Treatment of Electroplating Rinse Solution by Continuous Membrane Extraction and Diffusion Dialysis

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Abstract

This paper studies the recovery and concentration of Zn^{2+} and Cu^{2+} metal ions from industrial rinse water containing a mixture of Zn^{2+}, Cu^{2+}, Ca^{2+}, Mg^{2+}, K^+, and Na^+ salts. Transport and separation experiments were performed in a continuous membrane extraction (CME) system, i.e. in the membrane system composed of two contactors with a cation-exchange polymer membrane (Neosepta CMX) and an organic liquid (liquid membrane) circulating between. The organic solution was composed of kerosene and di-(2-ethylhexyl)-phosphoric acid or salicylaldoxyoxime (Acorga P-50) as the active extractant/carrier. The feed solution has been taken from a rinsing tank working in an industrial electroplating plant. Sulfuric acid (1 M) was applied as the stripping medium for metal ions. The total flux of target metals (Zn^{2+} and Cu^{2+}) in the MHS with Acorga P-50 or D2EHPA was 97.1% and 71.4%, respectively. The product of the CME process can be further de-acidified by diffusion dialysis with the use of an anion-exchange membrane (Neosepta AFN-7). The coefficients of separation, enrichment, and up-hill transport characteristics indicate that the CME system with Acorga P-50 can be considered a part of a technology for the efficient recovery of Cu^{2+} and Zn^{2+} in metal finishing plants.

Keywords: membrane extraction, diffusion dialysis, electroplating rinse solution

Introduction

The recovery and separation of different metals ions, including Zn^{2+} and Cu^{2+}, is a common problem of hydro-metallurgy solved by applying some extraction or liquid membrane methods [lj. The same metal ions appear in many other industrial effluents, e.g. in the solutions after metal-finishing activities [2, 3], after leaching solid residues in incineration plants [3], and during the production of viscose fibres [4, 5]. Zinc, copper and other valuable metals can be recovered, concentrated, separated and then recycled in a factory by using a respective technology. There is a widely accepted opinion that membrane separation methods [5] are most efficient and economi-

cal, especially for processing large volumes of dilute aqueous solutions containing different metal ions in a mixture. This conviction is supported by some early industrial attempts to use the emulsion liquid membranes for the recovery of Zn^{2+} in the viscose fibres industry [4-6]. This technology enabled us to concentrate Zn^{2+} up to 25-50 g/dm^3 and reduce the Zn^{2+} content in a feed to - 0.3 mg/dm^3. Similar results can be achieved in respect to Cu^{2+} [7].

Our interest in this field is directed towards the utilization of electroplating rinse solutions produced after finishing some products with copper or zinc. Note that Donnan dialysis [8], as the standard membrane method, was checked successfully [9-14] for the recovery and active concentration of various metals. This method is, however, inapplicable for processing the solutions containing

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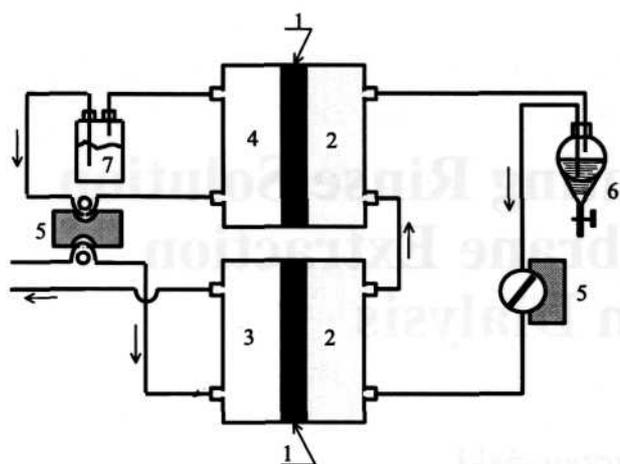Correspondence to: Prof. R. Wódzki

Fig. 1. Scheme of a continuous membrane extraction (CME) system: cation-exchange membrane (1), organic phase - liquid membrane (2), extraction (3) and re-extraction module (4), pump (5), organic phase reservoir (6), receiver (7).

salts of Ca, Mg, K and Na of concentrations higher or comparable to those of Zn and Cu. This is a result of rather low ability of cation-exchange membranes (CEM) to separate metal ions of the same valence [2, 14] as well as of some changes in CEM selectivity when in contact with solutions containing a mixture of uni- and divalent cations [15]. More advantageous and promising seems to be the use of various liquid membranes containing an appropriate carrier/extractant of Zn^{2+} and/or Cu^{2+} (see rev. in ref. [5]). To develop a practical liquid membrane (LM) system, we designed an experimental multimembrane hybrid system (MHS) with a circulating liquid membrane (LM). This MHS configuration can be regarded as equivalent to a membrane extraction device. The system (see Fig. 1) is related to the MHS with a bulk liquid membrane (BLM) [16-18], mechanical agitation of which is replaced by pumping the organic phase between two separated membrane contactors. This reconstruction allows us to obtain a system which would be easy to resize up to required operational efficiency. Therefore, before industrial implementation of a small MHS pilot plant we checked CME performance using a real industrial solution as the feed phase. Usually, all the coupled processes realized in the liquid membrane systems resulted in up-hill transport of selected species from the feed to receiver containing counter-transported substance. In the case of the process described herein, the active transport of Zn^{2+} or Cu^{2+} is coupled to the opposite directed transport of hydrogen cation from the stripping solution [16, 18]. As a consequence, the resulting concentrate (stripping solution) also contains a considerable amount of sulfuric or other acid, concentrations of which should be lowered before recycling the proper component. For this reason the studies were extended to test the method of diffusion dialysis for de-acidification of the product after separation and concentration with the use of the continuous membrane extraction system.

