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The recovery and the separation of metal ions from galvanic wastewaters

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ABSTRACT

This paper investigates a method for the recovery and the separation of metal ions from two galvanic wastewater types using two different polymer inclusion membranes (PIMs). The main aim of this work was to present results of the transport of metal ions from acidic and alkaline galvanic wastewaters. Membranes with acetylacetone and di(2-ethylhexyl)phosphoric acid were used for removal of metal ions from alkaline and acidic wastewaters, respectively. Additionally, the obtained PIMs were characterized by attenuated total reflectance Fourier transform infrared Spectroscopy and scanning electron microscopy. A characterization of membrane structures was presented along with its impact on the efficiency of the process of transporting metal ions. The obtained results showed that both studied membranes efficiently separated the investigated metals from their mixture. The highest recovery factors were obtained for iron(III) (97.01%) and nickel(II) (68.09%) ions.

Keywords: Galvanic wastewater; Polymer inclusion membrane; PIM; Metal ion separation; Metal recovery

1. Introduction

Galvanic wastewater contains high amounts of heavy metal ions (e.g. Cr, Mn, Fe, Ni, Cu, Zn and others) [1,2]. Significant presence of such elements causes these wastewaters to be toxic. Hence, it is necessary to remove metal ions from wastewaters generated by galvanizing plants and other industries, before they are drained into a sewage system.

The removal of metal ions from wastewaters is usually achieved by conventional processes like neutralization and precipitation. Lime precipitation is one of the most effective methods of treating galvanic wastewaters, in which the concentration of toxic metal ions is above 1,000 mg/L [3,4]. Complexation reactions are also frequently implicated in precipitation processes. Our earlier research has shown that β-diketones and its derivatives are a group of ligands particularly suitable for this purpose [5,6].

The discussed conventional methods are among the cheapest ones, but their effectiveness is not always satisfactory. Major disadvantages include an incomplete removal of metal ions from the wastewaters and the production of inconvenient sludge [7,8].

Commonly used methods also include ion exchange and electrochemical methods. Sofinska-Chmiel and Kolodynska [9] presented an investigation of sorption on chelating ion exchangers with *bis*(2-pyridylmethyl)amine and aminophosphonic functional groups: Dowex M4195, Lewatit® MonoPlus TP 220, Purolite S 940 and Purolite S 950. Kobya et al. [10] described a process of removing Cr(III), Ni(II) and Zn(II) from galvanic rinse wastewater by electrocoagulation using iron plate electrodes. The obtained results showed that electrocoagulation could reduce metal ions to a very low amount.

These two types of methods (ion exchange and electrochemical methods) are more effective than simple precipitation, but they require a lot of energy, and thus they are economically inattractive and costs. Therefore, the best results are achieved when several different methods are combined in one process. Three steps of decontamination can be applied for the removal of nickel(II), copper(II) and zinc(II)

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ions from galvanic baths [11]. At the first stage, Khalchenko [11] applied the method of coagulation. Thereafter, electrochemical treatment with an addition of sodium chloride using a ruthenium oxide-coated titanium anode and cathode was run. Purification was completed using vermiculite-based sorbents.

In the literature, there are a number of publications about innovative methods, which are suitable for removal and recovery of metals from wastewaters, in which concentration of metal ions is much below 1,000 mg/L. These processes include, for example, adsorption on new sorbents, electrodialysis and membrane filtration [12].

Electrodialysis was used by Dydo et al. [13] to produce highly concentrated metal solutions from a diluted stream. These authors also described the recovery and concentration of nickel(II) ions from real electroplating wastewater. The resulting values showed that the metal content in the solution after the electrodialysis process was two times higher than in the initial solution. Hosseini et al. [14] prepared a comprehensive review of membrane-based processes, which included reverse osmosis, nanofiltration, ultrafiltration, complexation–ultrafiltration, microfiltration, polymer inclusion membranes (PIMs), electromembranes, hybrid processes, liquid membranes, emulsion liquid membranes and membrane-based solvent extraction [15]. In this review the authors cited a number of original publications, which included characteristic and efficiency of the listed methods in relation to the treatment of metal plating wastewaters and recovery of metal ions.

