Review

Metal Recovery from Wastewater Using Electrodialysis Separation

Maria del Mar Cerrillo-Gonzalez [ID]**, Maria Villen-Guzman ***[ID]**, Jose Miguel Rodriguez-Maroto**[ID] **and Juan Manuel Paz-Garcia**[ID]

Department of Chemical Engineering, University of Malaga, 29010 Malaga, Spain;
mcerrillog@uma.es (M.d.M.C.-G.); maroto@uma.es (J.M.R.-M.); juanma.paz@uma.es (J.M.P.-G.)
* Correspondence: mvillen@uma.es

Abstract: Electrodialysis is classified as a membrane separation process in which ions are transferred through selective ion-exchange membranes from one solution to another using an electric field as the driving force. Electrodialysis is a mature technology in the field of brackish water desalination, but in recent decades the development of new membranes has made it possible to extend their application in the food, drug, and chemical process industries, including wastewater treatment. This work describes the state of the art in the use of electrodialysis (ED) for metal removal from water and wastewater. The fundamentals of the technique are introduced based on the working principle, operational features, and transport mechanisms of the membranes. An overview of the key factors (i.e., the membrane properties, the cell configuration, and the operational conditions) in the ED performance is presented. This review highlights the importance of studying the inter-relation of parameters affecting the transport mechanism to design and optimize metal recovery through ED. The conventional applications of ED for the desalination of brackish water and demineralization of industrial process water and wastewater are discussed to better understand the key role of this technology in the separation, concentration, and purification of aqueous effluents. The recovery and concentration of metals from industrial effluents are evaluated based on a review of the literature dealing with effluents from different sources. The most relevant results of these experimental studies highlight the key role of ED in the challenge of selective recovery of metals from aqueous effluents. This review addresses the potential application of ED not only for polluted water treatment but also as a promising tool for the recovery of critical metals to avoid natural resource depletion, promoting a circular economy.

Keywords: metal separation; membrane; selectivity; purification; industrial effluent

1. Introduction

During recent decades, the rising population and industrialization have increased demand for the Earth's natural resources and the occurrence of subsequent environmental problems. One of these problems is the generation of large amounts of wastewater containing metals that are a risk to the population and ecosystems due to their toxicity [1]. Some metals affect biological function and can accumulate in different organs, causing hazardous effects [2]. The most prevalent metals found in wastewater are Al, As Cd, Cr, Cu, Hg, Pb, Ni, Zn, Co, Fe, and Mn, and their composition in wastewater differs according to the type of industry (see Table 1). The main sectors that contribute to this problem are mining, smelting, foundries, and other chemistries such as textiles and refineries [2].

The negative effect of some metals in wastewater makes it necessary to treat these industrial effluents before discharging to reduce the pollution. The conventional method to remove metals from industrial effluents has been chemical precipitation, adjusting the pH of the effluents, and removing the precipitated particles through sedimentation or filtration [3]. Other chemical-based separation methods include coagulation/flocculation

and flotation. These methods can be applied to treat industrial effluents with high metal concentrations. Although these methods are simple and require inexpensive equipment, they involve a large amount of chemicals to reduce metal concentrations and a large-volume sludge formation which requires post-treatment [4]. As an alternative method, adsorption is widely selected to remove metal from aqueous effluents. Several studies have focused on developing cheaper and more efficient adsorbent materials in the last decade, for example, natural materials, industrial by-products, or biological and agricultural waste [5]. However, biosorption (i.e., adsorption with biological materials) has some shortcomings, such as a lack of specificity in metal binding, large amounts of biomass required if the biosorption capacity is low, and a limited reusability of biomass after desorption for real applications in industrial effluents [6]. Another method applied to remove metals from aqueous effluents is ion exchange due to its higher ion selectivity and the reusability of ion-exchange material. The main drawbacks of this technology are high operational costs, which limit application at industrial scale, and the formation of fouling by solids and organic compounds contained in industrial effluents [6]. Electrochemical processes based on passing a direct current through an aqueous solution containing metal between electrodes have also been widely studied. Metal selectivity, no consumption of additional chemicals, high efficiency, and lower amounts of sludge produced are the main advantages of these processes. However, electrochemical technologies possess some drawbacks, such as a high dependence on the pH values of aqueous effluents and high operational costs related to electrical energy requirements and electrode replacement [3].

Table 1. Typical metals found in industrial wastewater, data from [3].

Industries	Al	As	Cd	Cr	Cu	Hg	Pb	Ni	Zn	Co	Fe	Mn
Paper mills				x	x	x	x	x	x			x
Organic chemistry	x	x	x	x		x	x		x			
Fertilizer	x	x	x	x	x	x	x	x	x			
Petroleum refinery	x	x	x	x	x		x	x	x			
Steel works		x	x	x	x	x	x	x	x	x		
Aircrafts	x		x	x	x	x		x			x	
Textile mills				x								
Power plants				x								
Pharmaceutical		x	x	x	x		x	x	x			
Engineering			x	x	x		x	x	x		x	
Metal smelters		x										
Electroplating			x					x	x			
Mining								x				
Ferromanganese production											x	x

Some alternative technologies to conventional methods are based on pressure-driven membrane processes, such as ultrafiltration, nanofiltration, and reverse osmosis [7]. Another membrane technology is electrodialysis (ED), which involves the migration of cations and anions through ion-exchange membranes under the effect of an electric field. This technique has been employed industrially to treat saline waters and brines. However, its selective separation of charged species offers excellent advantages, increasing its interest for treating water containing metals. Some advantages related to the selective separation of ions are the high separation efficiency, low operating pressure, small operating footprint, no need for adding chemicals, and reduced sludge formation. Moreover, this technology can treat effluents with low concentrations of metal ions. All these advantages make electrodialysis one of the most effective and promising technologies for treating industrial effluents [8].

The potential of electrodialysis is not only focused on treating wastewater effluent-containing metals but also on the revalorization of waste and promoting the circular economy. This work presents an overview of the state of the art of this technique, summarizing the current research and industrial applications of electrodialysis.

2. Methodology and Review Structure

This review was guided by the Kitchenham framework for literature reviews [9], including the three main stages: planning, conducting, and reporting results. Prior to searching the available literature related to the main topic, the need and novelty of this review must be defined. In this step, the research questions were defined, and the keywords were selected to filter the information that could answer the research questions (Table 2).

Table 2. Research questions and keywords that guided the review.

	Research Questions
Q1	What are the fundamentals of electrodialysis?
Q2	Can electrodialysis be used to treat wastewater?
Q3	Is electrodialysis used to separate metals from industrial wastewater?

Once the research questions and keywords were selected, the data extraction and article selection were performed. For that, we considered mainly works from the last fifteen years (2008–2023), which were published in three databases: Scopus, Web of Science, and Sciencedirect. The search terms were the same for all databases, "electrodialysis" and "metals", with additional strings of "wastewater" and "recovery", and they were searched in the title, abstract and keywords. Table 3 presents the number of works that matched with our research terms in each database.

Table 3. Research results in databases using the selected search terms.

Database (2008–2023)	Electrodialysis and Metals	Electrodialysis and Metals and Wastewater	Electrodialysis and Metals and Wastewater and Recovery
Scopus	676	239	111
Web of Science	648	185	111
Sciencedirect	227	80	44

Finally, the results obtained are presented and discussed. For that, the current work has been organized into five sections in total. First, a general introduction presents the environmental challenges posed by metal contamination in industrial wastewater, and the potential of electrodialysis to the circular economy as a promising and efficient treatment technology. The current section outlines the structure of this review, and the methodology followed to filter and select the information. In the third section, the operational principles and the mass transport mechanism of the process are presented to understand the fundamentals of the electrodialysis process. The fourth section presents the state of the art of the application of electrodialysis for water treatment. The section is divided into three subsections. In the first one, the general application of electrodialysis is presented, particularly focused on desalination and industrial wastewater treatment. The second and third subsections are focused on the use of electrodialysis not only to treat industrial wastewater but also to recover metals. The difference between these two subsections is the number of metals recovered from effluents (i.e., recovering only one or multiple metals from the mixture). Finally, the fifth section contains the conclusions reached from the discussion of the information presented in the current review work.

3. Fundamentals of Electrodialysis Processes

3.1. Operational Principle

The working principle of ED consists of the migration of cations and anions through cation-exchange membranes (CEMs) and anion-exchange membranes (AEMs), respectively, induced by an applied electric field set between a pair of electrodes. In a simple electrodialysis cell (Figure 1), a pair of membranes is used. Anions migrate towards the anode, and cations towards the cathode, resulting in an overall decrease in the feed stream salt concentration. The membranes are separated by channels ending with the electrode compartments.
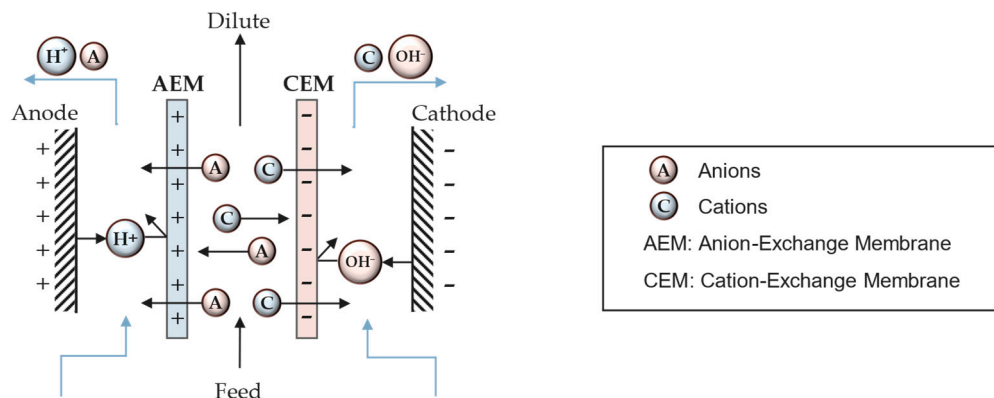
Figure 1. Schematic of a simple (two-membrane) electrodialysis cell.

