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Separation of the selected metals from aqueous solutions using electrochemistry

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Abstract

A periodically interrupted galvanostatic deposition of zinc from the selected industrial wastewaters containing ZnSO₄ was performed. Experimental arrangements comprised the following types of the cathode vs. anode couples: Ti vs. Pt; Ti vs. Pt-Ti (i.e. Pt-film on Ti); Cu vs. Pt; Cr-Ni (steel) vs. Pt; and in some cases Zn-Fe vs. Pt; C (graphite) vs. Pt a Ti vs. Au-Ti (i.e. Au-film on Ti), as well. At constant current densities *i*, the changes of pH, the electric conductivity, the deposited amount or concentrations of Zn and the corresponding consumption of electric energy had been periodically (each hour within a period of 5 hours) registered. Under proper experimental conditions the obtained 2D or 3D diagrams outlined a value of the separation efficiency between 65 % and 90 %, extraordinarily to be even higher than 90 %. The best cathodic materials were Ti, Cu or Cr-Ni. A very good separation efficiency of Zn²⁺ was reached by the described nanofiltration procedure using the membrane AFC 40, also. Its rejection was higher than 98 % and under special conditions even higher than 99 %. Both treatments to Zn-separation (the electrochemical or nanofiltration one) were compatible to each other.

Abstrakt

V této disertační práci byla prováděna periodicky přerušovaná galvanostatická depozice zinku z vybraných průmyslových odpadních vod obsahujících ZnSO₄. Experimentální uspořádání zahrnovalo následující typy kombinací katoda vs. anoda: Ti vs. Pt; Ti vs. Pt-Ti (tj. Pt-film na Ti); Cu vs. Pt; Cr-Ni (ocel) vs. Pt a v některých případech rovněž Zn-Fe vs. Pt; C (grafit) vs. Pt a Ti vs. Au-Ti (tj. Au-film na Ti). Pravidelně (každou hodinu po dobu 5 hodin) byly měřeny při konstantních proudových hustotách *i* změny pH a vodivosti κ . Za vhodých experimentálních podmínek 2D a 3D diagramy naznačily hodnoty účinnosti separace mezi 65 % a 90 %, mimořádně dokonce i vyšší než 90 %. Nejlepšími katodovými materiály byly Ti, Cu nebo Cr-Ni. Velmi dobré účinnosti separace Zn²⁺ bylo take dosaženo pomocí popsané nanofiltrace s využitím membrány AFC 40. Rejekce NF membrány byla vyšší než 98 % a dokonce za určitých podmínek vyšší než 99 %. Oba způsoby Zn separace (elektrochemický či nanofiltrační) se vzájemně doplňovaly.

Keywords

Electrodeposition, nanofiltration, wastewater treatment, zinc

Klíčová slova

Elektrodepozice, nanofiltrace, čištění odpadních vod, zinek

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Introduction

Current environmental and health issues include the management of industrial wastewater. At the same time, the emphasis is on introducing waste-free technologies. It is known that wastewater treatment is a necessary - albeit costly - process. Frequent pollutants in these cases are heavy metals. It is important that these metals are separated from waste water efficiently without the use of a number of auxiliary chemicals so as to avoid subsequent environmental pollution by other agents.

addition to membrane and other processes, technologies based In on electrochemical actions take their significant place in this field. Selecting a purification process or combinations thereof generally depends on the particular needs of the task. In industrial waters, this approach is typical and it was similar in the described case. In it, it was about cleaning or even recycling zinc from a model or real samples of rinsing water, whose composition corresponds to industrial waters at Glanzstoff-Bohemia s.r.o. To the importance of this topic, for example, the database of the Integrated Pollution Register (IRZ) can be mentioned, where the following organizations are listed among the largest polluters in the Czech Republic in the area of zinc and its compounds emissions to waste water for 2016: Glanzstoff - Bohemia s.r.o. (52 001 kg/year), ŠKODA AUTO a.s. (7 603 kg/year) and Vodovody a kanalizace Pardubice, a.s. (3,709 kg /year) [1]. In an effort to improve these facts, two project proposals were submitted in the TAČR EPSILON 2015 TH1011234 program, A new technology for removal and regeneration of zinc from technological and wastewater at Glanzstoff - Bohemia s.r.o. and TAČR EPSILON 2016 TH02030791 A technology of wastewater treatment from viscose, cellulose and paper production by metal separation and organic matrix. Proposing a technology for the separation and recycling of zinc in the manufacturing process of the Glanzstoff - Bohemia s.r.o. company, two projects were engaged within the contract research - SD 353006/2015/30350 New technologies for removing pollutants from process and wastewater at Glanzstoff – Bohemia s.r.o. and SD 373002/2017/30350 An optimization of production from the perspective of using Fuzy logic control system - separation of hemicelluloses in slush lve and Zn regeneration.