In the recent years, phosphonium ionic liquids have been proposed as carriers of zinc(II) and iron(III) from chloride acid solutions [16]. The recovery factors of iron(III) and zinc(II) have been established at 60% and 89%, respectively. Cyphos IL 101 has been proposed for the removal of zinc(II) and iron(III) from an alkaline chloride solution. This carrier has been found to be effective for the recovery of iron(III), while the transport of zinc(II) has been less efficient [17]. Kolev et al. [18] reported that zinc(II) could be selectively and quantitatively separated from aqueous solutions containing cadmium(II), cobalt(II), copper(II) and nickel(II) at pH of 3.0, when the PIM was composed of 45% D_2EHPA and 55% PVC. Using a D_2EHPA/CTA membrane, 73.4% of Fe(III) could be removed from chloride solution containing Mn(II), Ni(II), Co(II) and Cu(II) ions [19].

Like the chelating membrane extractants, β-diketone compounds are well suited as the membrane carriers for divalent metal ions separation, especially Cu(II) ions [20]. The recovery of zinc from galvanic wastewater using the 1-octyl-4-methylimidazole membrane extraction method was used [21]. 96% and 84% of zinc ions were recovered from chloride and sulphate wastewater solutions, respectively.

When the best method for the removal of metal ions from wastewater is to be selected, not only should its advantages and disadvantages be taken into account. The key is to choose a method for an individual parameter of galvanic wastewater. It is also important to consider the costs and efficiency of an installation.

In this paper, a method for the recovery and the separation of metal ions from two galvanic wastewater types was considered. The studies were performed using PIMs based on cheap polymer matrix (polyvinyl chloride, PVC) and commercial carriers (acetylacetone and/or di(2-ethylhexyl) phosphoric acid). A characterization of the membrane structures and its impact on the efficiency of the process of transporting metal ions was presented.

2. The experiment

2.1. Materials

The PIMs were prepared using acetylacetone (acac, Avantor Co., Gliwice, Poland) or di(2-ethylhexyl)phosphoric acid (D_2EHPA, Sigma-Aldrich Co., Saint Louis, Missouri, USA) as carriers, a PVC suspension with an average molecular weight of 72,000 Da (ANWIL Company, Wloclawek, Poland) as a matrix polymer, *bis*(2-ethylhexyl)adipate (DAO, Sigma-Aldrich Co., Saint Louis, Missouri, USA) as a plasticizer and tetrahydrofurane (THF, Avantor Co., Gliwice, Poland) as a solvent. All reagents were used as received. Ammonia, ammonium nitrate, sodium nitrate and nitric acid were of analytical grade (Avantor Co., Gliwice, Poland). Double-distilled water with a conductivity of 0.1 μS/cm was used for the preparation of aqueous solutions. The pH of the feed solution was adjusted using an ammonium buffer (in the case of membranes with acac) or sodium nitrate (in the case of membranes with D_2EHPA). Nitric acid was used to prepare a receiving solution.

2.2. The preparation of PIMs

The PIMs were obtained by the casting method in the same way as we described in our earlier paper [22]. Two types of membranes were made. The optimal composition of the first membrane (**1**) was 20 wt.% acac, 10 wt.% DAO, 70 wt.% PVC, and it was used to separate metal ions from alkaline solutions. In the case of acidic wastewater solutions, the second membrane (**2**) composed of 60 wt.% D_2EHPA, 5 wt.% DAO and 35 wt.% PVC was applied. Fig. 1 presents the structure of components used for the preparation of PIMs.

D_2EHPA/PVC membranes are stable during the process of transport carried out for 108 h [23], while acac/PVC membranes have been noted to be stable for 72 h [24].

