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Remediation and recycling of inorganic acids and their green alternatives for sustainable industrial chemical processes†

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The uses of inorganic acids as a solvent, leachant, and lixiviant are widespread in many commercially important industrial processes, including mining, metallurgy, metal-processing, nuclear fuel reprocessing, pickling, cleaning, leaching, etching, electroplating, metal-refining, and many others. Unchecked disposal of acidic waste into the environment poses serious threats to the flora and fauna as well as results in corrosion of metallic structures, undesired changes to the pH of soil and water, and many other problems. Because of their potentially harmful effects on the environment, acid recovery from acidic waste solutions is a crucial problem in addition to the resource preservation. Therefore, greener solvent based chemical processes have been gaining increasing attention in recent years. However, it is unclear whether the greener solvent will replace the inorganic acids in the foreseeable future. At present, developing efficient and sustainable methods for recovering and recycling inorganic acids from industrial effluents offers a co-operative approach to lessen the serious ecological disturbances, over exploitations of resources, and financial effects. The recovery and recycling of acids from acidic waste solutions has been proposed using a variety of methods such as solvent extraction, ion exchange resin, membrane technology, or hyphenated technologies which is a combination of two or more integrated technologies. The membrane technology is one option for recovering and recycling of inorganic acids that is easy to use, affordable, and environmentally benign. This is due to the small and straightforward equipment needed, better throughput, and lack of chemical requirements or secondary waste production during the acid recovery process. It is important to note that hyphenated technologies are very effective for zero waste discharge, do not require any further post-processing or chemical agents, along with other advantages inherent to the selected methods. The many procedures for recovering acids and water from waste solutions documented in the literature will be examined in this review, along with their benefits and drawbacks, as well as any problems that need to be fixed before they can be used on an industrial scale.

Environmental significance

Acidic waste products from the mining, resin regeneration, hydrometallurgy, electroplating, and numerous chemical industries pose risks to the environment's flora, fauna, and ecological stability. A huge amount of aqueous acidic wastes is thought to be produced annually worldwide. Thus, creating sustainable green technology and recycling acid from watery waste streams are both crucial from an environmental perspective. Membrane technology, which produces no secondary waste and is effective in recovering acids with high purity, is a promising approach. One of the most popular membrane technologies is based on diffusion dialysis using anion exchange membranes. For the commercial use of membrane technology, a number of challenges must be handled, probably in combination with other suitable methods for the circular economy leading to zero waste discharges.

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1. Introduction

Numerous industries such as the hydrometallurgy, electroplating, acidic vanadium leaching, and aluminum foil industries, and nuclear fuel fabrication and reprocessing facilities frequently use inorganic and organic acids as a solvent, leachant, or lixiviant.[1–4] Therefore, it is not possible to prevent the generation of extremely toxic and corrosive acidic waste water, the discharge of which is strictly forbidden.[5–7] However, acidic

wastewater is frequently released into the environment untreated, endangering both human health and the ecology. The most often used inorganic acids in various industrial operations are H_2SO_4, HNO_3, HCl, and H_3PO_4.

In metal processing industries such as electroplating, one of the important stages in the metal finishing process is washing metal surfaces using an acidic solution. This is typically done by "pickling" or submerging the metal in an acid bath. Pickling is a crucial stage in the hot-dip galvanizing process because it removes oxidized layers from the surface of fabricated steel parts.[8,9] For pickling, various acids such as HCl, HNO_3, or H_2SO_4 are employed. The used pickling solutions are regarded as hazardous wastes because of their corrosive nature, high acid level, and metal contents. The Environment Protection Agency (EPA) hazardous waste list states that spent pickle liquor with 5–10% free acid and 5–15% ferrous ions is categorized as hazardous waste.[10] The cost and environmental impact of the hot-dip galvanizing industry are significantly impacted by way of disposal of the pickling solution. In several industries, zinc is often produced *via* electrowinning by eliminating the contaminants from the used electrolytic solution through a bleed.[11,12] A typical bleed composition is 15 to 16% H_2SO_4, 5 to 10% $ZnSO_4$, 4.5 to 5% $MgSO_4$, 1 to 5% $MnSO_4$, 200 ppm chloride, 300 to 400 ppm Ca, and trace amounts of Fe, Ni, Co, Cu, and Cd.[13] Therefore, $ZnSO_4$ and H_2SO_4 are the two most important components, and these can be recycled into the process if contaminants are eliminated. Also, in the metal plating and finishing industries, aluminum anodizing is a key process in which aluminium parts are anodized and etched using sulfuric acid (H_2SO_4) and sodium hydroxide (NaOH). Along with this, the oxide scale from the surface of metals is removed using the pickling procedure with acid baths.[14] Therefore, these industries also produce waste streams with significant flow rates of alkali and acid.[15,16]

The manufacturing of semiconductors and liquid crystals involves a number of steps, such as resistor coating, light exposure, etching, resistor removal, and rinsing, all of which produce significant amount of acid waste. The aluminum–molybdenum alloy or silver placed on the glass substrate is dissolved during the etching process using mixed acids that include acetic acid, nitric acid, and phosphoric acid. The amount of waste acid produced during the etching and cleaning procedures is increasing fast due to the rapid growth of the semiconductor and liquid crystal industries in Korea, totaling to over 90 000 tonnes in 2005.[17] At present, it would probably continue to rise unless an effective treatment method is implemented. The acid waste (etching waste) generated by the use of the etching solution often contains metals like Al and Mo together with 50–70% phosphoric acid, 2–10% nitric acid, and 1–10% acetic acid.[18] These numbers vary based on the etching process's reaction conditions and reaction states.

In the nuclear, chemical, and metallurgical industries, HNO_3 is employed as a dissolving agent.[19–22] Due to the usage of nitric acid in dissolving, extraction, fuel manufacturing, and other processes, the nuclear industry's fuel reprocessing is also one of the main sources of high concentrations of nitric acid in aqueous waste. Additionally, a significant amount of radioactive corrosion and fission products, including Mo, Zr, Sr, Cr, Ni, Mn, Y, La, Ce, Pr, Nd, and Sm, are present in this highly acidic waste.[23] The major objective of the remediation for such radioactive waste is to produce these radionuclides with a high specific activity in a small amount of acid, and nitrate-free solution that can be safely and readily stored or immobilized in suitable matrices.[24]

Apart from this, acid mine drainage (AMD), a problem that affects mining companies worldwide, results in one of the major uncontrolled release of acid to the environment.[25] AMD is a pervasive and potentially harmful source of contamination

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from mine sites even after mining has been stopped. When rocks and sediments containing sulfide minerals like pyrite and pyrrhotite are exposed to the atmosphere in an oxidizing environment, AMD waters are created, which are best described as low pH, high metal, and high sulfate-bearing waters.[26–29] Both biotic and abiotic, or inorganic chemical oxidation processes, can result in pyrite oxidation. Degradation of biological and abiotic materials can be brought about by oxygen (direct oxidation) or oxygen plus iron (indirect oxidation).[30] Apart from sulfuric acid soil, these mining sources also include piles of ore and rock debris, open cuts, tailing pits, and dams.[27] AMD also contains iron, aluminum, and zinc as well as other potentially toxic elements. Regular releases of untreated AMD carry the risk of contaminating nearby water sources and sediments, which would be detrimental to biodiversity.[31] The United States, Canada, Australia, and South Africa all appear to have sizable mining operations.[32–41] The United States (US) Forest Service forecasts that AMD from coal mining in the eastern US will contaminate more than 6000 km impacted by acid discharges from 20 000 to 50 000 mines in the western half of the country, which exposed forest lands to these discharges.[33–35] AMD has been attributed to be due to a significant number of abandoned mine sites and the enormous volume of pyrite-bearing tailings from coal and gold mines in these countries. However, AMD contains acid in only pH ranges in contrast to the acid waste generated during various industrial processes which have high acidity generally in the mol L^{-1} range.

At present, the inorganic acids cannot be separated from these industrial manufacturing operations. The generation of these inorganic acids raises a number of questions, nevertheless, about their potential effects on the environment and sustainability.

2. Implications of acid discharges to environment

Inorganic acids can significantly damage the environment due to their corrosive nature and are potential for pollution, if not handled properly. The major environmental effects associated with inorganic acids are described below.

2.1. Ecological impacts

Inorganic acids, when released into water bodies can cause water pollution by lowering the pH of water. Acidic water can harm aquatic ecosystems, disrupting the balance of aquatic organisms and impairing their growth, reproduction, and overall health.[29,30,42,43] Acidification can harm these organisms directly or indirectly by disrupting food chains and altering the composition of aquatic communities.[44–48] Aquatic organisms, such as fish, amphibians, and invertebrates, are particularly sensitive to changes in pH. Acid rain, caused by the deposition of acid-forming pollutants, can further impact terrestrial ecosystems, including forests and sensitive plant species.[48] Acidic water can also leach metals such as aluminum and mercury, and other contaminants from soils and sediments. These potentially toxic elements are generally hydrolyzed above

pH 4 and remain as precipitates/insoluble substances under normal environmental conditions. These metal contaminants, however, turn very soluble at pH 3, and as a result, their concentrations in ground water may rise above the level that is not acceptable for use by humans. This may further exacerbate water pollution.[49,50]

2.2. Corrosion and infrastructure damage

Inorganic acids are highly corrosive substances that can damage the infrastructure, including pipelines, storage tanks, and equipment.[51–53] Acidic substances can corrode metals, leading to structural failures and leaks.

2.3. Air pollution

Inorganic acids can release toxic fumes and gases when exposed to air, particularly at higher temperatures.[44] For example, sulfuric acid can release sulfur dioxide (SO_2), a major contributor to air pollution and acid rain. Nitric acid can release nitrogen oxides (NO_x), which are potent air pollutants that contribute to smog formation and respiratory issues. These emissions can have regional and even global impacts on air quality and ecosystem health.

2.4. Water pollution

Wastewater treatment is a pressing problem that affects people worldwide because it poses serious risks to ecological systems and the quality of available drinking water.[4,54,55] The issues are consistently made worse by the industry's rapid development and the rise in living standards.[56–58]

2.5. Soil and land pollution

Improper disposal or accidental spills of inorganic acids can contaminate soils and land areas. Acidic substances can alter soil pH, making it inhospitable for many plant species. Acidic soil can also cause the leaching of nutrients and essential minerals, reducing soil fertility and impacting agricultural productivity.

In general, to mitigate the environmental effects associated with inorganic acids, it is important to implement proper handling, storage, and disposal practices, which includes:

(1) Using appropriate containment systems and protective measures to prevent leaks and spills.

(2) Implementing effective treatment processes to neutralize and remove/recycle inorganic acids from wastewater before discharge.

(3) Employing proper waste management techniques to minimize the release of acids into the environment.

(4) Promoting the use of green alternatives and sustainable practices to reduce reliance on inorganic acids.

(5) Adhering to environmental regulations and standards to minimize the potential environmental impacts.

By adopting responsible practices and considering alternative solutions, industries can minimize the negative environmental effects of inorganic acids and work towards more sustainable and environmentally friendly chemical processes.

3. Sustainability and circular economy

The sustainable use of inorganic acids in industrial applications depends on several factors, including their production, use, disposal, and potential alternatives and require consideration of the following points.

3.1. Environmental impact

Inorganic acids can have significant environmental impacts throughout their life cycle. The production of inorganic acids often involves energy-intensive processes and the release of greenhouse gases. Additionally, improper handling and disposal of inorganic acids can lead to water and soil pollution, as well as the emission of toxic fumes. Sustainable inorganic acid use requires minimizing emissions, reducing waste generation, and implementing proper disposal and treatment methods.

3.2. Resource efficiency

Inorganic acids are often derived from non-renewable resources, such as sulphur, nitrogen, or minerals. Sustainable practices involve efficient production methods, optimizing resource use, reducing consumption, and exploring alternative sources or processes, thereby reducing reliance on virgin materials.

3.3. Health and safety

Inorganic acids can pose risks to human health and safety, especially if not handled properly. Workers involved in their production and use may be exposed to corrosive substances and toxic fumes. Sustainable industrial practices prioritize worker safety through proper training, the use of personal protective equipment (PPE), and the adoption of less hazardous alternatives or processes.

3.4. Circular economy approach

Adopting a circular economy approach can enhance the sustainability of inorganic acid uses. This involves minimizing waste generation and exploring opportunities for recycling, reusing, or repurposing inorganic acids. Recycling and recovery technologies can reduce the need for new acid production, conserve resources, and minimize environmental impacts.

3.5. Exploration of green alternatives

As mentioned earlier, exploring and adopting green alternatives to inorganic acids can significantly contribute to sustainability. Organic acids, bio-based solvents, enzymatic processes, and supercritical fluids are examples of alternatives that offer reduced environmental impacts and improved safety profiles. Evaluating and implementing these alternatives can lead to more sustainable industrial chemical processes.

