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NaOH Recovery from MEROX Tower Waste Stream Using the Electrodialysis Process

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Electrodialysis with two different configurations was used for the recovery of NaOH from the waste stream of a MEROX tower. For this purpose, the effects of cell applied voltage and initial Na^+ concentration in the feed solution on NaOH recovery and current efficiency were studied. Results showed that the recovery and current efficiency were improved by increasing the initial Na^+ concentration. Also, increasing applied voltage had different effects on current efficiency. A NaOH recovery of about 70% and a current efficiency of 98% for a three-compartment cell at 15 volts showed that the method can be considered as a promising one for NaOH recovery from the waste stream of a MEROX tower.

Keywords current efficiency; electrodialysis; MEROX tower; NaOH recovery

INTRODUCTION

Caustic has been used widely in the oil and gas refinery operations since the earliest days of the refining industry because of its effectiveness in removing acidic components, such as mercaptans, H_2S, phenols, and inorganic or naphthenic acids, from crude oil and natural gas or their fractions. It is also widely used as a co-catalyst in the sweetening process of gas and petroleum industries, in which mercaptans (RSH) are converted to hydrocarbon disulfides (RSSR). Mercaptans are widely present in petroleum products. They cause foul odors and deteriorate the finished products. Due to their acidity, they are also corrosive to metals, which is harmful to storage and usage systems of oil products. It is, therefore, necessary to remove them either by extracting or by transforming them to harmless disulfides. In oil and gas industries, such processes are usually called sweetening (1).

The MEROX (an acronym for mercaptan oxidation) process is a proprietary catalytic chemical process developed by UOP used in oil refineries and natural gas processing plants to remove mercaptans from LPG, propane, butanes, light naphthas, kerosene, and jet fuel by converting them to liquid hydrocarbon disulfides.

UOP has developed many versions of the Merox process for various applications that include:

- Conventional Merox for extraction of mercaptans from LPG, propane, butanes, or light naphthas;
- Conventional Merox for sweetening jet fuels and kerosenes;
- Merox for extraction of mercaptans from refinery and natural gases;
- Minalk Merox for sweetening of naphthas. This process continuously injects just a few ppm of caustic into the feed naphtha;
- Caustic-free Merox for sweetening jet fuels and kerosenes. This process injects small amounts of ammonia and water (rather than caustic) into the feed naphtha to provide the required alkalinity; and
- Caustic-free Merox for sweetening of naphthas. This process also injects small amounts of ammonia and water (rather than caustic) into the feed naphtha to provide the required alkalinity.

The conventional Merox process for the removal of mercaptans from the hydrocarbon feed stream is a two-step process. In the first step, the feedstock is contacted in a trayed extractor tower with an aqueous caustic solution containing UOP's proprietary liquid catalyst. The caustic solution reacts with mercaptans to extract them. The reaction that takes place in the extractor is as follows:

$$2RSH + 2NaOH \rightarrow 2NaSR + 2H_2O \qquad (1)$$

The second step, referred to as regeneration, involves heating and oxidizing of the caustic solution leaving the extractor. The oxidation results in converting the extracted mercaptans to organic disulfides which are water-insoluble liquids to be then separated and decanted from the aqueous caustic solution. The reaction that takes place in the regeneration step is as follows:

$$4NaSR + O_2 + 2H_2O \rightarrow 2RSSR + 4NaOH \qquad (2)$$

After decantation of the disulfides, the regenerated "lean" caustic solution is recirculated back to the top of

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the extractor to continue the extraction of mercaptans. The net overall Merox reaction covering the extraction and the regeneration steps may be expressed as:

$$4RSH + O_2 \rightarrow 2RSSR + 2H_2O \quad (3)$$

The feedstock entering the extractor must be free of acid gases (CO_2 and H_2S). Otherwise, acid gases entering the extractor would react with the circulating caustic solution and interfere with the Merox reactions. Therefore, the feedstock is first "prewashed" in the prewash section of the Merox tower to remove acid gases using the caustic solution (2,3). This process can be represented by Eqs. (4) and (5).

$$H_2S + 2NaOH \rightarrow Na_2S + 2H_2O \quad (4)$$

$$CO_2 + 2NaOH \rightarrow Na_2CO_3 + H_2O \quad (5)$$

In this part of the tower, an excess amount of NaOH is used to achieve complete elimination of acidic gases; hence, a large amount of NaOH is periodically discarded via the spent caustic stream (4). This stream is a serious threat to the environment due to its sodium components (Na_2S, excess NaOH, and Na_2CO_3) requiring an appropriate waste stream process to reduce the negative impact to the environment.