2.3. The characterization of PIMs

The obtained PIMs were characterized by attenuated total reflectance Fourier Transform infrared (ATR-FTIR) spectroscopy and scanning electron microscopy (SEM).

The FTIR spectra of the membranes were measured with a Bruker Alpha Spectrometer in a wavenumber range of 450–4,000 cm^{-1}.

SEM images of the membranes were obtained with the Hitachi SU3500 SEM/EDS (energy dispersive spectroscopy) microscope operated at 10.0 kV. The membranes were visualized in 10.0 × 10.0 μm images.

2.4. Transport experiments and galvanic wastewater characterization

The transport experiments were carried out in a permeation module cell presented in our earlier paper [25]. A membrane film (of a surface area of 4.4 cm^2) was tightly

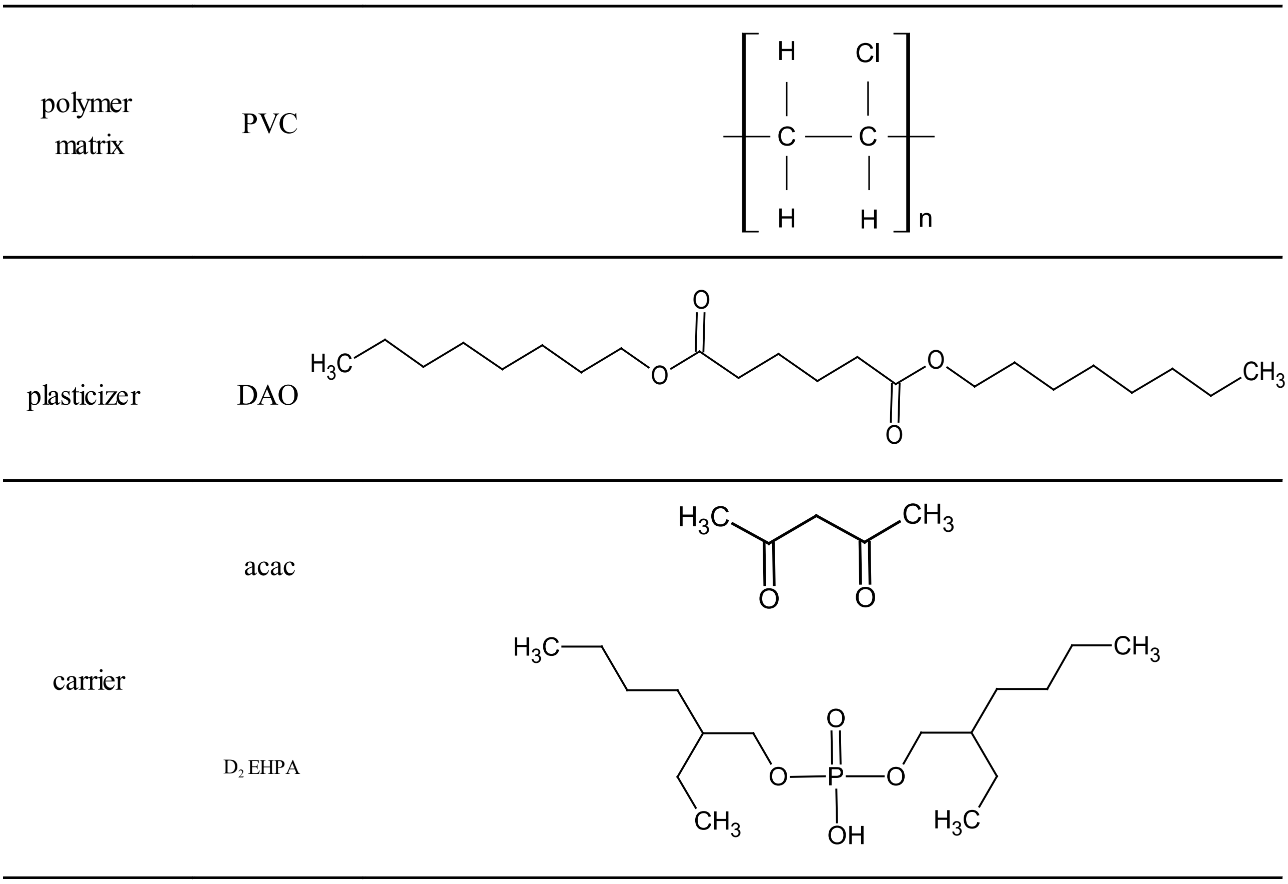


Fig. 1. Components of applied membranes: polyvinyl chloride (PVC), *bis*(2-ethylhexyl)adipate (DAO), acetylacetone (acac) and di(2-ethylhexyl) phosphoric acid (D_2EHPA).

clamped between two cell compartments. Transport studies were carried out with the use of galvanic wastewater sampled at two different galvanizing plants (A and B). A characterization of galvanic solutions investigated in this work is shown in Table 1.

For galvanic wastewater A, the feed phase was 30 mL of a galvanic solution and 15 mL of NH_4NO_3:NH_3 ammonium buffer. In the case of galvanic wastewater B, during the transport studies the feed phase constituted 45 mL of a galvanic solution with 0.1 M of $NaNO_3$.

The addition of the ammonium buffer causes the pH of the solution to increase. Under these conditions, the precipitation of iron(III), chromium(III), copper(II) and nickel(II) hydroxides takes place. It occurs with different pH values and in the following order:

$$\mathrm{Fe(III)} < \mathrm{Cr(III)} < \mathrm{Cu(II)} < \mathrm{Ni(II)}$$

pH 3.4 6.7 7.6 9.7

With higher pH values the obtained hydroxides are dissolved. Amphoteric metals like chromium pass into the solution in the form of hydroxo-complexes, for example, $[Cr(OH)_6]^{3-}$, according to the following reaction:

$$\mathrm{M(OH)}_x + y\mathrm{OH}^- \rightleftarrows \left[\mathrm{M(OH)}_{(x+y)}\right]^{(x-y)} \quad (1)$$

Albarède [26] stated that in the basic media at low concentration of Fe(III) ions, $Fe(OH)_3$ does not completely precipitate. Under such conditions, the $Fe(OH)_4^-$

Table 1
The composition of the tested galvanic wastewaters

Galvanic water waste	pH	Fe(III)	Ni(II)	Cu(II)	Cr(III)	Cl^-	SO_4^{2-}
		(mg/L)					
A	6.4	18.07	50.90	25.37	14.18	53.57	108.95
B	2.1	105.40	3.33	1.050	0.770	54.17	109.90

hydroxo-complex is formed, which is transported by the investigated membranes.

Copper and nickel ions along with a component of the ammonium buffer create the ammine complexes, $[\mathrm{Cu(NH_3)_4}]^{2+}$ and $[\mathrm{Ni(NH_3)_6}]^{2+}$. The reaction can proceed according to the mechanism of either of the two following equations:

$$\mathrm{M(OH)}_x + z\,\mathrm{NH}_3 \rightleftarrows \left[\mathrm{M(NH_3)}_z\right]^{x+} + x\,\mathrm{OH}^- \quad (2)$$

$$\left[\mathrm{M(OH)}_{(x+y)}\right]^{(x+y)} + z\mathrm{NH}_3 \rightleftarrows \left[\mathrm{M(NH_3)}_z\right]^{x+} + (x+y)\mathrm{OH}^- \quad (3)$$

Pure water and water with 0.1 M of $\mathrm{HNO_3}$ was used as the receiving phase in cases of galvanic wastewaters A and B (Table 1), respectively. Both, the feed and the receiving aqueous phases (45 mL each) were mechanically stirred at 600 rpm. The PIMs transport experiments were carried out at 20°C ± 0.2°C. Small amounts of the aqueous receiving phase were taken periodically via a sampling port equipped with a syringe and analysed by atomic absorption spectroscopy (AAS Spectrometer, AAS 240FS, Agilent) to determine the concentration of metal ions. The pH of the feed phase was kept constant (for A and B, the pH was 10.0 and 2.6, respectively) and controlled by means of a pH-meter (CX-731 pH meter, Elmetron, Poland), combined with a pH electrode (ERH-126, Hydromet, Poland). In order to initiate the process of transport twice under the same conditions, two samples were cut out from the original membrane films in the case of each membrane.

