

Electrodialysis-Based Separation Technologies: A Critical Review

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To support a sustainable industrial growth, chemical engineering today faces a crucial challenge of meeting the increasing demand for materials and energy. One possible solution is to decrease the equipment size/productivity ratio, energy consumption, and waste generation via process integration and optimization. This review focuses on the integration of electrodialysis with traditional unit operations and other membrane separations. Such integrations, due to their diversity and practicability, can be versatile tools to meet specific needs from chemical, biochemical, food, and pharmaceutical industries. © 2008 American Institute of Chemical Engineers AICHE J, 54: 3147–3159, 2008
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Introduction

Electrodialysis (ED) is a type of technology which arranges ion-exchange membranes alternately in a direct current field.^{1–23} As shown in Figure 1a, there are at least five elements complementary for ED applications⁴: (1) direct current supply, which proves effective to reinforce ion migration; (2) electrodes, where the oxidation/reduction reactions occur to realize the transformation from ionic conduction to electron conduction and thus provide the original driving force for ion migration; (3) ion exchange membranes, the key components which permit the transport of counter ions and block the passage of co-ions; (4) solvents, which make a continuum for ion transport by filling the space between electrodes and membranes; (5) electrolytes, the current carriers between cathode and anode. Owing to its distinguished functions, ED has been widely used to demineralize, concentrate and/or convert salt-containing solutions.^{4–9} Notably, a recent invention explored a new and broad space for ED development: bipolar membrane. As shown in Figure 1b, a bipolar membrane is a composite membrane consisting of a

cation-exchange layer and an anion-exchange layer and can split solvents (water and methanol, so far) into H^+ and OH^- / CH_3O^- at the interface under reverse potential bias. This solvent splitting technique is named electrodialysis with bipolar membranes (BMED),^{10–11} which has some preponderancies over solvent electrolysis, such as no gas or byproduct generation, lower voltage drop, maximal energy utilization, space-saving, and easier installation and operation.¹² Correspondingly, BMED has found more applications than other ED techniques in chemical or biochemical synthesis, food processing, and pollution control.^{1,2,4,10,13–22}

ED, however, is not so economically competitive as other membrane separations, such as reverse osmosis (RO), ultrafiltration (UF), and microfiltration (MF). The main reasons are the high cost of electrodes and ion exchange membranes (especially bipolar membranes) and relatively short life time of membranes when working in high-density electrical field. Accordingly, no ED applications can be considered industrially practical except desalination or concentration of electrolyte solutions using conventional ED (CED) or inorganic/organic acid production/recovery using BMED.¹ Naturally, CED or BMED are also high in capital cost, but they can provide products of higher quality or are more environmentally friendly than other mass separation techniques. Particularly, the integration of CED and /or BMED with other sepa-

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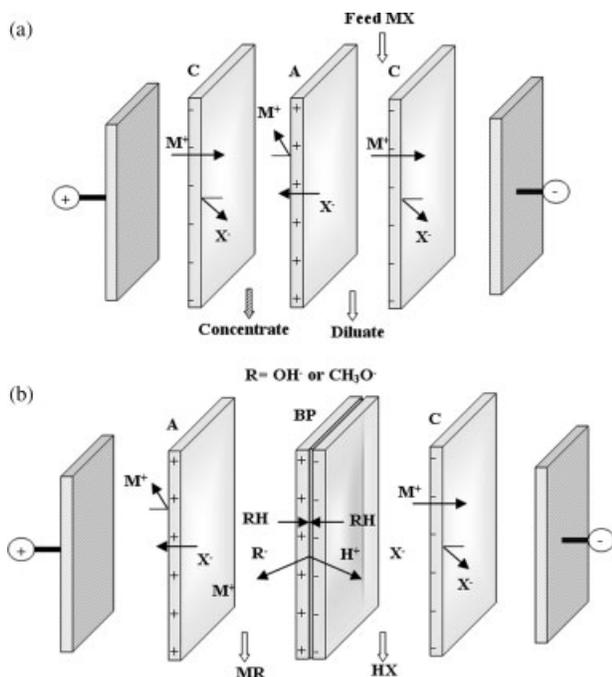


Figure 1. Schematic of (a) CED and (b) BMED.

BP, bipolar membrane; A, anionic membrane; C, cationic membrane; M^+ , cation; X^- , anion; CH_3O^- methoxide ion.

ration techniques provides versatile tools for industrial separations and thus has received more attention recently. These integrated processes are mainly classified as follows:

- The integration of ED with chemical unit operations, such as ion exchange, adsorption, electrolysis, extraction, complexation, stripping, absorption, and distillation, which are widely used in chemical separation and environmental protection.^{4,13,23–27}
- The integration of ED with pressure-driven membrane processes, such as microfiltration, ultrafiltration, nanofiltration, and reverse osmosis, which are often used in water treatment, feed pretreatment, fractionation of biochemical species, and concentration and desalination of sea water.^{28–38}
- The integration of ED with biochemical unit operations, such as fermentation, and membrane biological reactors, which are widely used in separation of biochemicals, production of organic acids from fermentation broth, and treatment of waste water.^{4,39,40}

Such integrations can achieve not only a synergic effect for a specific industrial separation but also an optimization on utilization of materials, energy, and space. In this sense, the integrations are a practical strategy for sustainable industrial growth—a challenge chemical engineering faces today. This review will present the recent progress on ED-based integrations for industrial separations.

Integration of ED with chemical unit operations

ED + Ion Exchange. Electrodeionization (EDI), a combination of ED with ion exchange, was proposed in the 1970s^{24,41} and turns out to be a reliable technique to treat solutions of low electrolyte content.¹ Its main application is to produce ultrapure water for semi-conductor production

and laboratory analyses. Its principle has been reported in many patents and papers.^{42–44} Different from conventional electro dialysis, EDI fills mixed-bed ion exchange resins or fibers in the diluate cell to increase the conductivity in the substantially nonconductive solvent-water. The diluate from EDI is almost completely deionized water. It is noticeable that at very low salt concentrations, water is split at the contact region between the cation- and anion-exchange resin beds and generates protons and hydroxyl ions. These generated ions will substitute the salt ions in the resins and thus regenerate in situ the exchange resins to some extent. Correspondingly, EDI can be performed continuously without chemical regeneration of ion-exchange resins and thus save a great amount of acids and bases needed for conventional ion exchange processes. Hence, the process is also called continuous electrodeionization (CEDI). As one of the large-scale applications, EDI or CEDI has been used to produce boiler feed water for power generation plants or ultrapure water for electronic industries. Figure 2 illustrates the comparison between EDI (Figure 2b) and conventional technique for production of ultrapure water (Figure 2a).¹

Although EDI is an advanced method for ultrapure water production, it still has shortcomings: incomplete removal of weak acids, incomplete deionization of water, and incomplete utilization of current.^{45,46} The main reason is that this kind of water splitting can not provide enough H^+ and OH^- for resin regeneration due to its low efficiency ($t_{H^+} = 4 \times 10^{-5}$ –0.11 for cation-exchange membranes, $t_{HO^-} = 0.03$ –0.6 for anion-exchange membranes⁴⁶), and some of the generated H^+ and OH^- ions recombine before regenerating the resins. These disadvantages can be overcome by using EDI with bipolar membranes.^{46,47} As shown in Figure 2c, the supply of H^+ and OH^- is guaranteed since BMED has a much higher water-splitting efficiency (t_{H^+} , $t_{HO^-} = 0.9$ –0.96⁴⁸). The recombination is avoided because cation- and anion-exchange resins are positioned in separate compartments. Besides, to suppress co-ion leakage and increase the diluate's purity, a protection compartment is added between diluate and concentrate streams. Hence, higher regeneration efficiency and lower outflow conductivity ($\kappa = 0.0556 \text{ S cm}^{-1}$; $\kappa(H_2O) = 0.055 \text{ S cm}^{-1}$; 25°C) can be achieved by optimizing the working conditions.^{46,47}