Continuous Membrane Extraction System

The application of any membrane method for the recovery of metals from industrial wastes requires, first of all, the enlargement of a membrane working area and the use of compact standard membrane modules. As pointed out by Kedem et al. in their pioneering patent [19], the MHS can be constructed from membrane modules, which are produced for the Donnan or diffusion dialysis (equipped with a proper ion-exchange membrane). As far as it concerns a liquid membrane itself, a possibly low operating volume of the organic phase is recommended. This can be accomplished by using supported liquid membranes (SLM), emulsion liquid membranes (ELM) [5] or rotating [20, 21] and creeping [22, 23] pertractors exploiting the BLM properties. However, none of these LM techniques eliminates the immanent instability of the LMs caused by different phenomena. The ELMs properties are strongly influenced by an osmotic water transport that lowers membrane effectivity [24-26]. A lifetime of supported liquid membranes is shortened by the leakage of their liquid component from porous support. Damage to these membranes may be caused by: slow emulsification [27], osmotic water transport and membrane wetting [28-30], the elution of a carrier [31, 32] and, finally, by the corrosion of membrane support [33]. The BLMs are adversely affected by the physicochemical instability of their interfaces at the presence of surface-active components [34-37]. Some of the above drawbacks can be eliminated by selecting a proper LM solvent, tailoring a carrier and surfactant (ELM only) composition. Other methods are based simply on the physical stabilization of the LM systems. For example, gelled supported liquid membranes [38, 39] can be prepared by the formation of a highly swollen gel in a porous membrane support. Another idea is to circulate the LM behind a porous separator, which stabilizes the interface between the organic and aqueous phases [40, 41]. This technique is known as the membrane extraction process (also: extraction with immobilized interface, non-dispersive extraction or perstraction). In order to improve the extraction and transport of ionic substances, the porous separator made up of inert polymer can be replaced by a hydrophilic, dense, ion-exchange membrane. This procedure leads from the interfacial liquid-liquid extraction to the "indirect ion-exchange extraction" first described by Korkisch [42] and further developed by Ho et al. [43], Kedem et al. [19, 44] and others [45, 46]. Such a change introduces a number of new qualitative features to the membrane system, e.g., higher selectivity against co-ions and the high sorption and permselectivity towards counter-ions. When the process of extraction is followed by the back extraction process, as presented in Fig. 2, the overall procedure can be regarded as continuous membrane extraction (CME). Generally, the CME process exhibits properties analogous to these observed for the pertraction (liquid membrane transport) with the flowing liquid membrane [47]. It is worth noting that the idea of MHS based on coupling of a solid ion exchange membrane with a liquid membrane, has its surprising justification as a biomimetic membrane system [48]. The assembly of an ion-exchange membrane and a liquid one is widespread among gram-positive bacteria where the transport of ions occurs

through two coupled biomembranes, i.e. the cell wall (ion-exchange biopolymer) and a quasi-liquid cytoplasma membrane composed of bilayered phospholipids.

The aim of this study was to design an experimental CME for recovering Zn^{2+} and/or Cu^{2+} in competition with other ionic solutes. According to the scheme presented in Fig. 1, the concept of this technique is quite simple, i.e. a solution of an organic phase (liquid membrane) flows between two ion-exchange membranes, which separate the feed (f), and strip (s) aqueous phases. The solutes are first exchanged with countertransported species through polymer membranes and then extracted into an organic phase by a selective extractant/ carrier. The reversed process occurs simultaneously at the stripping part of the CME system.

Diffusion Dialysis

The process of CME is driven by a high concentration, ca. 1 mol/dm^3, of sulfuric acid in the stripping solution. The resulting product, containing metal species of 0.1-0.2 mol/dm^3 concentration, should be de-acidified before recycling in a proper electroplating process. According to the membrane state-of-the-art, this can be achieved by applying the diffusion dialysis technique [49, 50], the efficiency of which to recover inorganic acids from various aqueous media has been proven elsewhere [50-55]. The separation of an acid and its salt by an anion-exchange membrane may occur because of the differences in the respective distribution coefficients (higher for the acid) and especially very high differences in the acid and salt diffusion processes amounting to one order of magnitude. This results in high permeation of the concentrated acid from its mixture with the salt and allows it to achieve high separation coefficients. The process can be realized in a simple diaphragm cell with any commercial anion exchange membrane [53] in the system: salt+acid/anion exchange membrane/water.

Experimental

Materials and Reagents

Organic phase - liquid membrane: The organic phase was prepared by dissolving di-(2-ethylhexyl)phosphoric acid (D2EHPA, purchased from Sigma) or 5-nonyl-salicyl-aldoxime (94%, Acorga P-50, Acorga Ltd.) in technical kerosene (product of MAKER, Poland, b.p. 124-174, viscosity 0.68 cP) to the concentration of 0.1 mol/dm^3. The solvent and reagents were used without any additional purification.