3.6. Regulatory compliance

Compliance with environmental regulations and standards is essential for sustainable use of inorganic acids. Regulations often aim to control emissions, manage waste disposal, and ensure worker safety. Adhering to these regulations and actively seeking ways to exceed compliance can promote sustainability and minimize environmental risks.

In general, the sustainability of inorganic acid use in industrial applications depends on a holistic approach that considers environmental, social, and economic aspects. By implementing sustainable practices, exploring alternatives, optimizing resource use, and prioritizing worker safety, industries can reduce the environmental impact associated with inorganic acid use and contribute to a more sustainable future. The key components of sustainability of inorganic acid waste management are illustrated in Fig. 1.

As discussed earlier, the circular economy of recycling inorganic acids involves the recovery, reuse, and regeneration of these acids to minimize waste generation, conserve resources, and reduce environmental impact. This requires a hybrid multitasking setup. It has been reported in the literature that membrane based technologies and integrated technologies are very effective for the circular economy of recycling inorganic acids and other resources including water with zero waste discharge.[59,60] However, there are no analyses indicating cost implications of circular economy by recycling of the resources from the aqueous wastes. When inorganic acids cannot be economically recovered or regenerated, these acidic waste waters should undergo proper treatment (pH adjustment and removal of hazardous components) and neutralization (termed remediation) to minimize their environmental impact. This ensures that the waste acid can be safely discharged or further processed without causing harm to the environment. Therefore,

Fig. 1 The factors influencing sustainability of inorganic acid use in industrial applications.

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the present review is focussed on three approaches of inorganic acid waste management *i.e.* (i) remediation of low acidic waste water, (ii) recycling of high acidic waste water, and (iii) green alternative to inorganic acids.

4. Remediation methods

Remediations methods are effective for the treatment of low acidity, typically in pH range, waste waters such as due to AMD. Active and passive remediation strategies can be employed for AMD remediation and comprehensive descriptions of several active and passive remediation techniques have been published earlier.[30,43,61–65] In general, passive treatment techniques precipitate metal sulfides by establishing reducing conditions and using organic materials as alkaline agents. One of the primary distinctions between passive and active treatment is the minimal or periodic maintenance and examination.[29] In situations with low acid loads and little change in the water flow rate, passive treatment applications may be economically advantageous. However, they are not appropriate for circumstances requiring more than 150 kg of $CaCO_3$ per day.[29] Aerobic wetlands, compost reactors, anoxic and open limestone drains and channels, bioreactors, and permeable reactive barriers are examples of passive treatment techniques. According to Wu *et al.*, the use of constructed wetlands (CWs) for the treatment of different industrial effluents, particularly acidic waste, has greatly evolved.[66] The CWs, usually referred to as treatment wetlands, are engineered systems that are created and built to enhance water quality while requiring relatively little external energy and being simple to use and maintain. As an alternative to traditional mechanical systems for treating wastewater from small towns, CWs have been installed all over the world.[67,68] According to the unique properties of industrial effluents, proper pretreatment, in-flow dilutions through re-circulated effluents, pH correction, plant selection, and intensifications in the wetland bed, such as aeration and bioaugmentation, are suggested. Despite advancements in design and operational strategies as well as the use of intensified systems, CW systems operating as standalone technologies are sometimes unable to meet the requirements of these new guidelines as a result of the deteriorating environment leading to stricter discharge standards, including the emphasis on effluent reuse. The development of treatment systems integrating CWs with other treatment technologies is mainly intended to achieve increased treatment efficiency.[69] Also, the wetland uses are limited to AMD with near neutral and low acidic properties (pH surpasses 4.5), and they are unable to cope with and adapt to sudden variations in water quality and flow rates.[70] Therefore, prior expert knowledge of the physical and chemical behavior of *in situ* treatment ponds or pits harboring AMD is required for the effective implementation of passive treatments such as wetlands. Although passive treatment takes little upkeep, refurbishment is usually necessary and adds to the expense.[71] Moreover, the toxic metal buildup and its associated long-term effects need to be carefully evaluated.

There are numerous primary chemical and physical active treatment strategies for AMD such as chemical neutralization, precipitation (pH control and electrochemical processes), sulphate reduction by biological/microbial mediation, flocculation, adsorption and ion exchange, and filtering, as well as crystallization.[72] Chemical neutralization is by far the most popular and widely used active primary treatment and broadly uses neutralizing agents such as caustic soda (sodium hydroxide), lime[73] and limestone,[74] fly ash,[75] natural clinker,[76] lignite,[77] magnesium oxide, and hydroxides.[77–81] Of these neutralizing agents, limestone, being inexpensive is most commonly employed.[82–85] The AMD treatment by neutralization and toxic element removal with unmodified and modified limestone has been evaluated by Iakovleva *et al.*[86] They have observed that the modification of limestone with sodium chloride and process water with high content of chlorides, sodium hydroxide and sodium carbonate are efficient and inexpensive methods of modification. However, in general, neutralization and precipitation through pH change alone is insufficient, particularly in the presence of metals like arsenic, molybdenum, mercury, selenium, and chromium. Therefore, a second phase of treatment is also required. Also, the majority of reducing agents have typically unpredictable process parameters, which is not desirable. Although electrochemical reduction provides a highly controlled and secure method of nitrate destruction, maintaining electrochemical reactors over long term poses a significant difficulty.[87] Additionally, the formation of watery sludge (greater than 90% water) containing potentially toxic elements is a major problem with the neutralization strategy. The cost of dewatering the sludge is considerable. Due to this, active AMD treatment methods are typically more expensive than passive ones, especially after the mining process has stopped.[88]

The industrial low acidic waste water discharges containing nitrate could be treated with the artificial denitrification processes.[89] Some of these methods are: bio-mediated denitrification,[90–95] catalyzed chemical,[96–102] electrochemical methods,[96,103–107] photocatalytic reduction,[108] and hydrothermal decomposition.[109,110] Although biological denitrification is a well-developed technology for converting nitrate to nitrogen, it is sluggish and difficult to manage, and the presence of other metal ions in the discharges inhibits bacterial growth. Similar to this, other systems have flaws that prevent them from being improved upon or applied, such as expensive capital expenditure, high energy and alkali consumption, and environmental damage.

The various remediation methods used for the mitigation of adverse effects of acidic waste water discharges are shown in Fig. 2.

5. Recycling and regeneration

Recycling of inorganic acids involves the recovery and reuse of these acids, reducing the need for new acid production and minimizing waste generation. Therefore, recycling and regeneration methods offer better approach than the remediation approach for the management of acidic aqueous wastes, particularly when the concentration of inorganic acids is high enough to make it viable for the circular economy.
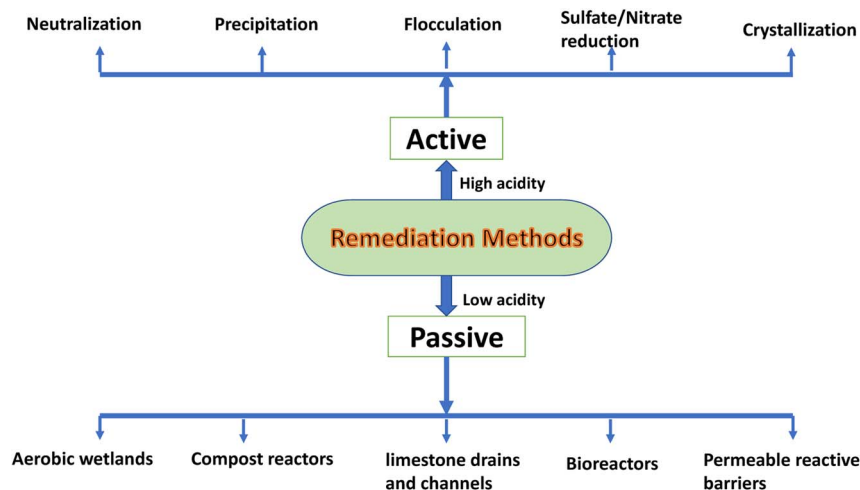
Fig. 2 Different practices used commonly for the remediation of acid in waste waters generated by the acidic mine drainage and industrial activities.

5.1. Regeneration by treatments

Removing metal ions and other components through chemical or physical processes is one of the main strategies for the regeneration and recycling of the acid from spent acidic solutions generated in the steel, electroplating, and semiconductor industries. Due to its strong acidity and oxidative capacity, piranha solution, a mixture of hydrogen peroxide (1 part) and sulfuric acid (3 parts), is frequently employed in the industrial processing, manufacturing, and laboratories especially to clean surfaces with organic contamination.[111-120] The electrochemical oxidation of hydrogen peroxide provides the basis for the regeneration of sulfuric acid from the utilized piranha solution.[121]

In the steel industry, HCl and H_2SO_4 solutions are typically used to treat steels, while mixtures of HNO_3 and HF solutions are used to treat carbon steels. Inhibitors are also included in pickling solutions to lessen the acidity of the pickling solutions' reaction with metals. These pickling solutions are deemed exhausted when the acid concentration falls by 75–85% while the metal content increases to 150–250 kg m^{-3}, resulting in a drop in the pickling rate. The extinguished baths are regarded as special hazardous wastes because of their caustic character and high concentration of acids and metals.[122] There are various methodologies for the treatment of spent pickling liquors to regenerate acids and recover metal salts as shown in Fig. 3.

A brief description of different strategies employed to recover acids from the spent pickle liquors is given below.

5.1.1. Pyrohydrolysis method. The spent pickle liquor is thermally degraded to transform the spent acid into hydrochloric acid and iron oxide at a high temperature in the presence of water vapor and oxygen as per eqn (1) in the fluidized bed acid regeneration process.[1,123]

$$4FeCl_2 + 4H_2O + O_2 \rightarrow 8HCl + 2Fe_2O_3 \tag{1}$$
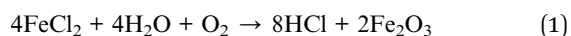
The fluidized bed reactor's (FBR) separating vessel receives the used pickle liquor, which is subsequently concentrated in a venturi loop using hot reactor gases. From this loop, a portion of the concentrated pickle liquor is continually supplied into the reactor's fluidized bed. According to eqn (1), the fluidized bed is made up of iron oxide granules, acid, and water that are evaporated at 850 °C, turning iron(II) chloride into iron(III) oxide and hydrochloric acid. The spray roasting method is an additional hydrochloric acid regeneration choice. While the equipment utilized varies slightly depending on the roasting procedure, the general operating principle remains the same. In the spray roasting reactor, the pyrohydrolytic separation of iron(II) chloride and water occurs at a temperature of around 450 °C. The heated reactor gases are cooled and the acid is pre-concentrated in a venturi recuperator, which receives the used acid. After that, the concentrate is sprayed from above directly into the fired reactor. The tiny drops evaporate as they fall because of the hot burn gases.[124] According to eqn (1), the ferrous chloride is separated into iron oxide and hydrochloric gas using steam and airborne oxygen. The iron oxide that results from this process is collected at the reactor's base and moved pneumatically to an oxide bin.
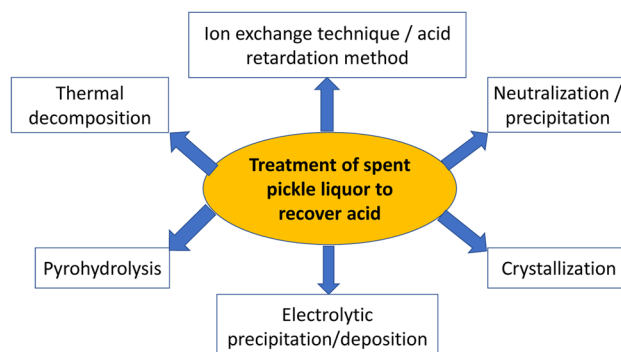

Fig. 3 Different techniques and methodologies employed for the regeneration and recovery of acids from the spent pickle liquors.

5.1.2. Neutralization and precipitation. The most common method for getting rid of iron is to precipitate it as a solid jarosite or goethite product.[125–127] Investigations revealed that it was not possible to precipitate individual metals selectively from solutions containing a high Fe^{2+} content without contaminating the precipitate with Fe and leaving a residue of Zn or another single metal ion in the solution when purifying spent pickling liquors and other bleed stream.[128,129] For the recovery of sulfuric acid from steel pickling liquid, Dufour et al. introduced the oxy-precipitation method.[130] Pourcelly et al. investigated the electro-transport recovery of sulfuric acid utilizing specialized anion-exchange membranes (AEMs).[131] By precipitating as basic sulphates, Lopez-Delgoda investigated the recovery of iron and acid from bio-oxidized sulphuric acid pickling waste.[132] As a result, acid is wasted, and the finished chemicals are of low value, requiring additional purification before being repurposed.

