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Transport of Cr(VI), Zn(II), and Cd(II) Ions Across Polymer Inclusion Membranes with Tridecyl(pyridine) Oxide and Tri-*n*-Octylamine

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ABSTRACT

An experimental investigation of chromium(VI), zinc(II), and cadmium(II) ions removal from acidic chloride aqueous solutions by transport through polymer inclusion membrane (PIM) with basic ion carriers [i.e., 4-(1′-*n*-tridecyl)pyridine N-oxide (TDPNO) and tri-*n*-octylamine (TOA)] is presented. The initial fluxes of all metal ions are higher for the less basic carrier (i.e., TDPNO). On the other hand, the more basic carrier (i.e., TOA) gives higher Cr(VI)/Cd(II) and Cr(VI)/Zn(II) selectivity coefficients. In long-term chromium(VI) transport experiments, the

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aqueous source and receiving phase were renewed every day, whereas the PIM remained the same as in the first run: the small decrease of permeability coefficient was observed, which can be explained by the partitioning of the carrier between the membrane and the aqueous solutions. A long-term experiment was conducted out to demonstrate the durability of PIMs. The application of PIM transport process for 99% removal of chromium(VI) from galvanic wastewaters is also shown.

Key Words: Polymer inclusion membrane; Removal; Toxic metal ions; 4-(1′-*n*-tridecyl)pyridine N-oxide; Tri-*n*-octylamine; Chromium(VI); Zinc(II); Cadmium(II).

1. INTRODUCTION

Chromium compounds are toxic for bacteria, plants, animals, and people. Human toxicity includes lung cancer as well as kidney, liver, and gastric damage. Chromium toxicity depends on its oxidation state, and, in general, chromium(VI) is much more toxic than chromium(III).

Batch solvent extraction with nitrogen-based extractants (e.g., amines and quaternary ammonium salts) was widely applied for chromium(VI) removal form aqueous solutions. Tri-*n*-octylamine (TOA),[1] tri-*iso*-octylamine,[2] and trioctylmethylammonium salts (Aliquat 336)[3] were used as extractants.

In recent years, a remarkable progress concerning the industrial applications of liquid membrane systems is observed. The systems of membrane transport include (1) bulk liquid membranes (BLMs), (2) emulsion liquid membranes (ELMs), and (3) supported liquid membranes (SLMs). The latter systems could be considered as an alternative for the industrial application of solvent extraction. Zouhri et al. reported the application of BLMs for Cr(VI) removal with Alamine 336 and dicyclohexano-l8-crown-6 as ion carriers.[4] The concentration and separation of chromium(VI) in SLM and ELM systems with Aliquat 336 as an ion carrier have also been described[5–7] as well as the study of further development of SLM systems containing tertiary amines and quaternary ammonium salts applied for Cr(VI) concentration and separation.[8,9]

Recently, a novel type of liquid membrane system called polymer inclusion membrane (PIM), was developed. The PIMs are formed by casting cellulose triacetate (CTA) from an organic solution to form a thin, stable film. This solution contains also an ion carrier and a membrane plasticizer (mostly *o*-nitrophenyl alkyl ethers). The resulting membrane is used to separate source and receiving phases; however, it does not contain an organic solvent for the transport of ionic species through PIM. A number of researchers used CTA membranes for carrier-mediated transport of metal ions from an aqueous source phase into an aqueous receiving phase. Sugiura et al. have studied the transport of zinc(II) and rare earth cations.[10,11] Transports of strontium(II), lead(II),[12] copper(II),[13] and chromium(VI)[14] have been investigated. Walkowiak et al. have studied the competitive transport of zinc(II), cadmium(II), chromium(III), and chromium(VI) across PIMs using tertiary amine-based carriers.[15] The chromium(VI) extraction and transport with 4-(1′-*n*-tridecyl)pyridine N-oxide (TDPNO) across the CTA-based PIM system were found to be strongly dependent on the concentration of sulfuric acid in the aqueous and source phases.[16]

The present article deals with the transport of chromium(VI) from chloride aqueous solutions by PIM with tertiary amine and N-oxide pyridine derivative as ion carriers. In this work, the effect of different plasticizer compounds on chromium(VI) transport across PIMs formed with CTA and polyvinyl chloride (PVC) matrices is presented. Stability of PIMs with TOA and TDPNO for chromium(VI) transport as well as separating properties of PIMs with TDPNO for chromium(VI), zinc(II), and cadmium(II) transport from hydrochloric acid solution have been studied.

