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Permeation of Cd(II) Ions through a Supported Liquid Membrane Containing Cyanex-302 in Kerosene

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ABSTRACT

The permeation of Cd(II) ions from aqueous phosphate medium through a supported liquid membrane (SLM) consisting of a flat disc cellulose nitrate membrane immobilizing a Cyanex-302 in kerosene as carrier has been investigated. The transfer of Cd(II) ions has been studied as a function of the stirring rate, the concentration of the extractant, the stripping solution, and the phosphate concentration in the feed. The experimental results are evaluated in terms of the permeation rate, the permeability coefficient, and the enrichment factor. The difference in the kinetic behavior of Cd(II), Cu(II), and Zn(II) when mixed together is used to improve the selective separation of Cd(II) by the investigated SLM system. The assessment of the conditions for the use of this system in pollution control of the environment with heavy metals produced from phosphate wastewater streams is discussed.

INTRODUCTION

The fate of toxic pollutants in the environment represents a main risk to human health. Cadmium is one of the main toxic pollutants characterized by a long environmental persistence and biological "half-time" which accounts for its bioaccumulation in individuals. Phosphate fertilizers produced from phosphate industries are one of the main sources of cadmium in agricultural soils (1, 2). With the use of fertilizers in agriculture, and due to the concentration process, Cd appears in alimentary products in harmful levels. In addition, the wastewater produced from phosphate in-

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dustries and released into water streams is highly acidic and contaminated with heavy metals which have a severe environmental impact. The development of new techniques for the recovery of Cd from the drainage water of phosphate industrial plants or its reduction to acceptable limits is an increasing demand. Supported liquid membrane (SLM) techniques, in which the extraction and stripping operations are combined in a single process and where the extractant usage is reduced, are more advantageous than conventional solvent extraction processes. The transport of Cd and Zn through an SLM containing bathocuproine in dibenzyl ether has been studied (3, 4). Alkylthiophosphinic reagents from the Cyanex series (5) have been successfully used for the extraction and separation of many metals (6). The extraction of Cd by mono- and dithiophosphinic acids was studied by Cytec Inc. (7, 8), and the best results were reported for the monophosphinic acid extractant (Cyanex-302).

In the present work the extraction of Cd(II), Cu(II), and Zn(II) by Cyanex-302 in kerosene from aqueous phosphate medium was studied under equilibrium conditions to select the suitable stripping solution and extractant concentration. The validity of the SLM technology for removal of heavy metals from aqueous phosphate medium was then tested using a cellulose nitrate flat sheet supported membrane in a two-compartment cell. The effects of the different parameters affecting the transfer rate and the permeability coefficient of the investigated SLM for metals transport were investigated.

The results are elaborated to assess the optimum conditions for the use of supported membranes in the reduction of heavy metals concentration in phosphate wastewater streams to acceptable limits.

EXPERIMENTAL

Materials

The aqueous phase was a buffer solution of NaH_2PO_4 and H_3PO_4 (B.D.H.) in equal molar concentrations giving pH 2 and having a phosphate concentration comparable to that in a wastewater stream (0.097 M). The carrier used was an organic solution of different concentrations of Cyanex-302 in nonaromatic kerosene. Hydrochloric acid, used as stripping solution, was an analytical reagent grade (AR) product of Prolabo. The investigated metal solutions were prepared from Cd, Cu, or Zn nitrate standards diluted with the phosphate buffer.

SLM Cell

The cell used consisted of two compartments separated by the supported liquid membrane and joined together by four stainless steel supports passing through the two compartments at the upper and lower parts of the cell. Each compartment has a capacity of 60 mL and was provided with a mechanical stirrer and a small opening on the top cover of the compartment to allow the withdrawal of samples for analysis. Cellulose nitrate discs MPS (USA) of 47 mm diameter, 0.45 μm pore size, and 70% porosity were used as the support (Fig. 1).

Procedure

In equilibrium investigations, equal volumes of the aqueous phosphate solution containing the investigated metal and the organic Cyanex-302/kerosene solutions were contacted for an hour. The two phases were completely separated by centrifugation, the metal concentration was determined in the aqueous phase, and the percent extraction was calculated.