The importance of zinc separation and recycling, in addition to the undisputed environmental benefit, has also a not negligible economic impact in the context of continued growth in world market prices [2-3], see Figure 1 showing zinc price developments since 2015.

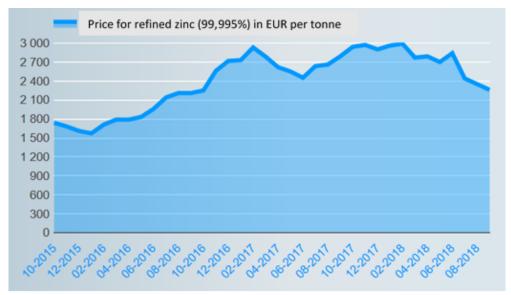


Figure 1 Zinc price growth since 2015 [4].

Annual losses in zinc emissions into waste water (52 t/year), is how only the business Glanzstoff - Bohemia s.r.o. represents the economic loss of about 3.6 mil. CZK. Ultimately, sanctions for long-term exceedances of ever stricter emission limits and remedial environmental measures could lead to a dampening of production for the upcoming 2019-2020 period.

The aim of this work was to obtain general information about the possibilities of separation of zinc from aqueous solutions of ZnSO₄ about concentrations used in viscose spinning. The composition of used model and potential real solutions corresponded to the technological conditions used in Glanzstoff - Bohemia s.r.o. In particular, it was about defining promising conditions in the mode of discontinuous (at regular intervals interrupted) process of Galvano static deposition of Zn, coupled with the same mode of monitoring and evaluation of its effects. The experimental set-up included successively the following selected electrode combinations, always referred to as cathode vs. anode: Ti vs. Pt; Ti vs. Pt-Ti (ie Pt-film on Ti); Cu vs. Pt; Cr-Ni (steel) vs.Pt and, under certain conditions, orientation wise eventually also the combination possibilities of Zn-Fe vs. Pt; C (graphite) vs. Pt and Ti vs. Au-Ti (ie Au-film on Ti). In own experiments, current densities, conductivity, pH changes and/or specific electricity consumption should be monitored at specified (approximately one-hour) time intervals.

Besides electrochemical measurements there should be, in a limited range a testing possibility of using nanofiltration (NF) to separate ions Zn^{2+} resp. ZnSO₄. In particular, there should be monitoring of the influence on selected operating conditions (concentration of Zn^{2+} ions of the sprayed on, volume flow of the sprayed on, pressure difference above and below the membrane and pH) on the removal efficiency of Zn^{2+} ions by NF membrane depending on time.

1. Theoretical Part

1.1 Electrochemical deposition

An electrochemical deposition introduces, in principle, an inverse analogous process on which galvanic cells operate, based on the dissolution of a metallic eg zinc cathode. Unlike the galvanic cell, which releases energy when dissolving the cathode, the electrochemical deposition consumes energy, and on the negatively charged cathode the oppositely charged metal ions are attracted by an electrostatic field. In doing so, however, there are simultaneous events that reduce its effectiveness, such as the decomposition of electrolyte, oxidation or reduction in its dissolved substances or their reaction on electrode surfaces, etc. The principle of electrochemical deposition is the storage of electrolyte by means of direct electric current. Substances that are subject to elimination are located in the electrolyte in form of ions. Under the influence of an electric voltage, an electric field is created which accelerates the movement of ions towards the counter-charged electrodes. The force F which results in the movement of ions is characterized by the following formula (4):

$$\mathbf{F} = \mathbf{Q} \cdot \mathbf{E}\mathbf{i} \tag{4}$$

where Q is the charge and Ei is the electric field strength [5].