5.1.3. Crystallization. Crystallization is one of the potential methods for wastewater treatment that has been heavily utilized in engineering applications recently, particularly for desalination, water, and salt recovery. The process has various benefits, including great effectiveness, reduced energy use, low costs, and little space requirement. Several crystallization techniques used in wastewater treatment are reviewed and summarized by Lu et al.[133] These procedures mostly include membrane distillation crystallization, drowning-out crystallization, reaction crystallization, and crystallization through evaporation. Exhausted pickling water could also be treated using the crystallization techniques. Salts and acids can be recovered with this method, and the latter can even be recycled.[9] The solubility relationships between water, sulfuric acid, and iron sulphate provide the basis for crystallization. The saturated solutions are generally chilled to crystallize the heptahydrate salt of iron sulphate, $FeSO_4 \cdot 7H_2O$.[1] There are three different heptahydrate crystallization procedures for regeneration depending on the cooling method i.e. indirect cooling crystallization, cyclone crystallization, and vacuum cooling crystallization. Therefore, the salt burden is reduced and wastewater emissions are significantly improved with the crystallization procedures.

According to Ozdemir et al., crystallization is an effective way to get rid of ferrous chloride in water after hydrochloric acid pickling.[134] To recover metals from used baths and the HNO_3/HF acid mixture, Kerstin and Rasmuson built a prototype plant with a continuous crystallizer.[135] Another crystallization method developed by Kerstin and Rasmuson is intended to treat pickling water that contains Fe(III) and Cr(III) ions.[136] In this method, while $Cr(III)F_3 \cdot 3H_2O$ and $FeF_3 \cdot 3H_2O$ precipitate, the mixture of regenerated acids (HF/HNO_3) is circulated. Galvez et al. investigated the crystallization procedures for recovery of HF and HNO_3 from exhaust baths, and they observed that the presence of Cr affects the speed of crystal formation.[137] In order to recover HF and HNO_3 and separate metals as fluorides from water stripped off, Hermoso et al. developed a crystallization technique.[138] This technique also offers nickel recovery with yields more than 72% and purity close to 100%. A method for making iron sulphate heptahydrate from pickling solutions that comprise $FeCl_2$, HCl, and H_2O is also patented by Kehrmann.[139] The PHAR (pickling hydrochloric acid regeneration) technique is illustrated by Brown and Olsen as having both technical and financial advantages.[140] By lowering the crystallization temperature from 270 K to 265 K, it is able to boost iron removal from 72% to 85%. In this procedure, sulfuric acid is introduced to the exhausted baths of hydrochloric acid, and when the temperature falls, iron sulphate heptahydrate crystallizes and hydrochloric acid is released. Energy use, prices, and CO_2 emissions are lowered with respect to old systems by 95%, 52%, and 91%, respectively. To regenerate HCl and make iron sulphate heptahydrate, Olsen and Blumenschein developed a technique for the treatment of spent pickling water that contains both HCl and $FeCl_2$.[141] In this instance, the regeneration is carried out using sulfuric acid, which, when reacting with $FeCl_2$ at ambient pressure, produces iron sulphate heptahydrate and HCl. While the acid is recycled, the salts are separated. Additionally, wastewaters are not produced, which lowers capital and operating costs. But this approach has the following drawbacks: (i) the crystallization requires considerable energy, (ii) it is challenging to remove strong metallic ions like Fe ions from the waste acids, and (iii) an economically viable way to handle the crystal that has been removed is not there.

5.1.4. Thermal decomposition. Another common approach for treating acidic waste is thermal breakdown, which involves spraying the waste acids, together with metal ions, into a furnace that is heated to temperatures between 600 and 1000 degree Celsius.[142] By absorbing the gases that are released when HCl or H_2SO_4 is broken down into H_2 gas, Cl_2 gas from chloride pickle liquor, and H_2SO_4 gas, SO_2 gas, and SO_3 gas from sulphate pickle liquor, Fe_2O_3 powder is created. This powder is then used to make magnetic materials. The recovered acids are employed again for material pickling and dissolving material. However, there are several problems in using the thermal decomposition-based approaches. Some of these are listed below.

(i) Significant energy consumption during the thermal decomposition of waste acid containing low Fe ions, which makes it economically not viable.

(ii) Loss of hydrochloric acid as HCl fumes.

(iii) Difficulty in maintaining the required Fe concentration in real applications.

(iv) Higher maintenance cost due to the corrosion of the equipment caused by wet Cl_2 and HCl gases.

5.1.5. Electrolytic precipitation and deposition. The recovery of HCl or H_2SO_4 from waste acids by eliminating metal ions via electrolysis has been the focus of numerous studies.[128,142,143] The cathodic compartment of the electrolysis cell, where metal ions electrodeposit on the cathode and Cl^- or SO_4^{2-} ions are transported through the anion exchange membrane, is introduced with waste HCl or H_2SO_4 and Fe metal ions in these procedures. Low yields and a low Fe electrolysis efficiency are the result of the ionization of HCl and H_2SO_4 to H^+ and Cl^- and H^+ and SO_4^{2-} ions, respectively, which is what causes the waste acidic solution to include a large quantity of free acids. The waste acid produced by emerging industries, however, cannot be treated using the aforementioned

procedure. In general, the waste acids contain the potentially toxic element ions with Fe^{2+} ions, which lead to contamination of the deposited iron.

5.1.6. Ion-exchange technique and the acid retardation method. In principle, by selectively adsorbing the hydronium ion on an anion exchange resin, acid can be recovered using ion-exchange. From discharge waters containing, for instance, ferric chloride or ferric sulphate, ion-exchange can recover part of the acids.[144–146] Most of the time, at least half of the initial concentration of acid can be recovered.[144–146] Because the acid can easily be removed from the resin with water, the process is reversible. Thus, it is possible to separate the free acid from the metal by alternately running the contaminated acid and water through a bed of this resin. Because of its low cost, simplicity, dependability, and outstanding performance, acid retardation is the most extensively employed procedure for the purification of mixed stainless steel pickle liquor.[147] Since the invention of the method in 1978, Eco-Tec alone has deployed hundreds of APU™ ion exchange systems in 30 different countries for a range of acid purification applications.[148] The APU system makes use of an ion exchange resin with the capacity to absorb potent acids from solutions while blocking their metallic salts. Recoflo, a patented ion exchange method,[149] achieves the desired separation efficiency through the use of short (60 cm) tightly packed beds of fine mesh resins and counter-current regeneration. Synthetic ion-exchange resins have been used for water softening or demineralization on a large scale for a long time. Even though they are successful at bringing ionic contamination levels down to low levels, these resins have historically lacked selectivity. Therefore, efforts have been made to increase this selectivity and efficiency through research. Nenov *et al.* used a powerful acid cation exchanger in the Na-form to remove arsenic from sulfuric acid from an arsenic-containing aqueous solution.[150] Using some anion exchange resins, sulfuric acid has been extracted from the acidic waste.[151–153] By studying the separation and recovery of H_2SO_4 from metal cations coexisting in the waste plating solution, it has been noted that the Wofatit SBW anion exchanger is effective until the relative acid concentration in the effluents reaches $C/C_o = 0.55$.[154–157] The cost of resin regeneration chemicals, which increases correspondingly with the amount of dissolved salts in the water, is what primarily determines the economics of ion-exchange.[145,146] However, using less expensive regeneration chemicals results in a significant reduction in resin regeneration costs.[145] Ion-exchange is useful for eliminating acids or metals for reusing, but it also requires a concentration step. The major disadvantage of the ion-exchange based method is requirement of the addition of chemicals to regenerate the exchange beds.[145–147] The problem is circumvented by the use of the acid retardation method which allows the undissociated acid to pass across a resin bed and then its adsorption by ion-exchange resins. The difference in osmotic pressure during water backwashing causes the adsorbed acid to be released. The ion exchange-based retardation technique allows for a partial acid recovery, but it also results in an increase in solution volume and a very dilute acid.

5.2. Solvent extraction

The purification and recovery of resources (metals) from waste solutions is accomplished using the well-known treatment technique known as solvent extraction.[144–146,158–162] The dispersion of a solute or solutes between two immiscible liquids or phases is known as solvent extraction. It frequently happens with organic and aqueous solutions. The organic phase typically consists of an extractant dissolved in a diluent, but a modifier and a synergistic agent may be needed in some circumstances.[158] While the synergistic agent is used to improve and enhance the extractant, the modifier is added to the system to improve its physical features like to cause phase disengagement after equilibrating the two phases. Nowadays, due to technological advancements, rising consumer demand for higher purity products, and call for more environmentally friendly transportation methods, a higher number of stable solvents (extractants) are available for use in hydrometallurgy. These solvents have the potential to exhibit excellent selectivity for a specific metal ion. When the flow rates of waste water and the concentration of the solute are both high, solvent extraction is economically viable. But, when the concentration of the pollutant to be recovered is very low, it is not a feasible method.[144–146,158] However, the majority of acidic waste streams typically include low levels of acids, typically 10–20 g L^{-1}.[155–157] A major obstacle to the efficient concentration of diluted acidic solution through evaporation is the higher energy requirement. The ability to recover different acids has been attributed to a number of extractants, including TEHA (tris-2-ethylhexylamine), Alamine-336 (a mixture of trioctyl/decyl amines), TBP (tri-butyl phosphate), and Cyanex 923 (a mixture of alkyl phosphine oxides).[144–146,158–161]

5.2.1. Solvent extraction of H_2SO_4. TEHA, Alamine 336, and Cyanex 923 are the three most often used extractants for recovering H_2SO_4. The chemical formula of TEHA is $(CH_3(CH_2)_3CH(C_2H_5)CH_2)_3N$.[144–146,158] It is a tertiary amine. The literature provides a thorough description of the physical and chemical characteristics of TEHA.[163] The application of TEHA for the recovery of H_2SO_4 from acidic mining waste solutions has been documented by several authors.[144–146,158–161,163–168] Using 75% TEHA in kerosene, Agrawal *et al.* reported recovering H_2SO_4 from a zinc electrowinning bleed stream containing 173.5 g L^{-1} of H_2SO_4.[160] The findings demonstrate that TEHA had excellent acid extraction capabilities even in the presence of significant zinc concentrations. Tri-octyl/decyl amine is a component of Alamine 336.[144–146,158–161] Cyanex 923 is a combination of four trialkyl phosphine oxides. Because Cyanex 923 possesses advantageous qualities including less hydrolysis and low solubility in water, various researchers have looked into the extraction of acids using this extractant.[158,169–171] Because it doesn't require dilution, it has an advantage over other phosphine oxides.[169] Because Cyanex 923 showed a favorable balance between its ability to extract sulfuric acid and to be stripped by water, Rickelton suggested using it as a viable extractant for the recovery of H_2SO_4.[172]

5.2.2. Solvent extraction of HCl. TEHA, Alamine 336, Aliquat 336, Cyanex 923 and TBP are the most frequent extractants

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used for HCl extraction and recovery.[158,166–168,173–175] According to Eyal and Canari,[168] ion pair formation enables the extraction of HCl using straight chain aliphatic amines diluted in alcoholic diluents. A two-step process of anion addition and amine protonation may be used to describe this mechanism. The removal and recovery of HCl from a secondary resource's leach fluid was studied by Sarangi *et al.* utilizing extractants such TBP (tri-butyl phosphate), Cyanex 923, Alamine 336, and Aliquat 336.[174] Sarangi *et al.* studied the extraction of HCl and found the extraction in the order as: Alamine 336 > Cyanex 923 > Aliquat 336 > TBP.[174] Although Alamine 336 was the most effective HCl extractant, water could not be used to strip the extracted acid from the organic phase. In contrast, other extractants like Aliquat 336, TBP, and Cyanex 923 can easily be removed from the acid using water. In terms of extraction and stripping efficiency, the author came to the conclusion that Cyanex 923 is the promising choice for HCl recovery.

5.2.3. Solvent extraction of nitric acid. TBP is an industrial-scale solvating extractant used for the reprocessing of spent nuclear fuel.[19] TBP is typically used to extract bulk uranium, thorium, and plutonium in high concentration nitric acid medium.[19,175,176] Historically, the PUREX process has been the most researched solvent extraction method for recovering uranium and plutonium from spent nuclear fuel.[19] In PUREX, an aqueous phase comprising used fuel that has been dissolved in strong nitric acid comes into contact with an organic phase made up of TBP in a kerosene diluent.[19] Trivalent fission products and transuranics are left behind when the TBP selectively recovers hexavalent and tetravalent actinides from the aqueous phase.[19,176] Additionally, leaching, etching, and electrowinning waste solutions are known to yield HNO_3 when TBP is used to recover it.[175,176] Utilizing various extractants, such as TBP and TOP, Hoon-Shin *et al.* evaluated the suitability of HNO_3 recovery from waste etching solution (TOP: tri-octyl phosphate).[176] The waste solution under investigation contained 19.6 g L^{-1}, 260 g L^{-1} CH_3COOH, 460 g L^{-1} HNO_3, 113 g L^{-1} HF, and 460 g L^{-1} HNO_3. According to preliminary findings, solvents such 2-ethylhexyl alcohol (EHA), decanol, octanol, heptanol, and hexanol were more selective for acetic acid (HAc) than HNO_3, although tri-octyl phosphate (TOP) and TBP showed more favorable extraction of HNO_3 in comparison to HAc. In the case of TBP in a single contact, it was found that the extraction of HNO_3 was approximately 46% *versus* a coextraction of 32% HAc, and TOP was 35 and 22% for HNO_3 and HAc, respectively.[176] When in contact with strong acids, the phosphoryl (P=O) group in TBP and TOP can behave as a strong Lewis-base, which allows it to form acid–base complexes.