The stripping experiments were carried out by shaking equal volumes of the organic solution loaded with maximum extracted concentration of the investigated metal and aqueous solutions containing different molarities of H_2SO_4 or HCl. After centrifugation and phase separation the concentration of the stripped metal in the aqueous phase was determined and the percent stripped was calculated.

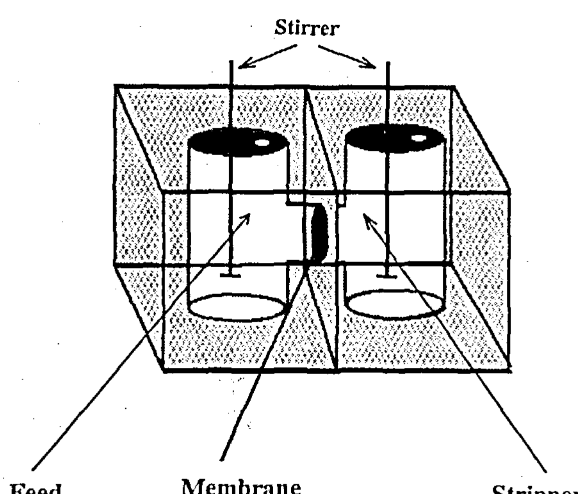

FIG. 1 Supported liquid membrane (SLM) cell.

In all cases the concentrations of Cd, Cu, and Zn were determined in the aqueous phase using a Dionex Ion chromatograph (DX 500).

In the mass transfer reactions through the SLM, the support was soaked in the Cyanex-302/kerosene solution for 24 hours, then put between two filter papers to remove excess solution. The membrane was fixed between the two half-cell. One compartment was filled with the feed solution and the other with the strip solution (50 mL each). In general, and unless otherwise stated, the stirring speed of the feed and stripping solutions was fixed at 1670 rpm while the used concentration of Cyanex-302, $[PO_4^{3-}]$ in the feed, and HCl in the strip were 1%, 0.097 M, and 4 M, respectively. The molar concentrations of Cd, Cu, and Zn were fixed at 4.45×10^{-4}, 4.1×10^{-4}, and 2.84×10^{-5} M. The experiment began by starting the stirring motors in the two compartments of the cell. At different time intervals, aliquots of 0.1 mL each were withdrawn from the feed and strip solutions, and the concentration of the metal in these aliquots was analyzed as mentioned before. The apparent rate constant (k) of Cd(II) transport was obtained from the slope of $\ln C/C_0$ vs t plot according to the relation

$$\ln C/C_0 = -kt$$

or

$$\log C/C_0 = -kt/2.303 \qquad (1)$$

where C_0 and C are the initial concentration of Cd in the feed and its concentration at time t, respectively.

Based on the value of k, the permeability coefficient (P) of the membrane was calculated according to the following equation (9):

$$P = kV/A\epsilon \qquad (2)$$

where V is the volume of the feed solution, A is the area of the SLM, and ϵ is the porosity of the support film.

RESULTS AND DISCUSSION

Equilibrium Investigations

Experiments on the extraction and stripping of divalent Cd, Cu, and Zn ions under equilibrium conditions were carried out before the transfer experiments through the SLM cell to select the suitable stripping solution and extractant concentrations. The effect of Cyanex-302 concentration on the extraction process was investigated by using different volumes of the extractant in kerosene giving 0.1, 0.5, 1, 5, 10, and 20% v/v. The results represented in Fig. 2 indicate that less than 1% Cyanex-302 in kerosene is enough for complete extraction of Cd or Cu. The extraction of 2.84 × 10^5 M Zn(II) increased from 12 to 88% with the increase of [Cyanex-302] from 0.1 to 20% (Fig. 2).

Investigations on the stripping by sulfuric or hydrochloric acid of the organic solutions loaded with Cd showed better results with the use of HCl. Investigations on the use of 0.1, 0.5, 1, 2, 3, 4, 5, and 6 M HCl showed that maximum stripping of Cd (87%) was reached with 3 M HCl (Fig. 3). In addition, investigations on the stripping of Zn and Cu by HCl in the same concentration range showed that maximum stripping of 93% for Zn was reached at 2–6 M while Cu was nearly not stripped by HCl in the investigated concentration range.