2. EXPERIMENTAL PART

2.1. Chemicals

TDPNO with formula weight 277.45 is a white, crystalline powder, which was synthesized by Golubski.[17] The melting point of TDPNO purified by crystallization from hexane solution is 61–63°C. The organic compounds (i.e., TOA, Aliquat 336, dichloromethane, tetrahydrofuran, PVC, and CTA) were purchased from Fluka and used without further purification. The following membrane plasticizers were used: dioctyl phthalate (DOP), *o*-nitrophenyl pentyl ether (ONPPE), *bis*(2-ethylhexyl) adipate (DOA), tricresyl phosphate (TCF), and *tris*(2-ethylhexyl) phosphate (TOF); they were also purchased from Fluka. Aqueous solution of inorganic compounds (i.e., potassium dichromate, sodium hydroxide, and hydrochloric acid solutions) were prepared from analytical grade reagents (POCh, Gliwice, Poland).

2.2. PIM Preparation

A solution of the support (CTA), the ion carrier, and the plasticizer in dichloromethane was prepared. A portion of this solution was poured into a membrane mold comprised of a 9.0-cm glass ring attached to a glass plate with CTA–dichloromethane glue. The organic solvent was allowed to evaporate overnight and the resultant membrane was separated from the glass plate by immersion in cold water. The membrane was soaked in aqueous solution of 0.1 M HCl for 12 hr and stored in distilled water.

2.3. Membrane Transport Experiments

The membrane was clamped between two cylindrical, water-jacketed half cells (volume 50 mL), described earlier.[14] The average membrane thickness was 28 μm (measured by digital ultrameter of A 2002M type from Inco-Veritas with 0.1-μm standard deviation over four readings). The total effective membrane area exposed to both phases was 6.0 cm^2. Both the source and receiving aqueous phases (50 cm^3 each) were stirred at 600 rpm with synchronous motors. The permeation of chromium(VI) was monitored by periodically sampling the source phase, and chromium was analyzed after appropriate dilution by an Perkin Elmer atomic absorption spectrophotometer.

The kinetics of the PIMs transport can be described as a first-order reaction in metal-ion concentration:[18]

$$\ln\left(\frac{c}{c_\mathrm{i}}\right) = -kt \tag{1}$$

where c is the metal ion concentration at some given time in the source phase (M), c_i is the initial concentration of metal-ion concentration in the source phase (M), k is the rate constant (sec^{-1}), and t is the time of transport (sec).

To calculate k values, the plots of $\ln(c/c_\mathrm{i})$ vs. time were used. The relationship of $\ln(c/c_\mathrm{i})$ vs. time was found to be linear, which was confirmed by high values of determination coefficients ($r^2 \geq 0.98$). The permeability coefficient (P) was calculated as follows:

$$P = -\left(\frac{V_\mathrm{s}}{A}\right) \cdot k \tag{2}$$

where V_s is the volume of aqueous source phase and A is an effective area of a membrane. The initial flux (J_i) was determined as equal to:

$$J_\mathrm{i} = P \cdot c_\mathrm{i} \tag{3}$$

3. RESULTS AND DISCUSSION

3.1. Effect of Plasticizer on the Transport Cr(VI) Across Membranes with TOA

At first, transport of chromium(VI) ions through PIMs containing TOA as ion carrier and various plasticizers was studied. Membrane plasticizers differ in physical properties, especially in viscosity and dielectric constant. Previously, Bartsch et al.[19] demonstrated that the use of *o*-nitrophenyl alkyl ethers as a solvent in CTA membranes resulted in the decrease of sodium cation transport with increase of alkyl group length. They found that the dielectric constant and viscosity of the solvent were important parameters determining the stability of metal ions complexes formed in the organic membrane phase. Blank experiments, in the absence of carrier, with a support and plasticizer only yield no significant flux across PIM. To understand the influence of plasticizer nature on chromate ions transport through PIM, membrane with different compounds (i.e., DOP, ONPPE, DOA, TCF, and TOF) were prepared and tested at 30°C. The initial Cr(VI) fluxes, which were obtained from slope line of the semilog of c/c_0 vs. time, and several physicochemical properties are presented in Table 1. Transport of chromium(VI) from acidic aqueous solution across PVC or CTA immobilized membranes containing 1.0 M TOA (based on plasticizer) into 0.1 M NaOH aqueous solution was investigated. The initial fluxes of chromium(VI) transport through PVC

Table 1. Properties of membrane solvent (plasticizer) and values of chromium flux through PIMs containing different plasticizer.