Ion-exchange membranes: The Neosepta CMX cation-exchange membrane (Tokuyama Co., Japan) was used for constructing the CME system. The membrane contains sulfonic ion-exchange groups attached to the polystyrene based backbone. A polymer mesh additionally reinforces the membrane. The standard ion-exchange capacity of the membrane (dry sodium form) is 1.5-1.8 mequiv./g [56]. Membrane water content is 0.25-0.30 g H$_2$O/g, and its thickness in the swollen state is
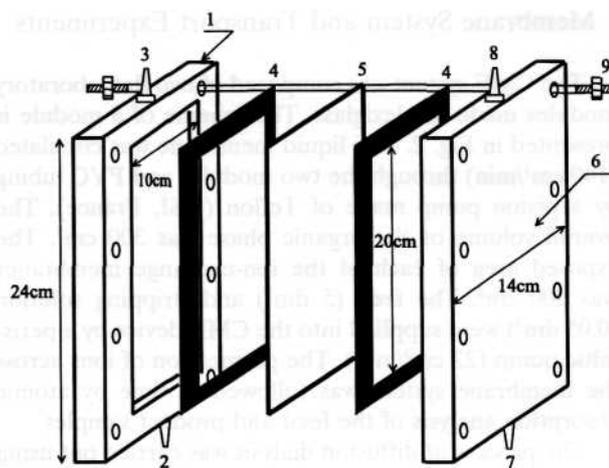

Fig. 2. Scheme of a membrane module for the CME system: feed or stripping solution chamber (1), feed or stripping solution input (2) and output (3), packing ring (4), cation exchange membrane (5), organic phase - liquid membrane chamber (6), organic phase - liquid membrane input (7) and output (8), clamping (9).

0.17-0.19 mm. Before use in transport experiments, the membrane was immersed in a 1 M sulfuric acid solution with constant stirring in order to "clean it up" and obtain its starting H$^+$ form. Thereafter, the free acid was desorbed from the membrane by repeated washing in deionized water. In this form the membrane samples of respective dimensions were used in the feed and strip contactors. The Neosepta AFN-7 membrane (Tokuyama Co., Japan), devised especially for diffusion dialysis, was used in the respective experiment. The membrane contains the styrene-divinylbenzene-vinyl pyridine copolymer thereafter quaternized to generate strongly basic anion exchange groups. The basic characteristics of the membrane are as follows: water content 0.45 kg H$_2$O/kg dry Cl$^-$ form, exchange capacity 2.22 mol Cl$^-$/kg swollen form, and thickness 0.0165 cm in the swollen form. The membrane was converted into its Cl$^-$ form by soaking in a NaCl solution (1 mol/dm^3) followed by careful washing in distilled water.

Solutions: The feed solution for the CME process was taken out from a rinsing tank operating at the electroplating installation in APATOR S.A., Torufi. The solution was produced while washing some metal elements after copper etching. The pH of the solution was 2.2 and its composition (expressed in mol/dm^3) was as follows: Cu^{2+} (5.1 x 10^{-3}), Zn^{2+} (2.7 x 10^{-4}), Ca^{2+} (2.9 x 10^{-3}), Mg^{2+} (4.7 x 10^{-4}), Na$^+$ (7.5 x 10^{-4}), K$^+$ (1.8 x 10^{-4}), and the equivalent content of chloride and nitrate anions. Stripping solution was prepared by dissolving reagent grade sulfuric acid in distilled water to the concentration of 1 mol/dm^3. In the second CME run, followed by the diffusion dialysis experiment, the synthetic solution of the composition parallel to the real industrial solution was applied. The solution was prepared from respective nitrates (reagent grade) each of 1x10^{-3} mol/dm^3 concentration.

Membrane System and Transport Experiments

The CME system was composed of two flat laboratory modules made of plexiglass. The scheme of a module is presented in Fig. 2. The liquid membrane was circulated (140 cm^3/min) through the two modules and PVC tubing by a piston pump made of Teflon (OSI, France). The overall volume of the organic phase was 300 cm^3. The exposed area of each of the ion-exchange membranes was 200 cm^2. The feed (5 dm^3) and stripping solution (0.05 dm^3) were supplied into the CME device by a peristaltic pump (22 cm^3/min). The permeation of ions across the membrane system was followed in time by atomic absorption analysis of the feed and product samples.

The process of diffusion dialysis was carried out using one of the contactors applied in the CME after replacing the cation exchange membrane with the Neosepta AFN-7 anion exchange membrane. At the beginning of the experiment the compartments of the cell were filled with the acidic solution containing concentrated CuSO$_4$ or with distilled water by pumping the liquids from the external reservoirs of the volume 85 cm^3 and 10 dm^3, respectively. During the experiment the pH and Cu^{2+} concentration in the solutions separated by the membrane were measured. All the experiments were carried out at room temperature (20-25°C).

Characterization

Stripping rates of ionic species during the CME processes were determined from the sets of primary data in the form of feed and strip concentration vs. time. Transport rates are expressed below as the stationary transport rates defined by Eq. (1 and 2):

$$J_M = \Delta Q_s / \Delta t, \qquad \text{mol/cm}^2\text{s} \qquad (1)$$

$$\Delta Q_s = \Delta[M]_{s,t} V_s / 1000 A_s \qquad \text{mol/cm}^2 \qquad (2)$$

Q_s denotes the amount of metal species transported to the receiver after the time *t,* through 1 cm^2 of the stripping CEM area $(A_s$ cm$^3)$, V_s (cm^3) is the volume of the stripping solution, $[M]_{s,t}$ (mol/dm^3) is the concentration of metal species at time *t*. The results can be reported also using the concentration (or enrichment) factor *(CF)*. This quantity is defined as the ratio of metal concentration in the receiver solution after the time *t* to the initial feed concentration:

$$CF = [M]_{s,t} / [M]_{f,t=0} \qquad (3)$$

To evaluate the separation ability of the CME system towards a mixture of the above-specified cations, the fractional stripping rates *(F),* and the separation coefficients (α) were calculated. Because of the multi-ionic character of the feed it was necessary to calculate both the individual, α^{Mk}_{Mi} and the overall, $\alpha^{Mk}_{\Sigma M}$, separation coefficients defined by Eq. (4) and (6), respectively.