Membrane technology has proved its advantages in the field of separation processes. Electrodialysis (ED) is a membrane process in which ions are transported through ion permeable membranes from one solution to another under the influence of an applied electrical potential (5). Today, the ED process is widely used in many applications for the removal or recovery of pollutant ions from waste streams (6–8). For example, ED is used for the removal of radioactive ions from low and intermediate level radioactive liquid wastes using inactive coexisting salts as ionic carriers of very small amounts of radioactive ions (9). As another application, NaOH and H_2SO_4 have been recovered using the ED process from the secondary liquid waste created by the regeneration of ion-exchange columns (10).

Other examples of the ED process applications for metal ion removal or recovery include the research reports published on the separation of strontium and cadmium ions in a system containing EDTA as a complexing agent by using a three-compartment ED Cell (11), transport of vanadium (III) and iron (II) ions through the Nafion 117 cation-exchange membrane (12), removal of copper ions (13,14) and zinc ions (15), heavy metals removal from a tin/zinc electroplating rinse solution (16), and nickel ions recovery from dilute solutions (17).

Many researchers have also investigated ED processes used for the removal of acid, salt, and heavy metal mixtures from aqueous solutions (18); boron compounds removal from natural and waste waters (19); elimination of nitrate from ground water (in regions where agricultural activities are highly intensive) (20); removal of fluoride from geo-thermal water (21); recovery of organic acids from waste salt solutions derived from the manufacture of cyclohexanone (22); and salt recovery from a process stream containing organic contaminants (23).

In this work, NaOH recovery from the waste stream of a MEROX tower using the electrodialysis (ED) process was investigated. For this purpose, the negative impact of sodium sulfide on the membranes had to be considered. Since the highly corrosive sodium sulfide destroys the anion and cation exchange membranes, the MEROX waste stream cannot be directly fed into the membrane system. Thus, its toxic sodium sulphide salt must be initially converted to other harmless innocuous salts by a suitable method such as the SEROX process (24) according to Eq. (6) below.

$$3Na_2S + 4O_2 + H_2O \rightarrow Na_2SO_4 + Na_2S_2O_3 + 2NaOH \quad (6)$$

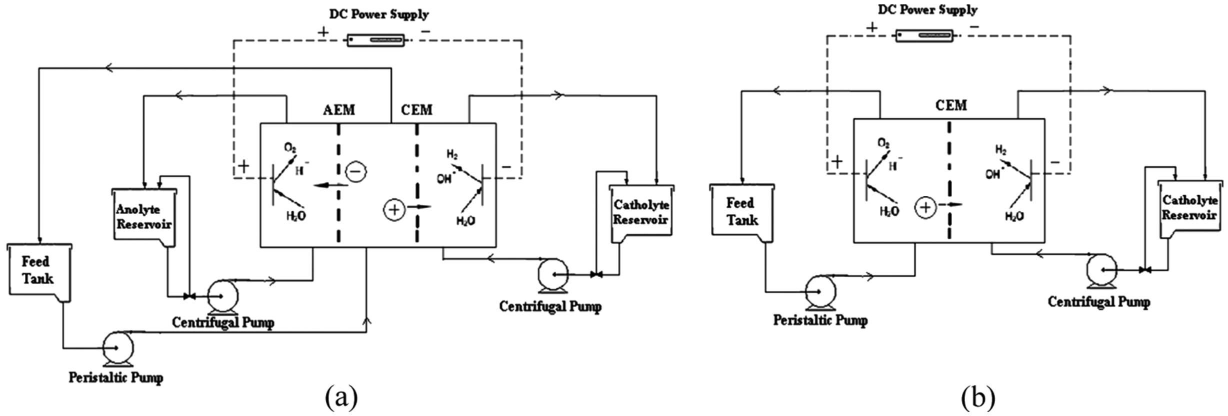
The converted stream containing sodium components (Na_2SO_4, $Na_2S_2O_3$, NaOH, and Na_2CO_3) can be subsequently used as the feed into the membrane system for NaOH recovery. Hence, the experimental work was carried out using a synthesized waste stream similar to the SEROX process output. During the experiments, the effects of such parameters as applied voltage and feed concentration on NaOH recovery, and current efficiency for Na^+ were studied.