According to Hesford and Mckey,[177] TBP extracted mineral acids in the following order: H_2SO_4 > HF > $HClO_4$ > HNO_3 > H_3PO_4 > HCl. Lee *et al.* carried out tests in a related investigation to recover important metals and regenerate nitric acid from the spent nitric acid solutions.[178] According to one study, 50% TBP was used in five counter-current stages with a three-volume ratio of organic (O) to aqueous (A) to extract 95% of the nitric acid from a feed solution containing 250 g L^{-1} of nitric acid. Hoon-shin *et al.* studied the removal of HNO_3 using distilled water at 60 °C. At an O/A ratio of 1.5, a five-stage counter-current

test resulted in a stripping efficiency of over 94%.[176] After stripping, a high purity product of 99.8% HNO_3 was obtained.[176] When employing distilled water as a stripping agent, similar results were obtained indicating that nitric acid was removed from the loaded organic phase that contained 80 g L^{-1} nitric acid. After five interactions, there was a noticeable recovery of nitric acid (>99%) in the aqueous phase.[175–182] There are several reports on the recovery of HNO_3 using organo-phosphorous based extractants.[182]

5.2.4. Solvent extraction of phosphoric acid. For the recovery of H_3PO_4 from various waste solutions, several researchers have reported employing various extractants such as methyl isobutyl ketone (MIBK) and TBP.[183–188] Because of its immiscibility with the aqueous solution, high selectivity to phosphoric acid, and simple recovery, TBP is an efficient extractant for extracting phosphoric acid.[183] TBP was utilized by Yagodin *et al.* as the extractant for the H_3PO_4 extraction, and they discovered that the extraction increased with the H_3PO_4 concentration.[185] The distribution coefficient, D increased from 0.20 to 0.52 with undiluted TBP at 20 °C, with 15 to 82% increase in H_3PO_4 (by weight) in the aqueous feed.[186] The extraction of H_3PO_4 included the creation of hydrated mono- and di-solvates at a temperature of 20 °C. With an increase in feed H_3PO_4 content, H_3PO_4 predominated.[185] Methyl isobutyl ketone (MIBK) and TBP were mentioned by Ahmed *et al.* as being used for phosphoric acid recovery. It was claimed that while TBP extraction needed to be done at higher temperatures due to its comparatively high viscosity, but phosphoric acid extraction using MIBK could be done at ambient temperature.[187] TBP, however, outperforms MIBK in terms of extraction selectivity for phosphoric acid. The extraction, washing, and stripping procedures constitute the purification procedure.

5.3. Membrane based methods

Membrane based methods are most promising for the recycling of acids from aqueous wastes containing higher concentrations of inorganic acids. The important membrane-based methods and their effective combination based integrated technologies for inorganic acid recoveries are described below.

5.3.1. Nanofiltration and reverse osmosis. Nanofiltration is a pressure-driven membrane separation method that is regarded as an intermediary between reverse osmosis (RO) and ultrafiltration (UF). Both, RO and NF are widely used for water purification, or the removal of salts from water. Both of these processes are pressure-driven, but nanofiltration is thought to be superior for wastewater purification since it has high selectivity and permeate fluxes at relatively lower pressures than reverse osmosis.[188–198] Because of these benefits, NF membranes have been employed in a number of disciplines, including the treatment of acidic wastewater.[197,199–210] It facilitates the penetration of water and monovalent ions (such as H^+) while restricting the transport of divalent and multivalent ions (such as $Fe^{2+/3+}$, Zn^{2+}, *etc.*) by taking advantage of the Donnan (charge) exclusion and size exclusion properties of the NF membrane (molecular weight cutoff, MWCO = 80–2000 Da).[206] In addition to aqueous compositions (acidity and ion concentrations),

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solute transport of both charged and non-charged species across the membrane depends on the properties of the membrane active layer such as the composition of the active layer, the content of free acid–base groups, acid–base properties, free volume, and pore-size distribution. Rejections in every instance follows the dielectric exclusion trends ($M^{3+} > M^{2+} > M^{+}$).[208] The mechanistic comparison of RO and NF for separating salt, acid and water is shown in (Fig. 4). Several studies have shown the separation of inorganic acids such as hydrochloric acid, sulfuric acid, phosphoric acid, and nitric acid, from acidic wastewaters, using NF membranes as feasible.[200–210] High metal ion rejection (>90%) and low acid rejections are seen in the studies using polyamide-based NF membranes at high sulfuric acid concentrations (below pH 2).[211–215] Using sulfuric acid wastewater from copper refining, aqueous sulfuric acid was purified using the NF membrane method.[205] Because of their poor acid stabilities, polyamide membranes were shown to be inadequate for treating effluents from the copper refining process in studies on both short- and long-term performance. The composite membrane made of polyacrylonitrile, in contrast, had remarkable acid stability.

The use of NF to treat hydrometallurgical streams provided a good alternative to established practices. The experimental results demonstrated that a semi-aromatic poly(piperazine amide) membrane may be used to recover strong acids (H_2SO_4 and HCl) from hydrometallurgical streams. When the pH is below 1.0, this membrane has a positively charged surface that favors the transport of anions while impeding the transport of metallic species that are present as cations.[216] For the recovery of phosphoric acid from leached sewage sludge ash, a cutting-edge treatment process has been developed. For the purpose of recovering H_3PO_4, a hollow ultrafiltration membrane has been modified and transformed into a nanofiltration (NF) LbL membrane using layer-by-layer (LbL) polyelectrolyte deposition.[217]

As NF exhibits strong rejections for multivalent ions (>90%), while permitting monovalent ions (like H^{+}) to pass through the membrane, it has the necessary qualities to regulate acidic mining waste. It must be emphasized that the most polymeric NF membranes based on polyamide are only stable at pH > 2.[218–223] The majority of investigations involving polyamide-based membranes at high sulfuric acid concentrations have demonstrated minimal acid rejection and high metal ion rejection. However, ongoing contact with acidic streams will cause the membrane to deteriorate.[219,220] The polyamide active layers have been protected by being coated with or having their chemical composition changed with sulfonated polysulfone groups in an effort to boost the stability of NF membranes in strongly acidic solutions.[224]

It is well known that positive charge can be introduced into the membrane surface in order to selectively separate out positively charged components, which has a substantial impact on the regulation of charge in NF membranes.[225] For the purpose of recovering hydrochloric acid, a water-based coating method was used to form an acid-recovering nanofiltration (NF) membrane that possesses both acid resistance and selective acid permeability. To accomplish this, a loose polyethersulfone NF membrane was dip-coated with branched-polyethyleneimine and an epoxy linker before being heated in a sealed oven with a high-humidity atmosphere. The resulting membrane had a positive surface charge with a zeta potential and showed the positive-charge separation membrane
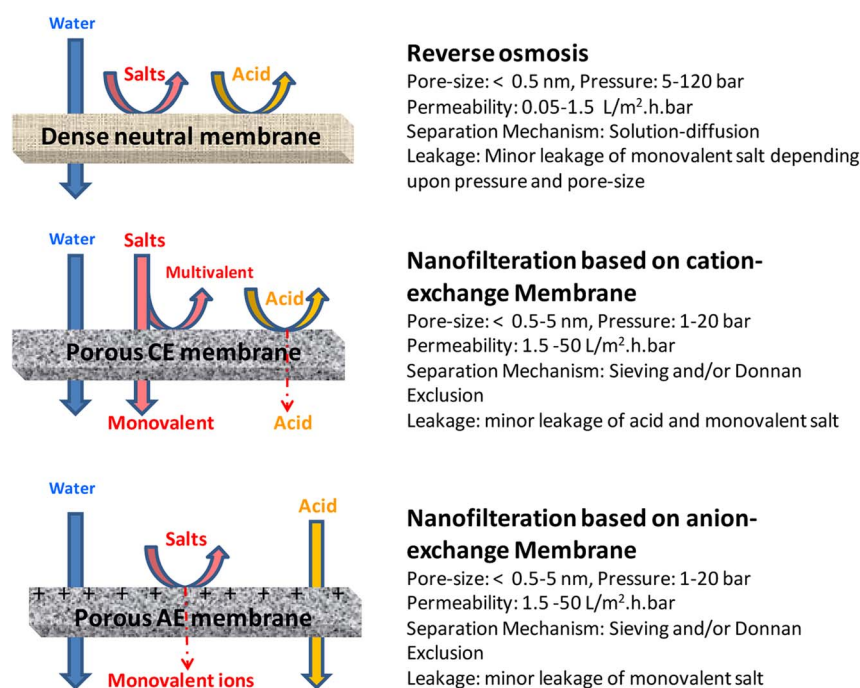

Reverse osmosis
Pore-size: < 0.5 nm, Pressure: 5-120 bar
Permeability: 0.05-1.5 L/m².h.bar
Separation Mechanism: Solution-diffusion
Leakage: Minor leakage of monovalent salt depending upon pressure and pore-size

Nanofilteration based on cation-exchange Membrane
Pore-size: < 0.5-5 nm, Pressure: 1-20 bar
Permeability: 1.5 -50 L/m².h.bar
Separation Mechanism: Sieving and/or Donnan Exclusion
Leakage: minor leakage of acid and monovalent salt

Nanofilteration based on anion-exchange Membrane
Pore-size: < 0.5-5 nm, Pressure: 1-20 bar
Permeability: 1.5 -50 L/m².h.bar
Separation Mechanism: Sieving and/or Donnan Exclusion
Leakage: minor leakage of monovalent salt

Fig. 4 Schematic illustration of separation of acid, salts, water in aqueous waste using reverse osmosis (RO) and nanofiltration (NF) membrane-based processes.

performance order of $MgCl_2$ > $MgSO_4$ > NaCl > Na_2SO_4. The selective permeation of hydrochloric acid was demonstrated by Mg rejection and Cl permeation studies to be achieved with Mg rejection over 95% and Cl permeation above 70%, allowing the acid to be recovered by getting permeate at the same pH as the input. Moreover, the NF membrane's selective separation capability and flow rate remained constant for a month.

Using a NF membrane, Mendoza-Roca et al. cleaned the acidic wastewaters from the pickling and tanning processes.[199] They obtained highly filtered water and attained substantial sulphate retention (>90%). However, the concentrate still contained all the acidic components and metal ions, which needed to be eliminated using customary procedures. Jakobs et al. also treated industrial nitric acid solutions with an NF membrane.[197] The nitric acid solution used in the manufacture of image tubes could be converted into a purified version attributed to the NF membrane's cation exclusion and acid permeation capabilities. The NF membrane method had a recycling rate of 80–90%. This outcome demonstrates unequivocally that acid wastewater can be filtered using NF membranes. The quantity of pollutants released is decreased by using NF membrane systems to recover sulfuric acid solutions from sulfuric acid wastewater generated during copper smelting. It appears that no research has been done to ascertain which kind of membrane is ideal for recovering sulfuric acid solution from wastewater used in copper refining. Moreover, the effects of highly acidic environments on membranes have not been extensively studied. Therefore, more investigation is required into the selective ion rejection capabilities and resilience of NF membranes in extremely acidic circumstances for the treatment of sulfuric acid wastewater.

Two polyamide membranes and a polyacrylonitrile-based membrane were successfully used to recover a pure sulfuric acid solution, as demonstrated by a combination of permeate flow, sulphate permeation, and metal ion rejection.[226] Because of their poor acid stabilities, polyamide membranes were shown to be inadequate for treating effluents from the copper refining process in studies on both short- and long-term performance. The polyacrylonitrile-based composite membrane, on the other hand, demonstrated outstanding acid stability and provided better than 90% metal ion rejection for 430 days, with the exception of calcium ions. The recovery performance in a 1-ton per day pilot-scale process employing copper-refining wastewater showed that, even at a 95% recovery rate, 90% of the metal ions were rejected.