The transport process is described by the first-order reaction:

$$\ln\frac{c}{c_0} = -kt \quad (4)$$

where c – the concentration of metal ions in the feed phase after time t (mol/m^3), c_0 – the initial concentration of metal ions in the feed phase (mol/m^3) at time t equal 0, k – rate constant (h^{-1}) and t – time of the transport process (h).

The ionic transport flux (J) refers to the quantity of metal ions (n) passing across the membrane area (A) per a unit of time (t):

$$J = -\frac{dn}{Adt} = -\frac{Vdc}{Adt}\left(\mathrm{mmol/m^2h}\right) \quad (5)$$

where V – volume of the receiving phase (m^3), n – quantity of metal ions (mol) and A – effective area of the membrane (m^2).

The initial flux (J_0) is described in turn by the following equation:

$$J_0 = \frac{V}{A}kc_0\left(\mathrm{mol/m^2h}\right) \quad (6)$$

where J_0 denotes the flux at $t = 0$.

A selectivity coefficient (S) is used for the quantitative description of the process of separating metal ions by PIMs:

$$S_{\frac{M_1}{M_2}} = \frac{J_{0,M_1}}{J_{0,M_2}} \quad (7)$$

Finally, the recovery factor (RF) describes the separation of metal ions from the feed phase into the receiving phase as follows:

$$\mathrm{RF} = \frac{c_0 - c}{c_0} \times 100\% \quad (8)$$

3. Results and discussion

3.1. Membranes characteristic

3.1.1. ATR-FTIR and SEM analysis

The FTIR spectra of the investigated membranes (**1** and **2**) were recorded within a wavenumber range of 450–4,000 cm^{-1}.

Fig. 2 shows the ATR-FTIR spectra of 100 wt.% PVC, 20 wt.% acac + 10 wt.% DAO + 70 wt.% PVC (**1**) and 60 wt.% $\mathrm{D_2EHPA}$ + 5 wt.% DAO + 35 wt.% PVC (**2**) membranes, respectively. The IRPal 2.0 program was used for the interpretation of infrared spectra.

The 100 wt.% PVC membrane spectrum showed that bands at 612 and 690 cm^{-1} were attributed to the bending modes of the C–H bonds, the bands at 1,254 and 1,335 cm^{-1} corresponded to the stretching modes of the C–F bonds (where F is Cl), the band at 1,426 cm^{-1} and the bands from 2,850 to 3,000 cm^{-1} corresponded to the stretching modes of the C–H bonds.

Additional bands were visible in the spectrum of membrane **1**, which was composed of acac, DAO and PVC. The spectrum showed bands from 1,075 to 1,320 cm^{-1}, which were attributed to the stretching modes of the C–O bonds; the bands at 1,725 cm^{-1} corresponded to the stretching modes of the C=O bonds.

The spectrum for membrane **2** (60 wt.% $\mathrm{D_2EHPA}$ + 5 wt.% DAO + 35 wt.% PVC) had characteristic bands from 900 to 1,050 cm^{-1}, which were attributed to the P–OR bonds.

