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# **Treatment of Heavy Metal Contaminated Process Waters by Physicochemical Methods Based on the Analogy of $\text{Cu}^{2+}$ and $\text{Ni}^{2+}$**

*Ph.D. Thesis Booklet written by*

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## 1. Objective and outline

In manufacturing industries enormous amount of high-salinity process water is generated, which salt content is limiting its further use. Consequently, desalination and process water treatment are priority in industrial water management. Beside of high salt content, heavy metal content makes the treatment process more complicated. Regarding this, several different technologies are available; precipitation, evaporation, ion exchange, complex forming, etc., but usually a combination of these represents the real solution for heavy metal removal. Among these methods, membrane processes are widely studied as environmentally friendly processes because of their advantages; no (or low levels of) chemical addition is required.

Since production technologies cannot be changed easily, more focus is given on the efficient treatment of wastes to reduce volume and/or lessen the concentration of pollutants to reach the emission limits. Dual goal can be achieved by process water treatment; to gain purified water and recover valuable compounds.

Electrodialysis (ED) is an emerging technology in drinking water production, *e.g.* seawater desalination or recovery of certain elements [1]. On the other hand, only a few reports are available where ED is used for metal containing high salinity waters, particularly not for real ones originating from industry. So, I found beneficial to investigate this upcoming treatment technique, and compare to well-known and proven technological solutions, like nanofiltration (NF).

Since the NF membrane rejects multivalent ions, it can be utilised for elimination of metal ions from liquid phase. In case of the most common heavy metal pollutant of the metal plating industry, by nanofiltration 47 – 98% copper removal efficiency [II; III; IV; V] could be achieved depending on the initial concentration and composition,

and transmembrane pressure. Although the copper concentration seemed to cover the ranges of real process water concentration, the total initial ion concentrations of the test solutions were far away from high salinity waters, even real process waters. Despite the low initial copper concentration, the total salinity had great influence on copper rejection in case of real process water [V], resulting in a reduced rejection to half (41 – 45%) than that of the model solutions (94 – 98%) [VI].

General problem in electroplating industry is that alongside the loss of the plating bath during drag-out, the metal concentration in the rinsing bathes continuously increases. By electro dialysis of rinsing water, the metal content could be concentrated and recycled to the main bath. Therefore, metal concentration could be restored as well as the water content of the recycled stream can compensate the loss caused by evaporation. As a result, both materials' loss can be reduced [VII]. ED was successfully applied for the treatment of synthetic solution simulating rinsing water of bright nickel electroplating bath. After electro dialysis the specific electric conductivity of the model solution was decreased significantly and the purified fraction was reused as rinsing water. It was estimated that in case of real process water treatment the concentrated fraction enriched in nickel could be recycled to the electroplating bath [VIII]. Although prosperous results were achieved for synthetic solutions, electro dialysis has not been used for treatment of metal contaminated real process waters.

The main goal of this project and my dissertation is to develop a treatment technology for heavy metal contaminated high-salinity process waters, what is highly efficient regarding the elimination of inorganic pollutants and energy consumption as well, keeping in mind the possibility of industrial implementation, after proper up-scaling.

## 2. Applied techniques and methods

In each membrane technique experiments the key characteristic of the membranes were determined; pure water- and permeate flux, rejection, demineralisation rate for NF, while demineralisation rate, percentage extraction and separation coefficient for ED. The conductivity, pH,  $\text{COD}_{\text{Cr}}$ , concentration of the followed ions ( $\text{Ni}^{2+}$ ;  $\text{Cu}^{2+}$ ;  $\text{Na}^+$ ;  $\text{Cl}^-$ ;  $\text{SO}_4^{2-}$ ;  $\text{NO}_3^-$ ) were measured as well. In case of ED experiments electric energy up-take was followed too.

### 2.1. Nanofiltration

NF experiments were performed on a universal bench-scale membrane filtration apparatus (CM-Celfa P28) in batch system and cross-flow mode. Desal DL flat sheet membrane was utilised with an active membrane area of  $28 \text{ cm}^2$ . The applied transmembrane pressure was adjusted to 30 bar and the isotherm experiments were performed.

### 2.2. Electrodialysis

ED is a membrane technique, which applies electric field gradient as driving force. This technique enables the separation of mineral compounds from feed solution, while moving dissociated ions through

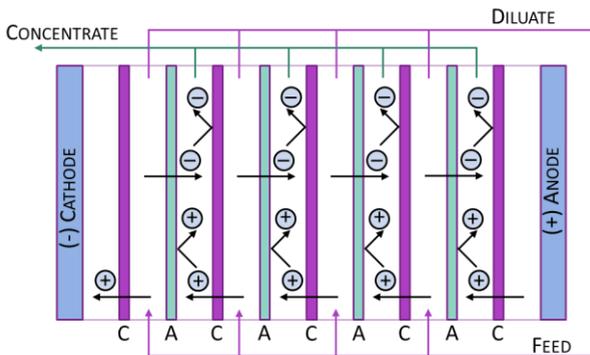


Figure 1. Principle of ED

ion-permeable selective membranes, forming two separated flows; a deionised flow called diluate and a concentrated flow called concentrate, as it is illustrated in *Figure 1*.