Plasticizers	Viscosity (centipoise)	Initial flux of Cr(VI) (μmol/m^2 sec)	
		CTA	PVC
None	—	15.7	3.1
DOP	78	24.2	4.63
ONPPE	7.58	45.0	19.5
DOA	13.7	43.2	18.0
TCF	58	30.0	8.3
TOF	12	43.5	18.5

Note: Source aqueous phase: 0.0020 M Cr(VI), 1.0 M HCl; receiving aqueous phase: 0.10 M NaOH; membrane: 1.6 cm^3 plasticizer/1.0 g CTA, 1.0 M TOA based on plasticizer volume. The experiments were conducted at 30°C.

immobilized membranes with TOA as an ion carrier, and various plasticizers, are shown as a function of viscosity of plasticizers in Fig. 1.

The initial fluxes of Cr(VI) increase linearly in the following order of plasticizers: DOP < TCF < DOA < TOF < ONPPE, (i.e., with their viscosity decrease). Comparing PIM and liquid membranes in facilitated flux of Cr(VI) transport, it was observed that the rate reaction between Cr(VI) and amine was influenced by the boundary layer of the microporous polymer as well as by organic boundary conditions such as viscosity and polarity. The viscosity of organic solvent influences on the diffusivity of chromium(VI) and TOA complex in the membrane liquid, and on the total volume of the organic phase, which is determined by porosity and tortuosity of the membrane. However, the highest value of initial flux was observed for CTA membranes with ONPPE and was equal to 45.0 μmol/m^{2}sec. The rapid transport with carrier dissolved in ONPPE results from a higher affinity of TOA to chromium(VI) ions in more polar (dielectric constant, $\varepsilon = 29.15$) environment of membrane organic phase. The high dielectric constant allows amine protonation and formation of chromate–amine complex in the organic phase. For PVC membranes, however, a lower value of initial flux for ONPPE (i.e., 23.5 μmol/m^{2}sec) was observed. As shown in Fig. 1, the relationship between the initial fluxes of chromium(VI) and the viscosity of membrane solvent is linear in the CTA and PVC membranes. This behavior

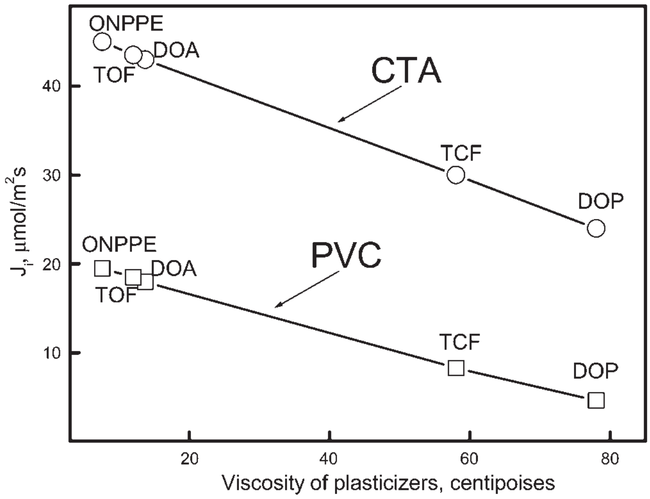

Figure 1. Influence the viscosity of plasticizer on chromium(VI) transport across CTA and PVC membranes containing 1.0 M TOA based on plasticizers. Source phase: 0.02 M Cr(VI) in 0.1 M HCl; receiving phase: 0.1 M NaOH.

can be explained by diffusion-dependent relation of Stokes–Einstein relation for diffusion coefficient (4):

$$D = \frac{kT}{6\pi\eta r} \tag{4}$$

where η is the viscosity of the solvent, D is the diffusion coefficient, r is the radius of the solute, k is the Boltzman constant, and T is absolute temperature.

