinity of seawater brine can also affect the process, by either increasing or decreasing solubility, depending on metal species²⁴. Overall, chemical precipitation is not preferred for heavy metal recovery from seawater and its relevant brines.

We note that seawater has been a major source of magnesium. A typical process first precipitates magnesium hydroxide by addition of strong base, following which acid is used to make magnesium chloride, and the pure magnesium is then recovered by electrolysis. In the past, the US produced almost half of all magnesium by precipitation. While some production of this type continues at the Great Salt Lake in Utah²⁵, a more economical method is in place in China by producing magnesium from ores such as dolomite²⁶.

Membrane filtration

Membrane filtration is frequently used in combination with other methods such as precipitation and deposition. This combination can remove not only heavy metals, but also suspended solids and organic compounds. The advantages of membrane filtration include high efficiency for removing literally all kinds of heavy metal ions and easy operation^{27–30}. Downsides of the method include high cost and difficulty of recycling related to materials fouling. Various types of membrane filtration methods such as ultrafiltration, nanofiltration, reverse osmosis, and electrodialysis can be employed, depending on the size of the contaminants^{31,32}.

Nanofiltration can separate monovalent metal ions from divalent or multivalent metal ions depending on ion size and charge³³. For example, lithium ions can be separated from dilute brine by nanofiltration³⁴; however, the performance of nanofiltration is limited by high salinity of

seawater brine because high osmotic pressure requires much energy to operate. Due to the high demand of lithium for the battery industry, various types of specific membranes for lithium have been proposed. Despite the general lack of selectivity for a specific ion in nanofiltration, metal ions such as lithium can be selectively recovered by ion-imprinted membranes³⁵⁻³⁹ and ion-sieve membranes^{40,41}. Electrodialysis using ion exchange membranes can also separate metal ions into different streams. This technology, which can be used for removal of divalent metal ions to purify seawater⁴², also enables the extraction of metals such as lithium chloride from high salinity water such as seawater brine⁴³. By using a monovalent selective ion exchange membrane, only monovalent metal ions such as sodium and potassium ion pass through the membrane to the cathode side and divalent metal ions such as magnesium and calcium ions are retained (Figure 1a)^{44,45}.

Lithium ions can be separated from calcium and magnesium ions by the same mechanism (Figure 1b). Further, not only divalent light-metal ions but also divalent heavy-metal ions can be separated from brines by electrodialysis, which has not been studied well yet.

In recent years, new membrane operations have been growing, such as membrane distillation (MD) and membrane crystallization, which might contribute to the development of interesting processes for extraction, purification, and crystallization of various minerals from the sea. MD is a thermally-driven process in which a hydrophobic porous membrane separates warm and cold solution streams. The hydrophobic nature of the membranes prevents the passage of liquids through the pores while allowing the passage of volatile solvents as a vapor⁴⁶. The high recovery factors that can be reached by MD, the rejection of almost 100% of the nonvolatiles present in the feed, and the greater fouling resistance to organic solutes and some inorganic solutes such as sodium chloride^{47,48} are interesting properties. The possibility to produce crystals in appropriate final structure, such as specific polymorphs, is also very attractive.

The treatment of brines discharged from seawater reverse osmosis (SWRO) desalination plants has emerged as a potential opportunity for the MD Crystallization technology, realizing in principle the strategy of a zero-liquid discharge. Appropriate softening processes have been described for removing Ca^{2+} , sulfates, and carbonates and producing Epsomite crystals at a very high level of purity from nanofiltration brines. The possibility to produce also highly concentrated LiCl solutions, approaching those used in LiCl crystallization, has been also demonstrated by vacuum MD^{49,50}.

In summary, membrane filtration is appropriate for separation of monovalent and divalent metal ions in seawater and for purification of separated salts. However, the lack of selectivity for a specific metal (except select ion-imprinted or ion-sieve membranes) is a bottleneck that should be addressed for metal recovery using membrane technologies.