The above results confirmed the presence of individual components in the membranes: a polymer – PVC, a plasticizer – DAO and carriers – acac or $\mathrm{D_2EHPA}$. This also suggested that there were no signs of covalent bond formation

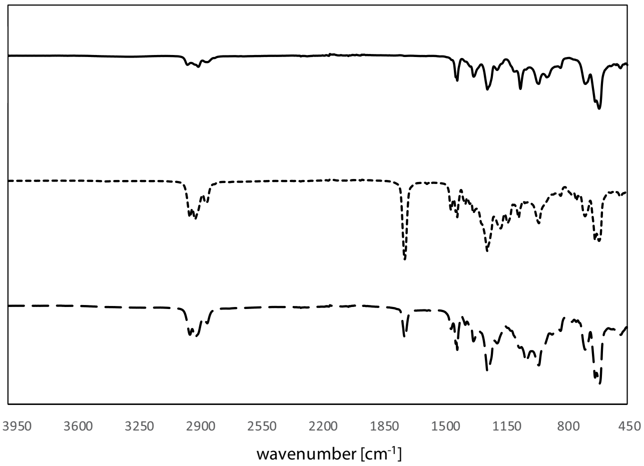


Fig. 2. ATR-FTIR of PIMs: —— 100 wt.% PVC; ---- 20 wt.% acac + 10 wt.% DAO + 70 wt.% PVC (**1**); – – – 60 wt.% $\mathrm{D_2EHPA}$ + 5 wt.% DAO + 35 wt.% PVC (**2**).

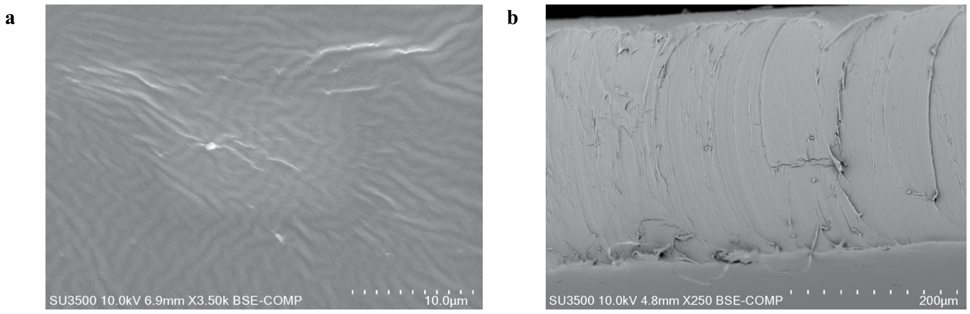
between the polymer, the plasticizer and a carrier. There could only exist van der Waals or hydrogen bonds.

The efficiency of transporting metal ions across PIMs depends on their microstructure, which is directly related to the distribution of the carrier along the polymer matrix. The SEM images provide an important quantitative (porosity and layer thickness) and qualitative (a dense and porous structure) analysis [27]. Fig. 3 presents SEM images of the surface and the cross section of the investigated PIMs (**1** and **2**).

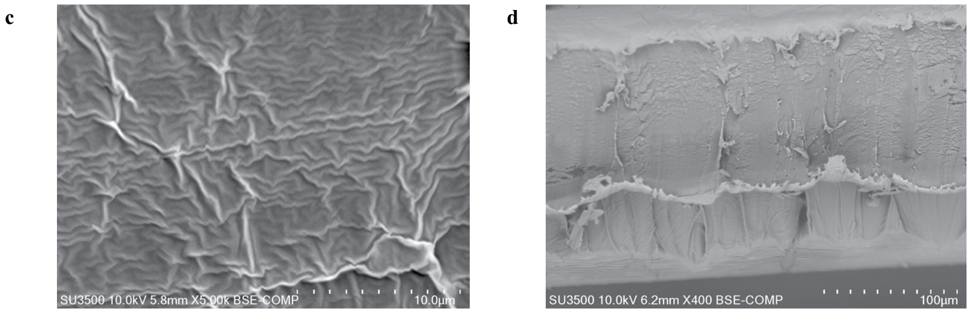
The SEM photomicrographs showed that both membranes had dense and homogeneous structures. Moreover, the images showed clear roughness of the film surfaces. In the case of membrane **2** the roughness was much more visible, which confirmed the results obtained in our previous paper [22]. The film roughness of **1** and **2** was 4.17 and 6.15 nm, respectively. Carriers could crystallize in the membrane and, for example, D$_2$EHPA molecules migrated to the membrane surface, causing its roughness and porosity.