The resulting membrane contained average 27 wt% PVC, 19 wt% TOA, and 54 wt% plasticizers (ONPPE). The unusually low content of plasticizer in PIMs used in our experiments is due to good plasticizing properties of tertiary amine, serving as an ion carrier. We studied also the removal of chromium(VI) from dilute aqueous solutions. Concentrations of chromium(VI) in drinking water range from about 0.003 to more than 0.005 mg/dm^3; typical values appear between 1 and 6 μg/dm^3. The concentration of chromium in drinking water depends significantly on geographical location. In the next run with the source/receiving phases volume ratio equal to 1, we show the possibility to reduce the chromium concentration in water from 1.0 to 0.0025 mg/dm^3 in 12 hr of PIM process. Experimental conditions were as follows: aqueous source phase contained 1.0 ppm Cr(VI) at adjusted pH value ≤ 4.5, NaOH concentration in receiving phase was equal to 0.010 M, and the 1.0 M TOA content in membrane was based on ONPPE plasticizer. This content of Cr(VI) in the aqueous phase is below permissible limit in drinking water in Poland (State Communicate of Standard of Poland Council of Ministers, *Standard 1140 for Drinking Water*, Decree No. 134, 2002); this limit is equal to 0.003 mg/dm^3.

In the next series of experiments, we were looking for the optimal plasticizer concentration of ONPPE in PIMs, used for transport of chromium(VI). The obtained results are shown in Fig. 2. At 0.8 cm^3 ONPPE/1.0 g CTA for TOA and 4.0 cm^3 ONPPE/1.0 g CTA the ion carrier causes the PIM saturation and the transport rate is maximal for TOA and TDPNO equal to 18.2 and 10.5 μmol/m^{2}sec, respectively.

3.2. Distribution Coefficients of TOA and TDPNO in PIM Systems for Chromium(VI) Transport

The ion-exchange chromium(VI) extraction by tertiary amine and TDPNO is described by the following equilibrium:

$$s\mathrm{TDPNO}_{(\mathrm{org})} + \mathrm{H}^+_{(\mathrm{aq})} + \mathrm{HCrO}^-_{4(\mathrm{aq})} = (\mathrm{TDPNO})_s \cdot \mathrm{H_2CrO}_{4(\mathrm{org})} \tag{5}$$

$$s\mathrm{TOA}_{(\mathrm{org})} + \mathrm{H}^+_{(\mathrm{aq})} + \mathrm{HCrO}^-_{4(\mathrm{aq})} = (\mathrm{TOAH})_s\mathrm{HCrO}_{4(\mathrm{org})} \tag{6}$$

where s is the stoichiometry factor of an ion carrier in organic phase.

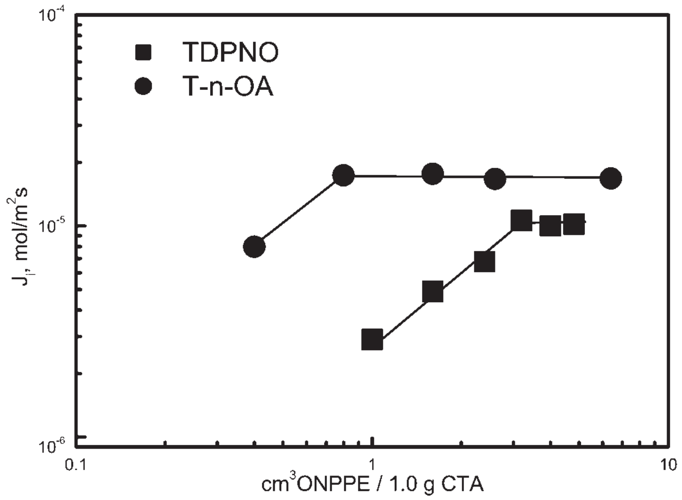

Figure 2. Relationship between initial fluxes and plasticizer content in membrane for chromium(VI) transport with TOA and TDPNO as ion carriers.