The two-membrane ED cell results in the production of an acid and a base from the fed salt. The unit cell is formed by an AEM, a CEM, and a channel in-between where the concentrated salt solution is fed. The application of an electrical current between the electrodes promotes the dissociation of water at the electrodes [10].

Multichannel cells consist of a system of alternative membranes creating channels which produce diluted and concentrated outflows (Figure 2). The flow containing ions is fed in the channels between membranes. Anions migrate toward the anode crossing the AEM but they are retained in the compartment due to the presence of an adjacent CEM. In this channel, there are also cations coming from the opposite directions, migrating to the cathode through the CEM, but they are blocked by the AEM. This means the migrated anions and cations remain blocked in the same compartment, creating a concentrated channel. On the other hand, the adjacent channels to the concentrate are denoted as dilute channels due to the reduction in both anion and cation concentrations. The combination of an AEM, a concentrated channel, a CEM, and a dilute spacer is known as a cell pair.
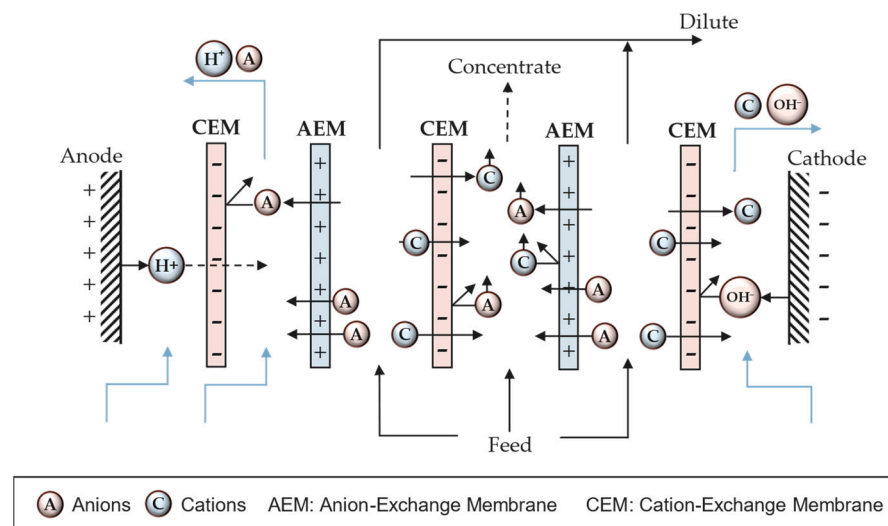

Figure 2. Depiction of a multichannel electrodialysis stack.

In aqueous solution, water electrolysis reactions are expected to take place: namely, water oxidation at the anode, Equation (1), and water reduction at the cathode, Equation (2).

$$\text{Anode}: \ 2H_2O \rightarrow 4H^+ + O_2 \uparrow + 4e^- \tag{1}$$

$$\text{Cathode}: \ 2H_2O + 2e^- \rightarrow H_2 \uparrow + 2OH^- \tag{2}$$
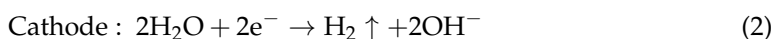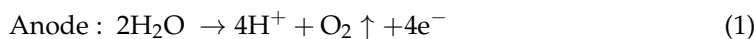
However, different electrochemical reactions may occur depending on the nature of the involved ions. For example, in the presence of chloride ions, chlorine gas can be formed at

the anode. Similarly, certain metal ions may electrodeposit at the cathode surface. Different cell configurations can be used to prevent certain electrochemical reactions. Figure 2 shows a CEM at the anode end to prevent the anion, assumed to be Cl^-, from reaching the electrode surface and forming Cl_2 gas.

The development of membrane technologies has allowed new cell configurations, expanding the application of electrodialysis [11]. An interesting enhancement is the use of bipolar membranes in the cell stack (Figure 3). A bipolar membrane (BM) is composed of an anion-exchange layer (AEL) and a cation-exchange layer (CEL), and does not allow anions and cations through it. This phenomenon promotes the dissociation of water available within the thin layer between AEL and CEL into protons (H^+) and hydroxyl (OH^-). This cell configuration generates an acidic and alkaline compartment on both sides of the bipolar membrane due to H^+ and OH^- crossing the CEL and AEL, respectively [12].
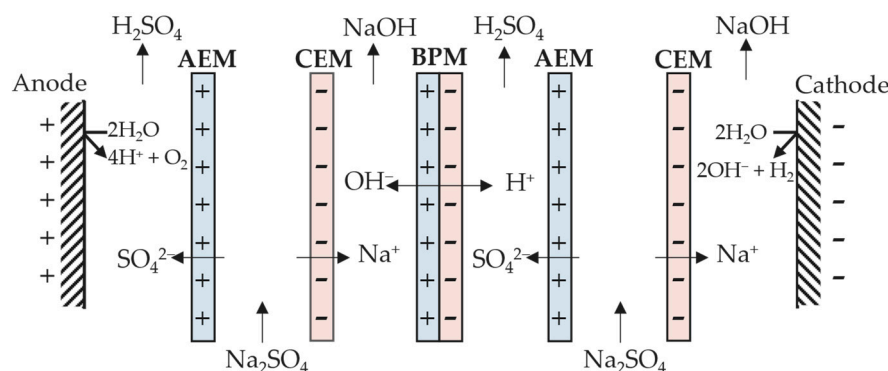

Figure 3. Depiction of a three-compartment electrodialytic cell with a bipolar membrane.

The use of monovalent anion-exchange membranes (MVAs) and monovalent cation-exchange membranes (MVCs) has been recently proposed to selectively separate ions in different ED compartments [9]. In this case, an MVA is used in the cell, which allows only the migration of monovalent anions, producing two compartments: one with multivalent anions retained and the other with monovalent ions (Figure 4). This process is classified as "selectrodialysis". In addition to using MVAs and MVCs, selectrodialysis can be achieved using different pH and chelating/complexation agents.
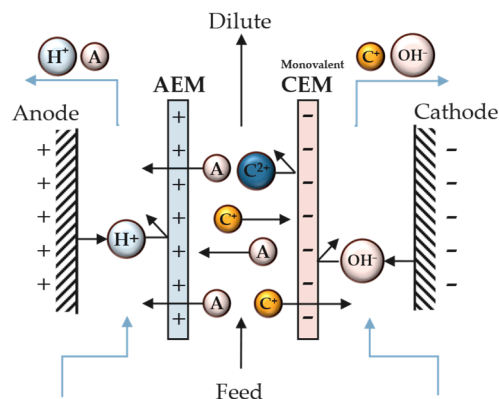
Figure 4. Scheme of a unit cell with a monovalent cation-exchange membrane.

One of the main drawbacks in the membrane processes is the fouling of their surfaces, caused by suspended particles or the precipitation of dissolved solids. Solid particles cause the deterioration of the membranes, increasing their electrical resistance with a subsequent lowering of the ED performance. In addition to performing pretreatments and cleaning procedures to prevent surface fouling, electrodialysis reversal (EDR) has been proposed to mitigate the fouling problem [13]. The technique consists of switching periodically the polarity of electrodes to force the migration of charged components to the

opposite direction [14]. Several studies reported the success of EDR systems due to their self-cleaning mechanism.

3.2. Mass Transport Mechanism

Mass and charge transport in electrolyte solutions and ion-exchange membranes is described with the same set of equations. Under an electric field, ions are mainly transported by electromigration. Diffusion transport becomes significant at the boundary layers, near the membranes and the electrodes, due to high concentration gradients. The coupling of these transport mechanisms is known as electrodiffusion and can be described by the Nernst–Plank transport equation, which considers the diffusive, electromigration, and convective flux to calculate the total flux of ions, J_i (mol/m^2/s):

$$J_i = -D_i^* \nabla c_i - \frac{z_i F D_i^*}{RT} c_i \nabla \varphi + c_i u \quad ; \quad i = 1, 2, \ldots, N_i \tag{3}$$

where c_i (mM) is the concentration, D_i^* (m^2/s) is the effective diffusion coefficient, z_i is the ionic charge, F ($\approx$95,485 A/mol) is the Faraday constant, φ (V) is the electric potential, and u (m/s) is the velocity of water. The term $z_i F D_i / RT$ (m^2/s/V) is known as the ionic migration coefficient. The set of equations is completed with the following electroneutrality condition:

$$\sum_{i=1}^{N_i} c_i z_i = 0 \tag{4}$$

At the submicro scale, at the interface of the electrically charged membranes, the electroneutrality condition does not hold, and electrical double layers form. This can be described by means of the Poisson equation:

$$\nabla^2 \phi = -\frac{F}{\varepsilon} \sum_{i=1}^{N_i} c_i z_i \tag{5}$$

where ε (F/m) is the medium permittivity ($\varepsilon = \varepsilon_0 \varepsilon_r$; $\varepsilon_0 \approx 8.85 \times 10^{-12}$ F/m and $\varepsilon_r \approx 80.2$ for water at 20 °C).