CED + BMED + Complexation. Separation is a necessary procedure in many industries, such as agro-food, biochemical, and chemical industries. This procedure is easy in some cases but very touchy in other cases, e.g., separation of cobalt and nickel ions. Cobalt ions (Co^{2+}) and nickel ions (Ni^{2+}) have the same charge and sign, and similar mobility (53 and 50 $S \text{ cm}^2 \text{ eq}^{-1}$ for the limit equivalent conductances of Co^{2+} and Ni^{2+} , respectively; 25°C, aqueous⁴⁹), and it is impossible to efficiently separate them by traditional unit operations such as extraction or complexation. But if BMED is incorporated, this problem can be solved as long as BMED acquires the selectivity for either Co^{2+} or Ni^{2+} . Figure 3 shows the principle of separating Co^{2+} and Ni^{2+} via coupling of BMED with complexation.¹³ In Compartment 2, most of Ni^{2+} ions are immobilized by the specific complexing agent HR and thus separated from the migrating flux of Co^{2+} and Ni^{2+} . The immobilized $Ni^{2+}(NiR_2)$ is then fed into Compartment 6 and released by substitution with H^+ ions, which are generated by the water splitting. Meanwhile,

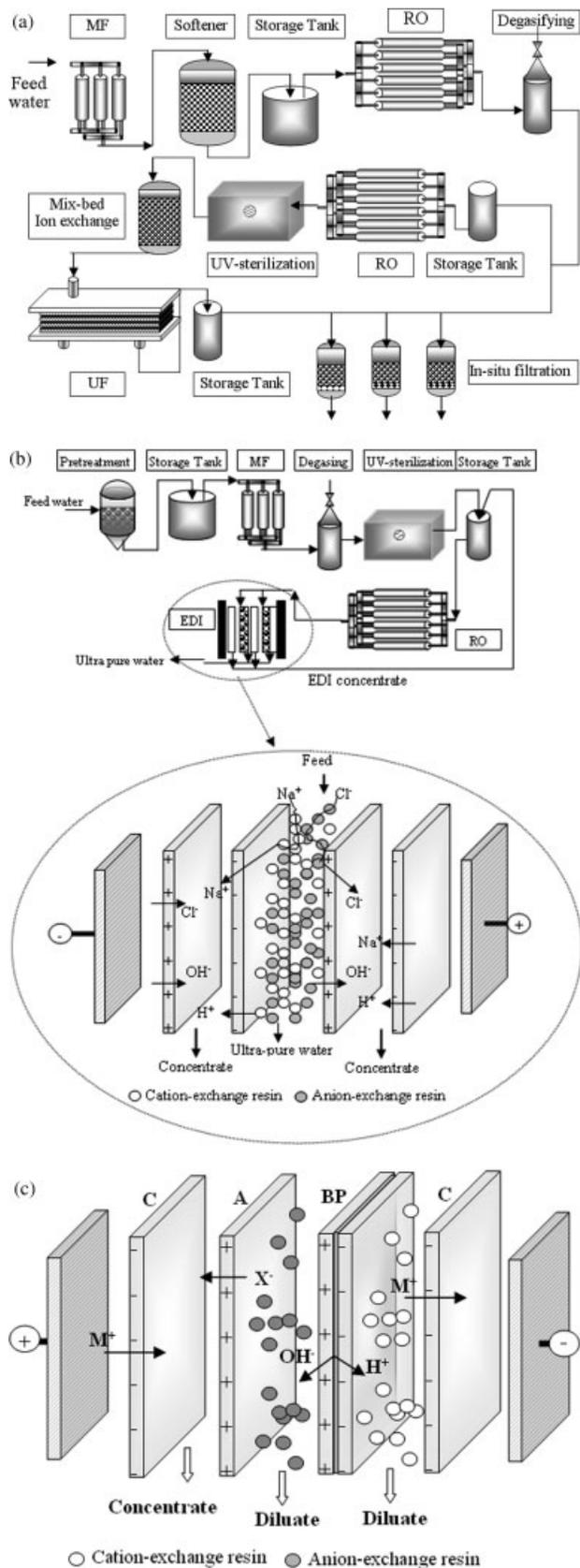


Figure 2. Comparison between (a) conventional technique, (b) EDI, and (c) EDI + BMED for production of ultrapure water.¹

the complexing agent HR is regenerated. As concerns the OH^- ions generated by the bipolar membrane, they are mixed into the HR stream to neutralize the acid produced in the complexing process. Through this technological symbiosis, a concentration ratio of Co/Ni can be attained as high as 20:1 in the concentrated CoCl_2 solution (Compartment 4) and 1:20 in the concentrated NiCl_2 solution (Compartment 5). In this case, BMED supplies H^+ ions to regenerate the complexing agent and OH^- ions to maintain the pH for complexation, whereas HR offers the ion selectivity to BMED. Obviously, these two technologies achieve a synergic effect on resource recycling.

ED + Adsorption. An example is enrichment of K^+ and/or I^- from seawater. Admittedly, seawater contains many unexploited resources and its utilization is strategically important to the development of society. The enrichment of potassium (K^+) and iodine (I^-) has been a difficult task in ocean chemical industry though there is an available method. This method is adsorption using clinoptilolite, which has an extraordinary affinity for K^+ and I^- . Nonetheless, there exist some touchy problems, such as the difficulty in ion desorption, fragility of clinoptilolite, and low separation efficiency. A promising solution is to couple BMED with adsorption. Figures 4a, b respectively show the cell configurations for extraction of K^+ or I^- . In these processes, the adsorbent is localized in the BMED stack and enriches K^+ or I^- before a direct current switches on. Then adsorbed ions are released by substitution with the H^+ or OH^- ions generated by bipolar membranes after a direct current field is applied. The preliminary results showed that the separation factors can attain as high as 8.2 for K^+/Na^+ and 10.2 for I^-/Cl^- . Interestingly, if Figures 4a, b are incorporated (Figure 4c), simultaneous enrichment of K^+ and I^- can be realized.

The above integration can also be extended to treatment of the wastewater containing heavy metals.²⁴ Generally speaking, the adsorption and desorption processes of metal cations

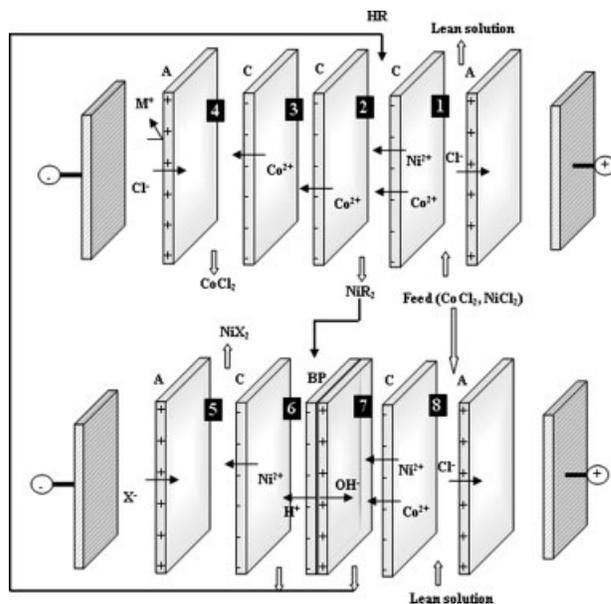


Figure 3. Simultaneous separation of Co^{2+} and Ni^{2+} by integrating BMED with complexation.