On the basis of mathematical model described by Danesi and Hill,[18,20,21] the mass transfer across SLMs (transport limited by diffusion in membrane and by the total re-extraction of metal ion at PIM/receiving phase), and the permeability coefficient are proportional to the distribution coefficient of the transporting species, under proper hydrodynamic conditions at the source phase/PIM interfaces:

$$P \approx \frac{D_0 K_{ex}[\mathrm{HCrO_4^-}]_{eq}}{d_0}[\mathrm{carrier}]_{eq}^{s} \tag{7}$$

where D_0 is diffusion coefficient of metal complex in membrane, d_0 is thickness of membrane, and K_{ex} is extraction constant of the equilibrium (5) or (6).

Making the following assumptions:

- $[\text{metal complex}]_{eq} < [\text{carrier}]_{eq}$ even when all chromium forms, taking into account at negligible level compared with the carrier initial concentration;
- none or only very poor extraction of the aqueous salting agent by the ion carrier;
- $[A^-]_{eq} \approx [A^-]_0$ if chloride concentration gradients are properly maintained throughout the experiments ($[\mathrm{Cl}^-]_0 = 0.1$ M in the source aqueous solutions).

The mass balance equation applied to the carrier gives for the *n*th repeated transport experiment:

$$[\text{carrier}]_{n+1} = \frac{[\text{carrier}]_n}{(1 + r/K_{\text{p})}} = \frac{[\text{carrier}]_0}{(1 + p/K_\text{p})^{n+1}} \tag{8}$$

where $[\text{carrier}]_0$ is the initial carrier concentration in the PIM,

$$p = \frac{V_\text{s} + V_\text{r}}{V_\text{PIM}} \tag{9}$$

where V_r is the volume of aqueous source phase, V_PIM is volume of plasticizer in membrane, and K_p is the apparent distribution constant of the carrier between the PIM and both aqueous source and receiving aqueous solutions.

In repeated transport both aqueous phases are renewed everyday, whereas the PIM remains the same as in the first run. The decrease of the permeability coefficient is given by relations (7) and (8) and can be explained by the distribution of carrier between the PIM and the aqueous solution.

$$\begin{aligned} P^{(n)} &= \frac{D_0 K_\text{ex}[\text{HCrO}_4^-]_\text{eq}}{d_0}[\text{carrier}]^s \approx \frac{D_0 K_\text{ex}[\text{HCrO}_4^-]_0}{d_0} \cdot \frac{[\text{carrier}]_0^s}{(1 + p/K_\text{p})^{ns}} \\ &= \frac{P^{(1)}}{(1 + p/K_\text{p})^{(n-1)s}} \end{aligned} \tag{10}$$

The semilogarithmic variation of log $P^{(n)}$ vs. the number of runs can be presented as follows:

$$\log P^{(n)} = \log P^{(1)} - (n-1) \cdot s \cdot \log\left(1 + \frac{p}{K_\text{p}}\right) \tag{11}$$

For HCrO_4^- transport through PIM with TOA and TDPA, where $s = 1$ and $p = 1000$, Eq. (11) was found as equal (Fig. 3):

For TOA

$$\log P^{(n)} = (-0.645) - (n-1) \cdot s \cdot \log\left(1 + \frac{1000}{85654}\right) \quad r^2 = 0.9885 \tag{12}$$

For TDPNO

$$\log P^{(n)} = (-0.700) - (n-1) \cdot s \cdot \log\left(1 + \frac{1000}{99501}\right) \quad r^2 = 0.9952 \tag{13}$$

From Eqs. (12) and (13), the empirical values of distribution coefficient $\log K_\text{p}$ for membrane system studied for TOA and TDPNO was estimated to equal to 4.93 ± 0.15 and 4.99 ± 0.08, respectively. The relations given above are approximate, which implies that uncomplexed carrier should be