The performance of an electrodialysis treatment depends on numerous variables, such as the membrane properties, the cell configuration, and the operational conditions. Regarding the transport mechanisms, the most important parameters are the electric current applied, the electrical conductivity of the electrolytes and the membranes, the concentration and pH of the electrolyte solutions, and the stream flow rate. All these parameters are inter-related between each other, and the study of their effects is essential to design and optimize the process.

Ion-exchange membranes (IEMs) are crucial elements of any ED process, and their characteristics play an important role in the performance of the process. Membrane properties can be divided into physicochemical (e.g., thickness) and electrochemical properties (e.g., permeability, selectivity, charge density, and area resistance) [15]. IEMs are dense polymeric membranes containing fixed charges in the polymer matrix, which can selectively enable the passage of oppositely charged ions (counter ions) while obstructing similarly charge ions (co-ions). The enhancement in the permselectivity between counter and co-ions as well as between counter ions with different (monovalent and multivalent) or equal valences (Cl$^-$ and NO$_3{}^-$) has allowed the expansion of IEMs to multiple applications [16]. However, improving the permselectivity involves an increase in cross-linking in the polymer matrix, which also results in an increase in the area resistance, which is not desirable from the point of view of energy efficiency. Thus, membrane designers must find a balance between permselectiviy and area resistance. Lu et al. [16] elaborated a comprehensive review of IEMs, focused on the progress of membrane manufacturing techniques, ion transport mechanisms, and experimental approaches to determine ion selectivity. In the same line, Tekinalp et al. [17] published a review on cation-exchange membranes and their

properties for selective metal separation by electrodialysis. They discussed the counter ion selectivity based on the membrane properties and the operational conditions, emphasizing the implication of the boundary layer at the membrane surface in the transport ratio of competing counter ions.

The Intensity of the applied electric current is also one of the key factors in an electrical separation process. By default, operating with the highest possible current density is desirable to increase the driving force and achieve the maximum ion flows. However, high electric current values have drawbacks, such as increased energy requirements, possible membrane damage, and increased concentration polarization at the membrane surfaces. [8]. Concentration polarization appears due to the difference in transport numbers of the ions (i.e., the fraction of the current carried by each ionic species) in the solution and the membranes. In the solution electrolyte, the ionic current derives from the transport of both cations and anions. In the membrane, the ionic current is only transported by the counter ions inside the membranes, resulting in a higher transport number through the membranes than in the solution. This phenomenon leads to the formation of concentration gradients at the solution–membrane interface, decreasing the concentration with respect to the bulk in the dilute compartment and increasing it in the concentrate compartment.

Depending on the applied current density, the concentration of specific ions can deplete near the surface membrane of the dilute region, which means there may not be any available ions to transport the current in that region. The current density that generates the depletion of the ion concentration to zero is known as the limiting current density. Working over the limiting current density is not recommended due to the increased electrical resistance and voltage drop, negatively affecting the process efficiency [18]. Furthermore, when approaching the limiting current density, the lack of ions in the system promotes the migration of protons and hydroxides, which are replenished through the water self-ionization reaction. This phenomenon is referred to as water splitting [19].

The ion concentration in the feed solution plays an important role in the process's efficiency. A low concentration in the solutions involves low ionic conductivity, affecting ions' migration across the IEMs due to lower diffusion- and electromigration-driven forces. On the other hand, high concentrations of ions can cause some problems. First, the recovery rate of the target ions can be reduced because the residence time is insufficient to separate the desirable number of ions. Second, although electrical resistance decreases, applying a high value of electric current is necessary to mobilize the ions to the recovery compartment. Finally, in the case of metallic ions, a high concentration can cause their precipitation if the pH is not appropriate. Hence, one of the first parameters that should be decided in designing an ED stack is the feed flow, and then, the concentration of the dilute and concentrate output flows.

The pH is also an important parameter, especially when the feed flow contains metallic ions, in which the ED treatment is typically carried out at low pH to avoid metal precipitation. However, low pH affects ED variables such as concentration polarization, current efficiency, and energy consumption [20]. Protons are ions with the highest molar conductivity ($350.1\ \Omega^{-1}\ cm^2\ mol^{-1}$ at 25 °C [21]). So, when the pH is low, protons are the predominant current transporter in the systems, affecting the recovery efficiency because the current is used to mobilize the protons instead the other cations.

Controlling the pH and optimizing its value is crucial to the excellent performance of ED treatment. According to Abou-Shady et al. [20], who studied the effect of pH on the separation of Pb(II) and NO_3^- from aqueous solution by electrodialysis, the optimal pH range for metallic ion solutions is between 3 and 5. Operating at pH < 3 makes the technique noneconomical due to high energy consumption, while operating at pH > 5 has undesirable effects, such as metal precipitation.

Water electrolysis tends to generate an acidic medium and an alkaline medium in the anode and cathode compartments, respectively. The alkalization of the catholyte may produce the precipitation of salts and hydroxides, while the acidification of anolyte leads to an increase in the energy consumption due to the high ionic conductivity of protons.

Furthermore, water electrolysis reactions involve the formation of O_2 and H_2 at the anode and cathode, respectively, which may produce polarization at the electrodes due to attached bubbles and overpressure in the compartments.

4. Application of the Technique

4.1. General Application

Electrodialysis has been applied for the desalination of brackish water. The first commercial ED equipment was sold by Ionics Inc. (Watertown, MA, USA) in 1954 to Arabian-American Oil Co. and installed in Saudi Arabia to produce demineralized water. Since then, the use of ED to remove salt from brackish water has extended to the United States and Europe. However, in the last decade, with the development of new membrane technologies, electrodialysis has become an alternative to reverse osmosis for seawater desalination [22]. An example of this is the Maspalomas desalination plant (Spain), built in 1986. Initially, the plant featured electrodialysis reversal technologies, which were replaced by reverse osmosis membranes in 2006 due to the need to increase its capacity (33,500 m^3 per day) [23].

Even so, electrodialysis has an economic advantage in a certain feed water salt composition range [24]. Electrodialysis is normally used in small- and medium-size plants (100–20,000 m^3/day) with a water salinity of 1–5 g/L of total dissolved solid (as higher salt contents entail higher energy requirements), while reverse osmosis (RO) is recommended for the desalination of water with dissolved solid concentrations higher than 10 g/L [22]. Moreover, some of the advantages of ED compared to RO are high water recovery rates, long lifetime of membranes, and less membrane fouling when using electrodialysis reversal. On the other hand, one of the disadvantages is that neutral toxic components, such as some viruses or bacteria, are not removed, and the produced water needs a post-treatment to be potable [18]. Another disadvantage of electrodialysis is the relatively high energy consumption, 2.6–5.5 kWh/m^3, compared to the energy requirement of reverse osmosis, 1.5–2.5 kWh/m^3 [25].

Although reverse osmosis leads in the water desalination market due to its advantages, ED combined with RO has a great potential [26–30]. RO generates large volumes of concentrate, typically 10–50% of the feed flow, that is usually discharged into the sea or treated by evaporation. With the aim of reducing the environmental and economic impact of the process, ED has been proposed to recover water and other valuable products from the RO concentrate, thereby minimizing the volume of discharge and contributing to the zero liquid discharge system [10]. In short, the role of ED is concentrating the RO waste even more to obtain an enriched stream of ions that favors the recovery of these ions in subsequent steps, and other streams of freshwater that can be mixed with the RO dilute, to increase the recovery of water in the process [27]. Brackish water is first treated with RO, and, subsequently, the concentrate stream is fed to an ED stack, increasing the concentration of total dissolved solids (TDs) from 1% to 10% and enhancing the overall water recovery from 82.5% (RO) to 92.1% (RO + ED).

In addition to brackish water desalination, other important applications of conventional electrodialysis are the demineralization of industrial process water and industrial wastewater treatment. In an industrial process, water is usually demineralized and neutralized before being used as process water to avoid equipment corrosion. Moreover, industrial wastewater is usually treated before being discharged to other water bodies due to its high salt concentration or toxic constituents that pose a risk to the environment. Because of the huge volume of water required in industrial processes, especially in cooling systems, a typical practice is reusing a fraction of treated wastewater to, on one hand, save costs related with the supply of fresh water, and, on the other hand, reduce wastewater discharge. Electrodialysis is particularly appropriate for the treatment of cooling water blowdown since high recovery rates and high brine concentrations can be achieved [31]. Furthermore, the temperature operation range of ion-exchange membranes is suitable for most cooling systems [22].

Regarding the treatment of wastewater, several applications of ED have been investigated to enhance the properties of municipal wastewater effluents. The reuse of tertiary treated effluents from wastewater treatment plants (WWTPs) is considered one of the solutions to the scarcity of water resources. However, conventional tertiary effluents are not always suitable for use, as some quality standards are not achieved. For example, the high salinity of effluents from WWTPs hinders the reuse of water for irrigation. Hence, ED can be used to reduce the salinity content of the effluent from WWTPs [32].

