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REMOVAL OF Cr(VI), Zn(II) AND Cd(II) IONS BY TRANSPORT ACROSS POLYMER INCLUSION MEMBRANES WITH BASIC ION CARRIERS

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An experimental investigation of chromium(VI), zinc(II), and cadmium(II) ions removal from acidic chloride aqueous solutions by polymer inclusion membrane (PIM) transport 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. Also the application of PIM transport process for removal of 99% chromium(VI) from galvanic waste waters is shown.

Key words: polymer inclusion membranes, separation, chromium(VI), zinc(II), cadmium(II)

INTRODUCTION

Chromium is regarded as a toxic element in the environment. Toxicity of chromium compounds depends on its oxidation states, *i.e.* chromium(III) and chromium(VI), which are regulated in different ways (Kimbrough et al., 1999). Chromium(VI) was recognized to be much more toxic than chromium(III). Chromium(VI) compounds were found to be toxic for bacteria, plants, animals and people. Human toxicity includes lung cancer, as well as kidney, liver and gastric damage. Chromium(VI) is one of major toxic elements present in environmental samples. For this reason, the application of liquid membranes for Cr(VI) removal from aqueous solutions was evaluated.

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Batch solvent extraction was used widely for chromium(VI) removal from aqueous solutions. As extractants were used tri-*n*-octylamine (Horn et al., 1994; Chilukuri et al., 1998), tri-*iso*-octylamine (Huang et al., 1991), trioctylmethylammonium salts such as Aliquat 336 (Lo and Shiue, 1998). Another option of chromium(VI) removal from aqueous solutions is the application of tertiary amines and quaternary ammonium salts as carriers in the membrane transport in microporous hollow-fiber modules (Yun et al., 1993; Yang et al., 1996; Alonso et al., 1996; Ortiz et al., 1996). The process, called also nondispersive solvent extraction (NDSX), offers a very large interfacial area per unit equipment volume without any dispersion. Recent years have seen a remarkable increase in the applications of liquid membranes in separation processes. These membranes include bulk liquid membranes (BLMs), emulsion liquid membranes (ELMs) and supported liquid membranes (SLMs). Ho and Sirkar (Ho and Sirkar, 1992) provide a good overview of membrane processes.

The applications of SLMs with tertiary amines and/or quaternary ammonium salts as ion carriers used for chromium(VI) concentration and separation have been shown in several papers (e.g., Chiarizia, 1991; Chaudry et al., 1997; Wang et al., 1998). A common problem for SLMs is the loss of membrane solvent and/or carrier to the both aqueous phases. As a result, SLM-based process have not been exploited industrially owing their poor durability.

An alternate approach to the problem of SLM stability has been related with the organic liquid phase immobilized within a porous structure. Recently, a novel type of liquid membranes systems, called polymer inclusion membranes (PIMs) has been developed. The PIMs are formed by casting as a support cellulose triacetate (CTA) from an organic solution to form a thin, stable film. This solution also contains an ion carrier and a membrane plasticizer (mostly *o*-nitrophenyl alkyl ethers). The resultant membrane does not contain organic solvent but is able to maintain the transport of ionic species through and may be used to separate source and receiving phases in PIM systems.

CTA membranes were used for carrier mediated transport of Cr(VI) ions from an aqueous source phase into an aqueous receiving phase. Walkowiak et al. have studied the competitive transport of zinc(II), cadmium(II), chromium(III) and chromium(VI) across PIMs using tertiary amines-based carriers (Walkowiak et al., 2000). The chromium(VI) extraction and transport with 4-(1'-*n*-tridecyl)pyridine N-oxide across the CTA-based polymer inclusion membrane system were found to be strongly dependent upon the concentration of sulphuric acid in the aqueous and/or source phase, respectively (Wionczyk et al., 2001).