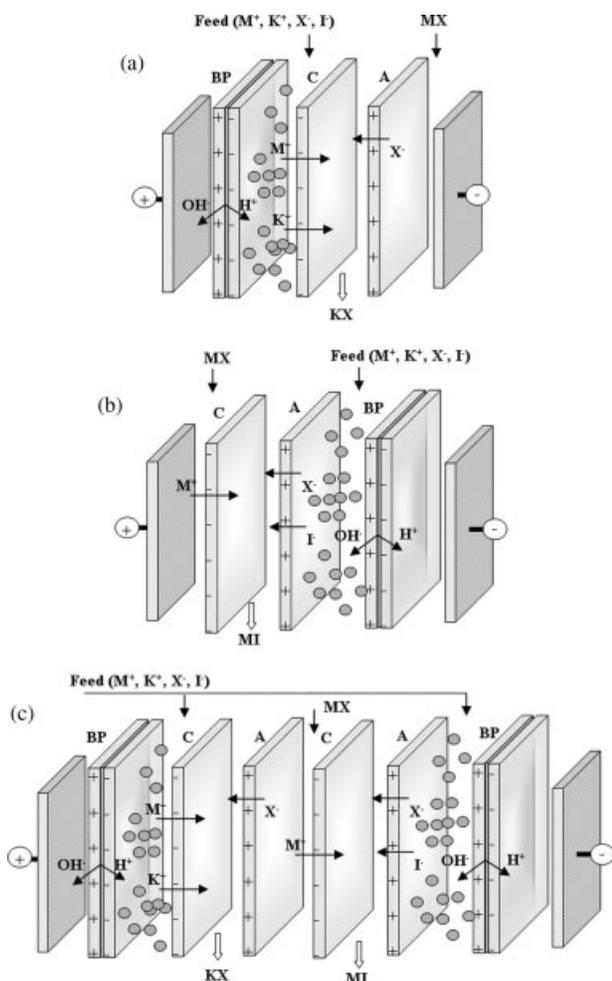
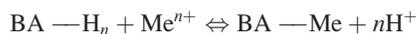


Figure 4. Integration of BMED with adsorption to enrich (a) potassium, (b) iodine, and (c) both from seawater.

K⁺, potassium ion; I⁻ iodine ion; ●, clinoptilolite.

on the bonding agents can be expressed by the following equations:



where, BA—H_n, H, and Meⁿ⁺ represent the bonding agent, adsorbent, and heavy metal ion, respectively. In this case, the bonding depends on chemical composition of the polymers used and can be either of ionic or chelate form. Table 1 lists

some bonding agents and their loading capacities to some heavy metal ions.²⁴ The complex formed (BA—Me) is to be removed from the water in a separation stage via ultrafiltration. As shown in Figure 5, the concentrates generated by this process are then to be treated using BMED, where the adsorbed heavy metal ions are replaced by the H⁺ ions generated by water splitting, and converted to their hydroxide sludge (Me(OH)_n in the compartment containing OH⁻. Obviously, efficient and rapid separation of metal ions and unlimited capacity of treatment are two advantages; moreover, higher selectivity can be achieved if specific complexing agents are employed.

Another example for integration of ED with adsorption is membrane capacitive deionization (MCDI).⁵⁰ Generally, CDI is a technique based on the electro-adsorption of ionic species using charged high-specific-surface-area electrodes,⁵¹ and ion-exchange membrane are not necessary for CDI to function. Nonetheless, CDI can function better if ion-exchange membranes are added. As illustrate in Figure 6, cation- and anion-exchange membranes are inserted between electrode and spacer and thus can prevent cations and anions from being adsorbed while electrodes are being discharged. This modification using ion-exchange membranes can achieve a higher salt removal rate than CDI. Furthermore, MCDI, due to its low energy consumption (1.96 kWh m⁻³), is competitive with RO and ED for desalination of daily wastewater discharged from thermal power plants.⁵⁰

BMED + Ion Exchange + Extraction. The conventional method for Cu²⁺ recovery is extraction and back-extraction; i.e., Cu²⁺ is extracted at alkaline pH by using naphthenic acid as extractant and kerosene as medium, and back extracted by changing pH from alkaline into acidic. This method involves complicated processes; furthermore, it has many shortcomings: low separation efficiency, significant loss of solvents, and liquid flooding or bubbling during operation. Here gives a better solution to Cu²⁺ recovery: coupling BMED with extraction and ion exchange (Figure 7).¹³ In this process, cupric ions are extracted from the mixture solution using the organic extractant HR at a slight alkaline pH, which is maintained by the OH⁻ ions supplied by the bipolar membrane. The cation-exchange resins act as the bridge for cation transport and effectively decrease the resistance of the compartment filled with HR. The bound Cu²⁺ ions are circulated to the other compartment along with the organic solution and released by substitution with the H⁺ ions from water splitting. Meanwhile, the extractant HR is regenerated. The preliminary tests showed that the process was dramatically affected by the ion exchange resins and current density. When gel ion-exchange resins are used, an

Table 1. Some Bonding Agents and Their Properties²⁴

Bonding agents (BA)	Molecular Mass/ Particle Size	Concentration of BA, g dm ⁻³	Maximum Loading Capacity, mg g ⁻¹ of BA			
			Cu ²⁺	Ni ²⁺	Co ²⁺	Pb ²⁺
Carboxymethyl Cellulose	<50 kDa	4.0	37	34	34	120
Pectine	30–100 kDa	1.5	364	339	n.d.	n.d.
Polyethylenimine	12–25 kDa	0.2	1475	1368	n.d.	n.d.
Dendritic Polyamidoamine	7.5 kDa	4.0	55	33	n.d.	n.d.
Strong-Acid Cation Exchanger	5–10 μm	4.0	79	88	82	288

n.d., not determined.

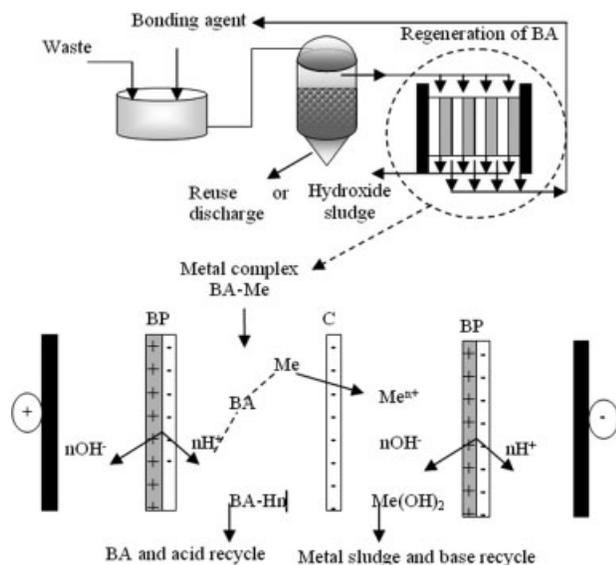


Figure 5. Treatment of wastewater containing heavy metals by integrating BMED with complexation.²³

average efficiency of 90% can be achieved if the process is operated below 50 mA cm^{-2} .⁵²

BMED + Absorption + Stripping/Distillation. The first application of such integration is to remove SO_2 from flue gases.⁵³ SO_2 was initially removed from the gas mixture via alkaline scrubbing. The spent solution is then regenerated by BMED into alkali and sulfurous acid. The alkali is recycled to the initial absorption stage; the sulfurous acid is stripped under high vacuum for production of SO_2 , which can attain a high concentration up to 95% and is further processed to obtain sulfuric acid or elementary sulfur. This application has been industrialized as SoxalTM flue-gas desulfurization due to its high current efficiency (85%) and economical competitiveness.^{53,54} This principle can also be applied to remove other acidic gases, such as CO_x or NO_x .

Recently, a more promising method for SO_2 removal is absorption using amines (R), especially alkanolamines, instead of inorganic alkalis.^{55,56} The amine regeneration and SO_2 recovery can be achieved simultaneously by heating the

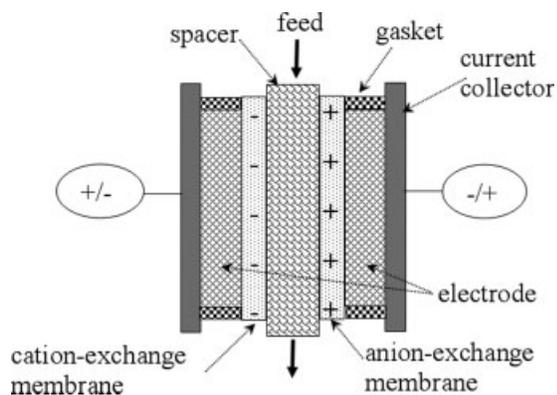


Figure 6. Schematic of membrane capacitive deionization.⁵⁰

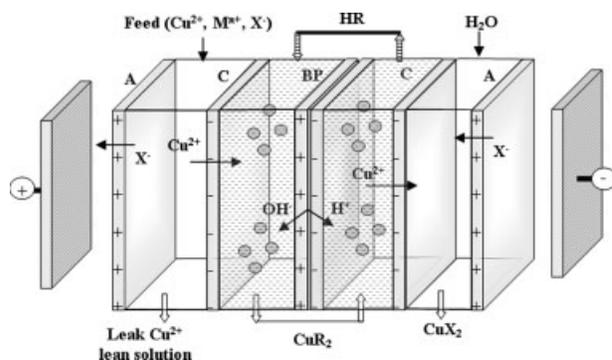


Figure 7. Concentration of copper from mixture solutions.