The economic and technical feasibility of applying ED to tertiary effluent has been reported in several studies [10]. Goodman et al. [33] investigated the capacity of a system based on EDR to remove salts from treated municipal wastewater. The pilot plant was constituted by a multimedia filtration unit and an EDR system with a capacity of 144 m^3/day. After prefiltration and coagulation–disinfection with $Fe_2(SO_4)_3$ and NaClO, the effluent was transferred to the multimedia filtration unit, then to the EDR system to remove the salt. The pilot plant reduced the total dissolved solid from 1104 mg/L to 328 mg/L, thus below the limit of 375 mg/L indicated by the Australian government and World Health Organization [34]. Moreover, the conductivity of the recycled water was reduced by 72%, demonstrating that the EDR-treated water is a viable alternative resource to provide quality water for agriculture. Gally et al. [32] evaluated the application of ED to turn sewage effluent into water with a proper quality to be reused as industrial water. The results confirmed the efficiency of ED in the reduction in electrical conductivity and the extraction of a high percentage of ions, especially, the removal of corrosive (Cl^-) and encrusting (Ca^{2+}, Mg^{2+}) ions.

In addition to reducing the salinity of wastewater for reclamation, electrodialysis has the potential to produce value-added streams. Llanos et al. [35] investigated the combined used of electrodialysis to, on one hand, reduce the conductivity of wastewater effluent, and, on the other hand, electrochemically (ECh) synthesize hypochlorite in the anolyte, which can be used as disinfectant. The integrated ED-ECh process achieved a final dilute and disinfect stream with a total electrical consumption of 1.03 Wh dm^{-3} and using a reduced volume of the anolyte (volumetric ratio anolyte/dilute 4:96).

In terms of revalorization, municipal wastewater (MWW) also has the potential to be a source for the recovery of nutrients, such as nitrates, phosphate, and potassium, which can be used as fertilizers. In this context, electrodialysis has been studied to be used as a pre-treatment step to concentrate the stream and enhance the subsequent precipitation/crystallization steps of nutrients [36]. Mohammadi et al. [37] studied the recovery of nitrate from MWW using single- and a two-stage electrodialysis processes. Under the optimized operational conditions (flow rate of 60 L h^{-1}; a four cell pairs; dilute-to-concentrated volume ratio of 2/0.5), the nitrate concentration in the dilute channel reached zero with a concentration ratio of 4.6 and energy consumption of 1.44 kWh/kg NO_3^-. The nitrate concentration ratio was enhanced by the two-stage process, and reached a ratio of 19.2 with an energy consumption of 4.34 kWh/kg NO_3^-. Cai et al. [38] developed an electrodialysis process with a magnesium anode to recover phosphate and ammonia as struvite from synthetic wastewater. The pilot-scale ED system removed 65% of phosphate from the wastewater stream, which had a phosphate concentration of 10 mg L^{-1}, while the phosphate concentration in the anode chamber was kept at 30 mg L^{-1} to promote the precipitation of phosphate with magnesium as struvite. In another study, carried out by Rota et al. [39], electrodialysis was proposed to treat solutions with a low phosphorus concentration with the aim of recovering it. The experiments were carried out in a five-compartment electrodialysis cell with two AEMs and two CEMs. Working under limiting current density conditions (0.6 mA cm^{-2}), a concentration factor of 9.7 was reached, obtaining a product stream with phosphate concentration of 0.120 g L^{-1}.

4.2. Applications to Wastewater Containing Metals

In recent years, electrodialysis has been expanded to the concentration and recovery of metals from industrial effluent. The development of new membrane materials has

enhanced the techniques to treat acidic industrial effluents. The following section presents different approaches to concentrate and recover different metals typically contained in industrial wastewater.

4.2.1. Single Metal Recovery from Aqueous Effluents

The most relevant results of several studies dealing with the use of electrodialysis applied to remove metals from aqueous effluents are summarized in Table 4.

Liu et al. [40] proposed using a bipolar membrane electrodialysis system (BMED) to remove arsenic from copper slag obtained as waste during the hydrometallurgical process. They studied the effect of experimental parameters such as current density and particle size on the recovery and removal of metals. The procedure followed consisted of three steps: (a) use of a BMED system to leach metals from the copper slag and separate some metallic cations, (b) separation of solid and liquid phases, and (c) use of a BMED system to recover arsenic and remove metallic cations from the liquid phase. This method was found to be effective in the recovery of arsenic (more than 79% in the form of H_3AsO_4) and the removal of metal cations. The potential use of electrodialysis for arsenic removal from geothermal water has also been evaluated [41]. The operational parameters optimized were the pH, As concentration, and the discharged voltage. Results showed a reduction of more than 90% in arsenic within 60 min.

The combination of leaching and electrodialysis processes as a method to reduce the concentration of cadmium in phosphate ore was found to be an effective method. The influence of operational parameters such as reaction time, the chemical properties and concentration of the extracting agent, liquid-to-solid ratio, pH, temperature, and current density was evaluated. From the results, it was concluded that a relevant reduction in cadmium content in phosphate ore was not achieved by using simple batch leaching. However, results showed that the percentage of cadmium removed was up to 84% at optimum conditions (current density of 10 mA/cm^2) [42].

As a carcinogenic, mutagenic, and toxic metal, a lot of efforts have been made to reduce the amount of chromium. Liu et al. [43] evaluated the development of an electrokinetic system improved by a BM to recover Cr(VI) in the form of H_2CrO_4 from chromite ore processing residue. The electrolyte concentration in anode and cathode chambers was observed to have a direct effect on the cell voltage, resulting in optimal electrolyte concentrations: 0.6 mol/L HNO_3 in the anode chamber and 1.0 mol/L $NaNO_3$ in the cathode chamber. Regarding current density, the optimal value was 3.0 mA/cm^2. This study was carried out in cells equipped with different numbers of chromite ore processing residue chambers. Results showed that two- and three-chamber-equipped systems had higher current efficiency and lower specific energy consumption values. Under optimal experimental conditions, the Cr(VI) recovery efficiencies were higher than 80%. Similarly, the recovery of Cr(III) and Cr(VI) as Na_2CrO_4 (a relevant raw material in several areas of manufacturing) using a modified bipolar membrane electrodialysis system was also proposed as a promising method to treat industry waste containing heavy metals [44,45].

Liu et al. [46] studied bipolar electrodialysis (BMED) and electrodeposition processes to recover copper contained in hazardous sludge produced by electroplating processes. The authors evaluated the influence of the number of sludge compartments equipped in the system, concluding that the specific energy consumption decreased with the number of compartments. The removal of copper from sludge was up to 96%, and the recovery in the form of copper foil via electrodeposition was 57% under optimized conditions (current density of 50 mA/cm^2, pH solution less than or equal 0.5, and initial copper concentration less than or equal 4 g/L). Hernandez et al. [47] proposed the recovery of copper from pregnant leaching solutions using a reactive electrodialysis cell equipped with two anion-exchange membranes and a bipolar electrode. Under optimized conditions (temperature of 55 ºC, current density of 80 A/m^2, and flow rate of 100 mL/s), the copper recovery was up to 99%. Both works confirmed that further work should be carried out to optimize the copper recovery rate and reduce the specific energy consumption.

Table 4. Summary of main results of studies focused on ED applied to treat aqueous effluents with recovery of a single metal.

Metal	Sources	Recovery (%)	Time	Max V	Current Density (mA cm^{-2})	Energy (kWh/g)	Feed	pH	Membrane	Ref.
As	Copper slag	96.50	45 h	9	3	-	-	-	BPMs	[40]
As	Geothermal water	91 As(III) 98 As(V)	60 min	25	-	-	5 mg/L As(III) 60 mg/L As(V)	8	CMB and AHA	[41]
Cd	Phosphate ore	84.30	24 h	8	10	-	50 mL 0.5 M Acetic acid + 2 g phosphate ore	4.5	CEM and AEM	[42]
Cr	Chromite ore	82	350 h	5	3	0.395	50 mL water $NaNO_3$ + 50 g solid	13.5	BPMs	[43]
Cr	Aqueous solution	87.8 Cr(III)	24 h	4	0.5	0.73	5 g/L Na_2SO_4	12	BPM, CEM and AEM	[44]
Cr	Chromium slag	70.6 Cr(VI)	300 h	-	3	-	50 mL water + 50 g solid	-	BPMs	[45]
Cu	Electroplating sludge	96.4	5 h	-	50	5.3	4 g/L Cu^{2+}	0.5	BPM, CEM, AEM	[46]
Cu	Pregnant leaching solutions	99.2	5 h	2.5	8	2.11	2.5 g/L Cu^{2+}	-	-	[47]
Ni	Electroless plating bath	82.34	3 h	-	3.5	0.0182	325 mg/L Ni^{2+}	3	AEM	[48]
Ni	Electroplating sludge	94	28 h	-	20	-	S/L ratio 1:15	-	BPM and CEM	[49]
Pb	Lead battery manufacture	75	4 h	40	-	7 kWh/m^3	5 mg/L Pb^{2+} 1000 mg/L SO_4^-	-	AEM: PC SA CEM: PC SK	[50]
Zn	Electroplating waste	86.6	60 min	-	2.5	-	0.748 M $ZnSO_4 \cdot 7H_2O$ + Citric acid	4	CMH-AMH Ralex membranes	[51]
Li	Spent LIB leachate	63.91	3 h	15	-	-		7	-	[52]

(BPM: bipolar membrane; CEM, CMB, CMH: types of cation-exchange membranes; AEM, AHA, AMH: types of anion-exchange membranes).