As specified earlier, in comparison to RO, NF permits greater permeate fluxes, although it is still very effective in retaining organic molecules and multivalent salts.[227] Moreover, NF has a membrane isoelectric point (IEP) that is known to be between 3 and 6 and to be charged. As a result, at acidic pH, the membrane surface displays a positive charge,[228,229] a characteristic that has a direct impact on the mechanisms regulating NF retention. This allows the positively charged NF membrane to effectively reject multivalent metal cations while allowing acidic anions to pass through the membrane nearly unhindered when treating acidic fluids.[230] Because of these features, NF is a very promising method for removing metal species from acid streams. In contrast, RO is a very effective procedure for

retaining dissolved salts and organic molecules with low molar masses, achieving 99% retention.[227] Its primary use is in the desalination of seawater, where it generates 20% of the world's desalinated water.[231] Due to its qualities, RO has grown more and more appealing as a method for treating industrial effluents, especially when water recovery is sought.[232,233] According to Ahsan et al.,[234] RO can be used to change the concentration of existing solutions because it also generates a highly concentrated stream while creating a high quality permeate. By utilizing RO, those authors were able to produce a concentrate with an acid concentration that was 400% higher than the feed acetic acid solution.

Several studies have reported the integration of NF and RO for the treatment of acidic streams polluted with metals. Purification of phosphoric acid,[235,236] nitric acid used in the manufacture of picture tubes,[237] recovery of metals and acids from electroplating effluents,[238] and purification of sulfuric acid are its few uses.[239] In addition to the aforementioned applications, the combination of NF and RO has shown to be a viable treatment for pressure oxidation process effluent, a waste product from the gold mining sector.[240] In this work, four flat-sheet NF membranes were used to study the separation of phosphoric acid from washing waste waters.[203]

The major problem associated with NF and RO are fouling of membranes and degradation of membranes (such as polyamide) in high acidity over a period of time, and high energy consumption. For sustainable application of RO and NF for acid recovery, these problems should be addressed along with possibility of coupling this method with other membrane-based technologies for the management of generated waste with high salt content. Ceramic NF membranes have a great degree of chemical stability, which makes them effective for handling acidic waste.[220] Nonetheless, it is necessary to create ceramic NF membranes with smaller pore sizes in order to lessen convective flow's influence on ion transport. This might facilitate greater ion rejections by ceramic NF membranes.

5.3.2. Membrane distillation. The membrane distillation (MD) technique makes use of a hydrophobic microporous membrane, which restricts the entry of feed water while selectively allowing vapor to pass through the membrane. The main driving force behind the process is a change in vapor pressure caused by the temperature difference between the feed and permeate streams.[241–243] The vapor is produced at the feed side of the membrane, transported across it, condensed, and collected from the permeate side. Therefore, the MD based process produces freshwater of excellent quality, thereby finding applications in brine water desalination and wastewater treatment. The working concept of the MD process is illustrated in Fig. S1 (ESI†).

MD is a combination of thermal and membrane desalination. Both the thermal energy, required to heat the feed solution, and the electrical energy, needed to power the circulation pumps, are consumed in MD systems. Therefore, a low-grade heat source and condenser are necessary for this process. Being an energy-intensive process, the technology immediately lost its appeal because it was discovered that MD required more energy than RO.[244] However, RO relies on expensive electricity

and the cost of electricity has increased, making it appear unsustainable. MD, on the other hand, can more easily utilize waste heat or solar thermal energy. Many benefits of MD-based acid recovery are:[245]

- A total (theoretical) rejection of non-volatiles such as cells, macromolecules, colloids, and ions.
- Reduced operational temperatures compared to traditional distillation.
- Reduced operating pressures compared to typical membrane separation techniques driven by pressure.
- Less sensitivity to process variable changes (*e.g.* pH and salts).
- Chemical resistance and good to exceptional mechanical properties.
- Smaller vapor gaps than with traditional distillation methods.
- It can be used to recover more fresh water from brine after RO.

However, there are limitations to MD-based processes, including their high energy intensity (even if heat is often of low-grade energy), sensitivity to surfactants, and the need for separate treatment for volatiles like hydrochloric acid, ammonia, or carbonates that pass through the membrane. The literature has generally identified four different configurations of the MD system, based on how the cold side permeate is handled.[246] These are:

(1) Direct contact MD (DCMD), in which liquid phases and the membrane come into direct contact. This is the simplest setup that can provide a respectably high flux. It can be used for applications like desalination and the concentration of aqueous solutions (like acids).[247]

(2) Air gap MD (AGMD), in which a space called an air gap sits between the condensation surface and membrane. Although this arrangement has the lowest flux, the energy efficiency is maximum. For the majority of MD applications, the air gap structure can be widely used, especially when thermal energy is expensive or scarce.[248]

(3) Vacuum MD (VMD), where the permeate side is air or vapor at lower pressure, and where the permeate is, if necessary, condensed in a different device. This arrangement is advantageous when volatiles are being eliminated from an aqueous solution.[249]

(4) Sweep Gas MD (SGMD), in which the created vapor is transported using stripping gas. This arrangement is employed when volatiles are eliminated from an aqueous solution.[250]

MD has found many potential applications such as production of high-purity water from salty water, removal of potentially toxic elements from waste water,[251] recovery of HCl from cleaning solutions in electroplating,[252] concentration of sulfuric acid to recover lanthanide compounds in the apatite phosphogypsum extraction process,[253] elimination of radioisotopes leading to reduction of nuclear industry waste volume,[254] and the removal of volatile organic components from diluted aqueous solutions.[255,256] A synthetic solution containing only H_2SO_4 and HCl was examined by Tomaszewska and Mientka for the separation of H_2SO_4 and HCl.[247] As the concentration of H_2SO_4 in the feed increases, it has been reported that the

presence of sulfuric acid in the feed reduces the solubility of HCl and hence increases HCl flux. Acid recovery from various process acidic solutions employing the MD approach was also described in the studies by Guiqing *et al.* and Tang and Zhou.[257,258] These studies of DCMD for acid recovery focused on treating mostly synthetic and particular real solutions. MD was examined using actual leach solutions that contained either HCl or H_2SO_4. The salt rejection rate for the H_2SO_4 actual leach solution was greater than 99.9%, and the concentration of free acid increased from 1.08 mol L^{-1} to almost 4.60 mol L^{-1}. The membrane rejected >99.9% of the acid.[259] Currently, MD has been primarily explored at the laboratory scale such as for treatment of wastewater from a power plant (in Singapore) and for wastewater treatment in a chemical plant (The Netherlands).[260–266] Along with this, some of the pilot plants undergoing field trials are for RO concentrate treatment, ground water treatment, and solar heat utilization.[267–269] The concept is viable, although it has some practical problems, like scaling on MD membranes.[270] In rural Victoria, Australia, a RO-MD trial using a solar-powered direct contact MD system produced results that were comparable.[271] Flux decreased as a result of membrane scaling, however it was quickly restored with an acid clean. The possibility of lessening scaling on MD membranes has not yet been investigated extensively. The idea of minimizing the usage of extra chemicals is of importance in remote mining operations. Considering that the scaling salts are most likely to occur in the higher temperature area of the DCMD hot cycle loop, a filter might be used to catch them before they reach the membrane.

At present, MD based processes have not been used for the recovery of acids other than laboratory scale. However, MD has potential when used in combination with other processes for the recovery of acids and aqueous waste treatment.

5.3.3. Diffusion dialysis. Among the different methods, diffusion dialysis (DD) is a well-recognized membrane based technique for the effective recovery of acids and alkalies in waste discharges from a variety of industrial effluents.[272,273] For acid recovery, anion-exchange membranes and for alkali removal, cation-exchange membranes are used. The process was first reported for the separation of small molecules from a mixture.[274] In this process, the solutes spontaneously pass through the ion-exchange membrane from the high concentration side to the low concentration side.[273] Therefore, the transport is based on the difference in chemical potential of solute over an ion-exchange membrane, with observation of Donnan criteria of co-ion rejection and preservation of electrical neutrality.

5.3.3.1. Advantages and disadvantages. Out of all membrane-based processes, DD is particularly attractive due to its cost-effective nature as no pressure or electric power is needed for driving the separation and hence the energy consumption is low. Only power is required for solution pumping. This leads to lower installation and operating costs.[273,275–278] One such interesting account of the economic benefits of a continuous flow diffusion dialyzer plant has been given in ref. 276, where processing 10 tonnes per day of waste solution to recover sulphuric acid has been discussed. It has

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been estimated that the major economic benefits are achieved from the saving of chemicals and within a short span of time, the high profits could recover the investment costs. The DD process also results in recovering pure acids due to the high selectivity of AEMs for acids. Moreover, the DD process supersedes all the other acid recovery processes owing to its environment friendly nature as it is free of any chemicals or post-processing.

However, in general for a DD process, the processing capacity and efficiency is relatively low (*e.g.*, 11.3 L m^{-2} d^{-1} for the commercial DF-120 membrane with an acid recovery of 85–90%), thus requiring large membrane areas for industrial applications.[273] This drawback is due to the low acid permeation of AEMs used. Besides, the process consumes huge quantity of water in the receiver compartment.

5.3.3.2. Systems studied. The DD process has been comprehensively applied for the acid recovery of both inorganic as well as organic acids. In inorganic acids, the majority of studies have been focused on recovery of hydrochloric acid[279] and only a few studies are there on the recovery of sulphuric acid,[280,281] nitric acid[282,283] and hydrofluoric acid.[284,285] Different types of organic carboxylic acids have also been recovered using the DD process.[286,287]

5.3.3.3. Basic principle of a DD process. As stated earlier, the DD process is based on the spontaneous transport of counter-ions due to their concentration gradient, wherein Donnan exclusion and electro-neutrality conditions are maintained.[272,273] When an anion-exchange membrane separates a two compartment system with the feed containing the acidic solution (AX) and the receiver containing water, as shown in Fig. 5, the anions *i.e.* the X$^-$ are allowed to transport across the membrane and the cations A$^+$ are repelled as a result of Donnan criteria of co-ion rejection. But since the receiver is electrically neutral, the positively charged H$^+$ ions also drag along with the anion, X$^-$, thereby preserving the electrical neutrality condition.[288] The diffusion of H$^+$ ions is preferred relative to other cations, owing to their smaller size, monovalent nature and higher mobility. The proton mobility has been reported to be an order of magnitude higher than those of other cations in

aqueous solution owing to its diffusion *via* some special transport mechanisms, such as the vehicle mechanism and Grotthuss mechanism.[289–292] In the vehicle mechanism, the proton moves through the medium as a water cluster by molecular diffusion, while in the Grotthuss mechanism, the protons move from oxygen to oxygen by simultaneously breaking and forming hydrogen bonds. Therefore, in a DD process, a net transport of HX, *i.e.* acid from the feed to the receiver takes place, leading to its recovery.

5.3.3.4. Models. The species permeation in a DD process is chiefly described by two types of models such as the solution-diffusion model and the three-phase membrane model.[273,293] In the solution diffusion model, the transport of species across the concentration gradient is governed solubility/interaction of the species with the membrane matrix. The species may interact with the membrane *via* electrostatic or non-electrostatic interactions. In a DD process, the separation between the protons and the metal ions is achieved owing to their difference in the solubility and mobilities in the membrane. The second model, the three-phase membrane model, segregates the membrane matrix into three regions: a hydrophobic region, comprising the hydrophobic membrane matrix which is responsible for membrane stability, a functional group containing active region; and an interstitial region. This model attributes the transport of acids to the hopping mechanism of anions and the dragging mechanism of protons and other cations through active and interstitial regions in an anion-exchange membrane. In the literature, different approaches such as the Nernst–Planck equation, Teorell–Meyer–Sievers,[294] and a lumped parameter model[295] have been used to theoretically model a DD process.[296]

5.3.3.5. Efficacy of diffusion dialysis. The acid is generally desired to be recovered from a solution containing a mixture of other salts. Therefore, it is important to assess the process in terms of preferential separation of the acid over other salts. The permeation rate of protons will directly govern the acid recovery rate and is designated as the acid diffusion coefficient (*U*). This can be calculated as:

$$U = \frac{M}{A \Delta C}$$

where *M* is the amount of the component transported in moles per h, *A* the effective area in square meters, and ΔC the average concentration of the two chambers in moles per cubic meters and defined as below[297,298]

$$\Delta C = \frac{C_f - C_r - C_d}{\ln\left(C_f - C_r\right)/C_d}$$

Here *C* is the acid concentration. The subscripts f, r and d represent the feed, recovered acid and depleted solution (dialysate), respectively. Here, it should be noted that there will be volume changes in the cell chambers during the water transport through the membrane and therefore $(C_f - C_r - C_d) \neq 0$ during the experiment.[298]

The separation factor (*S*) with respect to one species over another is given as the ratio of dialysis coefficients (*U*) of the two species present in the solution:
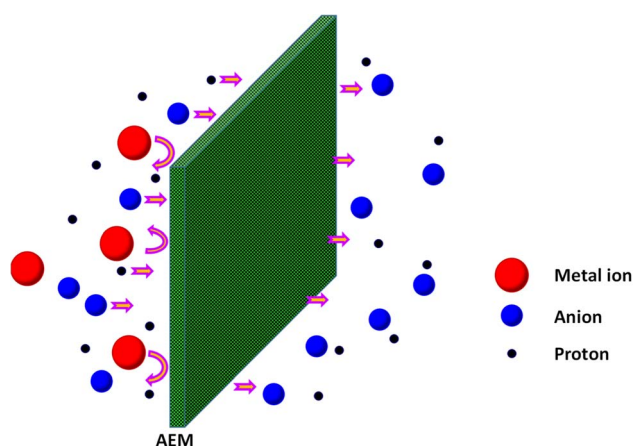

Fig. 5   Basic principle of a diffusion dialysis process.

$$S = \frac{U_{\text{H}}}{U_{\text{M}}}$$

The % acid recovery can be represented as:

$$A = \left(\frac{Q_{\text{r}} C_{\text{r}}}{Q_{\text{f}} C_{\text{f}}} \right) \times 100$$

where Q is the volumetric flow rate.