$$\alpha^{M_k}_{M_j} = \frac{[M]_{k,s}[M]_{j,f}}{[M]_{j,s}[M]_{k,f}} \qquad (4)$$

$$\alpha^{M_k}_{\Sigma M} = \frac{[M]_{k,s} \sum_{j \neq k}[M]_{j,f}}{[M]_{k,f} \sum_{j \neq k}[M]_{j,s}} \qquad (5)$$

The mixture emerging from the membrane system should be different from that entering on the feed side, i.e. both α^{Mk}_{Mi} and $\alpha^{Mk}_{\Sigma M}$ ought to be higher than 1 when the separation is reached. Another simple measure of the separation ability is the fractional flux *(F)* related to specific stationary rates:

$$F = \frac{J_{M_k}}{\Sigma J_M} \qquad (6)$$

Results and Discussion

The solution coming from a rinsing tank could be treated long enough to maintain a constant, and possibly low concentration of target Zn^{2+} and Cu^{2+} ions. It means that these metals should be recovered at a rate sufficient to balance their inflow. On the other hand it might be necessary to deplete solutions to a few mg/dm^3 before the reuse or discharge the rinsing medium. The experiments we carried out and reported here were focused to the simulation of constant recovery from feed reservoirs of a large volume. Consequently, the quantity to consider is the steady-state up-hill flux, i.e. the rate of active concentration of Zn^{2+} and/or Cu^{2+}.

It can be expected that the CME separation ability depends mainly on the composition of an organic phase, and specifically, on the properties of a extractant/carrier. Many compounds could be exploited for selective extraction and transporting of Zn^{2+} and Cu^{2+}, among which phosphoric acid derivatives and some hydroxyoximes seem most useful. The acid-based carrier, di-(2-ethyl-hexyl)-phosphoric acid attracts special attention because of its selectivity towards Zn^{2+} cations [18, 57-60], its very low solubility in water, and good solubility in many organic solvents [18]. The second reagent used in this study (Acorga P-50) is a representative of efficient Cu^{2+} extractants belonging to the salicylaldoximes class [61]:
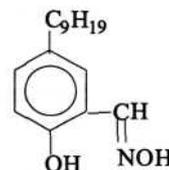
It was proved by Szpakowska et al. [62, 63] that Acorga P-50, alike other oximes, exhibits good transport properties in liquid membrane systems, although its selectivity in the presence of other competing ions has not been fully recognized. Therefore, it would be interesting to discover whether this reagent would be able to separate Cu^{2+} from the real industrial and multicomponent solutions.

Table 1. Transport and separation characteristics of the CME process with D2EHPA.

M	Transport[*] Stripping rate J_M mol/cm²s	Transport[*] Fractional rate F	M_k \ M_j	Separation coefficient[**], α_{Mi}^{Mk} Cu	Separation coefficient[**], α_{Mi}^{Mk} Zn	Separation coefficient[**], α_{Mi}^{Mk} Ca	Separation coefficient[**], α_{Mi}^{Mk} Mg	Separation coefficient[**], α_{Mi}^{Mk} K	Separation coefficient[**], α_{Mi}^{Mk} Na
Cu	2.72×10^{-13}	0.038	Cu	1	0.002	0.26	0.25	0.01	0.033
Zn	4.86×10^{-12}	0.676	Zn	416	1	109	104	4.2	13.9
Ca	5.71×10^{-13}	0.079	Ca	3.8	0.009	1	0.96	0.04	0.13
Mg	2.03×10^{-14}	0.003	Mg	4.0	0.01	1.05	1	0.04	0.13
Na	1.41×10^{-12}	0.196	K	99.8	0.24	26.2	25.0	1	3.3
K	5.95×10^{-14}	0.008	Na	29.9	0.07	7.8	7.5	0.3	1
Total	8.19×10^{-12}	1.000							

*) calculated from the strip composition after 10 h of the extraction run,
**) calculated from the feed and strip composition after 70 hrs of the extraction run.