Cu^{2+} , cupric ion; \square , the aqueous-organic phase containing the extractant HR; \square , aqueous phase; \circ , cation exchange bead.

formed amine sulfite. Whereas, more amine sulfate ($\text{RH}_2^+\text{SO}_4^-$ or $[\text{RH}^+\text{SO}_4^-]$) will be formed in the circulation because of oxidation of sulfur dioxide and/or amine sulfite, and it can not be regenerated by heating. The heat-stable salt not only decreases the efficiency of desulfurizing operation but also causes a secondary pollution and waste of resources. Our laboratory has applied BMED to conversion of such heat stable salts. Figure 8 presents a closing loop comprising desulfurization and recycling of desulfurizing agents, where the thermal regeneration unit is used to convert amine sulfites while BMED is used to convert the heat-stable amine salt.¹⁹ In such a way, the desulfurizing process is kept from amine loss and runs stably and efficiently. The results of BMED experiments indicated that the low energy con-

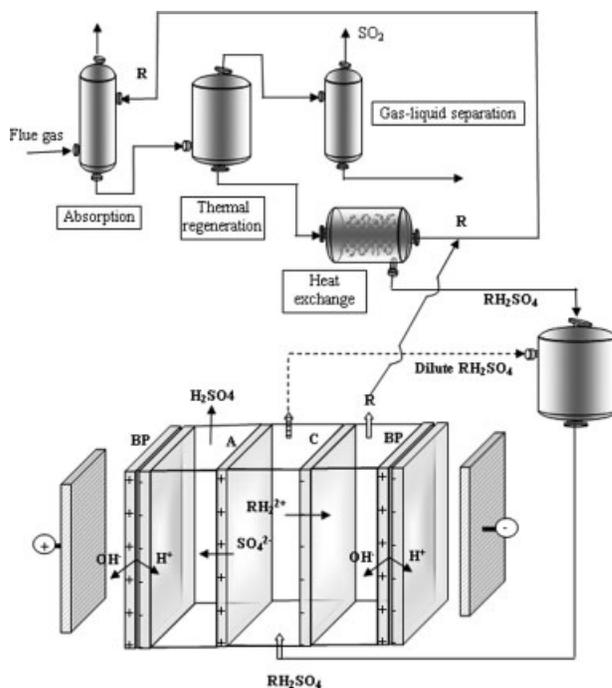


Figure 8. Regeneration of heat stable desulfurizing agents by using BMED.¹⁹⁻²⁰

R, amine; RH_2SO_4 , amine sulfate.

Table 2. Organic Amines Used for Integration and the Corresponding Estimation of Process Cost^{19,20}

Molecule Name	Pz	MEA	DEA	DMEA
Molecular formula	C ₄ H ₁₀ N ₂	C ₂ H ₇ NO	C ₄ H ₁₁ NO ₂	C ₄ H ₁₁ NO
Ball-cylinder model				
pK _b ⁴⁹	4.27 (pK _{b1}) 8.66 (pK _{b2})	4.50	5.11	4.74
Operation conditions				
Current density, mA cm ⁻²	60	50	50	50
Effective membrane Area, cm ²	7.07	7.07	7.07	7.07
Concentration of Na ₂ SO ₄ , mol dm ⁻³	0.3	0.4	0.4	0.4
Concentration of amine sulfate, mol dm ⁻³	0.18	0.2	0.2	0.2
Stack configuration	BP-C-C	BP-C-A	BP-C-A	BP-C-A
Repeating unit number	1	1	1	1
Energy consumption, kWh kg ⁻¹ R	5.4	1.49	1.25	0.97
Process cost				
Total process cost, \$ kg ⁻¹ R	0.96	0.48	0.32	0.30
Total process cost, \$ mol ⁻¹ R	0.083	0.029	0.033	0.027

R, amines; Pz, piperazine; MEA, monoethanolamine; DEA, diethanolamine; DMEA, *N,N'*-Dimethylethanolamine.

sumption and high current efficiency were achieved using both support electrolyte and amine sulfate solutions of moderate concentrations and the stack of BP-C-C configuration. When applying a high current density to the BMED stack, it had a high current efficiency and energy consumption. The structure of amine molecules also has an important influence on the processes.²⁰ Table 2 gives a performance comparison based on the inherent properties of amine molecules.

Rapp et al. reported a similar interesting study on amine recovery— recovery of dimethylisopropylamine (DMIPA) from spent scrubbing solutions.⁵⁷ DMIPA along with air is often used as a curing catalyst for sand/epoxy resin mixture in the process of manufacturing aluminum casting moulds. The amine is not consumed but emits into a waste air stream (ca. 0.5 g amine per m³ waste air).¹ As shown in Figure 9a, DMIPA is recovered as amine sulfate in an acid scrubber, followed by neutralization and distillation to recycle amine. The process is complicated and consumes an additional chemical reagent: alkali.

Figure 9b shows a pilot plant-scale test for such purpose by integrating BMED with distillation.^{1,57} The waste air stream containing DMIPA is fed into an acid scrubber, and the free amine is converted into amine sulfate. The effluent, containing ca. 10% amine sulfate in a mixture with sulfuric acid, is then fed into a BMED unit, where the amine sulfate is converted back into free amine and sulfuric acid. The produced sulfuric acid is recycled to the acid scrubber, and the amine-water mixture is distilled to recover the amine and water. In the pilot plant test, the current utilization was reported to significantly depend on amine sulfate concentration and pH in the acid compartment due to proton leakage through the anionic membrane. At an amine sulfate concentration of 0.5 mol dm⁻³ and pH ~ 1, the current utilization was ca. 70%.⁵⁷

Integration of ED with pressure-driven membrane operations

Pressure-driven membrane operations include microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), and

reverse osmosis (RO). The integration of such operations with ED can be classified into the following categories: (a) press-driven membrane operations as pretreatment; (b) ED as

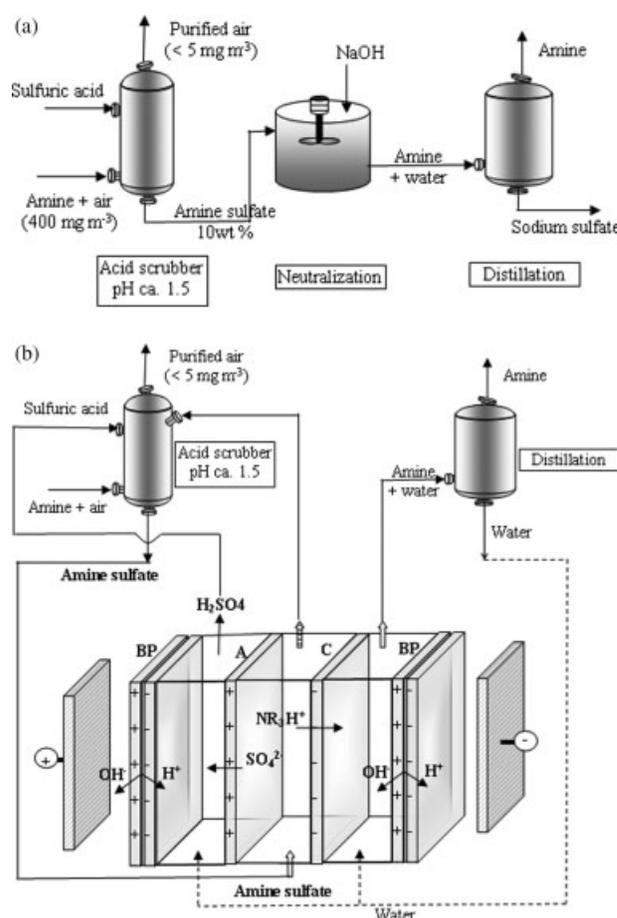


Figure 9. Recovery of dimethylisopropylamine sulfate:

(a) conventional process; (b) integration of BMED with distillation and absorption.¹

pretreatment, (b) pressure-driven membrane operations and ED cooperated as the main separation process.