MATERIALS AND METHODS

Schematic diagrams of the experimental setup for the ED (two-compartment & three-compartment) cells are illustrated in Fig. 1. The cells were made of Plexiglas and the compartments of each cell were separated from each other by either a cation exchange membrane (CEM) or an anion exchange membrane (AEM) as required. The effective area of the membranes was $9.5 \times 9.5\,cm^2$ and the thickness of all the compartments was equal to 8 mm. The properties of the ion-exchange membranes used in this work are listed in Table 1.

Prior to use, a pre-treatment process was carried out to remove impurities and to stabilize the membranes. For this purpose, the AEM and CEM were immersed in NaOH (1 M) and HCl (1 M) solutions for 24 h, respectively, followed by washing with distilled water. The pre-treatment process changed the anion and cation exchange membranes to hydroxide and hydrogen forms, respectively, before each experiment.

The electric field was imposed by an adjustable DC power supply (Model STAR 305, Iran) connected to a



(a) (b)

FIG. 1. Batch mode experimental setup of the ED system: (a) the three-compartment cell, and (b) the two-compartment cell.

platinum-coated titanium anode and a stainless steel cathode. The area of each electrode was equal to $8.7 \times 8\,cm^2$. The adjustable DC power source was able to supply voltage and direct current in the range of 0–40 V and 0–4 A, respectively. The feed solution was prepared by dissolving proper amounts of Na_2SO_4, $Na_2S_2O_3$, Na_2CO_3, and NaOH in distilled water according to the technical data of the SEROX unit of Kharg Petrochemical Company (Iran). These data are summarized in Table 2.

To start the experiment, equal volumes ($1000\,cm^3$) of 0.02 M NaOH and 0.02 M H_2SO_4 solutions were fed into the respective reservoirs and used as cathodic and anodic electrode rinses, respectively. The solutions were pumped into the cell by two submersible centrifugal pumps. The feed solution was introduced into the middle compartment of the three-compartment cell and the anodic compartment of the two-compartment cell at a flow rate of 45% on the basis of the peristaltic pump (Model Watson-Marlow 313S, USA) used in this work. This flow rate was equal to about 43 mL/min and this value was chosen to prevent concentration polarization phenomena based on our previous experiments (14).

TABLE 1
Physical and chemical properties of the membranes (Ionics, Watertown, MA, USA)

Property	Membrane type	
	AR204SXR412 (Anionic)	CR67, MKIII (Cationic)
Reinforcing Fabric	Acrylic	Acrylic
Specific Weight (mg/cm^2)	13.7	13.7
Thickness (mm)	0.5 mm	0.5 mm
Burst Strength (kg/cm^2)	7.0	7.0
Water Content	46% of wet resin only	46% of wet resin only
Capacity (meq/dry gram resin)	2.8	2.4

All the experiments were conducted over a period of 2 hours. Then a sample of the solution was taken from the cathodic reservoir to determine the concentration of NaOH by the titration method using 0.1 M HCl solution and phenolphthalein as titrant and indicator agents, respectively. Finally, by making Na^+ mole balance on the catholyte reservoir, a quantitative evaluation on the process performance was made by calculating NaOH recovery (R) using Eq. (7) below:

$$R(\%) = [\Delta(V \cdot C)/(V_f \cdot N_f)] \times 100 \tag{7}$$

where, $\Delta(V \cdot C)$ is the change in the number of the moles of NaOH (kmol) over the time period of t (s), and the parameters V_f and N_f represent the initial volume of the feed solution (m^3) and the initial concentration of Na^+ ion in the feed ($kmol/m^3$), respectively.

The performance of an electrodialysis process is usually evaluated in terms of the current efficiency which is a measure of how effective the electrical energy acts for the transfer of the desired ionic species across the ion exchange

TABLE 2
Composition of the feed solution

Component	Mole percent (%)
H_2O	99.667
NaOH	0.001
Na_2CO_3	0.061
$Na_2S_2O_3$	0.02
Na_2SO_4	0.251
Total Na^+ concentration ($kmol/m^3$)	0.371

membranes for a given applied current. Low current efficiencies indicate occurrence of water splitting in the dilute or concentrate streams, shunt currents between the electrodes, or back-diffusion of ions from the concentrate to the dilute compartment (25). In our study, current efficiency (η) for Na^+ transport was calculated using Eq. (8).

$$\eta(\%) = [\Delta(V \cdot C) \cdot z \cdot F/(I \cdot t)] \times 100 \tag{8}$$

where, I designates current (Amp), and F and z are Faraday's constant (96485 Amp · s/mol) and the charge of the Na^+ (equal to one), respectively.