Adsorption

Adsorption is indisputably one of the most popular methods for ion removal, and has attracted considerable attention due to its simplicity, convenience, and efficiency. Parameters such as pore size, internal structure, and functional groups determine sorption kinetics and uptake capacity to selectively remove specific compounds from contaminated effluent^{51,52}. For the treatment of industrial wastewater, the most suitable approach should be selected according to parameters such

as removal efficiency, working pH, initial ion concentration, and environmental impact. Economic considerations, such as capital investment and operational costs, are also important. From a scientific standpoint, the design and synthesis of new, effective adsorbent materials that are stable and reusable guide research directions. This has enabled very specific and selective interaction between various heavy metal ions and chelating groups. For this reason, adsorption has been the most studied ion capture method in academia over the past decade. Therefore, we examine adsorption in greater detail, including the advantages and disadvantages of representative materials, in order to point toward new research directions and application pathways.

Adsorption is superior to other techniques for removal of contaminants in terms of comparatively low cost, simplicity of set up, ease of operation, facile regeneration of adsorbents, and low generation of harmful byproducts. Traditional adsorption methods include activated carbon, clay, zeolites, and ion exchange resins, which are often thiol-functionalized to enhance performance⁵³⁻⁵⁵. Specifically, activated carbons have been the most popular due to low cost and abundance, although the kinetics and uptake are not satisfactory for highly concentrated or very dilute effluents⁵⁶⁻⁵⁹.

To overcome the limitations of slower kinetics and lower uptake, recent studies focus on making highly porous materials. Such materials can be built from periodic frameworks, which have inherent porosity and can be functionalized on demand. Actively-researched highly porous materials include metal-organic frameworks (MOFs)^{60,61}, covalentorganic frameworks (COFs)⁶², and porous organic polymers (POPs).

MOFs are made by assembling inorganic units and organic linkers by coordination bonds (Figure 2). The surface area values of such MOFs typically range from 1000 to 10,000 m² g⁻¹, potentially surpassing those of traditional adsorbents. Superior surface area together with tunability in building units, and their pore size, functionality, architectures, and compositions, together make them good candidates for adsorption of small molecule gas or solid contaminants^{63,64}. Synthetic versatility has enabled functionalization of electron-rich atoms such as sulfur (which has strong binding affinity to electron poor ion cations such as Hg²⁺, Cd²⁺, and Pb²⁺) on the backbone of MOFs for higher uptake of target molecules^{65,66}. MOFs are equipped with luminescence for sensing mechanism⁶⁷ and made into composite form for enhanced practicality⁶⁸. Overall, with versatile and powerful bottom-up synthesis, MOFs showcase fast kinetics, high uptake capacity, and selectivity, which clearly overcome limitations of traditional adsorbents. However, their instability in water limits their wide application in aqueous environments. Such organic-inorganic hybrid materials are even less stable in strong acidic conditions, making MOF-type adsorbents hard to recycle⁶⁶.

Alternatives to MOFs, COFs which only involve light organic elements (C, N, O, B, and Si) through strong covalent bonds (B–O, C–N, B–N, and B–O–Si), have emerged as an important class of porous materials with the equal advantages of designed structures, tunable pore size, and functionality. COFs via condensation reactions of building units show precise, well-defined structures with crystallinity, with comparatively high surface area, which can be greater than 4000 m² g⁻¹⁶⁹. Importantly, the strong covalent bond nature significantly enhances the materials' stability in harsh conditions⁷⁰.

The development of COFs inspired other organic networks, the so-called POPs, which, although not crystalline, are still highly porous and stable. More diverse synthetic coupling reactions including Sonogashira–Hagihara, Suzuki–Miyaura, Yamamoto, or Eglinton couplings are employed to make high performance POPs with additional thiol chelating groups^{70–72}. However, still cumbersome chemical treatments by strong acid or base are required to recycle the materials^{10,11,73,74}. Such intensive chemical processes are not desirable from a sustainability perspective¹⁰. For recovery of elements, sintering of the adsorbate-adsorbent complex is used, yielding highly pure ions^{75,76}. However, this method results in one-time use of the adsorbents. Instead of the traditional methods for recycling adsorbents and recovering ions, which required intense use of energy and chemical in an exhaustive way, we need highly accessible and convenient methods that will preserve environmental resources in a sustainable manner.