Mass Transfer Experiments through SLM Cell

Based on the equilibrium results, and selecting the best extractant and stripping conditions relative to Cd, two sets of kinetic experiments through the cell were carried out. In the first set of experiments the effect of stirring rate, [PO_4^{3-}], and [HCl] on the individual transfer of Cd through the SLM was separately studied. In the second set of experiments the optimum conditions derived from the individual transfer experiments of Cd were used to study its transfer in the presence of a mixture containing Cd, Cu, and Zn at three different concentrations of the extractant.

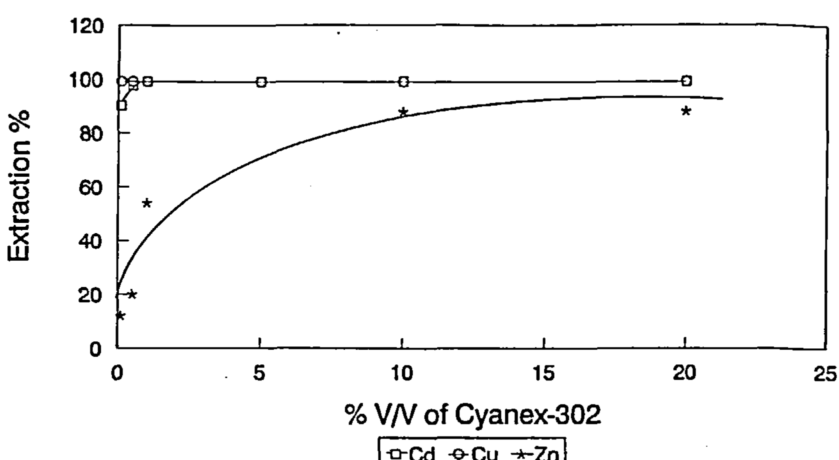

FIG. 2 Effect of Cyanex-302 concentration in kerosene on the extraction of Cd, Cu, or Zn from 0.097 M aqueous phosphate solution of pH 2.

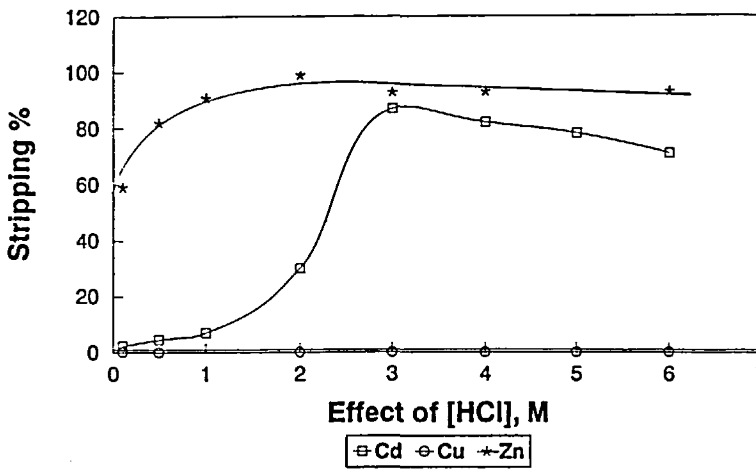

FIG. 3 Effect of HCl concentration on the stripping of Cd, Cu, or Zn.

(i) Individual Transfer of Cd through SLM

In supported liquid membranes the metal permeation process starts by diffusion of the metal from the feed solution to the external membrane layer followed by chemical reaction of the metal with the extractant at the external membrane interface. As the stirring speed is a hydrodynamic parameter, its effect on the diffusion process is more pronounced, i.e., as the stirring speed increases the diffusion process increases gradually until a region is reached where the diffusion remains constant with any further increase in the speed. Accordingly, the effect of stirring speed was studied by equally varying the stirring rate of the feed and strip solutions in the 390–1670 rpm range while fixing the other parameters. The plot of log C/C_0 versus t indicates that the increase in the stirring speed from 390 to 1250 rpm increases the diffusion process until a constant value is reached after 8×10^3 seconds at 1250 rpm or more (Fig. 4). In this region the diffusion contribution of the metal ions from the feed to the external layer of the membrane and through the aqueous film of the membrane surface to the strip solution is constant. Therefore a stirring speed of 1670 rpm was chosen for the investigations carried out on the effect of the other parameters on the permeation process.