RESULTS AND DISCUSSION

Different parameters can influence the performance of the ED process. In this work, the effects of applied voltage, concentration of feed solution, and cell configuration on the process performance were investigated.

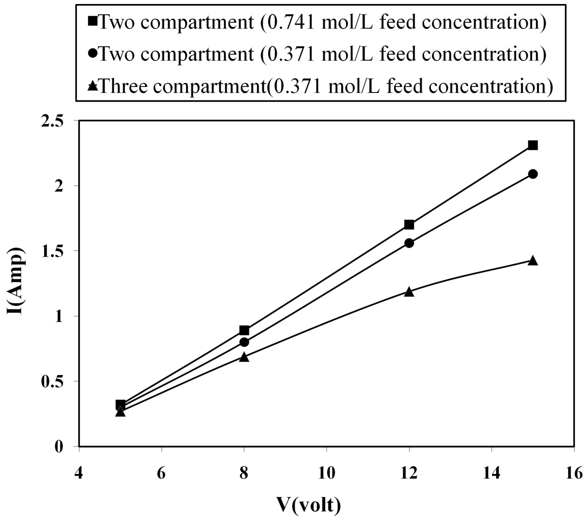


FIG. 3. Current vs. applied voltage for the two- and three-compartment cells.

Effect of Operational Parameters on ED Performance of a Two-Compartment Cell

In order to investigate the effect of feed concentration, experiments were performed at the two different concentrations of 0.371 and 0.741 mol/L of Na^+ ions in the feed. The former was chosen based on the data given in Table 2 and the latter is twice the former. Also, the applied voltage was adjusted at 5, 8, 12, and 15 volt. The results are presented in Figs. 2–4.

As it can be seen from Fig. 2, increasing the applied voltage led to the enhancement of NaOH recovery for both initial concentrations. Also, higher initial concentrations led to higher recoveries. These results can be explained by considering the effect of the driving force for ion transport through the membrane. Increasing applied voltage produces a stronger electric field which, in turn, leads to a higher driving force. On the other hand, at higher initial concentrations of Na^+ ion in feed solution, more Na^+ ions are available for competition with H^+ ions generated on the anode for current transport in the cell; thus, NaOH recovery will be greater for higher initial concentrations.

In Fig. 3, a slight difference is seen between the electrical currents for the two different initial concentrations. This is due to the lower electrical resistance of the solution with a higher concentration. However, this very small difference

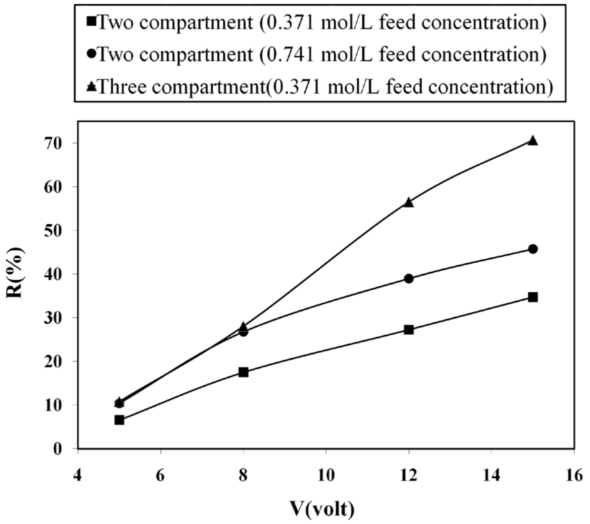


FIG. 2. NaOH recovery vs. applied voltage for the two- and three-compartment cells.