Electrochemical separation

Electrochemical methods for separations encompass a broad range of processes, ranging from traditional electrocoagulation and electrodeposition, to advanced materials for electrosorption and dialysis. Electrowinning and electrorefining of metal ions on an electrode surface through the reduction of metal cations, followed by their recovery, have been classical methods in hydrometallurgical fields for extraction of valuable ores⁷⁷. Direct conversion of metal cations into elemental metal, with facile recovery, is an attractive feature of this method. However, this approach involves relatively large capital investment and a costly supply of electricity, which has thus far hindered broad application of electrochemistry for ion recovery. Stringent environmental regulations and a strong scientific desire to discover new methods for efficient and effective ion recovery continue to motivate research in this field^{78,79}.

In general, electrochemically-based separations aim to provide a modular, sustainable, and potentially low energy alternative to conventional thermal processes. At the core of this mission, selectivity plays an important role. The recent investigation of a variety of selective electrosorption systems have pushed the applications and core mechanisms beyond traditional electrodeposition. Recently, selective electrosorption and release of ions (Figure 3a) has emerged as an attractive platform that overcomes the drawbacks of traditional adsorption methods^{80,81}. Through the use of electrochemically responsive redox-active materials, selective ion-capture and release can be achieved for a variety of target compounds of interest, in the presence of competing species and modulated solely by electrochemical potential. These ions can be either valuable compounds such as transition ions, valuable organics or biomolecules, or toxic pollutants from water and organic streams.

Redox-processes involve the transfer of electrons and the subsequent oxidation or reduction of a compound⁸³. When promoted by electrochemical potential, these processes can be channeled for energy storage, catalysis, or, as recently discussed, electrosorption processes. Conducting and redox-active polymers have been an attractive platform because of their tunable electronic structure, and also their ease of immobilization onto conductive surfaces. Whether it is by electropolymerization/electrodeposition or simple dip-coating, porous nanostructures with high capacitance and ion accessibility can be generated with these conducting polymers^{84,85}. Metallopolymers, in particular, can be powerful selective adsorption platforms due to their fast redox-reactions and selective adsorption mechanisms. Poly(vinyl)ferrocene and other ferrocene-derived polymers have shown strong affinity towards a variety of charged organic molecules,

which could be captured and released by specific chemical bonding ^{80,86}, as well as neutral contaminants, based on swings between hydrophobic and hydrophilic states ^{87,88}.

Within the context of ion recovery, these selective principles have been applied to transition metal oxyanions, with remarkable ion-adsorption capacity and kinetics such as in the case of arsenic and chromium ⁸². Not only were these harmful contaminants captured from solution, such as in the case of chromium, but they were also remediated at the electrode by electroreduction. Hexavalent chromium was shown to be transformed to its trivalent state, thus providing a means for value-added recovery. Arsenate was also found to be selectively removed. In both cases, these systems relied on a strong-charge transfer mechanism as the basis for selectivity over 20-fold competing electrolyte, including real wastewater matrices.

The redox-active receptors can be designed by pure organic means⁸⁹, such as in the case of functionalization of polyaniline materials with sulfur containing functional groups for the capture of mercury (Figure 4). In all these cases, the affinity of these active materials can be easily altered by application of a redox potential. While the natural state of the active materials, for example, allows for positive binding affinity to contaminants (heavy metal ions), a change in potential can trigger a repulsive charge to the materials that releases the contaminants. By constructing active materials with nanoscale morphology, kinetics can increase; and by functionalization of additional chelating groups, uptake capacity can be enhanced. Another example of functionalized electrodes for selective ion recovery is the harvesting of uranium from seawater by alternating current, in which the strong affinity of amidoxime adsorbents towards uranium is enhanced by the process of electrochemically-mediated deposition ⁹⁰.

Using different principles, electrochemical interfaces can be used in addition to extraction with ionic liquids to facilitate the removal of a range of valuable ions ⁹¹. Through the use of task-specific ionic liquids, ions can be extracted from a solution and up-concentrated. Subsequently, deposition onto a conductive surface from the ionic liquid allows for recovery of the metal, and recyclability of the ionic liquid ⁹². This overcomes traditional challenges in the use of solvent extraction, and reduces losses from the recovery of the ions from the ionic liquid.