The cations move toward the cathode, and conversely the anions move toward the anode. The cathode reaction is called the reduction and is given by the following equation (5):

$$M^{2+}(aq) + 2e^{-} \rightarrow M^{0}(s)$$
(5)

where M^{2+} is a divalent cation, 2 e⁻ is the number of exchanged electrons and M^{0} is a zero valent metal [6].

The entire electrochemical deposition process is shown in Figure 2.

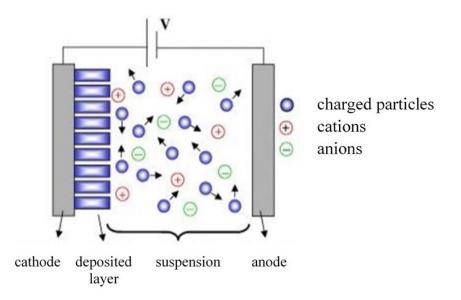


Figure 2 Schematic scheme of electrochemical deposition [7]

In industrial applications, electrodeposition is carried out in aqueous electrolytes, the so-called electrolytic baths. The basic component of these baths is the salt of the metal to be deposited. Furthermore, the presence of an auxiliary electrolyte is usually necessary mostly in the form of an acid or a base to promote the conductivity of the entire solution [8-9].

1.2 Nanofiltration

Nanofiltration (NF) is nowadays still a persistent pressure membrane process by which divalent ions can be selectively retained, while the rejection of monovalent ions is significantly lower. NF can be separated from a range of inorganic and organic substances with a molecular weight in the range of 200-1 000 Da. As a rule, nanofiltration works with lower pressure differences than reverse osmosis. However, it is necessary to overcome the osmotic pressure of the solution and therefore the magnitude of the pressure differences used in NF ranges from $10-40 \cdot 105$ Pa. In NF, the separation principle is based on a combination of sieve effect and different solubility (diffusivity). With these properties, nanofiltration ranks among attractive, everinnovative and less energy-intensive separation techniques that can be used to treat drinking water and process various industrial wastewater [10-13].

Nanofiltration membranes (1-3 nm pore size) allow separation of divalent ions from monovalent and they also can capture small organic molecules. The NF also found its application in the processing of waste industrial waters [10-14]. This can be illustrated by the figures presented in Figure 3, which graphically depicts the areas of NF utilization in terms of the number and focus of published works for the period

2008-2015 (based on the Scopus database). As can be seen from Figure 3, most publications (25 %) are concerned with the use of NF membrane processes in environmental issues.

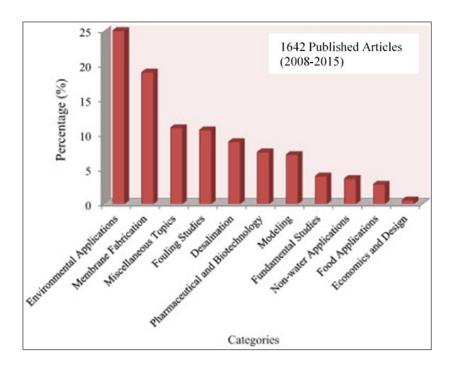


Figure 3 NF applications in various areas [14]

2. Experimental Part

2.1 Tested electrodes

Electrochemical deposition was made by using the following electrodes:

- cathode (Cr-Ni) Steel 17 240 Cr-Ni with active surface $S = 37 \text{ cm}^2$
- cathode (Ti) titanium with active surface $S = 37 \text{ cm}^2$,
- cathode (Cu) copper with active surface $S = 37 \text{ cm}^2$,
- cathode (Zn-Fe) galvanized iron with active surface $S = 37 \text{ cm}^2$,
- cathode (C) graphite with active surface $S = 44 \text{ cm}^2$,
- anode (Pt) platinum with active surface $S = 20 \text{ cm}^2$,
- anode (Pt-Ti) titanium with layer of platinum with thickness 0.1–0.15 μ m with active surface S = 37 cm²,
- anode (Au-Ti) titanium with layer of gold with thickness 0.1–0.15 μ m with active surface S = 37 cm²,
- anode (Pd-Ti) titanium with layer of palladium with thickness $0.1-0.15 \mu m$ with active surface $S = 37 \text{ cm}^2$.