Transport and Separation Ability of the CME with D2EHPA

The results presented in Fig. 3A in the form of the cumulative curves *Qs* vs. *t*, indicate stripping transport rates for the cations present in the feed. Using Eq. (1), these rates were calculated as the slopes of plots in their linear part. This linearity was observed usually after 10 hrs of a transport run. From the results collected in Table 1 it can be concluded that the values of specific rates can differ by two or more orders of magnitude, e.g., $J_{Zn} = 2.7 \times 10^{-13}$ and $J_{Mg} = 2 \times 10^{-14}$ mol/cm²s. Obviously, the selectivity of the CME system containing D2EHPA causes the flux of Zn^{2+} much higher than the flux of Cu^{2+}, in spite of lower Zn^{2+} concentration in the feed. As a consequence, the total fractional stripping rate of Zn^{2+} (0.676) and Cu^{2+} (0.038) attains 71.4%. Unfortunately, the high and nonrequired fractional flux of sodium (0.196) and calcium (0.079) was observed in parallel. This effect can be ascribed to relatively high total concentration of Na^+ and Ca^{2+} in the feed, i.e. 6.6×10^{-13} equiv./dm³ vs. 10.7×10^{-13} equiv./dm³ for Zn^{2+} and Cu^{2+} together. On the other hand, D2EHPA can lose its good extractant properties in the presence of sodium ions because reversed micelles are formed by di-(2-ethylhexyl)-sodium phosphate in an organic phase [64, 65]. These micelles can enhance the extraction of sodium and calcium cations [66]. In this case, CME selectivity cannot be assessed only by comparing steady-state stripping rates because of a high initial flux of sodium cations (see Fig. 3A). Thus, to characterize CME properties we used the coefficients $\alpha_{\Sigma M}^{Mk}$ which take into account the instantaneous composition of the external aqueous solutions. The plots of $\alpha_{\Sigma M}^{Mk}$ vs. time presented in Fig. 3B show that these coefficients change slightly during the transport run. The peculiarity of the observed dependence is that the coefficients related to Zn and Cu increase in time at the cost of the separation coefficients for uni-valent cations (Na^+, K^+). After ~ 70 hrs of transport time, the overall separation coefficient for Zn^{2+} reached - 40, which is satisfactory from a practical point of view. The separation ability of the CME system is also characterized by the individual separation coefficients α_{Mi}^{Mk} Their values (see Table 1) show that the highest selectivity was

attained for the pair Zn^{2+}-Cu^{2+} with $\alpha_{Cu}^{Zn} = 416$, and for Zn^{2+}-Ca^{2+} with o& = 109. Note that these coefficients (at least α_{Cu}^{Zn}) ^{can} be increased several times by lowering the concentration of D2EHPA in the liquid membrane [67]. However, in this case, the transport rates may diminish substantially to an unacceptable level from a practical point of view. The overall and individual separation coefficients allow us to establish the following selectivity order for the CME with D2EHPA: Zn > Na > K > Mg > > Ca > Cu.

The transport separation ability of the CME system leads to the active enrichment of the receiving solution in the target cations. The curves in Fig. 3C show that this process concerns mainly zinc ions and, unfortunately, to some degree, also sodium ions. As a result, the product solution is considerably "contaminated" by sodium ions, whereas the recovery of copper as a main component of the feed is ineffective.

Transport and Separation Ability of the CME with Acorga P-50

Cumulative stripping curves achieved in the CME system with Acorga P-50 are presented in Fig. 4A. The comparison of corresponding plots in Figs. 4A and 3A show that the results are quite different from those obtained with D2EHPA. According to the affinity of Acorga P-50 towards copper cations, a 30-fold increase of copper flux was observed. Simultaneously, the flux of Zn^{2+} decreased by 30%. Moreover, it is very important that, opposite the D2EHPA system, the flux of sodium becomes negligible. It supports the hypothesis that only the properties of D2EHPA are responsible for fluxes of sodium and calcium ions. The final result is that the flux of Cu^{2+} and Zn^{2+} attains 97.1% of total ionic flux in the system (see Table 2). After taking into account the concentrations of specific cations in the feed and strip, and calculating $\alpha_{\Sigma M}^{Mk}$ separation coefficients (see Fig. 4B), it can be concluded that the system still exhibits preference towards Zn^{2+} ions. The same conclusion can be drawn after analyzing the individual separation coefficients collected in Table 2, i.e. α_{Cu}^{Zn} is 5.6. Contrary to the D2EHPA system, all the coefficients for Cu^{2+}, except for α_{Cu}^{Zn} are higher than 1,
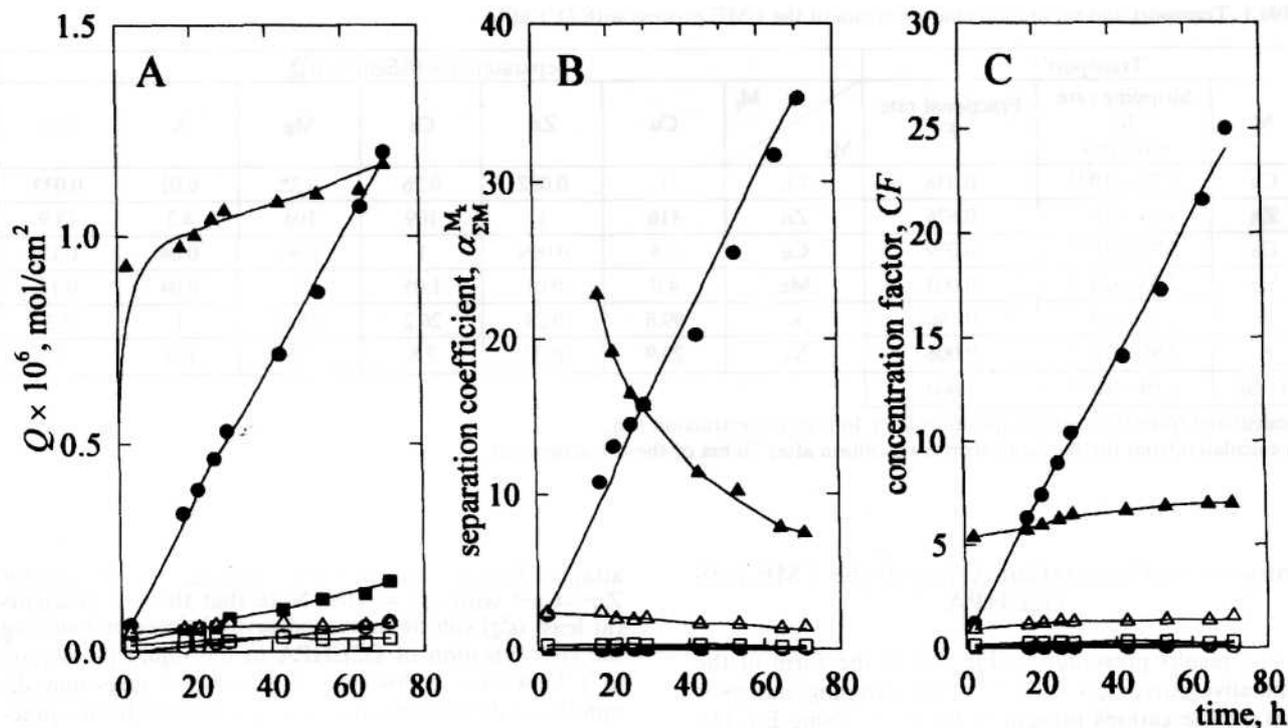
Fig. 3. Transport properties of the CME system with D2EHPA: (A) cumulative stripping curves, (B) overall separation coefficients, (C) concentration factors;
(•) Zn, (o) Cu, (■) Ca, (□) Mg, (▲) Na, (Δ) K.