5.3.3.6. Desirable membrane characteristics. AEMs are the critical component for the DD module. A promising AEM must possess high proton permeability, strong salt rejection, good thermal and chemical stabilities, proper water uptake, poor water permeability and low swelling ratio.[299–301] The membrane properties such as ion-exchange capacity, water uptake, and membrane thickness can govern the acid and other salt transport through the membrane. The commercial anion exchange membranes for acid recovery are generally homogeneous, and are prepared from different polymers such as poly(ether sulfone) (PES),[302] polysulfone (PSF),[303,304] poly vinyl chloride (PVC), poly-vinylidene fluoride (PVDF),[305] poly ether ketone, polystyrene (PS), poly phenylene oxide (PPO)[306–308] *etc.* Some of the commercial anion-exchange membranes explored for recovering acids are DF-120 (Shandong Tianwei Membrane Technology Co., China), Selemion DSV (Asahi Glass, Japan) and Neosepta (Tokuyama Co., Japan). The properties of these membranes have been compiled in detail in ref. 273. Though these membranes have good mechanical strength and stability, the polymer main chains are generally hydrophobic which restricts the ion permeability during the DD process. Some membranes with a hydrophilic matrix such as poly(vinyl) alcohol,[309–311] poly(ethylene) oxide *etc.* are available, but are not preferred for DD owing to their higher swelling leading to low mechanical stability. Also, these membranes have poor thermal and chemical stabilities. Nevertheless, hydrophilic nature of these membranes enhances the mobility of protons through the membranes and also retards fouling properties in the membrane. The unfavorable characteristics of these membranes have been dealt with by introducing cross-links in the polymer matrix using alkoxysilanes and aldehydes. Along with the homogeneous membranes, there have been several attempts to modify interfaces of ion-exchange membranes and synthesize asymmetrical membranes, to improve the membrane properties such as the ion transport and selectivity, thereby improving the efficacy of the DD process.[312,313] Lin *et al.* prepared asymmetric ultrafiltration membranes with a thin active layer (<1 μm thick) on a porous support and achieved significantly higher U_{H^+} and S compared to the commercial DF-120 membrane.[303] Kim *et al.* attempted to improve the properties of the commercially available Neosepta-AFX by interfacial polymerization of pyrrole and could achieve higher dialysis coefficients due to the repelling properties of poly(pyrrole) to cations.[313] In one of the studies based on poly(aromatic ether sulfone) (BPAES), series-connected hexacation segments could be synthesized using 1,4-diazabicyclo[2.2.2]octane (DABCO) and dibromomethane and a high separation factor of H^+ to Fe^{2+} ($S_{\text{H}^+/\text{Fe}^{2+}}$) = 127 and a dialysis coefficient of hydrogen ion (U_{H^+}) value of 18.92×10^{-3} m h^{-1} could be achieved.[314]

Also, most of the AEMs used in DD have quaternary ammonium groups as ion exchange groups. However, these ion-exchange groups have low thermal and chemical stability and low ion permeability compared with other ion exchange groups.[324] Some studies have reported the DD studies using membranes with pyridinium, imidazolium, and methyl-thiazolium functional groups.[311,315–324] Some of the relevant references on acid recovery by diffusion dialysis have been summarized in Table S1 (ESI†).

5.3.4. Electrodialysis. The ions in wastewater can be separated and concentrated using electrodialysis (ED). Regarding the use of waste acid recovery, it is stated that ED exhibits a reasonably high efficiency at low acid concentration and has recently been a subject of great interest.[325–327] The issue of low treatment efficiency in DD operation was often addressed by ED due to the electric field driven directional migration of ions. In ED, the transport of species is accelerated by the electric field. Anions and cations migrate through anion and cation exchange membranes, which promote the desired separation as depicted in Fig. 6, and shift between the cells towards charged electrodes with an electric field, respectively. Positively and negatively charged ions can be concentrated in different ways attributed to migration through IEMs.[328,329]

When compared to traditional selective technologies (such as adsorption, filtration, and IE), ED offers many benefits, including: (i) high ionic species separation efficiency, (ii) low operating pressure because there is no liquid movement across the membranes, (iii) the addition of functionalized membranes to selectively remove differently charged ions, (iv) a small operating footprint, (v) decreased sludge formation, and (vi) adoptable and easy to scale up.

Since ED concurrently creates streams that are both ion-rich and ion-deficient, it has been applied to a number of processes, including water desalination,[330] salt preconcentration,[331] acid/base reuse,[332] and precious metal and nutrient recovery.[333] The ED approach using cation-exchange membranes (CEM) proved successful in recovering acids from solutions containing salts ($NaNO_3$, $NaCl$, and Na_2SO_4).[334] Base solutions were utilized as the catholyte in the tests, and various sodium salts served as the anolyte. The outcomes demonstrate that, under the right conditions, electrodialysis appears to be a workable technique for the acid recovery. The recovery of diluted inorganic acids and sodium hydroxide is the subject of several published ED research studies. Bipolar electrodialysis was investigated by Trivedi *et al.* and Gineste *et al.* to concentrate diluted acid and caustic liquors utilizing salt solution.[335,336] With applied voltages between 10 and 25 V, this method produced concentrated compounds of excellent purity, but operating costs were considerable because of the significant electrical consumption. Inorganic acid recovery from pickling baths used in the stainless-steel industry was explored by Negro *et al.*,[337] while nitric acid recovery from ammonium nitrate-containing effluents was investigated by Ali *et al.*[338] The recovery investigation specifically for the aluminum industry was carried out by Greben *et al.*,[339] who successfully produced 140 g L^{-1} sulfuric acid with less than 1.2 g L^{-1} aluminum content by applying ED to a solution derived from electrolytic anodizing of aluminum.

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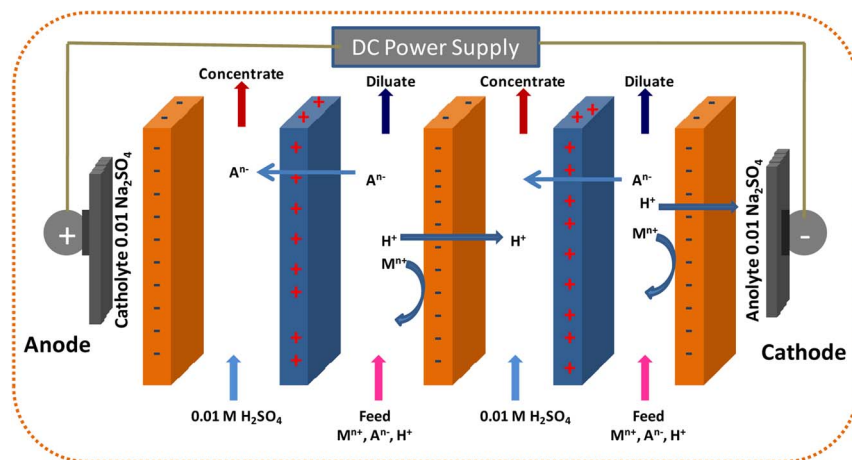*Environ. Sci.: Adv.*, 2023, **2**, 1306–1339 | **1319**

Fig. 6 Schematic of the ED cell configuration typically used for the recovery of acids and concentration of salts.

Nevertheless, anodizing plants' diluted acid liquors may include up to 20 g L^{-1} of aluminum in these.

To recover acids and water from diluted acidic wastewater streams from the aluminum anodizing industry,[340] the operating conditions in the ED process were adjusted. Studies on an industrial scale showed that thus produced concentrated acid and water solutions were of a high enough standard to be reused for the anodizing of aluminum. This lead to a 90% reduction in the amount of effluents delivered to the wastewater treatment facility and very low amounts of pollutants were released during ED treatment. The aluminum galvanic method was able to accomplish in a closed cycle, which reduces its negative effects on the environment and the economy. Overall, electrodialysis provides the aluminum sector a promising alternative.

Recovery of several commercial acids by ED processes has demonstrated that the AEM has a significant proton leak.[341,342] Therefore, research efforts had been concentrated on examining proton transport behavior in the ion-exchange membranes (IEMs) and incorporating the proton blockage mechanism in AEMs.[341–344] Due to the tiny hydrated ion radius of protons, some related studies show that the migration rate of protons is substantially higher than that of other cations in ED.[345,346] According to the "Grotthuss mechanism" and "vehicle mechanism",[347,348] the protonated water forms clusters for the former, and the protons move through the AEM as water clusters through molecular diffusion. The Donnan theory-based electrostatic repulsive force interaction is typically the best option to stop ion transmission.[349–352] The greater ion exchange capacity (IEC) of the membrane would, however, cause it to contain more water, which would facilitate more proton leakage.[344,345,353] This demonstrates the significance of water in proton transport. Consequently, utilizing weakly dissociated anion-exchange groups,[341,354] adding hydrophobic groups,[344,355] and enhancing crosslinking can improve proton blocking capabilities.[345] By grafting functional groups containing tertiary amine on the PVDF main chain, for instance, shows that acid-blocking in AEMs is possible.[355]

According to the description above, a high level of AEM stability and appropriate proton blockage performance are necessary for successful acid recovery. As a result, acid-conditioned PVDF-co-HFP is chemically stable and may be a promising option for acid recovery applications. It is anticipated that the AEM with cross-linking would exhibit the benefit of effective proton blockade. Yu et al. modified poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-co-HFP) with 1-vinyl-imidazole before crosslinking with 1,4-dibromobutane to create a sequence of proton blockage cross-linking in an AEM.[356] The PVDF-co-HFP-based AEM was reported to have an apparent asymmetric structure on its two sides, with a smooth and dense surface and a rough and porous surface. The fluorinated backbone of AEM's asymmetric structure and hydrophobicity result in greater proton blocking performance, higher electrical efficiency, and less energy-intensive acid recovery. Also investigated as a proton blocker in ED are polymer inclusion anion-exchange membranes (PIMs), which exhibit superior proton blocking without significantly impairing performance.[357] Jia et al. suggested the model assessments on an ED process for acid recovery for a potential prediction and effective optimization.[358] Using a series of thoughtfully planned studies, the detrimental effects of concentration diffusion and electro-migration on the acid recovery process were initially isolated. The undesirable movement of protons was shown to be significantly influenced by the potential gradient and concentration difference, according to the results. A thorough study of the features of the acid recovery system and ED stack configuration helps to accurately forecast the related negative contributions. In particular, the acid leakage is nearly proportional to the relevant driving forces. Proton selective membranes have a challenge in balancing perm-selectivity and ionic flux.[359] The production of acid–base pairs between basic 1-vinyl-imidazole(vi) monomers and acidified sulfonated poly(2,6-dimethyl-1,4-phenylene oxide) was suggested as a straight forward method for creating H^+ transfer channels in the membranes to address this problem (SPPO-H). The membranes are compacted and prevented from transferring Zn^{2+} by the
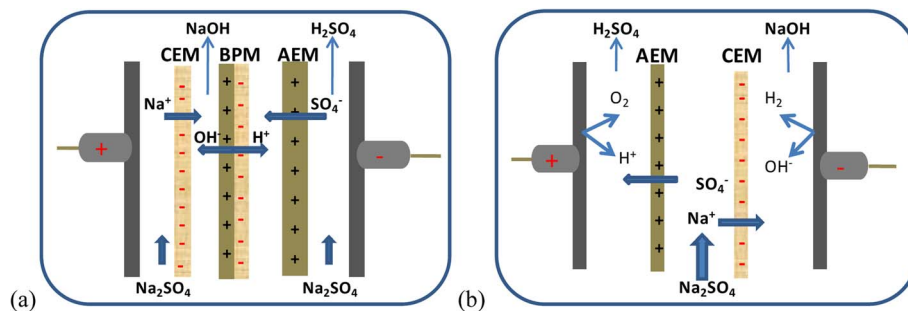
Fig. 7 Schematic representations of bipolar membrane electrodialysis (a) and electro-electrodialysis (b).

hydrogen bonding networks that are based on the acid–base interaction. On the other hand, electrostatic interactions between sulfonic acid groups and imidazole groups might facilitate the transfer of H^+, resulting in a sizable flux of H^+ through the membranes of such acid–base pairs. As a result, the finished membranes show a significant H^+ penetration but a very low Zn^{2+} leakage. This study demonstrates that zinc hydrometallurgy effluents can be treated using membranes having the acid–base pairs.