Pressure-Driven Membrane Operations as Pretreatment. This is the most common form to integrate ED with pressure-driven membrane operations. The purpose of using pressure-driven membrane operations as pretreatment is mainly to purify the feed and thus alleviate the membrane pollution in ED operation. MF and UF are often used, and the operation mode can be continuous or in batch.

Kim et al. reported a pilot-scale wastewater treatment and reuse system by integrating MF and ED.²⁸ MF removes suspending solids and heavy metal ions (immobilized by separating materials) from sewage while the following ED operation further purifies and desalinates the outlet. The results indicated that the treated water using such integration could meet the standards of water reuse and its quality remained stable for more than 6 months.

Two other applications are desalination of biochemical feeds and recovery of spent liquor. In these processes, MF is often used as the necessary procedure for pretreatment because it can remove biomass and unfermented residues. Take sodium glutamate production for an example, ceramic MF membranes proved effective in the pretreatment before recovery of ammonium sulfate from the supernate above isoelectric point.⁵⁸ Furthermore, if membranes of the pore size $0.2\ \mu\text{m}$ were used, the MF process could not only maintain a higher flux (up to $90\ \text{dm}^3\ \text{m}^{-2}\ \text{h}^{-1}$) and operation stability but also achieve an effective removal of macromolecular impurities (97.2% of TSS removal). TSS content in the retentate could attain as high as $50\ \text{g}\ \text{dm}^{-3}$, and protein content $20\ \text{g}\ \text{dm}^{-3}$. Such retentate could meet the requirement for subsequent protein recovery. The permeate after MF were further treated using ED and 80% of ammonium sulfate could be recovered at $170\ \text{A}\ \text{m}^{-2}$. Owing to MF pretreatment, membrane pollution is much alleviated during ED operation.

Apart from MF, UF is also necessary for high-quality pretreatment. Bruggen et al. employed UF to treat river water and refill it into surface water so as to balance the depletion of surface water caused by excessive exploitation.²⁹ The permeate from UF was further treated using ED or NF. ED could decrease the salt content effectively and the outlet could meet the standards of water refill; however, the permeate from NF had a high salt content (mainly monovalent ions). The integration of UF and ED is a desirable substitute for RO. For one thing, RO has a higher energy consumption and more serious pollution caused by concentrate discharge. For another, the permeate from RO will erode soil since it contains less salt than surface water.

In the case of enrichment of natural organic materials from river water, RO, however, is often used. Notably, inorganic salts are also concentrated during the enrichment, so ED is a further treatment for desalination. A typical example is to use RO for organic material enrichment and then ED for sulfate removal.³⁰

ED as Pretreatment. Such integration is often used on two occasions: (a) electro-acidification or electro-alkalization of biochemical feeds and subsequent filtration, and (b) treatment and reuse of electrolyte-containing wastewater.

In biochemical industries, proteins are often separated using isoelectric precipitation and subsequent UF. When it comes to adjusting pH to isoelectric point, addition of acid

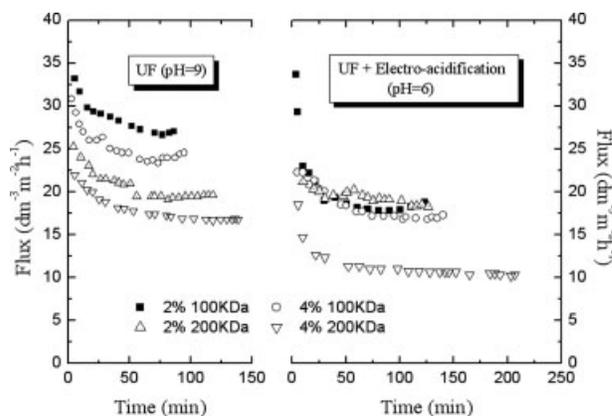


Figure 10. Plot of permeation flux vs. time (flow rate: $u = 0.24\ \text{m}\ \text{s}^{-1}$; mode: $V_D = 0.67$).³⁵

or base is the common method, but it often leads to a local pH extreme and thus denaturalization of proteins. In comparison, ED, especially BMED, is a better acidifying or alkalinizing technique since it supplies H^+ or OH^- at a mild and controllable rate and without salt introduction. These in situ techniques are also named electro-acidification or electro-alkalization.^{31,32} The subsequent UF operation can collect proteins from the feed and alleviate membrane pollution and maintain membrane flux in ED operation. Mondor et al. investigated such ED-UF integration for soy protein separation.³³⁻³⁴ They investigated three kinds of operating modes: (a) Electroacidification + UF (dead-end mode, membrane with a molecular weight cutoff of 100 kDa), feed pH: 6 or 7; (b) UF only (dead-end, 100 kDa), feed pH: 9; (c) addition of acid to adjust feed pH to 4.5 and precipitate. The results indicated that the integration achieved a higher removal of minerals (K^+ , Ca^{2+} , PO_4^{3-}) and thus a significant increase in protein solubility, i.e., an increase of 45% as compared to UF only. As for addition of acid, the proteins recovered have the similar quality as those using ED-UF integration, but its water consumption was twice as much. Alibhai et al. reported a comparisonal study on these protein separations.³⁵ The experimental conditions are as follows: protein concentration 2 wt % and 4 wt %, molecular weight cutoff 100 kDa and 200 kDa, operation mode permeation ($u = 0.24\ \text{m}\ \text{s}^{-1}$, water added: 67% of the feed volume), and feed pH 6 and 9. The flux-time plots are shown in Figure 10. The pure water flux of the membranes are $114\ \text{dm}^3\ \text{m}^{-2}\ \text{h}^{-1}$ (100 kDa) and $59\ \text{dm}^3\ \text{m}^{-2}\ \text{h}^{-1}$ (200 kDa, higher resistance and thus lower flux).³⁵ According to these flux data, gross resistance (R_g), reversible resistance (R_{rev}), irreversible resistance (R_{irrev}), and membrane resistance (R_m) can be calculated, as shown in Figure 11. On the whole, permeation flux decreases when using ED-UF integration, implying an increase in membrane resistance as compared to UF only. Note that this increase is mainly caused by the change in pH. At pH 6, proteins have more negative charges than those at pH 9 and thus pollute membranes more seriously. Furthermore, reversible resistance, as shown in Figure 11, accounts for most of the gross resistance.

Different from recovery of organic materials from river water, ED is used as pretreatment for treatment and reuse of electrolyte-containing wastewater. Its purpose is to desali-

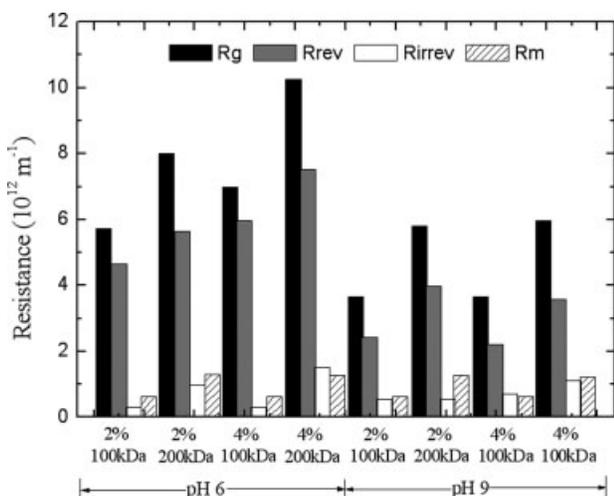


Figure 11. Resistance distribution at pH 6 (UF + Electro-Acidification) and pH 9 (UF only).³⁴

R_g , gross resistance; R_{rev} , reversible resistance; R_{irrev} , irreversible resistance; R_m , membrane resistance.

nate the wastewater and thus lighten the burden on subsequent NF or RO operation. For this kind of integration, the operation mode can be continuous or in batch.