The recovery of Ni from spent electroless nickel-plating baths with high concentrations of nickel and phosphorus was evaluated. The authors designed a two-chamber cell equipped with an AEM to couple electrodialysis and electrodeposition processes. The results confirmed that the experimental system allows the efficient recovery of Ni and the removal of P without using additional chemical reagents, which is associated with less pollution [48]. Alternatively, Liu et al. [49] designed a bipolar membrane electrodialysis system to recover nickel from electroplating sludge. They concluded that the H^+ produced during the electrodialysis process has a relevant influence on the solubilization of Ni from the solid matrix. The $Ni(OH)_2$ obtained during the treatment was found to have the same purity and physiochemical properties as commercial products, which is a promising result from the point of view of the circular economy.

Voutetaki et al. [50] proved the use of electrodialysis to treat aqueous effluents produced in the lead–acid industry. They implemented an ED pilot plant to separate the sulfate and lead ions, typically contained in battery industrial wastewater with a concentration of 500–2000 mg/L and 5 mg/L, respectively. The pilot-scale ED setup was formed by 66 cell pairs of CEMs and AEMs of 5 m^2 effective membrane area, operated in batch mode. It was found that the high concentration ratio of sulfate-to-lead ions (400:1) had a negative effect on the removal of lead. To improve this, different experiments were carried out to optimize the operational conditions, resulting in 75% of Pb with an energy consumption of 7 kWh/m^3 water treated, after 4 h at 40 V, 300 L/h, and a 90% dilute-to-concentrate tank volume ratio.

Babilas et al. [51] evaluated the formation of complex as a method to improve the electrodialysis technology applied to the selective recovery of zinc from industrial wastewater. They studied the effect of several chelating agents (i.e., citric, malic, and lactic acids) and the ion-exchange membrane type on zinc removal from wastes contaminated with ferric ions. The combination of electrodialysis with the addition of citric acid was found to be a promising strategy to selectively recover metals from aqueous effluents. The possibility of using a suitable chelating agent for electrodialysis has also been applied to the recovery of lithium from aqueous effluents. It should be noted that the recovery of lithium from solid matrices is gaining interest due to the increasing consumption of batteries. Xing et al. [52] proposed the addition of several chelating agents to improve the performance of the electrodialysis approach applied to synthetic lithium-ion battery solutions. The role of the chelating agent was dependent on the transitional metal content of the aqueous effluent. The application of bipolar-membrane-assisted electrodialysis under optimum conditions resulted in the recovery of 64% of lithium with a purity of 99%. The use of a chelating agent, such as chloride ions, has also been proven to treat Hg(II) ions to avoid its easy reduction to elemental mercury inside the cell and to increase the ED removal rate of Hg [53]. However, it has been tested in solid matrices instead of wastewater. In this context, experimental research is still needed to further improve the removal of Hg from water using electrodialysis. Sun et al. [54] proposed a model to optimize the electrodialysis process for the recovery of Hg from seaweed extracts. The optimal conditions were achieved at 7.17 V and 72.54 L/h with a Hg removal rate of 76.45% from an initial solution with a concentration of 5.04 mg/L. From simulation results, it was concluded that electrodialysis could be a promising technique to recover Hg from aqueous solutions.

This section summarizes how effluents containing different amounts of metal can be concentrated by applying ED. As can be concluded from the results, the experimental setup and conditions should be selected according to the properties of the aqueous effluent to recover the target metal effectively.

4.2.2. Multiple Metal Recovery from Aqueous Effluents

Industrial wastewater frequently contains metals that are used in different concentrations in many industry sectors; so, they are contaminants that cause serious environmental problems when discharged and their removal and recovery constitute an environmental

and economic challenge. Several studies focusing on the use of electrodialysis to recover multiple metals from aqueous effluents are summarized in Table 5.

Table 5. Summary of main results of studies focused on ED applied to treat aqueous effluents with multiple-metal recovery.

Metal	Sources	Recovery (%)	Time	Max V	Current Density (mA cm^{-2})	Energy	Feed	Stage	Membrane	Ref
Cr(VI)	Industrial effluent	97.9	90 min	25	-	38.57 Wh/L	50 mg/L	1	Ionac MC 3470	[55]
Ni		97.1					50 mg/L		Ionac MA 3475	
Fe	Printed circuit boards	-	50 min	30	50	-	-	1	PC Acid 60 (PCCell GmbH)CMH RALEX® (MEGA	[56]
Ni										
Cu										
Co	Sulfuric acid solution	93	5 h	-	5	-	0.01 M	1	MK-40 CEM	[57]
Zn		100					0.01 M		MK-40 AEM	
As(III)		58								
Se(IV)	Brackish water	80	-	25	-	-	50–1000 µg/L	1	-	[58]
Se(VI)		80								
Cu	Electroplating wastewater	90.7	25 min	12	22.5	-	22.3 mg/L	1	AMX Astom	[59]
Ni		90.2					24.4 mg/L		CMX Astom	
Ni	Lithium-ion battery leaching solution	99.8	180 min	18	-	9.65 kWh/mol	0.01 M	3	Neosepta AMXNeosepta CMXPCA PC 400D	[60]
Co		87.3				15.3 kWh/mol	0.003 M			
Li		99				-	0.003 M			
Mn		99				-	0.003 M			
Li	Lithium-ion battery leaching solution	66	144 h	-	1	-	1.75 g LiCoO$_2$	1	Neosepta CMX	[61]
Co		33					350 mL 0.1 M HCl			

(CEM, CMX: types of cation-exchange membranes; AEM, AMX: types of anion-exchange membranes).

Kirmizi et al. [55] used a self-designed electrodialysis cell to separately remove chromium(VI) and nickel(II) ions from aqueous effluents. The electrodialytic cell was divided into a compartment containing the diluted solution and two electrolyte compartments separated by a pair of AEMs (Ionac MA 3475) and CEMs (MC 3470). The cathode and anode were made of carbon fiber and stainless steel, respectively. Distilled water with pH adjusted to 3 with H$_2$SO$_4$ was used as the electrolyte solution, and Na$_2$SO$_4$ was added at 7 mM. This study observed that the removal efficiency decreased with increasing metal concentration, although high concentrations of metals can reduce the concentration polarization phenomenon and increase efficiency. This has been attributed to the fact that a reduced membrane retention time can negatively affect the process. For both Cr(VI) and Ni(II), increasing the voltage and Na$_2$SO$_4$ concentration had an increasing effect on energy consumption, while increasing the pH had a decreasing effect. An optimal removal of 92.3 ± 1% was achieved in 90 min for a 40 mL/min feed rate and 50 mg/L of Ni(II) ions at pH = 3, voltage value of 20 V, and energy consumption of approximately 30 Wh/L. In the case of Cr(VI), a removal of 97.9 ± 1% was achieved in 90 min for optimal values of 25 V and a feeding rate of 40 mL/min and 50 mg/L of Cr(VI) ions at pH = 3, with an approximate energy consumption of 40 Wh/L. Finally, it was concluded that it is necessary to operate with a high concentration of metal, a low voltage, and a low addition of salt to the electrolytes to obtain a high current efficiency.

In another study, Shestakov et al. [56] proposed electrodialysis to recover iron, nickel, and copper from wastewater generated in the manufacture of printed circuit boards, for which they used an electrodialytic system with PC Acid 60 (PCCell GmbH) and CM (H) RALEX® (MEGA) ion-exchange membranes. To each metal solution, sodium ethylenediaminetetraacetate with a molar ratio of Na$_2$EDTA/metal = 1:1.2 and 2–3 drops of a 40% aqueous solution of HNO$_3$ was added. When separating solutions containing one and all three salts of the target metals, the retention coefficients of the Ni^{2+} and Cu^{2+} cations differedsignificantly. In contrast, those of Fe^{3+} cations did not vary by more than 2–3%. When separating a multicomponent solution of three salts, the retention coefficients of Ni^{2+} and Cu^{2+} cations decreased compared to the corresponding values for mono salt solutions. In any case, electrodialysis separation of multicomponent solutions is an efficient method for exhaustive metal recovery, as applied to Fe^{3+} and Cu^{2+} cations.

Sadyrbaeva et al. [57] proposed a new method to extract cobalt and zinc ions from sulfuric acid solutions, silver and lead ions from nitric acid solutions, and copper ions from

hydrochloric acid solutions via electrodialysis with 1,2-dichloroethane liquid membranes with di-acid(2-ethylhexyl)phosphoric (D_2EHPA) and tri-n-octylamine (TOA) as a carrier. In this case, by using a current density of approximately 5 mA/cm^2 and times between 0.5 and 5.0 h, an almost complete extraction (93–100%) of the metals was achieved from aqueous solutions with an initial concentration of metallic salts of 0.01 M. The metal extraction rate decreased with the decrease in the pH of the starting solution and with the increase in the TOA concentration in the liquid membrane, establishing an optimum at 0.1 M, while the increase in the carrier concentration (D2EHPA) did not present significant effects, showing an optimum between 0.2 and 0.4 M.