Another unique advantage of using electrochemical systems is that certain conducting materials have powerful sensing capabilities. For example, the electrochemical activity of redox-active adsorbents is dictated by the number of free electrons in the materials. Donation of the electrons from the adsorbent to cationic metallic ions will cause a decrease in the adsorbents' electrochemical activity, while removal of the ions allows recovery of the electrochemical activity ⁹³. Finally, careful electrochemical engineering provides a unique role in reducing energy costs and providing synergistic processes ^{94,95}. In some cases, careful tuning of the redox-process on the counter-electrode has been found to drive ion-selectivity, suppress parasitic side-reactions, and enhance anion and cation uptake. In applications such as the case of hexavalent chromium capture, synergistic side-reactions and pH changes can help promote desirable electrochemical transformation, such as reduction of transition metals without added chemical reagents ⁸².

Overall, in terms of water economy and sustainability, electrochemical control of capture and release of contaminants, which allows recycling of capture media without the use of excess amounts of strong reagents, is a highly promising platform. Electrochemical approaches have the

advantage that adsorbents can become reusable without external chemical input. A wealth of organic, inorganic, and organometallic redox-active receptors are available, and matching them with specific charged ionic species will enable wide application of electrochemical systems. Along the way, discovery and implementation of binding mechanisms will facilitate the application of the method⁸³.

Regarding chemistry and materials for element extraction, we identify five criteria that ultimately lead to significant challenges that must be overcome in order to have safe and effective outcomes: high uptake, fast kinetics, long-term stability, selectivity, and recyclability (Figure 5). High uptake and fast kinetics are prerequisites for adsorbent materials. While most traditional adsorbents have some basic level uptake and kinetics, the other three criteria are dependent upon the design and synthesis of the adsorbent materials. Although porous materials can effectively remove large amounts of contaminants rapidly with good selectivity and stability, electrochemical means show greater potential to satisfy all five criteria. However, while electrochemical approaches present obvious benefits over traditional chemical methods, the chemical and mechanical robustness of the electrodes needs to be extensively studied and improved, and further studies of engineering design and scaleup are required before practical implementation of these technologies in industry is feasible.

Concluding Remarks

Metal separation technologies have been essential for contaminant removal and resource recovery from water and wastewater, and metal recovery can enhance the economic viability and environmental sustainability of water treatment systems. This paper reviewed and discussed these technologies from a chemical point of view, with perspectives on future directions. While chemical precipitation is not particularly selective for metal recovery, membrane filtration has potential for selective separation of monovalent and multivalent ions. Membranes are not suitable for the extraction of specific metal ions except for ion-imprinted or ion-sieve membranes. In terms of selectivity for a specific metal ion, adsorption with properly modified materials such as MOFs, COFs and POPs can take up a target metal selectively. To improve and facilitate the catch and release of a desired metal by adsorption, electrochemical separations can be used. However, significant technology gaps still confront metal separations. A detailed understanding of fundamental redox-ion binding is still needed, and the scale-up of electrochemical systems for practical, large-volume flow applications requires efforts in both engineering design and materials chemistry for the optimization of mechanical robustness, and electrochemical stability. Finally, while laboratory-scale approaches for each of these distinct methods for selective metals recovery exist, the integration of multiple approaches (e.g. adsorption and electrochemical separation) could lead to enhancements in the performance and efficiency of the overall process for practical industrial operations.

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Table 1. The different processes that can be used for element extraction. The major advantages and current limitations of these methods are based on data and observation from the literature.