ED experiments were performed on a laboratory scale ED-R unit (Membrain P EDR-Z/10-0.8) with 10 pieces of RALEX AM(H)-PP and 11 pieces of RALEX CM(H)-PP heterogeneous ion-exchange membranes with an effective area of 64 cm<sup>2</sup> each.

### ***2.3. Heat-pump vacuum evaporation***

Vacuum evaporation experiment was carried out on a pilot scale heat-pump vacuum evaporator (Veolia Water R150v03), which operates with R407C gas as working medium.

The momentary electric energy up-take for the whole system, the distillate's flowrate, the relative pressure (vacuum) in the cauldron and the specific electric conductivity of the distillate were monitored continuously. The specific electric conductivity of the initial feed and the final concentrate were determined at the start and end of the experiment, respectively.

### ***2.4. Mathematical modelling of ED***

Electrodialysis process can be described based on basic electrochemical rules, *e.g.* the resistance model. In case of real process waters a general characteristic parameter, the specific electric conductivity providing information on the total dissolved salt content. The aim was to set up a model in which conductivity acts as the key parameter. After determination of a semi-empirical model's parameters for pure NaCl and Na<sub>2</sub>SO<sub>4</sub> solutions at a given applied voltage, and knowing the initial conductivity values of the feed solution to be treated, the run-down of conductivity and absolute current, furthermore the necessary treatment time can be determined.

### 3. Results and theses

In course of my work, at first applicability of nanofiltration and ED was studied and compared, concerning high-salinity heavy metal containing model- and real process waters, originating from plating industry. Optimal operation conditions of both techniques were determined as well.

Evaporation is a common thermic method, which can produce similar low conductivity purified phase as the ED independently of the monovalent ion content of the feed, so these techniques were compared in aspect of the specific electric consumption related to 1 dm<sup>3</sup> produced purified water.

Finally, a model was elaborated according to the resistance model and Kohlrausch implication, in favour of describing the ED process and to estimate the results of ED treatment of process water having a given composition. The model could have a great benefit in case of implementation of ED technique to an industrial process chain for estimation the necessary operating conditions, in order to meet the required emission limits of the state, the required water quality of technological water for reuse or the required maximal conductivity proportional to concentration, to minimize the volume of hazardous liquid wastes.

Since the driving force of ED is electric field gradient, separation is based on the electric charge of ions. According this, the achieved results summarised in this dissertation regarding ED, as a matter of course, can be extended to all of the heavy metal ions present in electroplating processes (*e.g.* Sn<sup>2+</sup>, Zn<sup>2+</sup>, Co<sup>2+</sup>, Pd<sup>2+</sup>, Au<sup>+</sup>, Ag<sup>+</sup>, Cr<sup>3+</sup>, Cr<sup>6+</sup>, *etc.*) based on their analogue behaviour in electric field like Cu<sup>2+</sup> and Ni<sup>2+</sup> ions.

### ***Thesis 1***

It was revealed that electro dialysis (ED), which has been used in drinking water production and energetic industry for ten years, has not been established as a technique for treatment of heavy metal containing process waters yet. After experiments of model solutions, the ED technique was firstly applied for treatment of real process waters originating from electroplating industry. It was demonstrated that ED is an efficient method for the simultaneous removal of heavy metal ions and salts from artificial as well as real industrial process waters having specific electric conductivity up to 30000  $\mu\text{S}/\text{cm}$  initially. The minimal applicable voltage of this method was determined; 6 V or higher is recommended to be applied for the treatment of process waters with similar compositions.

Relevant publications: 1; 2; 5; 6; 8

### ***Thesis 2***

In aspect of treatment of heavy metal containing process waters, the efficiencies of nanofiltration (NF) and ED techniques were compared. It was revealed that both techniques represent similar efficiency and applicability for the removal of heavy metal ions; such as 81.0 – 89.6 % rejection of  $\text{Cu}^{2+}$  and  $\text{Ni}^{2+}$  for NF and 80.8 – 96.6% percentage extraction of  $\text{Cu}^{2+}$  and  $\text{Ni}^{2+}$  for ED, in the investigated 0.005 – 13.2 mg/l concentration range of them.