3.2. Transport

The transport of metal ions across PIMs containing acac or D$_2$EHPA as carriers was studied. The transport process was described by Eq. (4). In order to calculate the values of k, plots of $\ln(c/c_0)$ versus time were made (Fig. 4) individually for each galvanic wastewater. The straight line relationships of $\ln(c/c_0)$ versus time were obtained with high

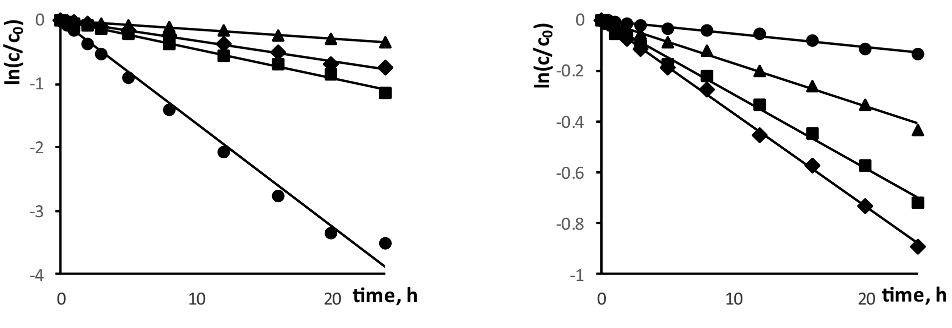


membrane **1**: 20 wt.% acac + 10 wt.% DAO + 70 wt.% PVC



membrane **2**: 60 wt.% D$_2$EHPA + 5 wt.% DAO + 35 wt.% PVC

Fig. 3. Surface (a and c) and cross section (b and d) SEM images of two types of investigated PIMs.



A
membrane **1**

B
membrane **2**

Fig. 4. The relation of $\ln(c/c_0)$ plotted versus time for Fe(III) ●, Ni(II) ■, Cu(II) ◆ and Cr(III) ▲ transport across PIMs with acac (**1**) or D$_2$EHPA (**2**) from galvanic water waste (A and B). Membranes: (**1**) 20 wt.% acac, 10 wt.% DAO, 70 wt.% PVC or (**2**) 60 wt.% D$_2$EHPA, 5 wt.% DAO, 35 wt.% PVC.

values of the determination coefficient (R^2, from 0.9848 to 0.9988). The rate constant values (k) for two independent transport experiments were averaged. The concentration of the metal in the feed phase was calculated as a difference in the initial concentration and the concentration determined in the receiving phase after time t.

The transport rate of metal ions (Fig. 4) decreased in the following order: Fe(III) > Ni(II) > Cu(II) > Cr(III) in the case of membrane **1** and Cu(II) > Ni(II) > Cr(III) > Fe(III) in the case of membrane **2**.

The selectivity of the transport of iron(III), nickel(II), copper(II) and chromium(III) ions from aqueous galvanic wastewater (A and B) by PIMs with acac (**1**) and D_2EHPA (**2**) as carriers is presented in Table 2.

The initial fluxes (J_0) for all metal ions present in the galvanic wastewater were 10 times higher for membrane **1** with acac than for membrane **2** with D_2EHPA. It depended on the carrier type. The selectivity order of metal ions during transport across membranes decreased, in the following order: Fe(III) > Ni(II) > Cu(II) > Cr(III) in the case of membrane **1** and Fe(III) > Cu(II) > Cr(III) > Ni(II) in case of membrane **2**. Both studied membranes efficiently separated the investigated metals from their mixture, but membrane **2** produced better results of separation. The highest selectivity coefficient was obtained for Fe(III)/Ni(II) and it equalled to 60.80 for membrane **2**, whereas the lowest was also obtained for Fe(III)/Ni(II), but for membrane **1** (1.33).

RFs which describe the metal separation processes were calculated as well. All values of RF are summarized in Table 3.