The removal of arsenite As(III), selenite Se(IV), and selenate Se(VI) from brackish water using an electrodialysis system was studied by Aliaskari et al. [58]. Contaminant removal was investigated at different pH values (3–11). The results showed that the removal of As and Se was pH-dependent since the loading of Se(IV), Se(VI), and As(III) species is pH-dependent. The removal of As(III) increased at pH > 9, while the removal of As(V), Se(IV), and Se(VI) decreased. Two sources of groundwater contaminated with As and Se were also investigated. The effect of chloride ion competition was studied by testing different values of salinity (ranging from 1 to 10 g/L of total dissolved solids). The results showed that increasing salinity resulted in delayed removal of As and Se. Additionally, various feed concentrations of Se(IV), Se(VI), and As(III) were investigated, ranging from 50 to 1000 µg/L. It was observed that higher feed concentrations of As and Se led to a higher molar flux, but the removal rates were not affected by the ion concentration. Furthermore, increasing the electrical potential from 5 to 25 V led to a significant increase in contaminant removal. The removal rates for As(V), Se(IV), and Se(VI) increased from less than 5% at 5 V to over 80% at 25 V. The maximum removal observed for As(III) was 58% at 25 V.

Min et al. [59] studied electroplating wastewater treatment using electrodialysis. The electrodialysis cell was equipped with five pairs of ion-exchange membranes and one pair of platinum-plated titanium electrodes. The CEM was CMX-SB (NEOSEPTA) and the AEM was AMX-SB (NEOSEPTA). The wastewater contained mainly copper and nickel with concentrations of 22.4 and 24.4 mg/L, respectively; its conductivity was 6300 µS/cm, and the pH was 2.18. The electrolyte solution contained 4% (*w/w*) Na_2SO_4. The voltage used (6 to 18 V) in the process was a very important factor in the separation efficiency. As it increased from 6 to 12 V, the separation efficiency of Cu^{2+} and Ni^{2+} improved, but if a higher voltage was applied (>12 to 18 V), concentration polarization occured, and the efficiency decreased. The optimal applied voltage, with a water conductivity of 6300 µS/cm, was 12 V with Cu^{2+} and Ni^{2+} removal efficiencies >99% after 25 min, with final concentrations of Cu^{2+} and Ni^{2+} in the concentrate of 1000 and 1200 mg/L and recovery rates of 90.7% and 90.2%, respectively. From the results, it is concluded that electrodialysis could effectively treat metallic industrial wastewater and recover significant amounts of metals.

Another field of interest in metal recovery is spent lithium-ion batteries. For this purpose, electrodialysis must be considered an emerging green process capable of recovering valuable metals from solid matrices. The main challenge of electrodialysis is the difficulty of separating various similarly charged metal ions due to the low selectivity of ion-exchange membranes. In order to improve the process selectivity, several complexing agents, such as ethylenediaminetetraacetic acid, citric acid, malic acid, and lactic acid, are used to form negatively charged complex anions so that ions with different charges can be separated. However, there are very few studies on applying electrodialysis for metal separation from spent LIBs.

In a study conducted by Chan et al. [60], they investigated the separation and recovery of lithium, nickel, manganese, and cobalt from mixtures obtained from spent lithium-ion batteries. The process involved three stages of electrodialysis coupled with EDTA using an AEM (PCA PC 400D) and a CEM (Neosepta CMX). In the first stage, at a pH of approximately 2, 99.3% of nickel was successfully recovered. In the second stage, at a pH of around 3, 87.3% of cobalt was separated. Finally, in the third stage, electrodialysis with a monovalent CEM (Neosepta CMS) was used to separate 99% of lithium from manganese.

The later breakdown of the EDTA-metal complexes, Ni (from stage 1) and Co (from stage 2), was carried out by adding a 2.0 M H_2SO_4 solution until the pH reached a value less than 0.5. The solid acid (EDTA) was recovered after filtration and washing with water and could be reused. Likewise, the H_2SO_4 solution recovered in the anode compartment could be reused. All metals recovered were more than 99% pure.

A new technique that combines hydrometallurgical extraction with electrodialysis to selectively recover lithium (Li) and cobalt (Co) from lithium-ion battery waste has been presented by Cerrillo et al. in a recent article [61]. The combined method helps reduce the consumption of leaching solution by regenerating the acid through electrolysis. Several extractions were conducted on $LiCoO_2$ powder to investigate the dissolution process of this common cathode material in lithium-ion batteries. A 0.1 M HCl solution was used as the extraction agent with a liquid-to-solid ratio of 200. The purpose of using hydrochloric acid was to test the effectiveness of chloride ions in reducing Co^{3+} to Co^{2+}. To ensure consistency, two cells were used in series for the hydrometallurgical–electrodialytic experiments. The electrodialytic cells consisted of three compartments separated by two Neopsepta CMX-fd CEMs. The anodic, central, and cathodic compartments were kept apart using these membranes. A CEM was used to separate the anode from the central compartment to prevent chloride ions from reaching the anode, which could otherwise oxidize and produce chlorine gas. The anode was made of titanium coated with metal oxides, while the cathode was made of stainless steel. The electrical current was kept constant at 50 mA, which corresponds to a current density of 1 mA cm^{-2}. The incoming $LiCO_2$-HCl suspension was continuously pumped from an external container to the central compartment of the electrodialysis cell, passing through a separatory funnel and a glass fiber filter that prevented particles from reaching the interior of the electrodialysis cell. The experiments led to the recovery of 62% lithium and 33% cobalt in the catholyte; 80% of the cobalt was electrodeposited on the cathode.

Siekierka et al. [62] proposed a method for selectively recovering metal transition cations from leaching battery waste using a reverse electrodialytic process. This approach generates energy while recovering the desired metals. Typically, the reverse electrodialytic process is used for energy production by leveraging the salinity gradient between seawater and river water. In this study, highly concentrated spent battery acid leachate is applied to generate a potential difference in the reverse electrodialytic cell due to the transport of ionic species across the membrane to a dilute solution. The system utilizes two commercial AEMs (ASE S-5158) and one central selective CEM (PAN-5C8Q) developed by the authors. Both electrodes use a 0.2 M sodium carbonate solution. Based on the analysis, it has been estimated that the maximum amount of energy that can be extracted per square meter is 0.44 watts. Furthermore, the potential power generation for all alkali and transition metal cations increased with the salinity of the high-concentration solution. The energy efficiency of the presented method was 45.5%. This technique holds great potential for managing waste batteries by converting them into valuable products like cobalt salts and producing additional electrical energy.

The combined recovery of metal ions contained in a mixture is a challenge from the point of view of the selectivity and purity of the recovered component. In this context, electrodialysis is a promising technology for the recovery of multiple metals from aqueous effluents, as was concluded from previously described works. These studies demonstrate the effectiveness of electrodialysis in diverse applications for metal recovery from a diverse variety of industrial wastewaters. However, most of the studies reviewed were carried out at the lab scale. So, experimental research is still needed to further improve the process and optimize the work conditions, with the aim of scaling the process to an industrial level.

5. Conclusions

Electrodialytic separation is a promising technique that offers new possibilities for the selective separation of metals from wastewater effluents, particularly from industrial sources. The specific design of the cell, in terms of the number of compartments, the dispo-

sition of the ionic-exchange membranes, the pH control, and the use of special membranes such as monovalent membranes or bipolar membranes, allow not only desalination but also the selective separation of target contaminants, which facilitates circular economy strategies within the field of wastewater treatment and management. The results obtained from experimental studies dealing with the optimization of ED applied to aqueous effluents containing metals highlight the importance of evaluating factors such as membrane properties, cell configuration, and operational conditions. Advances in membrane technologies have been focused on expanding the applications of ED, optimizing the performance of the technology, and overcoming some limitations, such as fouling or high costs due to the energy consumption required. A new opportunity for ED was opened with the use of renewable energy sources. Moreover, the production of gaseous streams, such as H_2 from water electrolysis, can be used to generate electricity. Nevertheless, further investigations are required to implement this technology at an industrial scale, since most studies have been carried out at the lab scale. Furthermore, it would be necessary to carry out an economic evaluation of ED scaling and a comparison with other separation techniques to demonstrate the applicability of ED in the field of metal separation from aqueous solutions.

Author Contributions: Conceptualization, M.V.-G. and J.M.P.-G.; methodology, M.d.M.C.-G. and M.V.-G.; investigation, M.d.M.C.-G.; writing—original draft preparation, M.d.M.C.-G., M.V.-G. and J.M.R.-M.; writing—review and editing, M.V.-G. and J.M.P.-G.; visualization, J.M.R.-M.; supervision, J.M.R.-M. and M.V.-G.; project administration, M.V.-G. All authors have read and agreed to the published version of the manuscript.

Data Availability Statement: No new data were created or analyzed in this study. Data sharing is not applicable to this article, since the information in the article has been obtained from literature revision (cited in reference section).

Conflicts of Interest: The authors declare no conflicts of interest.