Relevant publications: 1; 2; 7

### ***Thesis 3***

The effect of collective presence of heavy metal- and high salt contents on efficiency of NF was studied, at first in case of model solutions, followed by real heavy metal containing high salinity process waters. It was revealed that the rejection of ions was affected by their collective presence: though NF could reject 94 – 98% of the heavy metal ions till concentration of 4 g/l, the presence of monovalent ions (*e.g.* sodium- and chloride ions) have negative effect on the rejection of heavy metals,

resulting a decreased 12.5 – 90.5% rejection in a concentration range of 0.051 – 0.888 mg/l of the heavy metal, in the presence of 1.2 – 46.8 g/l monovalent ion ( $\text{Na}^+$  and  $\text{Cl}^-$ ) content.

Relevant publications: 1; 3; 7; 9

#### ***Thesis 4***

The effect of collective presence of heavy metal- and high salt content on ED's efficiency was studied as well, at first in case of model solutions, subsequently real heavy metal containing high salinity process waters. In contrast to NF, the ED represents significantly higher elimination efficiency in presence of monovalent ions. For real process waters up to 30000  $\mu\text{S}/\text{cm}$  specific electric conductivity, representing extreme high salinity, demineralisation rate of ED was higher than 91% and 99%, while those obtained for NF were 26% and 62% in case of the two studied samples representing this type of process waters.

Relevant publications: 1; 7

#### ***Thesis 5***

Energetic comparison between high-purity water producing heat-pump vacuum evaporation and ED techniques was established that the energy requirement of ED ( $0.059 \text{ kW}\cdot\text{h}/\text{dm}^3$ ) was one order of magnitude less than that of demonstrated for heat-pump vacuum evaporation ( $0.543 \text{ kW}\cdot\text{h}/\text{dm}^3$ ), however the same quality of purified water could be produced by both techniques.

Relevant publications: 4; 5; 6

#### ***Thesis 6***

In case of real process waters, the specific electric conductivity as general characteristic parameter provides information on the total dissolved salt content. Mathematical model based on the resistance model and Kohlrausch implication was set up for ED process, in which conductivity acted as the key parameter. At the same time semi-

empirical constants of the model were determined for pure NaCl and Na<sub>2</sub>SO<sub>4</sub> solutions treated at 6 V.

It was recognised that the most precisely fitting function on the absolute current values was the tangent hyperbolic:

$$I[A] = I_0 \cdot \left[ \tanh \left( -\frac{t[\text{min}]}{k_1} + k_2 \right) + 1 \right]$$

where  $I_0$  [A] is the initial absolute current,  $k_1$  [min] and  $k_2$  [-] are constants and  $t$  [min] is the operation time. Values of  $I_0$ ,  $k_1$  and  $k_2$  take up different values in case of different initial concentration solutions at different applied voltages.

### ***Thesis 7***

It was determined that with the help of the resistance model the absolute current could be calculated for the momentary specific conductivity value of the solution in case of a specific ED apparatus, as follows:

$$I = \frac{U}{n_{AM} \cdot R_{AM} + n_{CM} \cdot R_{CM} + R_D + R_C}$$

where  $U$  [V] is the applied voltage,  $n_{AM}$  and  $n_{CM}$  [-] are the number of anion- and cation exchange membranes, respectively,  $R_{AM}$  [ $\Omega$ ] is resistance of the anion exchange membrane,  $R_{CM}$  [ $\Omega$ ] is resistance of cation exchange membrane,  $R_D$  [ $\Omega$ ] is resistance of the diluate and  $R_C$  [ $\Omega$ ] is resistance of the concentrate.

Expanded:

$$I = \frac{U}{n_{AM} \cdot \frac{R_{AM,s}}{A_{AM,eff}} + n_{CM} \cdot \frac{R_{CM,s}}{A_{CM,eff}} + \frac{h}{\kappa_D \cdot A} + \frac{h}{\kappa_C \cdot A}}$$

where  $U$  [V] is the applied voltage,  $n_{AM}$  and  $n_{CM}$  [-] are the number of anion- and cation exchange membranes, respectively,  $R_{AM,s}$  [ $\Omega \cdot \text{cm}^2$ ] is

the surface resistance of the anion exchange membrane,  $R_{CM,s}$  [ $\Omega \cdot \text{cm}^2$ ] is surface resistance of cation exchange membrane,  $h$  [cm] is the flow length, *i.e.* the distance between the membranes defined by the spacers,  $A$  [ $\text{cm}^2$ ] is the cross-section of flow from the aspect of the ion transport, which is equal to the effective area of each membrane,  $\kappa_D$  [S/m] is the specific electric conductivity of the united diluate stream and  $\kappa_C$  [S/m] is the specific electric conductivity of the united concentrate stream, both measured in the joined streams after leaving the ED cell.