Table 2. Transport and separation characteristics of the CME process with Acorga P-50.

Transport[*)]			Separation coefficient[**)], $\alpha_{Mj}^{M_k}$						
M	Stripping rate J_M mol/cm²s	Fractional rate F	M_k \ M_j	Cu	Zn	Ca	Mg	K	Na
Cu	8.84×10^{-12}	0.721	Cu	1	0.18	9.70	17.2	2.10	2.80
Zn	3.05×10^{-12}	0.249	Zn	5.60	1	54.3	96.2	11.8	15.6
Ca	2.46×10^{-14}	0.002	Ca	0.1	0.02	1	6.20	0.22	0.29
Mg	9.64×10^{-15}	0.0008	Mg	0.06	0.01	0.56	1	0.12	0.15
Na	3.19×10^{-13}	0.026	K	0.47	0.09	4.60	8.10	1	1.3
K	1.10×10^{-14}	0.0009	Na	0.36	0.06	3.47	6.15	0.76	1
Total	1.23×10^{-11}	1.000							

*) calculated from the strip composition after 10 h of the extraction run,
**) calculated from the feed and strip composition after 70 hrs of the extraction run.

Table 3. Characteristics of the CME process with Acorga P-50 and the solution for treatment by diffusion dialysis technique.

	Cu	Zn	Ca	Mg	Na	K
Initial composition of the feed, mol/dm³	1×10^{-3}	1×10^{-3}	1×10^{-3}	1×10^{-3}	1×10^{-3}	1×10^{-3}
Final composition of the stripping solution (concentrate) mol/dm³	0.135	3.8×10^{-3}	2.5×10^{-4}	2.4×10^{-5}	3.8×10^{-5}	8.7×10^{-5}
Final concentration factor, *CF*	140.8	3.64	0.27	0.025	0.040	0.043
Final separation coefficient $\alpha_{Mj}^{M_k}$	610	0.104	0.008	0.001	0.001	0.001
Steady state stripping rate J_M, mol/cm²s	5.5×10^{-11}	8.8×10^{-13}	5.6×10^{-14}	8.6×10^{-15}	5.9×10^{-15}	8.1×10^{-11}

which considerably changes the selectivity order to: Zn > Cu > Na > K > Ca > Mg. Regarding the properties of hydroxyoximes in the extraction of Zn^{2+} and Cu^{2+}, the first position of Zn^{2+} in this order is rather surprising. At the feed pH = 2 only Cu^{2+} should be extracted and then transported, because it is possible to extract Zn^{2+} at higher pH values only, i.e. pH > 4. This discrepancy can be explained by assuming that the pH in the reaction zone located at the liquid membrane feed cation-exchange, membrane interface is higher than that in the bulk feed solution. This is possible due to the Donnan exclusion effect lowering the free sorption of strong electrolytes into the CEM phase. For an ideal membrane contacted with a dilute acid, the concentration of sorbed acid can be assessed as a squared bulk concentration [68], i.e. the internal interfacial concentration should be close to 1×10^{-4} (pH=4). This assessment is highly speculative; however, under transport conditions it is impossible to verify this value experimentally. Some information could be obtained only from concentration profiles, which we intend to calculate numerically during further model studies. Nevertheless, considering the composition of the feed and strip after the MHS-FLM operation one can conclude that Acorga P-50 is better than D2EHPA for removing Cu^{2+} together with Zn^{2+} from the used industrial solution. This conclusion is supported by both higher fluxes and the ability to transport Zn^{2+} and Cu^{2+} actively as characterized by respective concentration factors $CF > 1$ (see Fig. 4C).