Present work deals with the transport of chromium(VI) from chloride aqueous solutions by polymer inclusion membranes with tertiary amine and N-oxide pyridine alkyl derivative as ion carriers. The effect of plasticizer content on chromium(VI) transport across PIMs and separating properties of PIMs with tri-*n*-octylamine and 4-(1'-*n*-tridecyl)pyridine N-oxide for chromium(VI), zinc(II) and cadmium(II) transport have been studied.

EXPERIMENTAL PART

CHEMICALS

The 4-(1'-*n*-tridecyl)pyridine *N*-oxide (TDPNO) with formula weight 277.45 is a white, crystalline powder which was synthesised by Golubski (Golubski, 1998). The melting point of TDPNO purified by crystallisation from hexane solution is $61 \div 63^{\circ}\text{C}$. The organic compounds, *i.e.* tri-*n*-octylamine (TOA), dichloromethane, *o*-nitrophenyl pentyl ether (ONPPE) and cellulose triacetate (CTA) were purchased from Fluka and used without further purification. The aqueous solutions of inorganic compounds, *i.e.* potassium dichromate, zinc chloride, cadmium chloride, sodium hydroxide, sodium acetate and hydrochloric acid, were prepared from analytical grade reagents (POCh, Gliwice, Poland).

POLYMER INCLUSION MEMBRANE PREPARATION

Cellulose triacetate, an ion carrier and a plasticizer were dissolved in dichloromethane. 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. Dichloromethane 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 hours and stored in distilled water.

TRANSPORT STUDIES

Transport experiments through PIMs were carried out in a permeation cell in which the membrane film was tightly clamped between two cell compartments (Fig. 1). The average CTA membrane thickness was $28 \mu\text{m}$ (measured by digital ultrametr of A 2002M type from Inco-Veritas with $0.1 \mu\text{m}$ standard deviation over four readings). The effective membrane area exposed to both phases was 6.0 cm^2 . Both, the source and receiving aqueous phases (45 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, zinc, and cadmium was analyzed after appropriate dilution by an atomic absorption Perkin Elmer spectrophotometer.

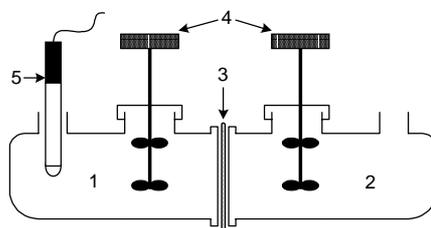


Fig. 1. Diagram of the transport cell: 1 - source phase, 2 - receiving phase, 3 - membrane, 4 - mechanical stirrers, 5 - pH electrode

Kinetics of PIM transport can be described by a first-order reaction in metal ion concentration:

$$\ln\left(\frac{c}{c_i}\right) = -kt \quad (1)$$

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

To calculate the value of k , a plot of $\ln(c/c_i)$ versus time was prepared. The values of rate constant for the duplicate transport experiments were averaged and standard deviation was calculated. The straight line relationships of $\ln(c/c_i)$ vs. time with high values of determination coefficient (r^2), i.e., from 0.9699 to 0.9918, were obtained.

The initial flux (J_i) was determined as equal to:

$$J_i = \frac{V}{A} \cdot k \cdot c_i \quad (2)$$

where V is volume of the aqueous source phase, and A is an area of effective membrane.

The selectivity coefficient, S , was defined as the ratio of initial fluxes for M1 and M2 metal ions, respectively.

$$S = J_{i,M1} / J_{i,M2} \quad (3)$$

The removal (R) of metal ions from the source phase into receiving phase was calculated as:

$$R = \frac{c_i - c}{c_i} \cdot 100\% \quad (5)$$

where c_i – the initial concentration of metal in the source phase.

RESULTS AND DISCUSSION

EFFECT OF PLASTICIZER CONTENT ON THE TRANSPORT Cr(VI) ACROSS PIM WITH TOA AND TDPNO

Initially, transport of chromium(VI) ions through PIMs containing TOA or TDPNO as ionic carriers and various plasticizer content was studied. Blank experiments, in the absence of carrier, yielded no significant flux across PIM containing only the support and plasticizer. To understand the influence of plasticizer on chromate ions transport through PIM, membranes with different content of *o*-nitrophenyl pentyl ether were prepared and tested at temperature 25 °C.