References

1. Ahmed, J.; Thakur, A.; Goyal, A. Chapter 1: Industrial Wastewater and Its Toxic Effects. In *Biological Treatment of Industrial Wastewater*; The Royal Society of Chemistry: London, UK, 2021; pp. 1–14. [CrossRef]
2. Briffa, J.; Sinagra, E.; Blundell, R. Heavy Metal Pollution in the Environment and Their Toxicological Effects on Humans. *Heliyon* **2020**, *6*, e04691. [CrossRef]
3. Shrestha, R.; Ban, S.; Devkota, S.; Sharma, S.; Joshi, R.; Tiwari, A.P.; Kim, H.Y.; Joshi, M.K. Technological Trends in Heavy Metals Removal from Industrial Wastewater: A Review. *J. Environ. Chem. Eng.* **2021**, *9*, 105688. [CrossRef]
4. Barakat, M.A. New Trends in Removing Heavy Metals from Industrial Wastewater. *Arab. J. Chem.* **2011**, *4*, 361–377. [CrossRef]
5. Villen-Guzman, M.; Cerrillo-Gonzalez, M.M.; Paz-Garcia, J.M.; Rodriguez-Maroto, J.M.; Arhoun, B. Valorization of Lemon Peel Waste as Biosorbent for the Simultaneous Removal of Nickel and Cadmium from Industrial Effluents. *Environ. Technol. Innov.* **2021**, *21*, 101380. [CrossRef]
6. Doble, M.; Kumar, A. Treatment of Waste from Metal Processing and Electrochemical Industries. In *Biotreatment of Industrial Effluents*; Butterworth-Heinemann: Oxford, UK, 2005; pp. 145–155. [CrossRef]
7. Goh, P.S.; Wong, K.C.; Ismail, A.F. Membrane Technology: A Versatile Tool for Saline Wastewater Treatment and Resource Recovery. *Desalination* **2022**, *521*, 115377. [CrossRef]
8. Arana Juve, J.M.; Christensen, F.M.S.; Wang, Y.; Wei, Z. Electrodialysis for Metal Removal and Recovery: A Review. *Chem. Eng. J.* **2022**, *435*, 134857. [CrossRef]
9. Kitchenham, B. *Procedures for Performing Systematic Reviews*; Keele University: Keele, UK, 2004; Volume 33.
10. Gurreri, L.; Cipollina, A.; Tamburini, A.; Micale, G. Electrodialysis for Wastewater Treatment—Part I: Fundamentals and Municipal Effluents. In *Current Trends and Future Developments on (Bio-) Membranes: Membrane Technology for Water and Wastewater Treatment—Advances and Emerging Processes*; Elsevier: Amsterdam, The Netherlands, 2020; pp. 141–192, ISBN 9780128168240.
11. Van der Bruggen, B. Ion-Exchange Membrane Systems—Electrodialysis and Other Electromembrane Processes. In *Fundamental Modeling of Membrane Systems: Membrane and Process Performance*; Elsevier: Amsterdam, The Netherlands, 2018; pp. 251–300. [CrossRef]

12. Pärnamäe, R.; Mareev, S.; Nikonenko, V.; Melnikov, S.; Sheldeshov, N.; Zabolotskii, V.; Hamelers, H.V.M.; Tedesco, M. Bipolar Membranes: A Review on Principles, Latest Developments, and Applications. *J. Membr. Sci.* **2021**, *617*, 118538. [CrossRef]
13. Hansima, M.A.C.K.; Makehelwala, M.; Jinadasa, K.B.S.N.; Wei, Y.; Nanayakkara, K.G.N.; Herath, A.C.; Weerasooriya, R. Fouling of Ion Exchange Membranes Used in the Electrodialysis Reversal Advanced Water Treatment: A Review. *Chemosphere* **2021**, *263*, 127951. [CrossRef]
14. Tanaka, Y. Chapter 2: Electrodialysis Reversal. In *Membrane Science and Technology*; Elsevier: Amsterdam, The Netherlands, 2007; Volume 12, pp. 383–404. [CrossRef]
15. Güler, E.; Elizen, R.; Vermaas, D.A.; Saakes, M.; Nijmeijer, K. Performance-Determining Membrane Properties in Reverse Electrodialysis. *J. Membr. Sci.* **2013**, *446*, 266–276. [CrossRef]
16. Luo, T.; Abdu, S.; Wessling, M. Selectivity of Ion Exchange Membranes: A Review. *J. Membr. Sci.* **2018**, *555*, 429–454. [CrossRef]
17. Tekinalp, Ö.; Zimmermann, P.; Holdcroft, S.; Burheim, O.S.; Deng, L. Cation Exchange Membranes and Process Optimizations in Electrodialysis for Selective Metal Separation: A Review. *Membranes* **2023**, *13*, 566. [CrossRef]
18. Moura Bernardes, A.; Zoppas Ferreira, J.; Siqueira Rodrigues, M.A. *Electrodialysis and Water Reuse: Novel Approaches*; Springer: Berlin/Heidelberg, Germany, 2014; ISBN 9783642402494.
19. Ebbers, B.; Ottosen, L.M.; Jensen, P.E. Electrodialytic Treatment of Municipal Wastewater and Sludge for the Removal of Heavy Metals and Recovery of Phosphorus. *Electrochim. Acta* **2015**, *181*, 90–99. [CrossRef]
20. Abou-Shady, A.; Peng, C.; Almeria, O.J.; Xu, H. Effect of PH on Separation of Pb (II) and NO_3- from Aqueous Solutions Using Electrodialysis. *Desalination* **2012**, *285*, 46–53. [CrossRef]
21. Dean, J.A. *Lange's Handbook of Chemistry*, 15th ed.; McGraw-Hill Professional Publishing: New York, NY, USA, 1999; ISBN 0-07-016384-7.
22. Strathmann, H. Electrodialysis, a Mature Technology with a Multitude of New Applications. *Desalination* **2010**, *264*, 268–288. [CrossRef]
23. Dow Water & Process Solutions Aumenta La Eficiencia de La Planta de Agua Municipal MasPalomas I | IAgua. Available online: https://www.iagua.es/noticias/espana/dow-water-and-process-solutions/17/02/22/dow-water-process-solutions-aumenta (accessed on 26 May 2022).
24. Generous, M.M.; Qasem, N.A.A.; Akbar, U.A.; Zubair, S.M. Techno-Economic Assessment of Electrodialysis and Reverse Osmosis Desalination Plants. *Sep. Purif. Technol.* **2021**, *272*, 118875. [CrossRef]
25. Soliman, M.N.; Guen, F.Z.; Ahmed, S.A.; Saleem, H.; Khalil, M.J.; Zaidi, S.J. Energy Consumption and Environmental Impact Assessment of Desalination Plants and Brine Disposal Strategies. *Process Saf. Environ. Prot.* **2021**, *147*, 589–608. [CrossRef]
26. Jiang, C.; Wang, Y.; Zhang, Z.; Xu, T. Electrodialysis of Concentrated Brine from RO Plant to Produce Coarse Salt and Freshwater. *J. Membr. Sci.* **2014**, *450*, 323–330. [CrossRef]
27. Xu, X.; Lin, L.; Ma, G.; Wang, H.; Jiang, W.; He, Q.; Nirmalakhandan, N.; Xu, P. Study of Polyethyleneimine Coating on Membrane Permselectivity and Desalination Performance during Pilot-Scale Electrodialysis of Reverse Osmosis Concentrate. *Sep. Purif. Technol.* **2018**, *207*, 396–405. [CrossRef]
28. Yan, H.; Wang, Y.; Wu, L.; Shehzad, M.A.; Jiang, C.; Fu, R.; Liu, Z.; Xu, T. Multistage-Batch Electrodialysis to Concentrate High-Salinity Solutions: Process Optimisation, Water Transport, and Energy Consumption. *J. Membr. Sci.* **2019**, *570–571*, 245–257. [CrossRef]
29. Korngold, E.; Aronov, L.; Daltrophe, N. Electrodialysis of Brine Solutions Discharged from an RO Plant. *Desalination* **2009**, *242*, 215–227. [CrossRef]
30. McGovern, R.K.; Zubair, S.M.; Lienhard, V.J.H. The Benefits of Hybridising Electrodialysis with Reverse Osmosis. *J. Membr. Sci.* **2014**, *469*, 326–335. [CrossRef]
31. Soliman, M.; Eljack, F.; Kazi, M.K.; Almomani, F.; Ahmed, E.; El Jack, Z. Treatment Technologies for Cooling Water Blowdown: A Critical Review. *Sustainability* **2021**, *14*, 376. [CrossRef]
32. Gally, C.R.; Benvenuti, T.; Da Trindade, C.D.M.; Rodrigues, M.A.S.; Zoppas-Ferreira, J.; Pérez-Herranz, V.; Bernardes, A.M. Electrodialysis for the Tertiary Treatment of Municipal Wastewater: Efficiency of Ion Removal and Ageing of Ion Exchange Membranes. *J. Environ. Chem. Eng.* **2018**, *6*, 5855–5869. [CrossRef]
33. Goodman, N.B.; Taylor, R.J.; Xie, Z.; Gozukara, Y.; Clements, A. A Feasibility Study of Municipal Wastewater Desalination Using Electrodialysis Reversal to Provide Recycled Water for Horticultural Irrigation. *Desalination* **2013**, *317*, 77–83. [CrossRef]
34. WHO. *Guidelines for Drinking-Water Quality: Fourth Edition Incorporating the First Addendum*; WHO: Geneva, Switzerland, 2017.
35. Llanos, J.; Cotillas, S.; Cañizares, P.; Rodrigo, M.A. Novel Electrodialysis–Electrochlorination Integrated Process for the Reclamation of Treated Wastewaters. *Sep. Purif. Technol.* **2014**, *132*, 362–369. [CrossRef]
36. Mohammadi, R.; Tang, W.; Sillanpää, M. A Systematic Review and Statistical Analysis of Nutrient Recovery from Municipal Wastewater by Electrodialysis. *Desalination* **2021**, *498*, 114626. [CrossRef]
37. Mohammadi, R.; Ramasamy, D.L.; Sillanpää, M. Enhancement of Nitrate Removal and Recovery from Municipal Wastewater through Single- and Multi-Batch Electrodialysis: Process Optimisation and Energy Consumption. *Desalination* **2021**, *498*, 114726. [CrossRef]
38. Cai, Y.; Han, Z.; Lin, X.; Duan, Y.; Du, J.; Ye, Z.; Zhu, J. Study on Removal of Phosphorus as Struvite from Synthetic Wastewater Using a Pilot-Scale Electrodialysis System with Magnesium Anode. *Sci. Total Environ.* **2020**, *726*, 138221. [CrossRef]
39. Rotta, E.H.; Bitencourt, C.S.; Marder, L.; Bernardes, A.M. Phosphorus Recovery from Low Phosphate-Containing Solution by Electrodialysis. *J. Membr. Sci.* **2019**, *573*, 293–300. [CrossRef]