The reverse permeation of acid ions and water, which results from a large concentration difference between the concentrated chamber and the dilute chamber, significantly reduces the concentration effect of the targeted acids that are separated from acidic effluents by the electrodialysis process.[360] For the recovery of HCl, HNO_3, H_2SO_4, and H_3PO_4 in comparison to the TWEDM membrane modules consisting of loose ion exchange membranes, Wang *et al.* proposed the TWEDMS membrane modules (fabricated by Shandong Tianwei Membrane Technology Co. Ltd.) consisting of compact ion exchange membranes.[360] The TWEDMS membrane modules can offer higher concentration differences and current efficiencies for the recovery of HCl, HNO_3, and H_2SO_4 because they suppress the reverse penetration of acid ions and water from the compact membrane structure. The ideal operating conditions must be attained in order to guarantee maximum ED performances. To achieve such ideal operating conditions, a dynamic optimization technique called the orthogonal collocation approach was used.[361]

The most notable difference between selective electrodialysis (SED) and regular electrodialysis (ED) is the use of a monovalent selective ion-exchange membrane in place of the common cation exchange membrane (CEM) or anion exchange membrane (AEM). Hence, this new electric-driven method has special benefits for monovalent and divalent ion fractionation, such as the separation of lithium and magnesium,[362–364] proton and metal ion separation,[365–367] $NaCl/Na_2SO_4$ separation,[368] and others. It is possible to separate the inorganic acids from the metal ion-containing solutions by utilizing the SED process's ion fractionation capability. The concept of SED for acid recovery has been put forward in several published publications.[365–367]

Contrary to electrodialysis, both electro-electrodialysis and bipolar membrane electrodialysis involve water electrolysis, as seen in Fig. 7. Both H^+ and OH^- ions are produced when water splits at the electrode or membrane interface (bipolar membrane). Water splitting in bipolar membranes, however, has a number of benefits, one of which is reduced electricity consumption.

Bipolar electrodialysis for the purification of bases and acids has also been studied. As an illustration, the acid recovery procedure utilized the waste solutions of acid (HCl or H_2SO_4) and iron salt obtained during standard electrodialysis.[369] In comparison to the feeding solution for traditional electrodialysis, bipolar electrodialysis produced an acid solution that was 51-fold (in the case of hydrochloric acid) and 63-fold (in the case of sulfuric acid) more concentrated. Iron salt was barely present in the recovered acid solution (0.12 and 0.13%). When compared to the feeding solution for the bipolar electrodialysis procedure, the base purification process produced a NaOH solution that was nine times more concentrated. The recovered base was contaminated to varying extents (1.75 to 2.50%). For the purpose of economically recovering chromic acid in plating operations, electro-electrodialysis (EED) is a promising technique.[370,371] In a single phase, rinse water treatment, removal of metallic contaminants from the process, and recovery of the plating chemicals from rinse water are all accomplished. In one process, it might be possible to recover chromic acid, get rid of metallic impurities, and clean static rinses. However, there are constraints on the process. The main ones are the applied AEM's weak resistance to the oxidative chromic acid solution and the increase in AEM resistance, particularly at the beginning of the process, as a consequence of the formation of polychromates in the membrane.

6.   Hyphenated methods

As shown in Table S2 (ESI†), there are various techniques for treating aqueous acidic wastes. However, it is clearly seen from Table S2 (ESI†) that none of these techniques support the circular economy's goal of zero waste discharge through the recycling of water, acid, and other materials. The majority of membrane processes generate concentrate streams that are highly metal-rich and can be used for: (i) selective precipitation for metal recovery, with the supernatant (*i.e.*, water) being discharged to natural receiving bodies or being recycled internally, (ii) solvent extraction and ion-exchange for the selective

recovery of a target metal (*e.g.*, REEs, Cu and Zn), and (iii) electrowinning for the electrodeposition of one particular metal (*e.g.* Cu). The recovery of a purified acid stream is quite practical with some technologies, such as NF, DD, and MD, and can be used for processes to: (i) dissolve the raw minerals, (ii) remove impurities from the metal surface, (iii) regenerate the solvent extractant, (iv) regenerate the ion-exchange resin, and (v) regenerate the electrolyte in the electrowinning baths. However, other technologies such as ED, FO, RO, and MD obtain a stream that contains water rather than acids. In this situation, water can be either discharged to the natural water receiving bodies or reused internally. The following describes a few of the hyphenated membrane technologies that use conventional techniques or other membrane methods that have been documented in the literature.

6.1. Diffusion dialysis-electrodialysis

By utilizing the anion-exchange membrane's permanent proton-metal ion selectivity, diffusion dialysis (DD) is a novel concentration-gradient membrane technique for acid recovery but faces problems such as high water consumption and insufficient acid recovery. It was proposed that an integrated system works better than the typical diffusion-controlled devices for acid recovery and gradually increases productivity and efficiency with "minimum water usage". One promising approach for recovering acids uses selective electrodialysis (SED), which employs a potential difference as its driving force.[372] By combining these two methods, acid reclamation efficiency could be overall improved. In recent years, DD and ED processes have been merged to recover a variety of resources. However, the DD and ED individually use water at different stages of cleaning and acid recovery when operated in non-continuous modes, requiring almost double the water volume as in any other technique. But, it is possible to obtain a single pass of recoverable permeate compartment attributed to the benefit of an integrated system. This approach results in a 50%

reduction in consumable water.[372,373] Although it takes longer than conventional DD methods, such an integrated system provides minimal treatment costs. Fig. 8 depicts the typical combining methods involving DD-ED.[374]

Zhang *et al.* published a high recovery ratio (74.9%) for the integrated technique to recover HCl from wastewater of chemosynthetic aluminum foil solutions.[375] According to this study, it is important to evaluate integrated systems, reclamation insights, and recovery phenomena for various acids derived from metallurgical wastewater models.[375] However, only the recovery of HCl through an integrated process has been documented; there have been no reports of the recovery of HNO_3 or H_2SO_4 using an integrated system. Due to their large quantities in metallurgical effluents,[376] the recovery of these acids is necessary. In an effort to enhance acid recovery and preserve water, Chen *et al.* built an integrated concentration and electro-driven membrane system.[377] They also established the nonlinear relationship between mass transfer and water usage in DD. According to the study's findings, selective electrodialysis used a 0.6 V cell potential difference at a 14.9 fold reverse concentration difference to recover 80% of the secondary acid. In this way, the integrated system reduced the water consumption in the DD unit by 50% while still achieving 93% acid recovery, with the concentrated acid reaching a concentration that was 13% higher than the initial concentration of waste acid. Also, the system demonstrated excellent potentially toxic element rejection (90%), exhibited clear benefits by requiring less alkali reagent and releasing lower amount of nitrates into the environment, and highlighted its enormous potential for industrial waste acid reclamation.

Upadhyay *et al.* explored the electrodialysis integrated diffusion dialysis system using poly(ethylene) based IEMs to recover and enrich acids from metallurgical effluent.[374] The pilot scale diffusion dialysis (DD) and electrodialytic (ED) cells were integrated in a series to compare performance, taking advantage of high-permselectivity and counter-ion transport numbers in membrane-driven processes. The poly(ethylene)-
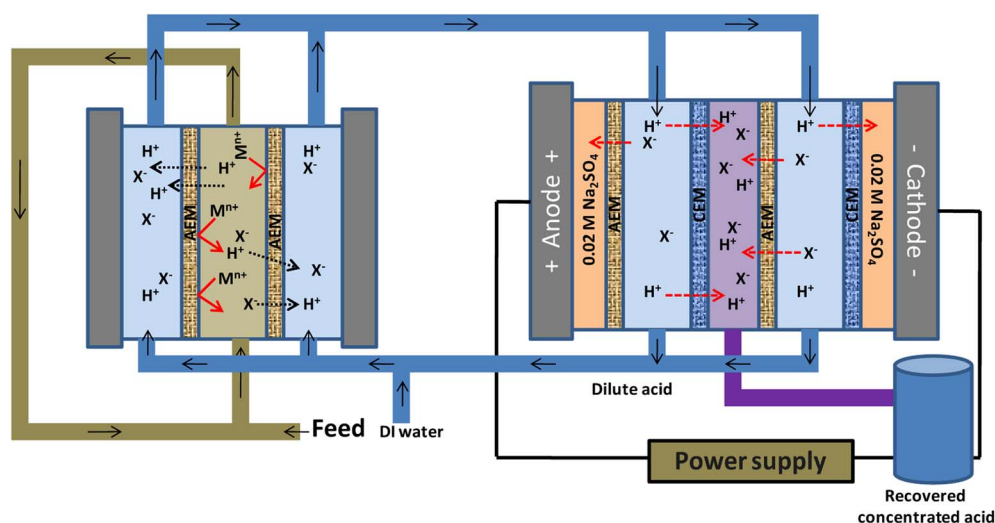

Fig. 8 Conceptual illustration of diffusion dialysis integrated selective electrodialysis cell for obtaining concentrated acids.

based inter-penetrating type cation and anion exchange membranes (In-CEM and In-AEM) were developed, which had ionic conductivities between 8 and 12 mS cm^{-1} and a counter-ion transport number (t_m) in the range of 0.80–0.95. The recoveries of HCl, HNO$_3$, and H$_2$SO$_4$ were assessed for process effectiveness using the proton dialysis coefficient (v_{H^+}), separation factor (S_f), and metal-ion leakage ($L_{Fe^{n+}}$). The counter-ion diffusivity, thermodynamic variables, dissociation coefficient, and ion's inherent trans-membrane properties for various acids were used to support this acid reclamation research. The v_{H^+} and S_f values for DD as a standalone technique were 0.35 to 0.50 $\times 10^{-3}$ m h^{-1} and 6–7, respectively. In contrast, the v_{H^+} and S_f were enhanced by 30 and 15 fold, respectively, employing the integrated system. The highest possible v_{H^+} values for HCl, HNO$_3$, and H$_2$SO$_4$ were 14 $\times 10^{-3}$ m h^{-1}, 11 $\times 10^{-3}$ m h^{-1}, and 10.2 $\times 10^{-3}$ m h^{-1}, respectively. The S_f values for HCl, HNO$_3$, and H$_2$SO$_4$ were 88.6, 91.0, and 106.0, respectively.

6.2. Nanofiltration-electrodialysis

It is anticipated that NF and SED will be cutting-edge technology for the acid recovery. It should be noted that the driving forces for the NF and SED are different, and the ion separation mechanisms for both types of membranes are also different. It is unknown which one is more suitable for treating industrial wastewater in terms of acid recovery, metal ion rejection, current efficiency, and energy consumption. As a result, Hussain *et al.* investigated selective electrodialysis and nanofiltration for acid recovery from molybdenum metallurgical wastewater.[378] A considerable amount of acidic wastewater containing significant levels of copper, molybdenum, and other non-valuable metals is generated by the molybdenum mining industry. Using a combination of selective electrodialysis (SED) and nanofiltration (NF), the separation of metal ions (Mo^{6+}, Fe^{2+}, Ca^{2+}, and Na$^+$) and recovery of sulfuric acid from molybdenum metallurgical effluent were examined in this work. SED was optimized using a constant voltage of 6 V and a volume ratio of 1 : 1 between the diluent and concentrate chambers, with the highest acid recovery being 89.6% and the highest Mo^{6+} rejection rate being 98.1%. In comparison, the NF process achieved the highest acid recovery rate of 59.1% and the highest Mo^{6+} rejection rate of 96.3% at an optimal operating pressure of 1.0 MPa. In terms of this wastewater treatment, a comparison of SED and NF reveals that SED is more competitive than NF due to its lower energy usage, higher acid recovery rate, and higher acid purity. Moreover, NF and SED together could achieve an acid recovery rate of approximately 94.2%. Also, it was possible to post-process the leftover solution into MoO$_3$ nanoparticles. In view of this, it's reasonable to conclude that SED and NF are both promising technologies for acid recovery from molybdenum metallurgical wastewater. Fig. 9 depicts the standard schematic flow sheet that was used in this work.[378]

6.3. Membrane distillation integrated technologies

Kesieme *et al.* examined the use of membrane distillation and solvent extraction for water and acid recovery from acidic mining waste and process solutions.[379] In this work, direct
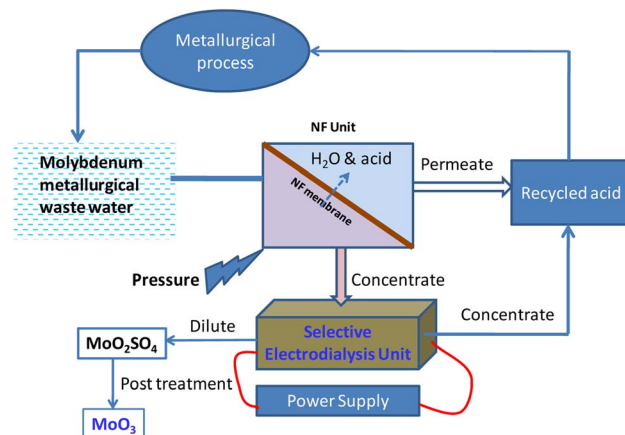