CME and Diffusion Dialysis

The Cu^{2+} concentrate acidic for further diffusion dialysis was prepared in the CME process with Acorga P-50. The results and characteristics of this treatment are presented in Fig. 5(A, B) and Table 3, respectively. The experiment was prolonged up to 450 h of continuous work, in order to check its performance and stability in long-time operation. As can be seen from experimental data (Fig. 5A, B), the system was operating steadily, attaining high concentration factors *(CF* = 141, Table 3) for selectively transported copper cations. This means that after ending the process, the up-hill transport index for Cu^{2+}, calculated as the ratio of actual concentrations in the stripping and feed solution, was as high as ca. 540. The product of the CME operation contained mainly the concentrated (0.14 mol/dm^3) solution of $CuSO_4$ in H_2SO_4 (~ 1 mol/dm^3). In order to diminish the content of sulfuric acid in the concentrate, the diffusion dialysis of H_2SO_4 into a large volume of distilled water has been carried out. Because the process has been realized in the closed system with limited volumes of solutions, the process of acid dialysis can occur only to equalize the acid concentration in the membrane adjacent solutions, i.e. to pH = 2. Because of the fast diffusion of sulphuric acid trough the Neosepta AFN-7 membrane, this equalization occurs after the relatively short time of 3-5 h (see plots in Fig. 5C). However, according to the mechanism of diffusion dialysis, the permeation of sulphuric acid is associated
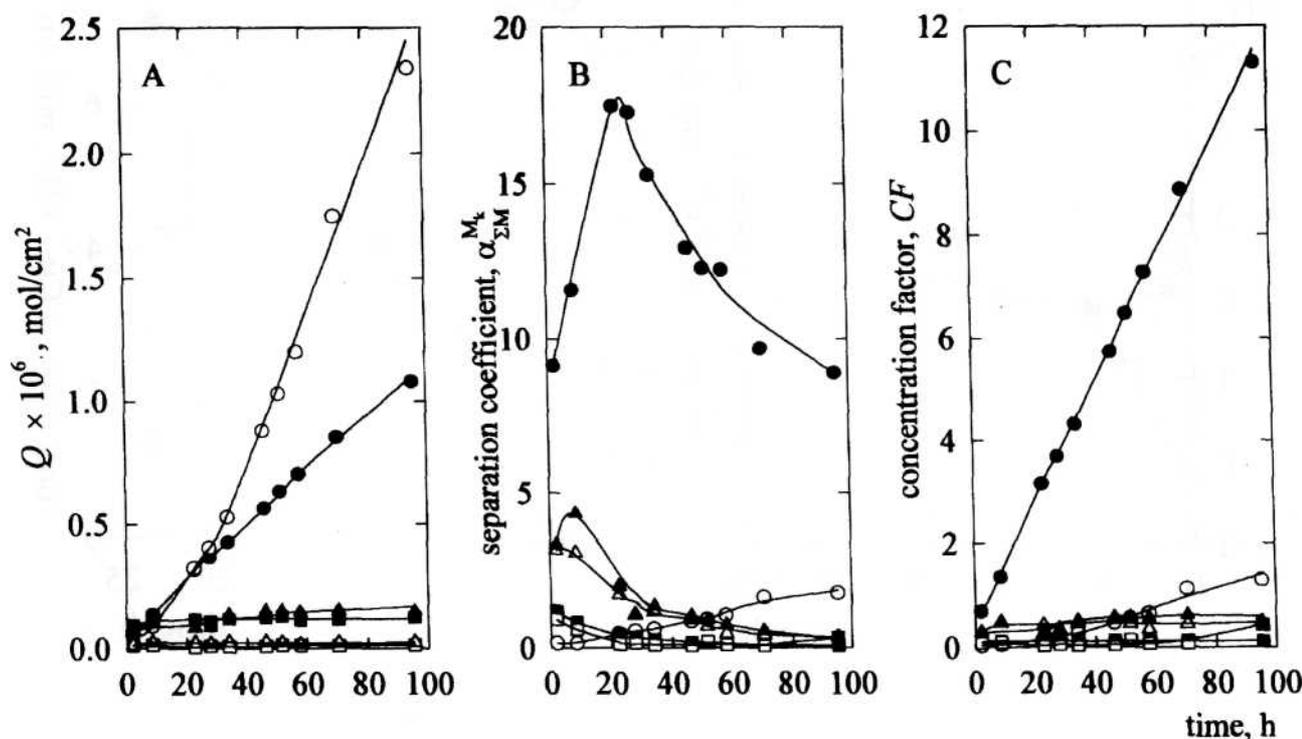