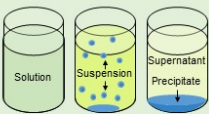
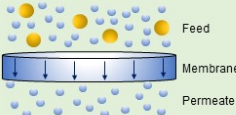
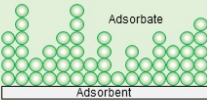
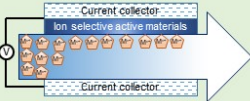
	Methods	Main advantages	Major challenges	Metals extractable
	<p>Chemical precipitation Chemicals react with contaminants to either form insoluble precipitates or change solubility of contaminants. Supernatant collected for reuse.</p>	<ul style="list-style-type: none"> • Effective for removing concentrated contaminants • Simple and inexpensive, therefore widely used 	<ul style="list-style-type: none"> • Generates large volume of sludge • Need extra steps to clean chemicals used for precipitation 	<p>Hg²⁺, Cd²⁺, Pb²⁺, Cu²⁺, Cr³⁺, and Zn²⁺</p>
	<p>Membrane filtration Pressure driven separation of particles larger than membrane pore size. Most effective when particles are sufficiently large.</p>	<ul style="list-style-type: none"> • Removes both organic and inorganic contaminants • High selectivity is often obtained when the correct size filter is used 	<ul style="list-style-type: none"> • Removes both organic and inorganic contaminants • Only efficient when used in combination with other methods • Surface fouling makes reuse difficult 	<p>Hg²⁺, Cd²⁺, Pb²⁺, AsO₄³⁻, Zn²⁺, Ni²⁺, Cu²⁺, Cr³⁺, and Ni²⁺</p>
	<p>Adsorption Porous adsorbent adsorbs contaminants. Kinetics and uptake decided by internal structure and composition.</p>	<ul style="list-style-type: none"> • Economical and facile to operate • High cost-effectiveness 	<ul style="list-style-type: none"> • Recycle of adsorbents and recovery of contaminants not facile • Adsorption kinetics and uptake capacity vary 	<p>Hg²⁺, Cd²⁺, Pb²⁺, Ag⁺, Au³⁺, Mn²⁺, Co²⁺, Cu²⁺, and K⁺</p>
	<p>Electrochemical separation Charge controlled electrodes can capture and release contaminants. Design of chemical specificity between electrodes and contaminants is key.</p>	<ul style="list-style-type: none"> • Selectivity obtained by design of materials interactions • Facile regeneration of materials and recover of contaminants 	<ul style="list-style-type: none"> • Large capital investment needed • Often challenging to obtain high uptake and fast kinetics 	<p>Hg²⁺, Cd²⁺, Pb²⁺, Cu²⁺, and Cr³⁺</p>

Figure Captions.

Figure 1. Electrodialysis with ion exchange membranes. (a) Configuration of electrodialysis module with monovalent selective ion-exchange membranes. Adapted from Zhang et al. ⁴². (b) Schematic diagram of ion migration in one-pair compartments of selective electrodialysis. Adapted from Guo et al. ⁴³. CIMS: cation exchange membranes, ACS: anion exchange membranes.

Figure 2. Porous adsorbents: MOFs and COFs. (a) Synthetic scheme for tetrahedral cage motif MOF and its interaction with mercury. Adapted from Yee et al. ⁶⁵. (b) Synthetic scheme for COF through condensation reaction of monomers and post-functionalization to include additional thiol chelating groups. Adapted from Sun et al. ¹¹.

Figure 3. (a) Scheme for redox-mediated electrosorption process for selective ion-recovery ⁸¹. (b) Application of redox-electrosorption to chromium & arsenic adsorption ⁸². (c) DFT optimized geometry for chromate adsorption onto ferrocene. (d) Selective adsorption of hexavalent chromium onto PVF-functionalized redox-electrode.

Figure 4. Reversible sorption and desorption of ions using conducting polymer. (a) Schematic representation of sulfur-functionalized conducting polymer nanofiber geometry and its selective interaction with mercury ions upon change of potentials. (b) Time-dependent cyclic voltammograms of the conducting polymer depends on the amount of mercury ions adsorbed. Adapted from Kim et al. ⁸⁹.

Figure 5. (a) The primary challenges for achieving efficient metal recovery from seawater and industrial water are high uptake, fast kinetics, long-term stability, selectivity, and recyclability. (b) A radar chart summarizing minimum satisfactory levels, current performance level of adsorption methods and electrochemical separations, and desired future directions that, can be achieved by combining advantages of adsorption and electrochemical separations as discussed (e.g. electrosorption).