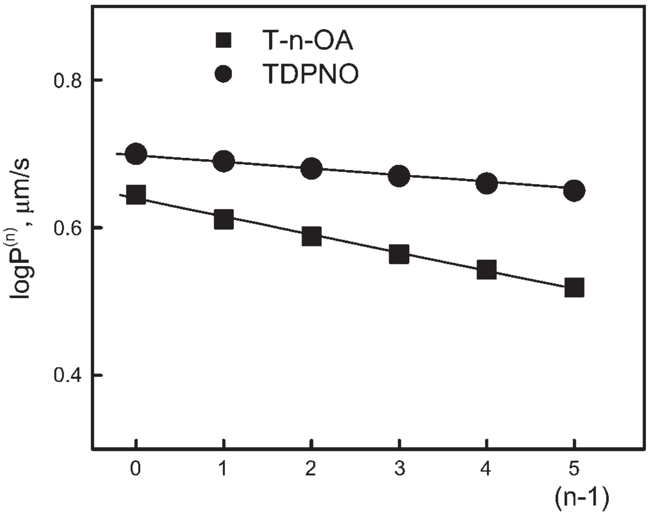

Figure 3. Logarithmic variations of chromium(VI) permeability coefficients vs. number of runs in repeated transport experiments with TOA and TDPNA. Source aqueous phase: 0.0010 M Cr(VI) in 0.10 M HCl; receiving phase: 0.10 M NaOH; PIMs: 1.0 M carriers based on the plasticizer, 0.8 cm^3 ONPPE/1.0 g CTA for TOA or 4.0 cm^3 ONPPE/1.0 g CTA for TDPNA.

surface active and partitioning at the interface membrane/aqueous source phase. The loss of undissolvent carriers in aqueous solutions is easier, because viscosity and polarity of the used plasticizer are higher.

3.3. Separation of Cr(VI), Zn(II), and Cd(II) from HCl Solution Through PIM Using TDPNO

The selectivity of chromium(VI), cadmium(II), and zinc(II) transport from aqueous chloride solutions by PIM with 1.0 M TDPNO as an ion carrier and 4.0 cm^3 ONPPE/1.0 g CTA depends on the basicity of carriers used (Fig. 4). As can be seen from Fig. 4, the initial fluxes of Cr(VI) are higher for TDPNO than for TOA (Fig. 2). This fact results from differences of those carriers basicities—the basicity constant of TOA ($pK_b = 5.8$) is much stronger in comparison with TDPNO ($pK_b = 12.9$).[22,23] For both carriers, when the HCl concentrations are 0.1 M in the aqueous source phase, the metal ion fluxes increase in the order: Zn(II) < Cd(II) < Cr(VI). On the other hand, the selectivity coefficients of chromium(VI)/cadmium(II)

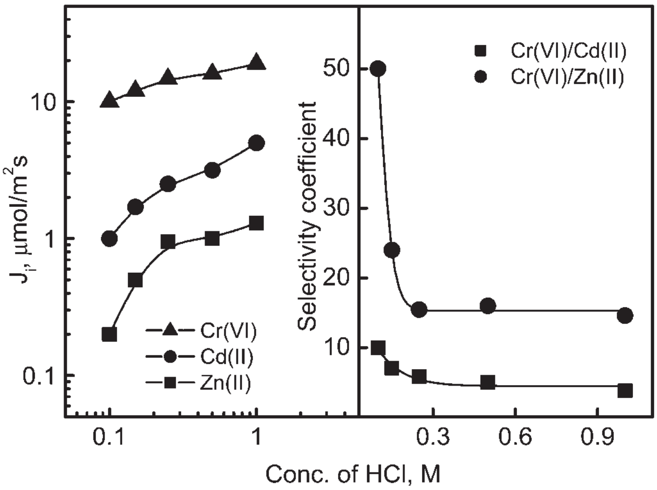

Figure 4. Relationship of initial flux values and selectivity coefficients with concentration HCl for competitive transport of chromium(VI), cadmium(II), and zinc(II) through PIM. Source phase: 1.0×10^{-3} M each metal ions in HCl solutions; receiving phase: 0.50 M CH_3COONa (pH = 8.0); membrane: 0.80 cm^3 ONPPE/1.0 g CTA, 1.0 M TOA; membrane: 4.0 cm^3 ONPPE/1.0 g CTA, 1.0 M TDPNO.

and chromium(VI)/zinc(II) are higher for TOA than for TDPNO. The selectivity coefficients for Cr(VI)/Cd(II) and Cr(VI)/Zn(II) from 0.5 M HCl were the highest for transport with TOA and were equal to 15 and 106, respectively.[24] The transport of Cd(II) through the membrane is much faster than in the case of Zn(II); this result can be explained by much higher value of extraction constant of Cd(II) and the fact that Cd(II) is present predominantly as its trichlorocadmate(II) complex in the solution, while Zn(II) exist as its tetrachlorozincate(II) complex.