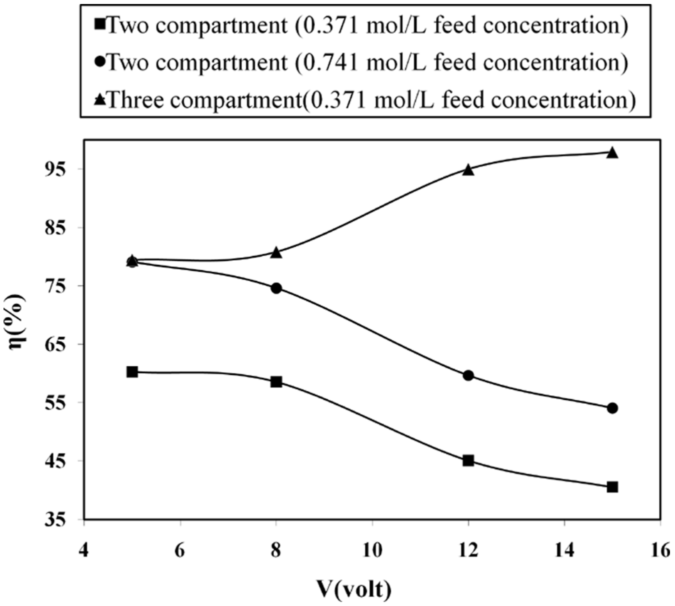


FIG. 4. Current efficiency vs. applied voltage for two- and three-compartments cells.

proves that the electrical resistance of the feed solution passing through the anodic chamber is not the predominant resistance and that the overall resistance of the cell has not changed considerably with increasing initial concentration.

It is clear from Fig. 4 that for the system with a higher initial concentration of Na^+ in the feed, the Na^+ current efficiency was higher. The reason for this effect is similar to the one explained earlier for the effect of initial Na^+ ion concentration on NaOH recovery. The same figure reveals that current efficiency decreases significantly with increasing applied voltage. This is due to the strong competition between Na^+ and H^+ ions for current transfer in the cell. By increasing the applied voltage, more H^+ ions are produced due to the anodic reaction of water oxidation and, therefore, current efficiency for Na^+ declines.

Comparison of the Performances of the Two- and Three-Compartment Cells

Figure 2 reveals that for both configurations, NaOH recovery increases with increasing applied voltage. The reason for this was already explained by considering the fact that by increasing the applied voltage, the driving force for ion movement through the membranes is enhanced, which leads to a higher NaOH recovery.

However, it is seen in Fig. 2 that NaOH recovery in the three-compartment cell is higher than that in the two-compartment cell. This can be understood by considering the competition between H^+ and Na^+ ions to be transferred through the cation exchange membrane. As said earlier, the feed solution in a two-compartment cell passes through the anodic chamber in which H^+ ions are produced via the anodic reaction. Therefore, there is a strong competition between H^+ and Na^+ ions to pass through the membrane. In the three-compartment cell, however, the feed is sent to the middle compartment which is separated from the anodic chamber by the anion exchange membrane and, therefore, H^+ ions generated in the anodic chamber cannot compete with Na^+ to move from the middle chamber into the cathodic one. As a result, NaOH recovery is higher in the three-compartment cell for any applied voltage.

Figure 2 indicates that the difference in NaOH recovery between the two configurations becomes larger at higher voltages. This can be attributed to the increasing competition between Na^+ and H^+ to be transferred through the CEM in the two-compartment cell by generating more H^+ ions at higher voltages, whereas this has no effect on the performance of the three-compartment cell.

As shown in Fig. 3, the electric current passing through the cell is higher for the two-compartment cell compared to that of the three-compartment cell. This is caused by the higher electrical resistance in the latter due to the extra compartment whose resistance is added to the overall cell resistance. This leads to a higher power consumption by the two-compartment cell. This is shown in Fig. 5.

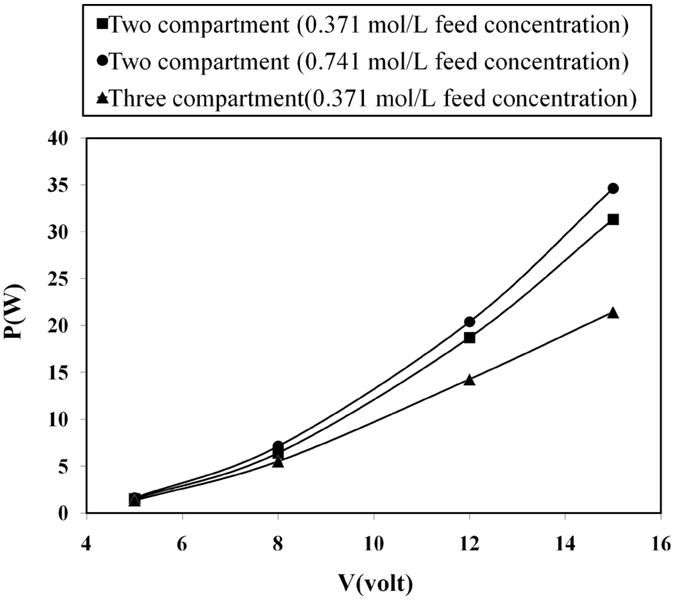


FIG. 5. Power consumption vs. applied voltage for the two- and three-compartment cells.