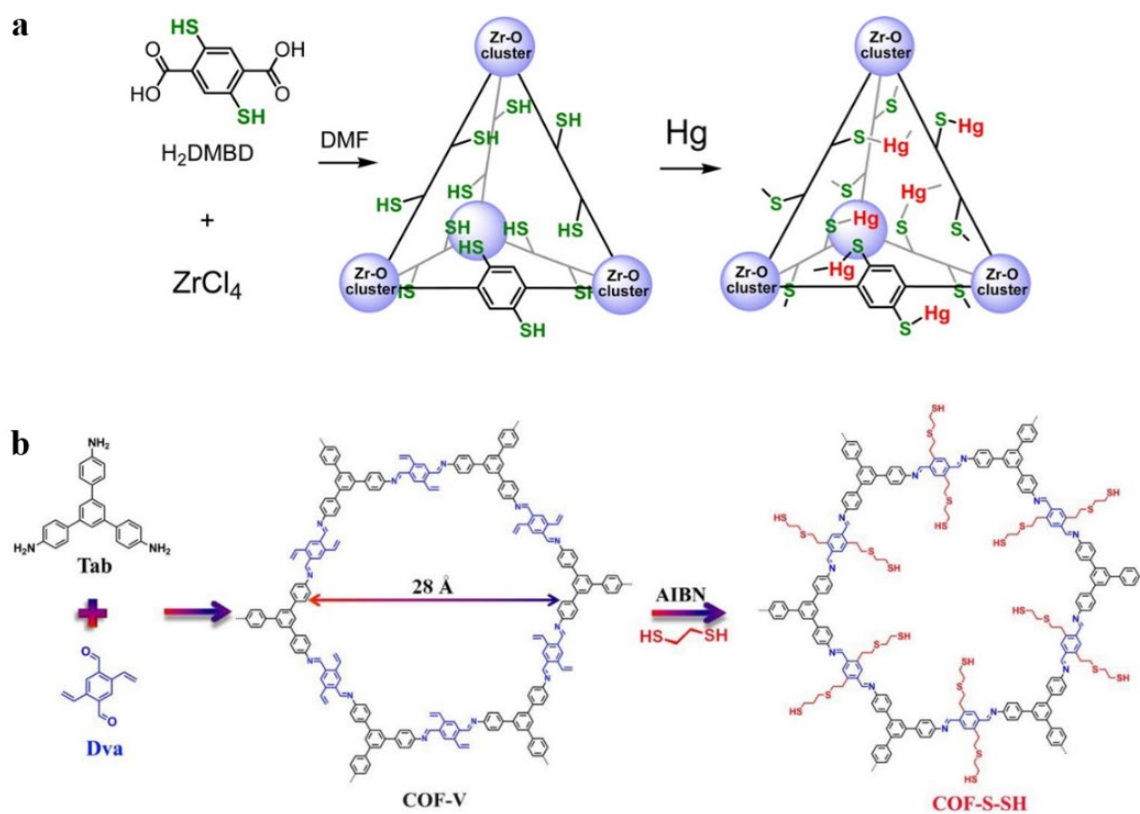


Figure 2.