The RF values were calculated using Eq. (8). The membrane with acac had definitely better properties of recovering metal ions in comparison with the membrane with D_2EHPA. The obtained results corresponded well with the results produced in our previous paper [15]. The highest recoveries of iron(III) (97.01%) and nickel(II) (68.09%) were obtained as an effect of transport across membrane **1**. In the case of membrane **2**, the recovery of copper(II) ions was the most effective (59.05%).

4. Conclusion

The results obtained in this paper show that the transport of metal ions from galvanic wastewater depends on the carrier type in the investigated membrane and it is more effective across a membrane with acac (**1**) than across a membrane with D_2EHPA (**2**). The initial fluxes (J_0) for all metal ions presented in the galvanic wastewater are higher for the membrane with acac. Metal ions are transported in the following order: Fe(III) > Ni(II) > Cu(II) > Cr(III) in the case of membrane **1** and Cu(II) > Ni(II) > Cr(III) > Fe(III) in the case of membrane **2**. Both studied membranes efficiently separate the investigated metal ions from their mixture, but membrane **2** produces better results of separation. The highest selectivity coefficient is obtained for Fe(III)/Ni(II) at membrane **2**.

Although the membrane with acac has the worse separation properties in comparison with the membrane with D_2EHPA, the final recovery factors for all metal ions transported across this membrane are definitely better. The highest recovery of iron(III) (97.01%) and nickel(II) (68.09%) is obtained.

The ATR-FTIR results confirm the presence of individual components in the membranes: PVC, DAO and acac or D_2EHPA. They also suggest that there are no signs of covalent bond formation between those components.

The efficiency of transporting metal ions across a membrane depends on its microstructure. The obtained SEM images show dense and homogeneous structures of surfaces

Table 2
Initial fluxes, selectivity order and selectivity coefficients for competitive transport of Cr(III), Fe(III), Ni(II) and Cu(II) ions across PIMs

Galvanic wastewater/membrane	Metal ion	Initial flux, J_0 (mmol/m^2 h)	Selectivity order	Selectivity coefficients, S
A/1	Fe(III)	5.9346	Fe > Ni > Cu > Cr	
	Ni(II)	4.4544		$S_{Fe(III)/Ni(II)}$ 1.33
	Cu(II)	1.4634		$S_{Fe(III)/Cu(II)}$ 4.06
	Cr(III)	0.4339		$S_{Fe(III)Cr(III)}$ 13.68
B/2	Fe(III)	1.0230	Fe > Cu > Cr > Ni	
	Cu(II)	0.0618		$S_{Fe(III)/Cu(II)}$ 16.54
	Cr(III)	0.0257		$S_{Fe(III)/Cr(III)}$ 39.73
	Ni(II)	0.0168		$S_{Fe(III)/Ni(II)}$ 60.80

The given values of the J_0 and S carry 0.1% tolerance.

Table 3
Recovery factors (RF) of Fe(III), Ni(II), Cu(II) and Cr(III) ions from the galvanic wastewater after 24 h transport across PIMs

Galvanic wastewater/membrane	Fe(III)	Ni(II)	Cu(II)	Cr(III)
	RF (%)			
A/**1**	97.01	68.09	52.54	28.35
B/**2**	12.31	51.35	59.05	35.06

The given values of the RF are of 0.1% tolerance.

of investigated membranes' films. The roughness of membrane **2** is much more visible than that of membrane **1**, which can cause a decrease in the recovery factors of the transported metal ions.

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Symbols

c — Concentration of metal ions in the feed phase after time t, mol/m^3
c_0 — Initial concentration of metal ions in the feed phase, mol/m^3
k — Rate constant, h^{-1}
t — Time of transport process, h
J — Ionic transport flux, mmol/m^2 h
J_0 — Initial flux, mol/m^2 h
n — Quantity of metal ions, mol
A — Effective area of the membrane, m^2
V — Volume of receiving phase, m^3
S — Selectivity coefficient
RF — Recovery factor, %

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