Pressure-Driven Membrane Operations and ED Cooperated as the Main Separation Process. In this case, neither of the two techniques is subordinate to the other but cooperate as the main separation process.

β -lg 142–148, the most potent antihypertensive sequence, is one of β -lactoglobulin tryptic hydrolysates and can only function well in high purity. Figure 12 illustrates the method for separation of this peptide using UF-ED integration.³⁶ The special component for this ED stack is UF membranes, which are positioned between cation- and anion-exchange membranes. Take separation of cationic peptides (Figure 12a) for an example, the feed containing β -lg hydrolysates is pumped into the compartment between anion-exchange membranes and UF membranes, and the product lies in the compartment between cation-exchange membrane and UF membranes. A KCl solution is used as electrolyte in product compartment. Driven by a direct current field, cationic peptides (P^+) transport through UF membranes into product compartment, and K^+ and Cl^- migrate out toward electrode compartments. Ionic and neutral species are separated after using UF membranes in the ED stack; moreover, membrane pollution is much alleviated. In the case of a multi-compartment stack (Figure 12b), Cl^- is blocked from passage by cation-exchange membranes and thus stays in feed compartments. Consequently, the changes of conductivity, pH, and concentration in all compartments are more complicated than those for the single UF membrane system.³⁶

To separate anionic peptides, one just needs to change the positions of product compartment, feed compartment, and electrodes.³⁷ If two UF membranes are positioned between the cation- and anion-exchange membranes (Figure 12c), cationic peptides, neutral molecules, and anionic peptides can be separated simultaneously.

A more interesting example is water desalination using RO-CED integration, which was recently proposed by Pelle-

grino et al.³⁸ As shown in Figure 13a, the RO membranes are hollow-fibers or tubes and form channels between alternating anion- and cation-exchange membranes. The packing density of fibers or tubes may be similar to that for CED spacers or other turbulence promoters. The entire system is under the high-pressure as needed for RO operation and produces two main streams: RO permeate and concentrated brine. As shown in Figure 13b, there exists an internal recycle of RO reject between CED flow channels. This RO-CED integration allows in-situ removal of some salts from the RO reject using CED and suppresses concentration polarization via electrophoretic flow. Its purpose is to lower the osmotic pressure at the RO membrane interface and save energy (and/or increase the recovery of pure water per unit energy input). As compared to CED followed by RO, this integration has lower energy consumption in regard to CED because all the channels are filled with higher concentration of salts and thus the entire stack has lower electrical resistance. The energy savings range from 10 to 20%; however, the conductivity of ion-exchange membranes is the limiting factor on energy savings.³⁸

Integration of CED and BMED

Such integration is mainly applied in biochemical industries^{39,59–61}; specifically, CED is used to desalinate inorganic electrolytes in the feed (thus named desalination electro-dialy-

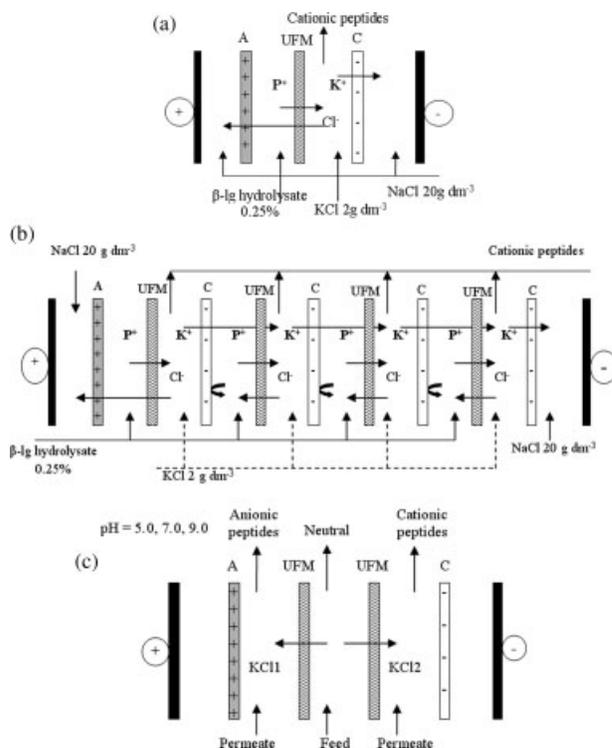


Figure 12. Fractionation of the peptides from β -lg tryptic hydrolysates using ED.

(a) One UF membrane for separation of cationic peptides, (b) four UF membranes for separation of cationic peptides, and (c) two UF membranes for simultaneous separation of cationic and anionic peptides.^{36–37} A: anion-exchange membrane; UFM: ultrafiltration membrane; C: cation-exchange membrane; P^+ : cationic peptides.

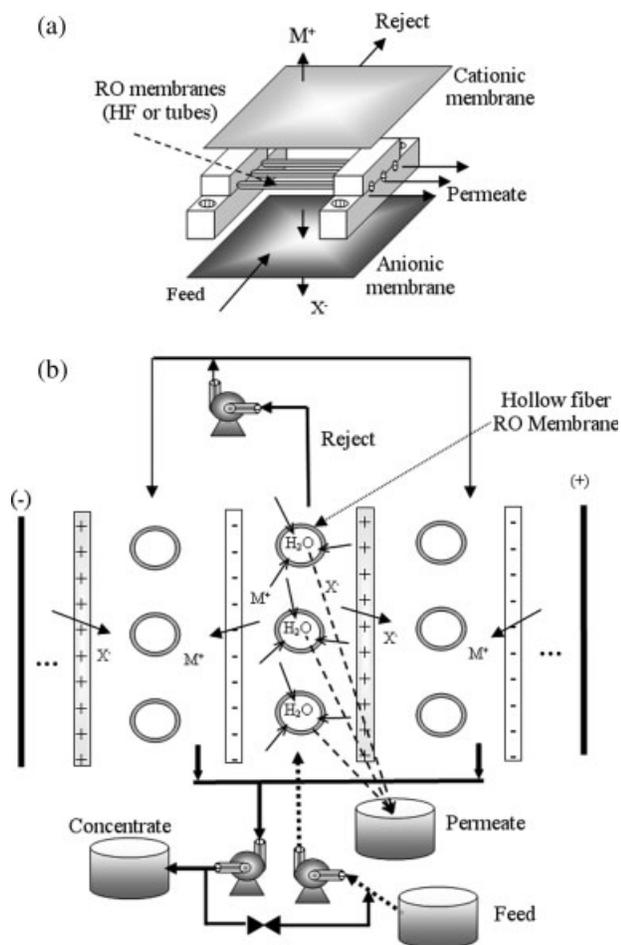


Figure 13. A novel concept for desalination-integrating RO with ED.

(a) Membrane cell; (b) stack configuration and process flow.³⁸

sis), and BMED are used for electro-acidification. Shown below are two examples.^{39,60,61}

Example I. Recovery of Mg and Proteins from Soy Tofu Whey. The ingredients of soy tofu whey include proteins (18.7 wt %), coagulant (MgCl_2 ; Mg^{2+} , 3.2 wt %), saccharide, and minerals; the former two ingredients can be separated for reuse in tofu making. Bazinet et al. used CED to desalinate the whey solution and recover Mg^{2+} and then BMED to recover the proteins.^{60,61} This integration not only achieves a higher efficiency than CED or BMED but also decreases the process cost and increases the productivity (c.f. Table 3).

Example II. Removal of Lipids from Cheddar Cheese Whey. The purpose of removing lipids is to stabilize cheese

whey, and the conventional method is centrifugation.³⁹ Bazinet et al. improved such removal process by adding BMED or CED-BMED for electro-acidification (Figure 14).^{39,61} After electro-acidification using BMED, the precipitation rate of cheese whey increased by 50%, but desalination using CED had no significant influence on whey precipitation. The precipitates obtained contained lipids and trace proteins while the whey solution had almost no lipids but proteins. The CED-BMED integration proved effective to obtain the whey proteins with lower salt content.