2.2 Tested membrane

A tubular NF membrane was utilized for all measurements. A commercially available type of membrane, AFC 40, PCI Membrane Systems (Poland), was utilized. Other parameters of the tested membrane are summarized in Table 1.

Structural parameters	
Material	Polyamide film
Maximum pH range	1.5–9.5
Maximum pressure [bar]	60
Maximum temperature [°C]	60
CaCl ₂ retention [%]	pprox 60
Membrane surface charge (pH=7)	Negative
Effective membrane area [cm ²]	240
Lenght of one tube [cm]	30
Internal diamater [cm]	1.25

Table 1 Characteristics of the tested membrane

2.3 Chemicals

Zinc sulphate heptahydrate p.a. Sulfuric acid 96% p.a. Sodium sulphate anhydride p.a. Ethyl alcohol 96% p.a. Demineralized water (conductivity $<1 \ \mu S \cdot cm^{-1}$) Lach-Ner, s.r.o., Czech Republic Lach-Ner, s.r.o., Czech Republic Lach-Ner, s.r.o., Czech Republic Lach-Ner, s.r.o., Czech Republic DEMIWA 5 RO, WATEK, s.r.o., Czech Republic

2.4 Methods

2.4.1 Electrochemical separation – electrodeposition

Galvanostatic electrochemical deposition was performed in solution of zinc sulphate. Its conductivity was adjusted by sodium sulphate anhydride. The pH of the solution was not adjusted. Solution of zinc sulphate as a model wastewater with Zn^{2+} concentration of 100 mg L⁻¹ was treated using an electrodeposition with flat plate electrodes with active area of electrodes of 37 cm² at current density 1-50 mA cm⁻², conductivity 1–5 mS cm⁻¹ and duration of 5 hours. After electrochemical treatment Zn²⁺ separated as a film of Zn⁰ has been dissolved in sulfuric acid and subsequently it has been recovered as ZnSO₄, because ZnSO₄ is one of the important precipitating agent during production of viscose fiber.

Both the anode and the cathode were weighed on analytical scales at specified time intervals. Control by gravimetry (Zn increase of weight on the cathode) is a fast, inexpensive and operative method for relatively accurate detection of the electrochemical deposition process. Likewise, gravimetry confirmed that due to the interfering phenomena undesirable products and processes on the cathode surface not accrued.

2.4.2 Membrane separation – nanofiltration

Two pieces of membrane were submerged into highly demineralized water (conductivity $< 1 \ \mu S \ cm^{-1}$). Before starting the main experiments, it was necessary to conduct compaction of the membranes. The tested membranes were stabilized for at least 2 h at the maximum pressure (30 bar) that was employed in this study. The permeate flow at different transmembrane pressures was measured by digital scales connected with personal computer (PC). Permeate flow was recalculated using density of permeate and membrane area to permeate flux. Permeate density was taken as being identical to pure water. After each experiment, the NF apparatus was cleaned with demineralized water until the permeate flux and permeability of the membrane were restored (3–4 h).

Experiments were performed at the following concentrations of zinc: 25, 50, 100 and 150 mg L⁻¹. Transmembrane pressures of 5, 10, 15, 20, 25 and 30 bar were applied on the NF apparatus. To investigate the maximum applicable pH range of the NF membrane, the pH values of the solutions in the experiments were adjusted to pH 3, 5 and 6.5. The dependence on the feed flow rate was also investigated by varying this parameter, with values of 9, 6 and 3 L min⁻¹. During all experiments, permeate fluxes were measured after stabilization of pressure and temperature and samples for ICP–OES analysis were collected after stabilization of the permeate conductivity. The last condition led to different duration of experiments.

For electrochemical deposition and nanofiltration experiments, analytical techniques were used: Inductively Coupled Plasma–Optical Emission Spectroscopy (ICP-OES), Total Organic Carbon (TOC) Determination with TOC/TN Formacs^{HT/TN} analyzer and Chemical Oxygen Demand (COD) VIS spectrophotometer DR 3900.