Fig. 4. Transport properties of the CME system with Acorga P-50: (A) cumulative stripping curves, (B) overall separation coefficients, (C) concentration factors;
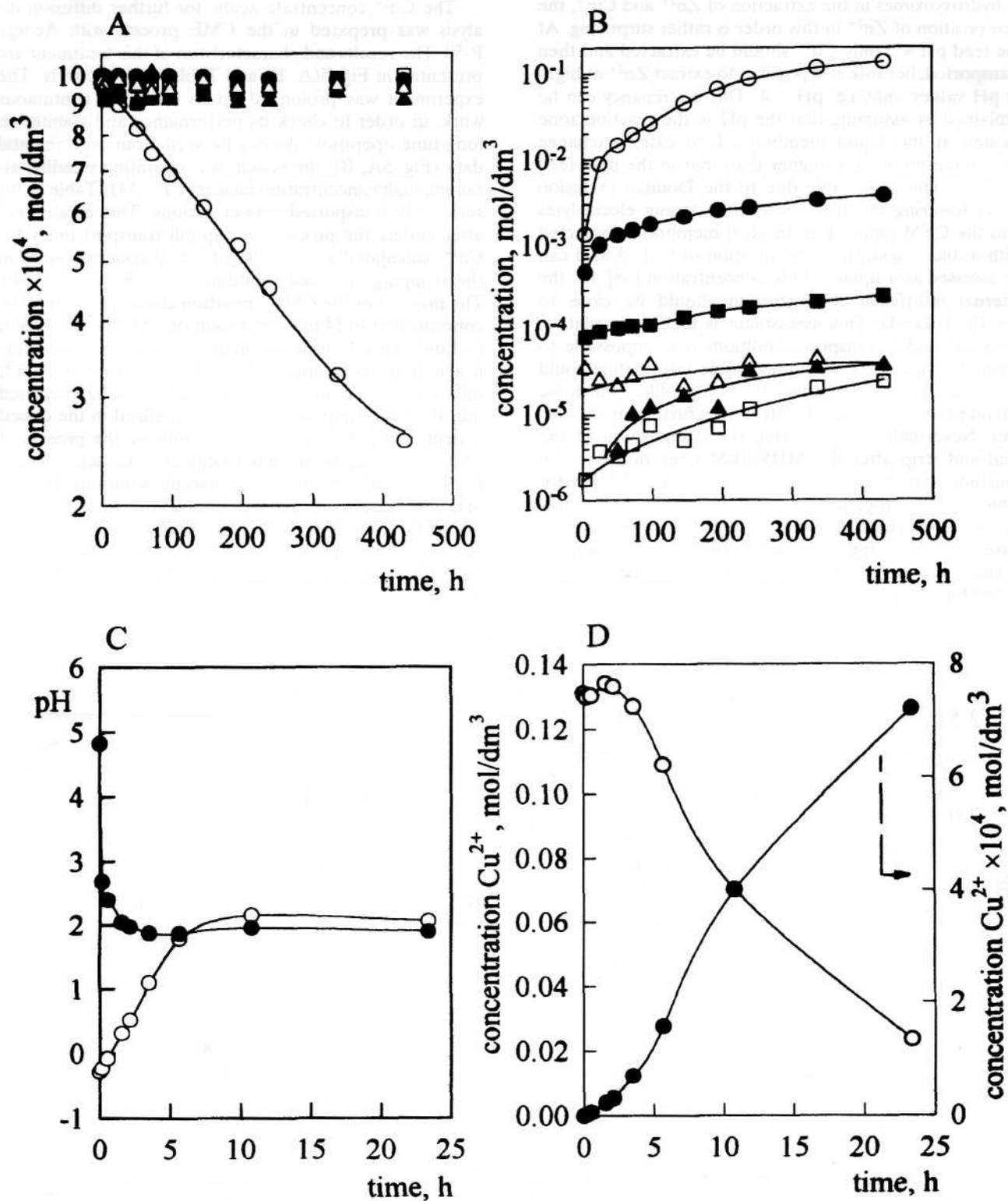(•) Zn, (o) Cu, (■) Ca, (□) Mg, (▲) Na, (△) K.

Fig. 5. Continuous membrane extraction (CME) (A, B) and diffusion dialysis (C,D) process for the recovery and concentration of Cu(II). Concentration vs. time dependence for metal extraction (A) from the feed and re-extraction (B) into the stripping solution: (•) Zn, (o) Cu, (■) Ca, (□) Mg, (▲) Na, (△) K. Diffusion dialysis of the Cu concentrate: changes in pH (C) and Cu concentration (D) in the concentrate (o) and acid stripping solution (•).

with the slow diffusion of salts from the CME product. Because this process is proportional to concentration differences across the polymer membrane (according to I-Fick's law for diffusion), the diffusion of Cu^{2+} was observed as a mutual process lowering the content of the target salt in the CME product. In the case of the studied system, this phenomenon results in the drop of Cu^{2+} concentration from 0.14 to 0.11 mol/dm^3 after the time when the diffusion of sulphuric acid practically disappears (equal pH of the membrane adjacent solutions). Under applied experimental conditions, it was observed that steady state fluxes for acid and salt were $0.7 \pm 0.1 \times 10^{-7}$ and $4.2 \pm 0.2 \times 10^{-10}$ mol/cm^{2}s, respectively. From these data the $H_2SO_4/CuSO_4$ diffusion dialysis can be evaluated as a very effective process because its selectivity (defined as the ratio of respective fluxes), attains the sufficiently high value of 166. Thus, the results of the diffusion dialysis treatment prove that this technique can be considered a very useful one for the utilization of metal recycling technology in the electroplating industry.

Conclusion

Some previous ideas concerning the applicability and function of the multimembrane hybrid system were verified by its enlargement and modification to the experimental CME system. The experiments proved that continuous membrane extraction can be regarded as feasible in the processing of industrial solutions containing Zn^{2+} and Cu^{2+}, to the degree resulting from the liquid membrane properties and a carrier used. The related equipment and materials are easy for reconstructing, resizing and regenerating, without the loss of stability and ability to work over a long time period. It is possible to recover and concentrate Zn^{2+} and/or Cu^{2+} from dilute aqueous solutions by using standard technical carriers (D2EHPA, Acorga P-50), technical kerosene, and commercially available ion-exchange polymer membranes (Neosepta CMX or AFN-7). The results indicated that both D2EHPA and Acorga P-50 can be used for the recovery of Zn^{2+}. In comparison to D2EHPA, the use of Acorga P-50 results in a 30-fold increase of Cu^{2+} transport rate and a decrease of Zn^{2+} transport rate by 40%. Moreover, the concentration factors and separation coefficients have indicated that Acorga P-50 is a good component for a liquid membrane system, preventing the transport of calcium and sodium ions. The application of the CME technique (with a properly chosen carrier) followed by processsing the CME product by diffusion dialysis allows us to recover and actively concentrate metal cations, and thus to prepare the resulting solution in a way conducive to its further recycling.

Acknowledgments

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