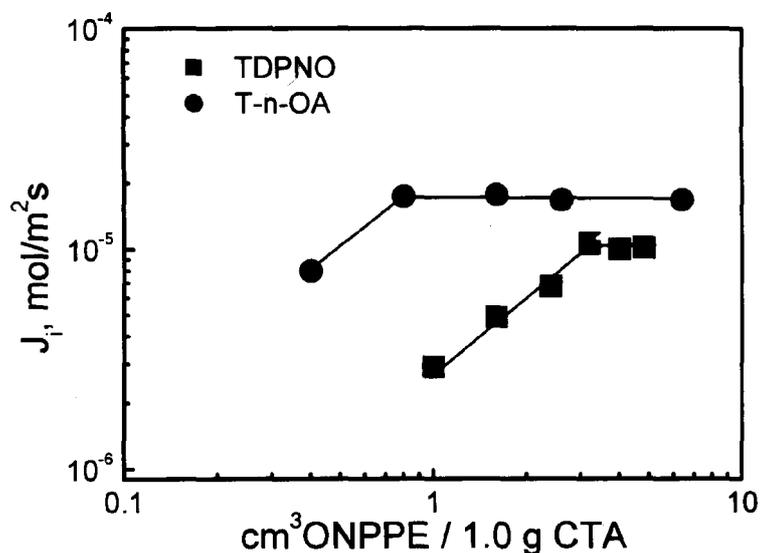


Fig. 2. Relationship between initial fluxes and plasticizer content in membrane support for chromium(VI) transport with TOA or TDPNO as ion carriers

SEPARATION OF Cr(VI), Zn(II) AND Cd(II) FROM HCl SOLUTION THROUGH PIM USING TOA AND TDPNO

The selectivity of chromium(VI), cadmium(II), and zinc(II) transport from aqueous chloride solutions by polymer inclusion membrane with 1.0 M TOA or TDPNO as a ion carriers, 0.80 cm³ and 4.0 cm³ ONPPE / 1.0 g CTA, respectively, depends on the basicity of carriers used (Table 1).

Table 1. The values initial fluxes and selectivity orders with selectivity coefficients for competitive transport of chromium(VI), cadmium(II), and zinc(II) through PIM. Source phase: 1.0 · 10⁻³ M each metal ions in 0.50 M HCl; Receiving phase: 0.50 M CH₃COONa (pH=8.0); Membrane: 0.80 cm³ ONPPE / 1.0 g CTA, 1.0 M TOA; Membrane: 4.0 cm³ ONPPE / 1.0 g CTA, 1.0 M TDPNO.

Carrier	Metal ions	Initial flux, J_i ($\mu\text{mol}/\text{m}^2\text{s}$)	Selectivity orders and selectivity coefficients
TOA	Cr(VI)	6.62	Cr(VI) > Cd(II) > Zn(II) 15 106
	Cd(II)	0.449	
	Zn(II)	0.062	
TDPNO	Cr(VI)	16.01	Cr(VI) > Cd(II) > Zn(II) 5 16
	Cd(II)	3.16	
	Zn(II)	1.01	

As can be seen from Table 1, the initial fluxes of Cr(VI), Cd(II), and Zn(II) are higher for TPNO than for TOA. This is caused by differences of those carriers basicities – the basicity constant of TOA ($pK_b = 5.8$) is much stronger in comparison with TDPNO ($pK_b = 12.9$) (Chmurzyński, 1996; Martell and Smith, 1974). On the other hand, the selectivity coefficients of chromium(VI)/cadmium(II) and chromium(VI)/zinc(II) are higher for TOA than for TDPNO.