3. Results and discussion

3.1 Electrodeposition with combination of electrodes Ti (cathode) vs. Pt (anode)

The titanium cathode and pure platinum anode were used for the described experiments. The conditions for experiments with combination of the electrodes Ti vs. Pt are summarized in Table 2.

Table 2 Summary of conditions	and efficiencies	achieved for	electrode	couple	Ti
(cathode) vs. Pt (anode)					

No.	к _{to} [mS cm ⁻¹]	I _{avg.} [mA cm ⁻ ²]	c Zn ²⁺ ICP 2 h [mg L ⁻¹]	c Zn ²⁺ ICP 5 h [mg L ⁻¹]	Zn ²⁺ removal 2 h [%]	Zn ²⁺ removal 5 h [%]	Ee 2 h [kWh∙m⁻³]	Ee 5 h [kWh∙m⁻³]
1.	2.75	1.02	78.88	70.01	21.12	29.99	0.81	2.13
2.	2.74	25.48	18.85	8.25	81.15	91.75	110.12	264.97
3.	2.75	25.49	12.30	10.24	87.70	89.76	162.46	420.93
4.	2.74	50.05	8.56	19.19	91.44	80.81	336.53	703.00
5.	0.50	9.56	70.62	39.97	29.38	60.03	86.18	237.75
6.	1.16	8.22	49.14	47.01	50.86	52.99	48.84	118.54
7.	4.34	8.17	46.23	6.55	53.77	93.45	21.36	55.74
8.	1,17	18.05	40.24	23.80	59.76	76.20	181.06	454.15
9.	4.34	42.82	19.44	11.37	80.56	88.63	323.77	693.19
10.	5.00	25.48	29.06	13.48	70.94	86.52	106.44	267.78
11.	2.00	42.82	9.83	4.34	90.17	95.66	332.33	822.75
12.	5.00	2.50	33.83	8.20	66.17	91.80	3.32	8.65
13.	5.10	1.41	48.30	14.70	51.70	85.30	1.73	4.38
14.	5.06	0.71	56.90	25.39	43.10	74.61	0.74	1.93

During experiments, 62.70 % of Zn was removed after 2 hours and 78.39 % of Zn after 5 hours on average. In real application it would be 83.69 % of Zn recovered on average from this amount. Residual concentrations of Pt were the same <0.05 mg L⁻¹ in the final electrolyte and in the electrode rinse as well.

Figure 4 and Figure 5 show the dependences on weight and concentration of Zn^{2+} on time during the experiments (electrodeposition of Zn on Ti-cathode) for current density i = 1.02-50.05 mA cm⁻². Irregular course of dependencies $\triangle Zn$ vs. t a c vs. t for t > 2 h was caused by the mechanical instability of the Zn coating.

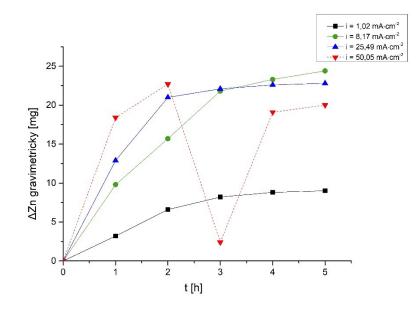


Figure 4 Increase of weight of deposited Zn on Ti-cathode with time during experiments with electrode couple Ti vs. Pt, t = 0-5 h, i = 1.02-50.05 mA cm⁻², $\kappa = 2.74-4.34$ mS cm⁻¹, T = 25 °C

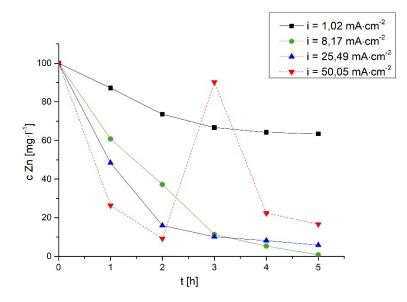


Figure 5 Decrease of Zn^{2+} ions concentration with time during their depolarization on cathode Ti vs. Pt , t = 0–5 h, i = 1,02–50,05 mA cm⁻², $\kappa = 2,74-4,34$ mS cm⁻¹, T = 25 °C

3.2 Comparison between the tested Ti vs. Pt and Ti vs. modified Pt-Ti anode for electrochemical deposition of model samples of wastewater

Figure 6 shows Ti (cathode) vs. Pt (anode) and Ti (cathode) vs. modified Pt-Ti (anode) after 5 hours of the experiments.