### ***Thesis 8***

It was recognised, that the most precisely fitting function on the specific electric conductivity values was the tangent hyperbolic:

- for the concentrate stream:

$$\kappa_C \left[ \frac{\mu\text{S}}{\text{cm}} \right] = C_1 \cdot \tanh \left( \frac{t[\text{min}]}{C_2} \right) + C_3 \quad (1)$$

- for the diluate stream:

$$\kappa_D \left[ \frac{\mu\text{S}}{\text{cm}} \right] = D_1 \cdot \tanh \left( -\frac{t[\text{min}]}{D_2} \right) + D_3 \quad (2)$$

where  $C_1$  [ $\frac{\mu\text{S}}{\text{cm}}$ ],  $C_2$  [min],  $C_3$  [ $\frac{\mu\text{S}}{\text{cm}}$ ],  $D_1$  [ $\frac{\mu\text{S}}{\text{cm}}$ ],  $D_2$  [min] and  $D_3$  [ $\frac{\mu\text{S}}{\text{cm}}$ ] are semi-empirical constants and  $t$  [min] is the operation time.

## **4. List of publications**

### ***Research articles***

- [1] C. Z. Torma, E. Cséfalvay: *Nanofiltration and Electrodialysis: Alternatives in Heavy Metal Containing High Salinity Process Water Treatment*. Chemical Papers 2018; 72 (5): 1115-1124.  
DOI: <https://doi.org/10.1007/s11696-018-0433-7>

- [2] C. Z. Torma, E. Cséfalvay: *Review of heavy metal containing, high salinity water treatment via nanofiltration and electrodialysis*. Proceedings of the 13<sup>th</sup> Conference on Heat Engines and Environmental Protection. 2018; pp. 153-160.  
ISBN: 978-963-313-280-7, DOI: –
- [3] C. Z. Torma, E. Cséfalvay: *Nanofiltration: a final step in industrial process water treatment*. Periodica Polytechnica Chemical Engineering 2017; 62 (1): 68-75.  
DOI: <https://doi.org/10.3311/PPch.10640>
- [4] Torma Cs. Zs., Cséfalvay E.: *Magas sótartalmú hulladékvizek kezelési lehetőségei: bepárlás és elektrodialízis*. Energiagazdálkodás 2017; 58 (4-5): 13-17. (in Hungarian), DOI: –

### ***Conference lectures and conference abstracts***

- [5] Torma Cs. Zs., Cséfalvay E.: *Hulladékvíz sótalanítás a galvániparban*. Magyar Víz- és Szennyvíztechnikai Szövetség: Innováció a szennyvíztisztításban és az ivóvízkezelésben Szakmai Nap – lecture Budapest, Hungary, 2018.11.07 (in Hungarian)
- [6] Torma Cs. Zs., Cséfalvay E.: *Elektrodialízis: nehézfém- és magas sótartalmú hulladékvizek hatékony kezelési lehetősége az iparban*. Magyar Víz- és Szennyvíztechnikai Szövetség: Dr. Dulovics Dezső Junior Szimpóziuma 2018. – lecture Budapest, Hungary, 2018.03.22 (in Hungarian)
- [7] C. Z. Torma, E. Cséfalvay: *Nanofiltration and electrodialysis: alternatives in high salinity process water treatment*. In: 44th International Conference of Slovak Society of Chemical Engineering – lecture and proceeding article Demänovská dolina, Nízke Tatry, Slovakia, 2017.05.22-26.  
Proceedings of the 44th International Conference of SSCHE, pp 108, ISBN: 978-80-89597-58-1
- [8] C. Z. Torma, E. Cséfalvay: *Influence of applied voltage on electrodialysis' efficiency in case of artificial and real heavy metal containing process waters*. In: 15<sup>th</sup> Workshop on Progress in Trace Metal

Speciation for Environmental Analytical Chemistry – lecture and proceeding article

Gdańsk, Poland, 2016.09.04-07.

TraceSpec 2016 Book of abstracts, pp 32, ISBN: 978-83-62984-36-7

- [9] C. Z. Torma, V. Horváth, E. Cséfalvay.: *Treatment possibilities of heavy metal containing process waters*. In: Műszaki Kémiai Napok 2016. – lecture and proceeding article  
Veszprém, Hungary, 2016.04.28  
Conference proceeding of MKN'16. pp 138, ISBN: 978-963-396-087-5

### *Others*

- [10] C. Z. Torma, V. Horváth, E. Cséfalvay: *Nehézfémek eltávolítása hulladékvizekből*. Magyar Tudomány Ünnepe 2016, MTA EK Energia és Társadalom. Budapest, Hungary – lecture

## **5. References**

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DOI: <https://doi.org/10.1016/j.seppur.2014.04.002>