APPLICABILITY OF POLYMER INCLUSION MEMBRANES IN ENVIRONMENTAL PROTECTION – UTILIZED OF TOXIC EFFLUENTS

As the costs of wastewater disposal increase, more emphasis is being placed upon the recovery and recycling of valuable chemicals contained within these streams. In the chrome-electroplating industry, rinsing of finished products generates toxic waste water containing chromium(VI) compounds. These waste waters decisive of a significant disposal problem. However, chromium, zinc, and cadmium compounds always present in such waste waters could be regarded as a valuable components which can be effectively removed and separated. The example illustrating such recycling of chromium compounds is presented below. The experiments were carried with the acidic waste water from electroplating plant. The volume source phase of 50 cm^3 industrial solution of acidified sodium chromate ($\text{pH } 1.0$, 250 ppm Cr(VI)) was placed in one compartment, and 50 cm^3 of dilute NaOH aqueous solution ($\text{pH } 12$) was placed in the other compartment. As can be noticed from Figure 3 the maximum removal of Cr(VI) after 30 hours of transport reaches 99%.

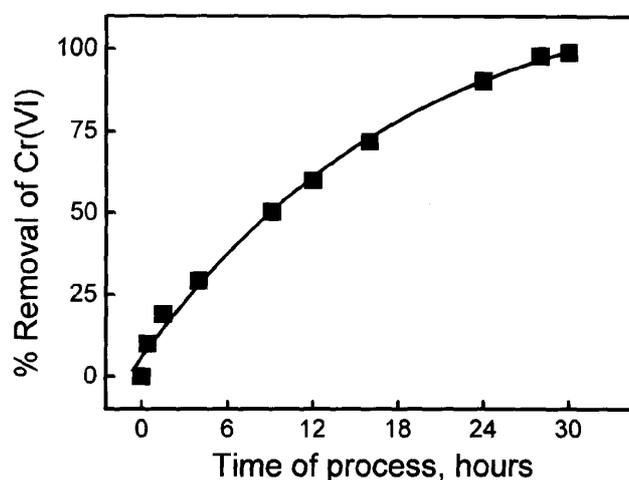


Fig. 3. Removal (%) of Cr(VI) ions from waste water by PIM transport.
Membrane: 0.80 cm^3 ONPPE / 1.0 g CTA, 1.28 M TOA

CONCLUSIONS

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. 4-(1'-*n*-tridecyl)pyridine *N*-oxide and tri-*n*-octylamine allow to separate metal ions; the selectivity orders were found 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, and 16.01, 3.16, 1.01, respectively. These results were discussed in terms of the basicity of ion carriers. Also the application of effective chromium(VI) removal (99 %) from galvanic waste waters using transport through PIM with TOA is shown.

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W pracy przedstawiono wyniki badań transportu jonów chromu(VI), kadmu(II) i cynku(II) przy użyciu polimerowych membran inkluzyjnych z trioctanu celulozy (CTA) zawierających jako przenośniki jonów n-tlenek 4-(1'-n-tridecyl)pirydyny (TDPNO) lub tri-n-oktyloaminę (TOA). W celu określenia najkorzystniejszego składu polimerowych membran inkluzyjnych zbadano wpływ ilości plastyfikatora w membranie na transport jonów chromu(VI). Maksymalną szybkości transportu Cr(VI) osiągnięto używając membrany z TDPNO zawierające więcej plastyfikatora w porównaniu z TOA, ze względu na dobre właściwości plastyfikujące amin. W przypadku transportu jonów Cr(VI), Cd(II) i Zn(II) za pomocą w/w zasadowych przenośników selektywność procesów malała w szeregu: Zn(II) < Cd(II) < Cr(VI). Membrany inkluzyjne z trioctanu celulozy zawierające TOA zastosowane do wydzielania jonów chromu(VI) z roztworów przemysłowych (ścieki z galwanizerni) pozwoliły na 99 % wydzielanie tego metalu po 30 godzinach procesu transportu.