Figure 4 shows that the current efficiency for Na^+ in the three-compartment cell enhanced with increasing applied voltage. This is due to the fact that H^+ ions in this configuration produced via the anodic reaction cannot migrate through the AEM toward the middle compartment so that Na^+ ions in this compartment are the only migrating species toward the cathodic chamber without any competitor. On the other hand, by increasing the applied voltage, the power consumed for Na^+ transport increases whereas the potion for other consumers such as current leakage and membrane resistance remains almost constant. The current efficiency for Na^+ transport, therefore, increases with applied voltage.

In contrast, by increasing the applied voltage and, thereby, the current density of the system, the current efficiency of Na^+ showed a falling trend in the two-compartment cell system. The reason is the same as that in the previous section with reference to Fig. 4. Also, the higher current efficiency of the three-compartment cell can be easily understood with regard to the same reasoning used for Fig. 2 and considering the effect of the competition between H^+ and Na^+ ions for passing through the cation exchange membrane in the two different configurations.

CONCLUSIONS

In this paper, the effects of such parameters as applied voltage and feed concentration on NaOH recovery from converted waste stream of the MEROX process were studied. Based on the results obtained, the following conclusions can be drawn:

1. Increasing the initial concentration of the feed solution had positive effects on both NaOH recovery and current efficiency but had no significant effect on the electrical current passing through the cell.
2. A higher NaOH recovery can be achieved by using the three-compartment cell; this can be further increased by applying a higher voltage to the cell.
3. Interestingly, current efficiency decreased with increasing applied voltage in the case of the two-compartment cell compared to the three-compartment cell.
4. Examination of the results obtained for the three-compartment cell reveals that a NaOH recovery of 70% and a current efficiency of 98% can be achieved at 15 volt.
5. At any applied voltage, the electrical current was lower for the three-compartment cell. This means that the voltage which yields higher recovery and current efficiencies in the case of the three-compartment cell also leads to lower power consumption (V × I) for this configuration. Therefore, the three-compartment configuration leads to a better performance not only in terms of higher NaOH recovery and current efficiencies but also with respect to reduced power consumption.
6. Finally, the implemented system showed that it can be used as a promising method to recover unused caustic from the waste stream of the MEROX process with high recovery and current efficiency.

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SYMBOLS

C	NaOH concentration, $\mathrm{kmol\,m^{-3}}$
F	Faraday's constant, 96485 $\mathrm{Amp \cdot s/mol}$
I	Current, Amp
M_n	Molar mass of NaOH, $\mathrm{kg\,kmol^{-1}}$
N_f	Initial concentration of Na^+ in feed, $\mathrm{kmol\,m^{-3}}$
R	Percentage recovery of NaOH
V	Volume of catholyte solution, $\mathrm{m^3}$
V_f	Initial volume of feed, $\mathrm{m^3}$
z	Charge of Na^+
t	Process time, s
$\Delta\ (V \cdot C)$	Change in the number of NaOH moles in the catholyte solution
η	Current efficiency for Na^+