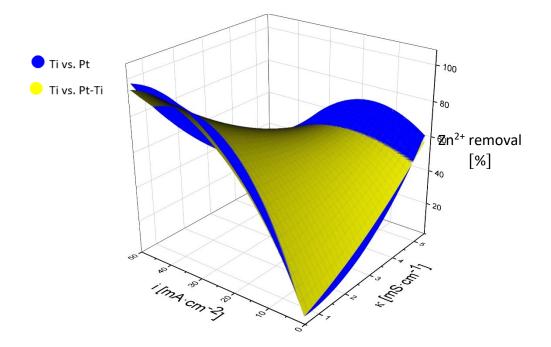


Figure 6 Removal of Zn²⁺, comparison between the electrodes pairs Ti vs. Pt and Ti vs. Pt-Ti, t = 5 h, i = 0.71–50.11 mA cm⁻², $\kappa = 0.50-5.10 \text{ mS} \cdot \text{cm}^{-1}$, $T = 25 \text{ }^{\circ}\text{C}$

3.3 Nanofiltration

Membrane AFC 40 which was experimentally tested during nanofiltration experiments is made of polyamide film with an effective membrane area of 240 cm² (two tubes, each with length of 30 cm and internal diameter of 1.25 cm), (Table 1). This membrane was selected based on previous measurements because it showed high rejection values for Co^{2+} ions with a high permeate flow rate as well [15]. Two pieces of membrane were inserted into the membrane module.

3.3.1 Dependence of rejection on concentration Zn²⁺ ions

The permeate flux was measured as a function of the pressure difference. The line in Fig. 2 indicates the pure water flux (PWF). The permeability (7.14 L h^{-1} m⁻² bar⁻¹) is the slope of this line. The feed volumetric flow was constant,

at 9 L min⁻¹, during this experiment. This value of the feed flow rate was chosen to minimize the effect of concentration polarization. In the concentration range of zinc sulphate (25–150 mg L⁻¹), it can be assumed that the permeate flux varied very little, because very low concentrations were utilized.

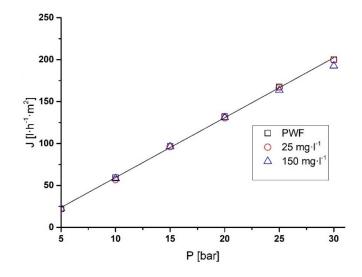


Figure 7 Comparison of fluxes, PWF, $c \operatorname{Zn}^{2+} = 25-150 \text{ mg L}^{-1}$, membrane AFC 40, feed flow 9 L min⁻¹, T = 25 °C, pH 6.5

The observed rejection increased very slightly with increasing concentration, especially at the smallest pressure difference (from 97.5 % to 98.5 % at 5 bar). Rejection was higher than 98% with all tested concentrations, except for the experiment with the lowest pressure and lowest concentration. (Table 3).

Duassuna		Rejecti	on [%]	
Pressure [bar]	Z	on of feed [mg·l	-1]	
[bai]	25	50	100	150
5	97.50	98.10	98.60	98.50
10	98.10	98.40	98.60	98.60
15	98.40	98.60	98.60	98.50
20	98.00	98.50	98.60	98.50
25	98.00	98.60	98.60	98.50
30	98.00	98.40	98.40	98.40