Fig. 9 Diagram of the NF-ED integrated molybdenum metallurgical process flowsheet for recovering metal ions and acids.

contact membrane distillation (DCMD) and solvent extraction (SX) are combined to recover acid and byproducts from acidic mining waste solution. By applying DCMD to concentrate the waste solution for effective acid and metal recovery using SX, it has been possible to obtain high water recovery and concentrate the acid for the reuse. Fig. 10 illustrates a proposed flow-sheet for recovering water, sulfuric acid, and metal values. H$_2$SO$_4$ concentration rose from 0.85 mol L^{-1} in the feed solution to 4.44 mol L^{-1} in the concentrate during the DCMD phase using the synthetic acidic waste solution. The efficiency of the metal and sulphate separation was >99.99%, while the overall water recovery was greater than 80%. The concentrated solution was first treated to recover water using DCMD, followed by sulfuric acid recovery using SX using an organic phase made up of 50% TEHA and 10% ShellSol A150 in octanol. From the waste solution, which contained 245 g L^{-1} H$_2$SO$_4$ and metals with varying concentrations, more than 80% H$_2$SO$_4$ was recovered in a single contact. With only 2.4 g L^{-1} H$_2$SO$_4$ remaining in the raffinate after three stages of consecutive extraction, approximately 99% of the acid could be removed. Using water at 60 °C, the extracted acid was easily separated from the loaded organic solution.
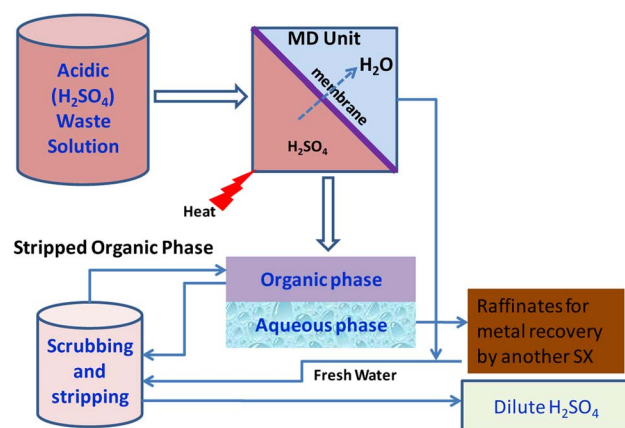

Fig. 10 A conceptual flow-sheet to recover water, sulphuric acid and metals (inorganic salts) by the integrated MD-SX process.

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A unique membrane-integrated waste acid recovery technique from pickling solution has been developed by Culcasi *et al.* combining membrane distillation (MD) and diffusion dialysis (DD) technologies with a reactive precipitation unit, where iron ions can be isolated from the zinc-rich solution, and can result in continuous treatment and regeneration of pickling solution.[380] To maintain ideal HCl and iron concentrations in the pickling tank and to separate iron and zinc ions in a reactive precipitation unit, the proposed method integrates DD and MD processes with a reactive precipitation unit. Fig. S2 (ESI†) provides a conceptual schematic illustration of MD-DD combined technology for the acid recovery.

A mixture of waste acids with aluminum and/or molybdenum impurities is produced during the etching operations used to make semiconductors. These waste acids include acetic acid (HAc), nitric acid (HNO_3), and phosphoric acid (H_3PO_4). By using vacuum distillation and diffusion dialysis, Kim *et al.* attempted to recover phosphoric acid from mixed waste acids of the semiconductor industry.[381] To recover phosphoric acid from mixed waste acids, diffusion dialysis using a newly developed anion exchange membrane technique was followed by vacuum distillation.

Many combinations of membrane distillation and other techniques are possible, including MD-ion exchange, MD-bioreactor (MDBR), MD-crystallizer, *etc.*[8,382] The simultaneous creation of both fresh water (>98% ion rejection) and solution concentration is made achievable by MD-ion exchange-based technology.[383] The benefits of this integration include: (i) the potential for simultaneous recovery of valuable low concentration elements (such as REEs) from AMD using a selective ion exchange adsorbent in a single system, (ii) the potential for improved performance of the ion exchange adsorbent due to increased AMD concentration (while producing high quality water) under MD and thermal conditions; and (iii) the reuse capacity of the ion exchange adsorbent.

The MDBR process combines a membrane bioreactor with MD to recover water while also treating wastewater. Submerged and stepwise are the two basic operational setups that are typically used.[384] The main advantages of this integration is that MDBR operates at low operating pressures and moderate temperature, achieving excellent rejection of nonvolatile compounds and producing high quality permeate that is independent of biological activity. In comparison to standalone MD, operation of an increased thermophilic biological process enables greater organic biodegradation, which delays membrane fouling and wetting. Furthermore, MD-crystallizer integration has also been studied.[385,386] This combination can concentrate feed solution while selectively crystallizing salt (close to zero liquid discharge). The integrated MD-crystallizer process reduces scaling on the MD membrane by continuously crystallizing salt. This small integrated system may produce high-quality water and recover valuable metals as salt crystals for small-scale treatment with low flow rates (like AMD), and hardly any chemicals are needed for the salt precipitation. Yadav *et al.* recently reviewed the membrane distillation crystallization technology for the zero liquid discharge along with resource recovery.[387] The

operational difficulties, such as crystal deposition (scaling) on the membrane surface, the pore wetting phenomena, and the economic implications are also examined in this review.[387] The appropriate membrane synthesis is highly important for any MD standalone or integrated technology.[388]

7. Emerging green alternatives

Green alternatives for inorganic acids involve the use of environmentally friendly substitutes that have reduced environmental impacts and are derived from renewable resources as described below.

7.1. Organic acids

Organic acids can often serve as greener alternatives to inorganic acids. These acids are derived from natural sources and can be biodegradable, making them more environmentally friendly. For example, citric acid, acetic acid (vinegar), and lactic acid are commonly used as alternatives to inorganic acids in various applications. They can be effective for tasks such as pH adjustment, cleaning, and metal processing.

7.2. Bio-based solvents

Bio-based solvents derived from renewable resources offer greener alternatives to traditional inorganic acids. Solvents such as limonene (derived from citrus fruits), ethanol (derived from biomass), or terpenes (derived from plant sources) can be used as substitutes in applications where inorganic acids are traditionally employed. These solvents are often less toxic, have lower volatile organic compound (VOC) emissions, and can be more readily biodegradable.

7.3. Enzymatic processes

Enzymes offer an environmentally friendly alternative to inorganic acids in various industrial processes. Enzymes are biodegradable proteins that can act as catalysts for specific reactions. They operate under milder conditions and can provide high specificity, reducing the need for harsh acids. Enzymatic processes can be employed in tasks such as cleaning, surface treatment, and organic synthesis.

7.4. Supercritical fluids

Supercritical fluids, such as carbon dioxide (CO_2) in its supercritical state, can be utilized as green alternatives to inorganic acids. Supercritical fluids possess unique solvent properties, making them effective in various applications. They are non-toxic and non-flammable, and can be easily separated from the product. Supercritical fluids can be employed in tasks such as extraction, cleaning, and synthesis, reducing the need for traditional acidic solvents.

7.5. Green chemistry principles

The principles of green chemistry advocate for the design and use of inherently safer chemicals and processes. By adopting these principles, industries can minimize the use of inorganic

acids and prioritize greener alternatives. This includes strategies such as using less hazardous reagents, optimizing reaction conditions to reduce waste and energy consumption, and designing processes that generate less hazardous by-products. It's important to note that the choice of green alternatives depends on the specific application, process requirements, and availability of suitable substitutes. Transitioning to greener alternatives for inorganic acids can contribute to sustainable industrial practices, reduce environmental impact, and promote a more circular and resource-efficient economy. One of the most promising alternatives to inorganic acids without the need to change existing technology is deep eutectic solvents (DESs). After their emergence as a concept some 15 years ago, DESs are today one of the most prominent areas of research within the larger fields of green chemistry and engineering.[389–392] The term "DES" typically refers to self-associating mixtures of two or more Bronsted/Lewis acids and bases that exhibit a "eutectic" character upon combination when compared to their native constituents and exhibit a "deep" (*i.e.* large) melting point depression.[390,393,394] The construction of a vast network of intra- and intermolecular interactions, specifically hydrogen bonding between the involved species, is responsible for the formation of such systems.[390,393] Numerous applications of DESs have been prompted by their "green" qualities *e.g.* minimal vapor pressure, lack of toxicity, ease of preparation, biodegradability, *etc.*[390,395–397] In addition to this, DESs have interesting physicochemical properties such as a broad polarity range, electrical conductivity, high surface tension, and good thermal stability.[390,394,398] The majority of DES applications at present have been in the metal finishing industry, and their relative toxicity must be compared to that of the aqueous mineral acids they are intended to replace. The environmental effects of the DES based on choline chloride and ethylene glycol in electroplating applications have been studied by Haerens *et al.*[399] Both components are easily biodegradable and have no negative environmental effects, and therefore, the resulting DES is no different.

DESs can offer adequate media for the industry's many technological objectives.[400,401] In appropriate systems, it may be possible to replace ecologically harmful metal coatings, deposit new alloys and semiconductors, and use new coating techniques to deposit corrosion-resistant metals like Ti, Al, and W.[402–404] When it comes to technologically significant plating systems like Ni, Co, and Cr, where many of the aqueous precursors are proven carcinogens, DESs may provide workable alternatives to get around regulatory constraints. DESs have been used to study a variety of metal reduction processes, including those involving Zn,[403–406] Sn, Cu,[407,408] Ni,[409] Ag,[410] Cr,[411] Al,[412] Co, and Sm.[413]

Stainless steels have generally benefited from electropolishing, but DESs have also made it possible to electropolish aluminum, titanium, Ni/Co alloys, and super alloys. Stainless steel has received the majority of attention when it comes to electropolishing in deep eutectic solvents, but aluminum, titanium, Ni/Co alloys, and super alloys have also been studied.[397] Using anodic electrolytic etching with an ethylene

glycol:choline chloride DES, a new process has been created for removing surface oxide scale from single crystal aerospace castings of nickel-based super alloys generally used in turbine blades.[414] This technique makes it possible to remove scale from cast components, allowing the detection of flawed components prior to the pricey and time-consuming heat treatment procedure.

In a recent review, it has been examined how crucial processes including metal winning, corrosion remediation, and catalyst preparation depend on the dissolving of metals and metal oxides.[415] The processing and reprocessing of metals is the source of a huge volume of aqueous waste, with the treatment of acidic and basic byproducts being both energy and chemical expensive.

Many deep eutectic solvents have been the subject of in-depth studies regarding the solubility of metal oxides. A number of metal oxides have been demonstrated to be dissolved by type III DESs,[416] and ligands like urea, thiourea, and oxalate are well-known complexants for many metals and can be added to the DES. Electrochemistry can be used to separate metals from complicated mixtures. However, this method has a drawback in that all of the liquids are completely miscible with water and cannot be used for a biphasic extraction. Three DESs based on choline chloride have been reported to dissolve 17 metal oxides in the elemental mass series Ti through to Zn.[417] The careful selection of the hydrogen bond donor was resulted in the selectivity for extracting specific metals from complicated matrices.[390]

In general, DESs have the potential to replace inorganic acids, but this field is still in its infancy, in part because of unknown cost and technological factors.

8.   Conclusions

Based on the review of the various technologies used to treat the aqueous acid waste produced by various industries, hyphenated technologies may be very effective for the circular economy and would have zero waste discharges into the environment. By combining membrane technologies with solvent extraction, ion-exchange, crystallization, precipitation, and other processes, numerous hyphenated technologies are made available. Combining two membrane technologies with distinct advantages is also possible, for example, diffusion dialysis with electrodialysis, membrane distillation or nanofiltration to produce pure and concentrated acid, salt remediation, and water reuse. However, the requirements for the acid waste produced by various sectors vary. Thus, it is necessary to integrate various approaches in order to fulfil the demand for a specific acidic waste discharge, to achieve the zero-waste discharge, and circular economy goals. Another interesting development would be the use of deep eutectic solvents as superior eco-friendly alternatives to inorganic acids. There has been a lot of research done on the potential uses of deep eutectic solvents in solvometallurgy, mineral dissolution, electroplating, and electropolishing, among other things. Deep eutectic solvents offer superior qualities to inorganic acids and are non-toxic, biodegradable, and recyclable, but still there are

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significant technological and financial barriers to overcome. Consequently, it may not be overstated to say that deep eutectic solvents could eventually replace inorganic acids in order to foster circular economy without putting undue strain on the environment or natural resources.

Author contributions

Conflicts of interest

The authors declare that they have no known conflict of interest that could have appeared to influence the work reported in this paper.

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