REFERENCES

1. Hobson, G.D. (1986) *Modern Petroleum Technology, Part I*, 5th Ed.; Wiley: New York.
2. Holbrook, O.L. (1997) *Handbook of Petroleum Refining Processes*; McGraw-Hill: New York.
3. Basu, B.; Satapathy, S.; Bhatnagar, A.K. (1993) MEROX and related metal phthalocyanine catalyzed oxidation processes. *Catal. Rev. Sci. Eng.*, 35: 571.
4. Kohl, A.; Nielsen, R. (1997) *Gas Purification*, 5th Ed.; PennWell: Tulsa, OK.
5. Kabay, N.; Demircioglu, M.; Ersz, E.; Kurucaovali, I. (2002) Removal of calcium and magnesium hardness by electrodialysis. *Desalination*, 149: 343.
6. Koter, S.; Warszawski, A. (2000) Electromembrane processes in environment protection. *Polish J. Environ. Studies*, 9: 45.
7. Nagarale, R.K.; Gohil, G.S.; Shahi, V.K. (2006) Recent developments on ion-exchange membranes and electro-membrane processes. *Adv. Colloid Interface Sci.*, 119: 97.
8. Huang, C.H.; Xu, T.W. (2006) Electrodialysis with bipolar membranes for sustainable development. *Environ. Sci. Technol.*, 40: 5233.
9. Sugimoto, S. (1987) Removal of radioactive ions from nuclear waste solutions by electrodialysis. *J. Nucl. Sci. Technol.*, 15: 705.
10. Miyagawa, M.; Mizutani, T.; Miki, M.; Ohuchi, I. (1979) Volume reduction system of radioactive waste by electrodialysis. *Karyaku Karyoku Genshiryoku Hatsuden*, Japan, 30: 351.
11. Gasser, M.S.; Nowier, H.G. (2004) Separation of strontium and cadmium ions from nitrate medium by ion-exchange membrane in an electrodialysis system. *J. Chem. Technol. Biotechnol.*, 79: 97.
12. Shim, J.B.; Oh, W.Z.; Lee, B.J.; Park, H.S.; Kim, J.D. (1999) Electrodialysis of vanadium (III) and iron (II) ions from a simulated decontamination solution. *Sep. Sci. Technol.*, 34 (10): 1963.
13. Öğütveren, Ü.B.; Koparal, S.; Özel, E. (1997) Electrodialysis for the removal of copper ions from wastewater. *J. Environ. Sci. Health A*, 32 (3): 749.
14. Mohammadi, T.; Moheb, A.; Sadrzadeh, M.; Razmi, A. (2004) Separation of copper ions by electrodialysis using Taguchi experimental design. *Desalination*, 169: 21.
15. Choi, K.H.; Jeoung, T.K. (2002) Removal of zinc ions in wastewater by electrodialysis. *Korecm J. Chem. Eng.*, 19 (1): 107.
16. Smith, W.H.; Foreman, T. (1997) Electrowinning/Electrostripping and electrodialysis processes for the recovery and recycle of metals from plating rinse solutions. *Sep. Sci. Technol.*, 32: 669.
17. Dzyaz'ko, Y.S.; Rozhdestvenskaya, L.M.; Pal'chik, A.V. (2005) Recovery of nickel ions from dilute solutions by electrodialysis combined with ion exchange. *Russian Journal of Applied Chemistry*, 78 (3): 414.
18. Rockstarw, D.A.; Scamehorn, J.F. (1997) Use of electrodialysis to remove acid, salt, and heavy metal mixtures from aqueous solutions. *Sep. Sci. Technol.*, 32 (11): 1861.
19. Mel'nik, L.A.; Butnik, I.A.; Goncharuk, V.V. (2008) Sorption–membrane removal of boron compounds from natural and waste waters: Ecological and economic aspects. *J. Water Chem. Technol.*, 30 (3): 167.
20. Kabay, N.; Yüksel, M.; Samatya, S.; Arar, O., Yüksel, Ü. (2007) Removal of nitrate from ground water by a hybrid process combining electrodialysis and ion exchange processes. *Sep. Sci. Technol.*, 42: 2615.
21. Arda, M.; Orhan, E.; Arar, O.; Yuksel, M.; Kabay, N. (2009) Removal of fluoride from geothermal water by electrodialysis (ED). *Sep. Sci. Technol.*, 44: 841.
22. Wang, Z.; Luo, Y.; Yu, P. (2006) Recovery of organic acids from waste salt solutions derived from the manufacture of cyclohexanone by electrodialysis. *J. Membr. Sci.*, 280: 134.
23. Tsai, S.P. Electrodialysis-based separation process for salt recovery and recycling from waste water. U.S Patent 5645703, July, 8, 1997.
24. Mazgarov, A.M. (1996) New process of petroleum and gas-condensate refining from low molecular mercaptans. *Gigiena Trudai Proffesional'nye Zabolevaniya*, 12: 11.
25. Shaffer, L.; Mintz, M. (1997) *Electrodialysis in Principles of Desalination*, 2nd Ed.; Academic Press: New York.