40. Liu, Y.; Dai, L.; Ke, X.; Ding, J.; Wu, X.; Chen, R.; Ding, R.; Van der Bruggen, B. Arsenic and Cation Metal Removal from Copper Slag Using a Bipolar Membrane Electrodialysis System. *J. Clean. Prod.* **2022**, *338*, 130662. [CrossRef]

41. Pham, M.T.; Nishihama, S.; Yoshizuka, K. Effect of Operational Conditions on Arsenic Removal from Aqueous Solution Using Electrodialysis. *Solvent Extr. Ion. Exch.* **2021**, *39*, 655–667. [CrossRef]

42. Benredjem, Z.; Delimi, R.; Khelalfa, A.; Saaidia, S.; Mehellou, A. Coupling of Electrodialysis and Leaching Processes for Removing of Cadmium from Phosphate Ore. *Sep. Sci. Technol.* **2016**, *51*, 718–726. [CrossRef]

43. Liu, Y.; Zhu, H.; Zhang, M.; Chen, R.; Chen, X.; Zheng, X.; Jin, Y. Cr(VI) Recovery from Chromite Ore Processing Residual Using an Enhanced Electrokinetic Process by Bipolar Membranes. *J. Membr. Sci.* **2018**, *566*, 190–196. [CrossRef]

44. Wu, X.; Zhu, H.; Liu, Y.; Chen, R.; Qian, Q.; Van der Bruggen, B. Cr(III) Recovery in Form of Na_2CrO_4 from Aqueous Solution Using Improved Bipolar Membrane Electrodialysis. *J. Membr. Sci.* **2020**, *604*, 118097. [CrossRef]

45. Dai, L.; Ding, J.; Liu, Y.; Wu, X.; Chen, L.; Chen, R.; Van der Bruggen, B. Recovery of Cr(VI) and Removal of Cationic Metals from Chromium Slag Using a Modified Bipolar Membrane System. *J. Membr. Sci.* **2021**, *639*, 119772. [CrossRef]

46. Liu, Y.; Lv, M.; Wu, X.; Ding, J.; Dai, L.; Xue, H.; Ye, X.; Chen, R.; Ding, R.; Liu, J.; et al. Recovery of Copper from Electroplating Sludge Using Integrated Bipolar Membrane Electrodialysis and Electrodeposition. *J. Colloid Interface Sci.* **2023**, *642*, 29–40. [CrossRef]

47. Hernández, J.; Tapia, J. Direct Copper Recovery from Pregnant Leaching Solutions (PLS), Using a Custom Electrolytic Cell, Based on Reactive Electrodialysis (RED). *Miner. Process. Extr. Metall. Trans. Inst. Min. Metall.* **2023**, *132*, 110–116. [CrossRef]

48. Yan, K.; Huang, P.; Xia, M.; Xie, X.; Sun, L.; Lei, W.; Wang, F. An Efficient Two-Chamber Electrodeposition-Electrodialysis Combination Craft for Nickel Recovery and Phosphorus Removal from Spent Electroless Nickel Plating Bath. *Sep. Purif. Technol.* **2022**, *295*, 121283. [CrossRef]

49. Liu, Y.; Lian, R.; Wu, X.; Dai, L.; Ding, J.; Wu, X.; Ye, X.; Chen, R.; Ding, R.; Liu, J.; et al. Nickel Recovery from Electroplating Sludge via Bipolar Membrane Electrodialysis. *J. Colloid Interface Sci.* **2023**, *637*, 431–440. [CrossRef]

50. Voutetaki, A.; Plakas, K.V.; Papadopoulos, A.I.; Bollas, D.; Parcharidis, S.; Seferlis, P. Pilot-Scale Separation of Lead and Sulfate Ions from Aqueous Solutions Using Electrodialysis: Application and Parameter Optimization for the Battery Industry. *J. Clean. Prod.* **2023**, *410*, 137200. [CrossRef]

51. Babilas, D.; Dydo, P. Selective Zinc Recovery from Electroplating Wastewaters by Electrodialysis Enhanced with Complex Formation. *Sep. Purif. Technol.* **2018**, *192*, 419–428. [CrossRef]

52. Xing, Z.; Srinivasan, M. Lithium Recovery from Spent Lithium-Ion Batteries Leachate by Chelating Agents Facilitated Electrodialysis. *Chem. Eng. J.* **2023**, *474*, 145306. [CrossRef]

53. Hansen, H.K.; Ottosen, L.M.; Kliem, B.K.; Villumsen, A. Electrodialytic Remediation of Soils Polluted with Cu, Cr, Hg, Pb and Zn. *J. Chem. Technol. Biotechnol.* **1997**, *70*, 67–73. [CrossRef]

54. Sun, J.; Su, X.; Liu, Z.; Liu, J.; Ma, Z.; Sun, Y.; Gao, X.; Gao, J. Removal of Mercury (Hg(II)) from Seaweed Extracts by Electrodialysis and Process Optimization Using Response Surface Methodology. *J. Ocean Univ. China* **2020**, *19*, 135–142. [CrossRef]

55. Kırmızı, S.; Karabacakoğlu, B. Performance of Electrodialysis for Ni(II) and Cr(VI) Removal from Effluents: Effect of Process Parameters on Removal Efficiency, Energy Consumption and Current Efficiency. *J. Appl. Electrochem.* **2023**, *53*, 2039–2055. [CrossRef]

56. Shestakov, K.V.; Lazarev, S.I.; Polyanskii, K.K.; Ignatov, N.N. Recovery of Iron, Nickel, and Copper in Waste Water from Printed Circuit Board Manufacture by Electrodialysis Method. *Russ. J. Appl. Chem.* **2021**, *94*, 555–559. [CrossRef]

57. Sadyrbaeva, T.Z. Membrane Extraction of Ag(I), Co(II), Cu(II), Pb(II), and Zn(II) Ions with Di(2-Ethylhexyl)Phosphoric Acid under Conditions of Electrodialysis with Metal Electrodeposition. *Theor. Found. Chem. Eng.* **2021**, *55*, 1204–1220. [CrossRef]

58. Aliaskari, M.; Ramos, R.L.; Schäfer, A.I. Removal of Arsenic and Selenium from Brackish Water Using Electrodialysis for Drinking Water Production. *Desalination* **2023**, *548*, 116298. [CrossRef]

59. Min, K.J.; Choi, S.Y.; Jang, D.; Lee, J.; Park, K.Y. Separation of Metals from Electroplating Wastewater Using Electrodialysis. *Energy Sources Part A Recovery Util. Environ. Eff.* **2019**, *41*, 2471–2480. [CrossRef]

60. Chan, K.H.; Malik, M.; Azimi, G. Separation of Lithium, Nickel, Manganese, and Cobalt from Waste Lithium-Ion Batteries Using Electrodialysis. *Resour. Conserv. Recycl.* **2022**, *178*, 106076. [CrossRef]

61. Cerrillo-Gonzalez, M.M.; Villen-Guzman, M.; Vereda-Alonso, C.; Gomez-Lahoz, C.; Rodriguez-Maroto, J.M.; Paz-Garcia, J.M. Recovery of Li and Co from LiCoO2 via Hydrometallurgical–Electrodialytic Treatment. *Appl. Sci.* **2020**, *10*, 2367. [CrossRef]

62. Siekierka, A.; Yalcinkaya, F.; Bryjak, M. Recovery of Transition Metal Ions with Simultaneous Power Generation by Reverse Electrodialysis. *J. Environ. Chem. Eng.* **2023**, *11*, 110145. [CrossRef]