Integration of ED with (bio)chemical reactions-ion-exchange membrane reactors

In many chemical and biochemical reactions, products or byproducts inhibit the reaction when a certain concentration is exceeded. This limits the product concentration, so additional separation and concentration steps are necessary. Furthermore, a continuous removal of reaction inhibitors can make the process continuous and more economical. A typical application is applied to fermentation, which is the common method for organic acid production.⁶² During fermentation, microbes favor a suitable range of pH, but the produced acid will decrease the system pH and suppress the activity of microbes. One solution is to remove the acid from fermentation broth using ED, especially BMED. On one hand, BMED can separate and produce organic acids in a separate compartment and thus eliminate the product inhibition in the broth; on the other, it can produce alkali to stabilize the broth pH. These technologies have been extensively reviewed.⁴

Under some circumstances, the feed has fewer ionic species, so it will cause a large voltage drop if fed into ED stacks. One way out is to use CED to concentrate the feed before pumped into membrane bio-reactors. Figure 15 illustrates such integration to treat the drinking water of high nitrate content.^{40,63} The ground water contaminated by nitrate results from agricultural activities and is not suitable for drinking. This water can be purified by integrating CED with membrane bioreactor (MBR). MBR allows efficient denitrification of the concentrate from CED while the diluate from CED has a nitrate concentration below the acceptable value (50 mg dm^{-3}).⁴⁰

Multiple Integrations. On some special occasions, more than two techniques are needed for integration to accomplish a target. Given below are some examples. Recycling of water and H_2SO_4 from the rinse of a lead battery production line.¹

Such rinse contains lead sludge, sulfuric acid, and a low level of heavy metals, such as chromium, copper, iron, and nickel. The goal is to recycle water and sulfuric acid but keep metals under the maximum tolerable concentrations¹: $\text{Cr} < 0.1 \text{ mg dm}^{-3}$, $\text{Cu} < 0.1 \text{ mg dm}^{-3}$, $\text{Fe} < 1.5 \text{ mg}$

Table 3. Comparison Between Several Electrodialytic Processes⁶⁰

Techniques	Mg Recovery (%)	Protein Recovery (%)	Energy Consumption (Wh)	Energy Consumption kWh kg^{-1} of Recovered Mg	Energy Consumption, kWh kg^{-1} of Recovered Protein
CED (30 min)	60	—	0.96	0.69	—
BMED (60 min)	14.3	22.7	0.34	1.70	0.6
CED (60 min) + BMED (60 min)	65	34.7	0.08 + 0.47	0.08 + 3.76	0.33

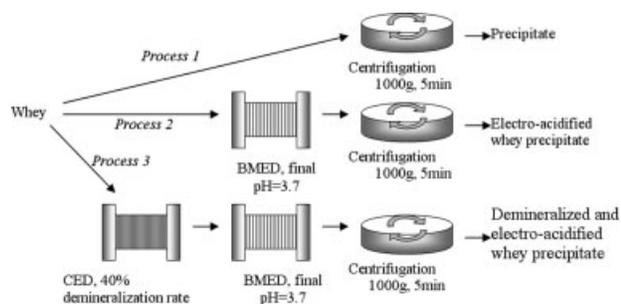


Figure 14. Treatment of cheddar cheese whey using CED and/or BMED before centrifugation.⁶¹

dm^{-3} , and $\text{Ni} < 0.1 \text{ mg dm}^{-3}$. To achieve this goal, Osmota GmbH (Germany) developed a multiple integration: CED-MF-NF-RO-precipitation-neutralization.¹ Figure 16 presents the flow sheet together with material balance at each step. The first step is to precipitate lead from wastewater in a settling tank. The supernate contains H_2SO_4 (ca. 30 g dm^{-3}), metal ions, and particles. MF is then used to treat the supernate; the retentate is recycled to sedimentation while the permeate is fed to NF to remove metal ions. Subsequently, CED is used to concentrate sulfuric acid using the permeate from NF. The obtained H_2SO_4 stream has a volume of $10.5 \text{ m}^3 \text{ d}^{-1}$ and a concentration of ca. 60 g dm^{-3} . The sulfuric acid left in the diluate from CED is totally recovered by RO. The permeate from RO has no sulfuric acid or metal ions and can be directly recycled to the rinsing tank. The concentrate from RO is partially recycled into ED and the left is used for neutralization. On the whole, 88 wt % of the sulfuric acid and 25 wt % of the rinse water are recovered. This results in reduction of costs for recovering water and sulfuric acid and substantial savings on neutralization and sludge disposal.

Utilization of High Salinity Waters. These high salinity waters include seawater, brackish water, and brine. Although not drinkable without treatment, they are a treasure of resources and of significance to the future of mankind. The key to

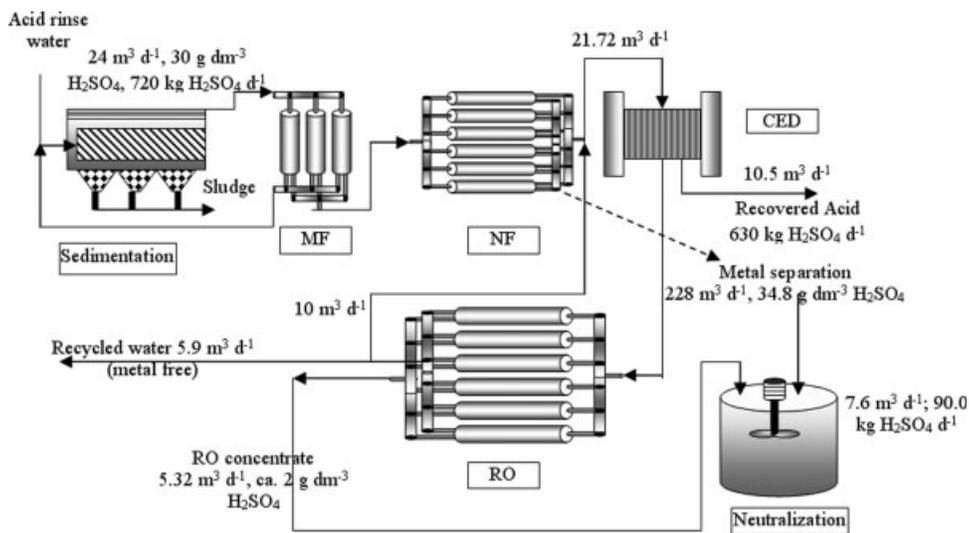


Figure 16. Recycling of spent rinse from a lead/acid battery production line.¹

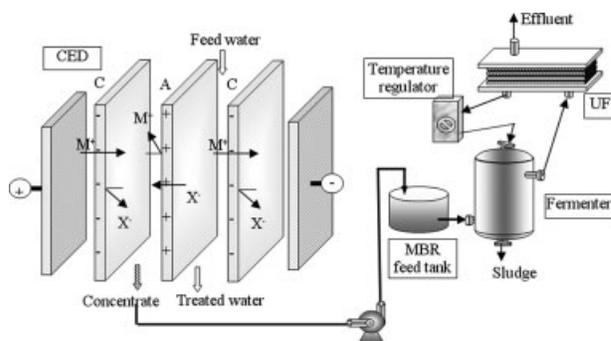


Figure 15. Denitrification of drinking water by using ED-MBR integration.⁴⁰

C, cation-exchange membrane; A, anion-exchange membrane.

utilizing them is how to separate and concentrate their ingredients. Figure 17 pictures a blueprint for such purpose.¹⁵

Route I. After pretreatments (sedimentation and/or filtration), RO is used for concentration. The concentrate is the raw material for (a) salt production and (b) acid and base production using BMED. The produced acid can acidify sea water or ground water before bromine extraction. The permeate from RO can be taken as fresh water.

Route II. ED is used to substitute RO and conducts the processes in Route I.

Route III. ED with mono-valent ion selective membranes is used to produce mineral water from deep sea water.

Route IV. NF or RO using bipolar or mono-polar membranes is used to separate and concentrate ions of different valence. In particular, integration of BMED with adsorption can enrich trace elements in seawater, such as K^+ and I^- .