3.4. Applicability of PIMs in Environmental Protection—Use of Toxic Effluents

With the wastewater disposal increase, more attention is paid to the recovery and recycling of valuable chemicals contained in these streams. In the chrome-electroplating industry, rinsing of finished products generates toxic wastewaters containing chromium. These wastewaters present a significant disposal problem and a loss of valuable raw material in the form of chromium, zinc, and cadmium which are mostly toxic. The experiments were conducted by using the acidic wastewater from electroplating plant. The source phase of industrial solution of acidified sodium chromate [50 cm^3; pH = 1.0, 250 ppm Cr(VI)] was placed in one compartment, and dilute NaOH solution (50 cm^3; pH = 12) was placed in the other one. The recovery of Cr(VI) transport as a function of process time is given in Fig. 5.

4. CONCLUSION

The PIMs containing basic carrier removed effectively chromium(VI) from acidic solution, and the transport is of a long-term integrity. The CTA or PVC immobilized membranes with basic carrier such as TOA or Aliquat 336 can be applied for effective removal of chromium(VI) from acidic aqueous solutions. The polymer inclusion membrane contained average 30 wt% PVC, 20 wt% TOA, and 50 wt% plasticizers. It was possible to reduce the concentration of chromium(VI) from 1.0 to 0.025 ppm in the aqueous source phase (i.e., below permissible limit in drinking water in Poland). The linear decrease of initial fluxes of Cr(VI) through PVC or CTA membrane with TOA vs. viscosity of applied plasticizers was found. The PVC- or CTA-based membrane systems possess important advantages

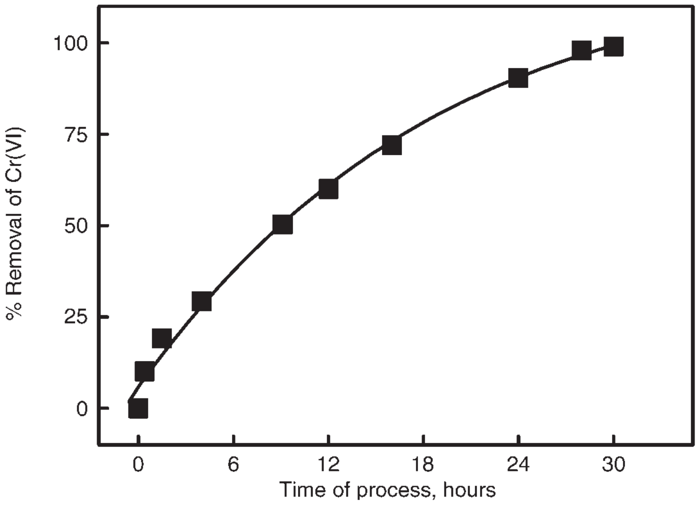

Figure 5. Recovery of chromium(VI) ions from wastewater in PIM with TOA. Membrane: 0.8 cm^3 ONPPE/1.0 g CTA, 1.28 M TOA. Receiving phase: 0.10 M NaOH.

over other liquid membranes (i.e., easy setup, high transport rate, and high repeatability). Detailed investigations of the other experimental variables on the chromium(VI) removal via polymer inclusion membranes are in progress.

The polymer inclusion membrane transport of chromium(VI), cadmium(II), and zinc(II) from acidic aqueous solutions using basic ion carriers is an effective method of selective removal of metal ions studied. The used ion carriers [i.e., TDPNO and TOA allow separation of metal ions; the selectivity increases as follows: Zn(II) $<$ Cd(II) $<$ Cr(VI). The initial fluxes of chromium(VI), cadmium(II), and zinc(II) for TOA and TDPNO were as follows: 6.62, 0.449, 0.062 μmol/m^{2}sec, and 16.01, 3.16, 1.01 μmol/m^{2}sec, respectively. These results were discussed in terms of the basicity of ion carriers. The partition coefficients membrane/source phase for TOA and TDPNO show the high stability of polymer inclusion membrane and its applicability in the long-term separation experiments. The small decrease of permeability coefficient results from the partition of the carrier between membrane and aqueous solutions. The application of effective chromium(VI) removal (99%) from galvanic wastewaters using transport through PIM with TOA is also shown.

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