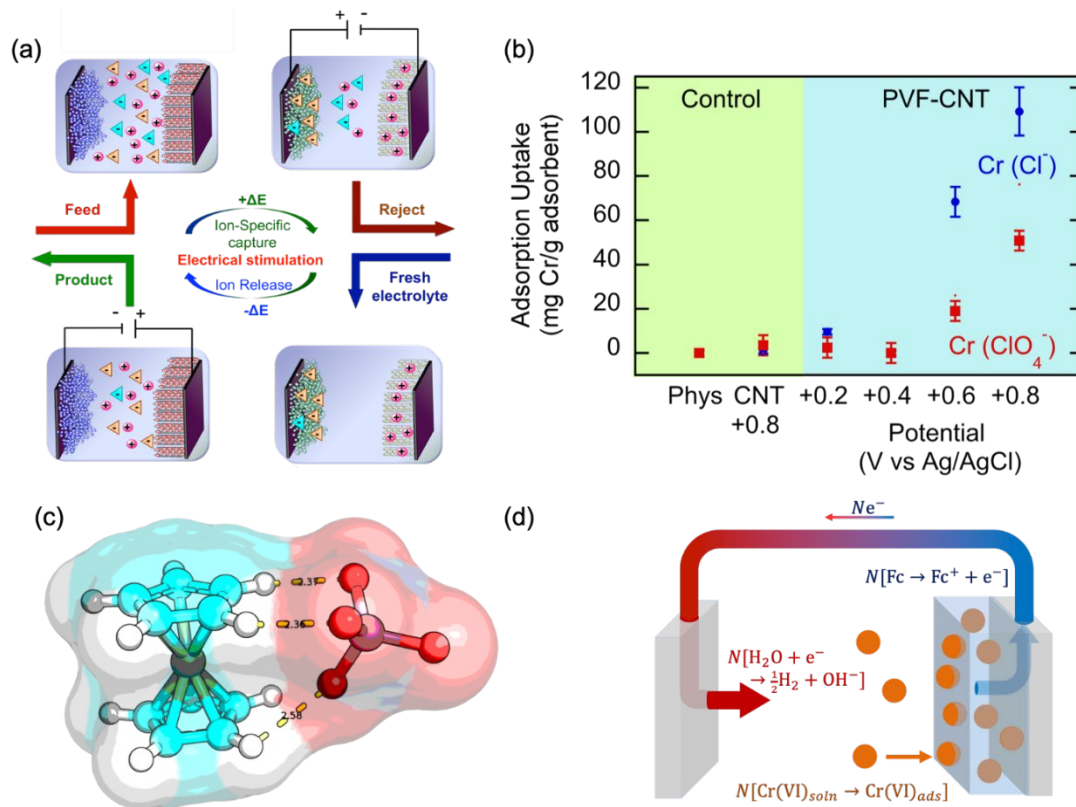


Figure 3.

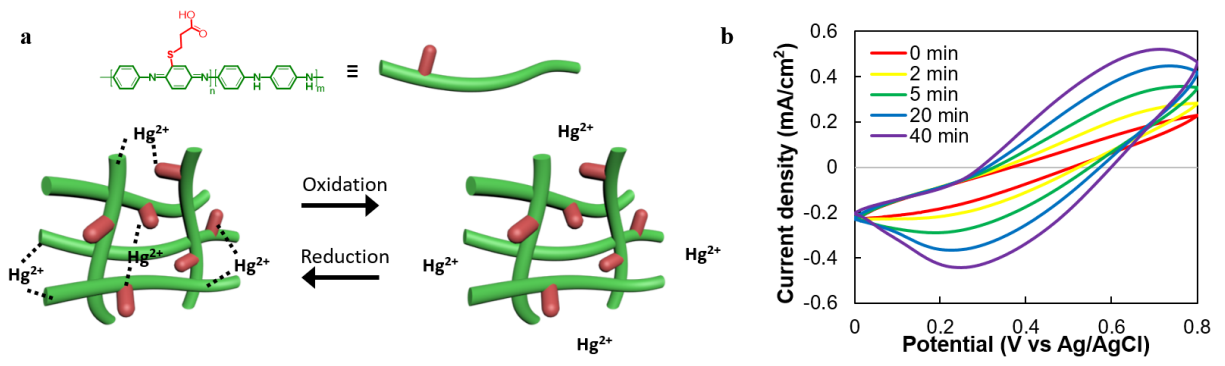


Figure 4.

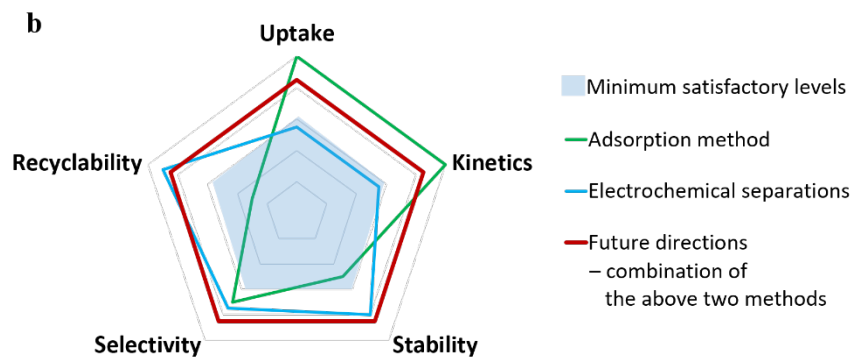
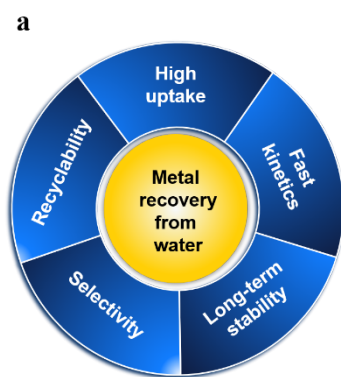


Figure 5.