Table 3 Observed rejections for all measured Zn²⁺ concentrations

Conclusion

In accordance with the focus and objectives of the presented dissertation were the results of both galvanostatic and nanofiltration separation of zinc from the monitored ZnSO₄ solutions presented and summarized in the previous chapters. In the case of electrochemistry, the findings leaned on electrolysis interruption and data collection at regular (hourly) intervals for 5 hours, its tabulation and evaluation. The experimental arrangement included gradually in particular the following selected electrode combinations, marked always in the order as cathode vs. anode: Ti vs. Pt-Ti (ie Pt-film on Ti); Cu vs. Pt; Cr-Ni (steel) vs. Pt and, furthermore, informatively and to a limited extent also the combination of Zn-Fe vs. Pt; C (graphite) vs. Pt and Ti vs. Au-Ti (ie Au-film on Ti). During them, the gradually increasing current densities were maintained and also under the given constant value also the monitoring of decreasing pH, slightly increasing values (as well as required also adjusted) k and especially significantly decreasing concentrations of c Zn^{2+} , correlating vice versa with the increasing weight of excluded Zn. From the deducted values of electrical quantities, electrolytic demands of electrolysis were simultaneously determined also. From the rendered 2D and later 3D diagrams, it emerged that the zinc separation efficiency at appropriate experimental parameters was between 65 % and 90 %, exceptionally even above 90 %. Although the separation of zinc occurred on all cathodes, the best results were achieved on the cathodes Ti, Cu and Cr-Ni (steel). Some of the limitations included the release of graphite particles into solution in case of C (graphite), increasing the dissolved Cr content, especially in the case of Cr-Ni (steel) used as anodes and further exfoliating the excreted Zn at current densities of about 50 mA·cm⁻² higher. This, however, does not fundamentally limit the principal utilization of electrolysis for the removal of Zn with the possibility of its subsequent recycling, given the favorable results described at other electrodes. Very good Zn²⁺ separation results were also achieved using (NF) nanofiltration with AFC 40 membrane. In most cases, rejection was greater than 98 %, with the highest values even above 99 % (at pH 3). With regard to other practical aspects of the use of NF-membranes, the possibility of their gradual clogging, the possibility of separating only Zn^{2+} ions and not directly recyclable Zn metal, etc., there appears to be an optimal utilization of the NF primarily in the purification process. It has been shown that both Zn^{2+} separation methods (eg, electrochemical and subsequent NF) can complement each other effectively.

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Participation in national conferences

KOČANOVÁ, **Veronika**, L. DUŠEK and L. NOVOTNÝ. Sacrificial anodes catalyzing electro-Fenton oxidation of wastewater, 3nd International Conference on Chemical Technology Mikulov 13. – 15. 4. 2015, lecture, p. 359, ISBN: 978-80-86238-82-1.

NOVOTNÝ, Ladislav, V. KOČANOVÁ, P. LANGÁŠEK and R. PETRÁŇKOVÁ. The Use of Selected Silver Amalgam Electrodes for a Potentiometric Indication of Technological Steps in Production of Demiwater, XXXV. Modern electrochemical methods, Jetřichovice 18. – 22. 5. 2015, lecture, p. 108, ISBN: 978-80-905221-3-8. **KOČANOVÁ, Veronika** and L. DUŠEK. Electrochemical corrosion of steel as a source of Fe^{2+} catalyst of Fenton reaction, XV. Workshop of Physical Chemists and Electrochemists Brno 26. – 27. 5. 2015, lecture, p. 51, ISBN: 978-80-210-7857-4.

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Self-education activities

Professional course in the area of occurrence and elimination of drug residues in the environment UCT Prague 27. 11. 2017 – 1. 12. 2017

Specialized seminar "Sampling of drinking water, groundwater and wastewater" Ekomonitor, Brno 23. 10. 2017

Specialized seminar "Presentation as an integral part of the scientific work" RNDr. Eva Juláková, CSc., Pardubice 4. 10. 2017

XXXIV. European Membrane Society Summer School, "Membranes in Biorefineries", Lund a Bäckaskog Castle, Sweden 26. 6. – 30. 6. 2017

Study stay – United Kingdom University of Central Lancashire, Preston, PR1 2HE. United Kingdom 2. 7. – 17. 7. 2016

Specialized seminar "Argumentative Writing in English", Mgr. Petr Kos, Ph.D., Pardubice 13. 6 – 14. 6. 2016

XXXII. European Membrane Society Summer School, "Integrated and Electromembrane processes" Stráž pod Ralskem/Liberec 21. 6. – 26. 6. 2015

IX. Summer Electrochemical School Mertrohm, Brno 28. 5. 2015

Specialized seminar "UNICOM – Academic/Conference Presentation Skills" Language centre University of Pardubice, Pardubice 24. 11. – 25. 11. 2014