The effect of phosphate concentration in the feed solution was studied by using two different phosphate concentrations, 0.013 and 0.097 M, while keeping the stirring speed at 1670 rpm as well as all other experimental

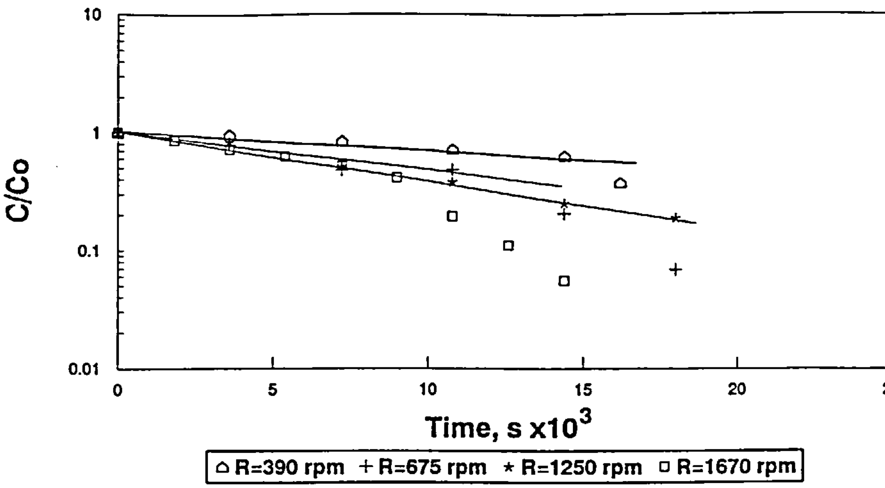

FIG. 4 Effect of stirring rate on the transfer of Cd through SLM containing 1% Cyanex-302 in kerosene.

conditions fixed as mentioned in the Experimental Section. The results of the log C/C_0 versus t relation shown in Fig. 5 indicate that an increase in phosphate concentration increases the transfer rate and the permeability coefficient of the SLM for Cd.

The increase in the concentration of the HCl stripping solution from 2 to 5 M, (Fig. 6) increased the transfer rate of Cd in the system when the experimental conditions were fixed as before.

The different values of the rate constant (k) and the permeability coefficient (P) at different stirring speeds, phosphate and hydrochloric acid concentrations evaluated from the slopes of the fitted straight lines according to Eqs. (1) and (2) are listed in Table 1.

(ii) Transfer of Cd in the Presence of Cu and Zn

In this set of experiments the transfer rate of Cd, Cu, and Zn from a feed solution containing a mixture of 4.45×10^{-4} M Cd, 4.1×10^{-4} M Cu, and 2.84×10^{-5} M Zn was studied at three different Cyanex-302 concentrations, namely 1, 10, and 20%. The results of the relative transfer of Cd in this mixture, represented as the log C/C_0 vs t relation, show a gradual increase in the transfer rate of Cd with the increase in extractant concentration (Fig. 7).

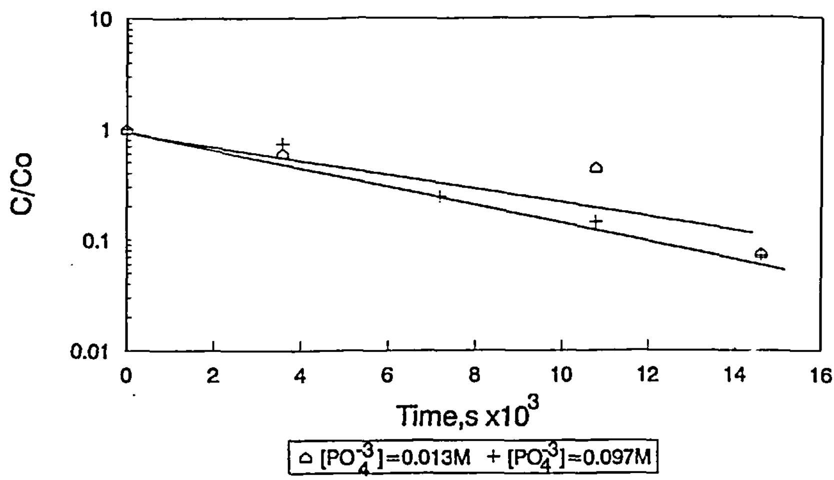

FIG. 5 Effect of phosphate concentration in the feed solution on the transfer of Cd through SLM containing 1% Cyanex-302 in kerosene.