Production of Gluconic Acid. Gluconic acid can be produced by catalytic oxidation of glucose into sodium gluconate followed by acidification using ion exchange (Figure 18a). The formed sodium gluconate can not be fed directly to ion exchange because there are some impurities in the so-

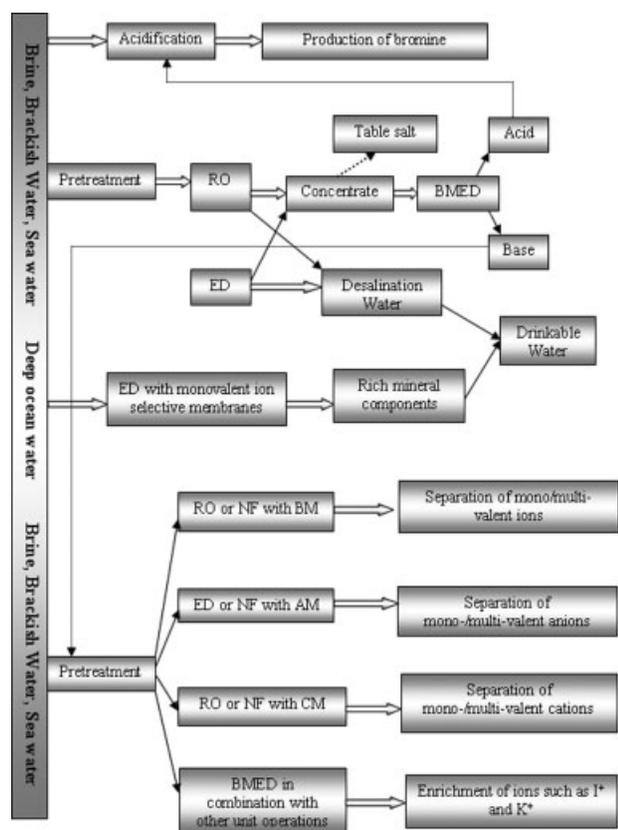


Figure 17. Resource utilization of high salinity water by using membrane technologies.¹⁵

RO, reverse osmosis; ED, electrodialysis; NF, nanofiltration; BM, bipolar membrane; AM, anion-exchange membrane; CM, cation-exchange membrane.

lution which prevent gluconic acid from crystallization. Consequently, a great amount of coal and electricity is consumed to supply the energy for purification of sodium gluconate: condensation under vacuum, crystallization, centrifugation, and drying. Obviously, this purification process generates air, water, and solid pollutions and adds much to the product cost. Besides, ion exchange is not an environmentally sound technique for acidification due to the use of acid and water for resin regeneration and the formation of salts during regeneration. To overcome the shortcomings, a multiple integration was developed recently in our research group: dissolution-oxidation-filtration-BMED-ion exchange-condensation-crystallization-drying (Figure 18b). In particular, BMED is the key technique to convert gluconate into gluconic acid as compared to the following ion exchange. In a 3-compartment BMED, the outlet from catalytic oxidation is fed into the salt compartment, and gluconic acid and NaOH are generated in the acid and base compartments, respectively. Under the optimized conditions, the conversion rate can attain as high as 98.6%, and current efficiency as high as 71.5%. Some technical details are listed in Table 4. The formed gluconic acid has a high purity and can be used directly for crystallization. The formed NaOH can be recycled as the base for catalytic oxidation. More than 90% of ion exchange can be replaced by BMED to achieve a better economy. Figure 19a presents a contrast between the feed and outlet of BMED,

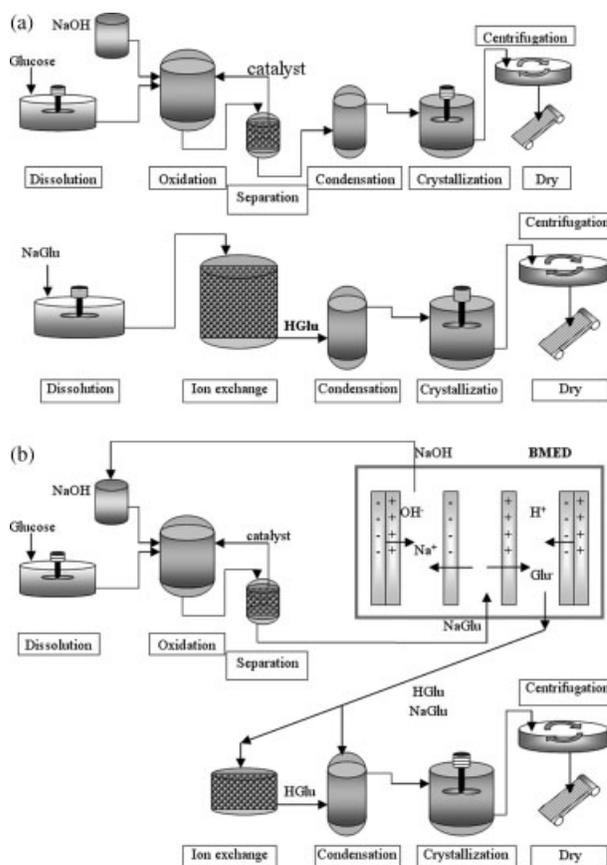


Figure 18. Production of gluconic acid:

(a) Traditional method, and (b) continuous production using BMED. NaGlu, sodium gluconate; HGlu, gluconic acid.

and Figure 19b shows the crystals of dextrose- δ -lactone (intramolecular condensation of gluconic acid) produced using the multiple integration.

Conclusions and Perspective

As exemplified and discussed earlier, ED-based integrations bring versatile solutions to the separations in chemical, biochemical, food, and pharmaceutical industries. By means of ED, some impractical or uneconomical separations can be realized in a cost-effective manner, such as separation of Co

Table 4. Production of Gluconic acid by Using BMED

Operation conditions	
Feed concentration (sodium gluconate), mol/L	1.5–1.7
BMED configuration	
The number of repeating units	10
Total membrane area, cm ²	24,000
Current strength, A	10
Operation performances	
Conversion rate (%)	98.6
Current efficiency (%)	71.5
Energy consumption (kWh kg ⁻¹)	1.03
The purity of gluconic acid (%)	98.4
The purity of NaOH (%)	96.3
Process Cost	
Process cost (CNY/kg)	2.81



Figure 19. Intermediates and final product of dextrose- δ -lactone (intramolecular condensation of gluconic acid):

(a) Feed solution (left, sodium gluconate) and outlet from BMED (right, gluconic acid); (b) dextrose- δ -lactone crystals. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

and Ni, enrichment of trace metals and preparation of ultrapure water. Nowadays, EDI is widely used in power generation plants or electronic industries to supply ultrapure water. BMED-integrated fermentation are used for clean production and recovery of some organic acids such as gluconic acid, lactic acid, and acetate acid ED-integrated UF/RO/MF/NF processes are widely used for water treatment, resources recovery, and environmental protection. Although some ED integrations, such as BMED + ion exchange, MCDI, BMED + adsorption, ED + extraction, and ED + absorption + stripping/distillation are not commercially available, they show highly technical and economical feasibility. They will be brought to industrial practice as long as the developers or users recognize that these separation technologies are versatile tools to cope with specific treatment requirements.

It should also be noted that ED-based separations are promising technologies for clean production and separation but have a long way to go before industrialization in most industries. The obstacles include the limited choice of membranes and the extremely high equipment cost of electrolysers. Ion-exchange membranes are costly, and ED itself has limited efficiency due to the membrane-related problems, such as concentration polarization, water splitting on monopolar membranes, and scaling. Besides, to date, many ED-based applications are limited to aqueous systems. The application in nonaqueous media, though feasible technically, are not available on an industrial scale due to the poor stability of membranes and spacers in organic solvents and the high electrical resistance which results in higher energy consumption and low current efficiency. Therefore, much work should be done to reduce the cost of membranes and electrodes and enhance cell configurations. Fortunately, in some applications, ED-based processes are preferable in spite of the cost disadvantage because they can provide products of higher quality or are more environmentally friendly. The increase in environmental awareness and raw material cost have accelerated the application of ED-based integrations, especially in highly industrialized and densely populated countries. In the long-term, ED-based integrations will replace single mass separations or some other integrated separations. Accordingly, researchers should give attention to interdisciplinary knowledge and solve some touchy problems, such as materi-

als design, apparatus design, process control, systematic integration, processes simulation, and operation optimization in ED-based separation processes.

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