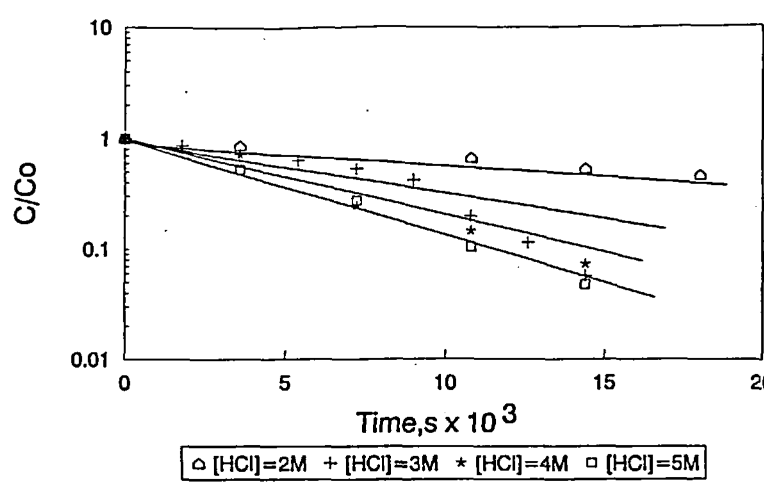

FIG. 6 Effect of HCl molarity in the stripping solution on the transfer of Cd through SLM containing 1% Cyanex-302 in kerosene.

TABLE 1
Effect of Stirring Rate, Phosphate, and Hydrochloric Acid Concentrations on the Permeation Rate Constant and Permeability Coefficient of Cd(II) Transfer through SLM Containing 1% Cyanex-302 in Kerosene

Parameter studied		Permeation rate constant (k), $s^{-1} \times 10^4$	Permeability coefficient (P), $cm \cdot s^{-1} \times 10^6$
Stirring rate, rpm	390	0.50	2.04
	675	1.01	4.20
	1250	1.12	4.63
	1670	1.12	4.63
$[PO_4^{3-}]$, M	0.013	1.53	6.30
	0.097	1.86	7.67
[HCl], M	2	0.42	1.73
	3	0.84	3.46
	4	1.53	6.30
	5	1.83	7.54

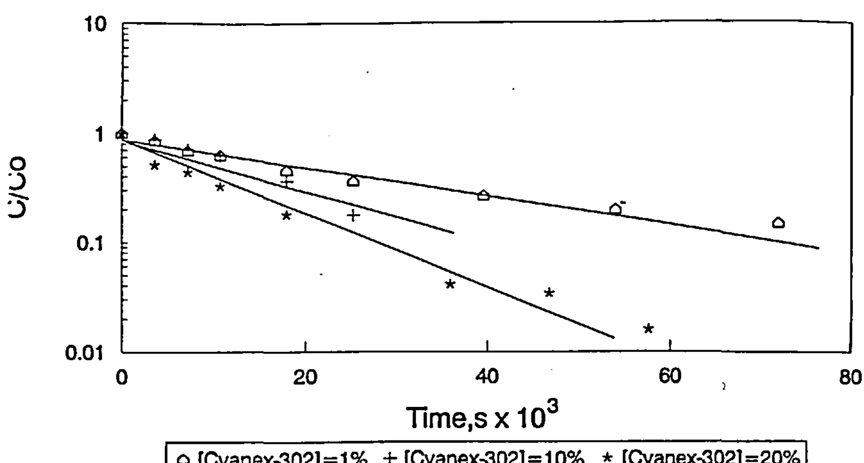

FIG. 7 Effect of Cyanex-302 concentration on the transfer of Cd through SLM in the presence of Cu and Zn in aqueous phosphate medium of pH 2.

One of the most common criteria used to evaluate a particular SLM system is "the enrichment factor" (Y) which is defined as the ratio of the concentration of the species in the stripping solution [S_s] to its initial concentration in the feed solution [S_f] (8):

$$Y = [S_s]/[S_f] \tag{3}$$

The enrichment factors of Cd in the present system evaluated at different time intervals in the three Cyanex-302 concentrations studied are given in Table 2. The tabulated data show that the enrichment factor increases with contact time within the same experiment and increases in general with an increase in the extractant concentration. An enrichment factor (Y) of about 4 was reached after 15, 7, and 5 hours in the cases of using 1, 10, and 20% Cyanex-302, respectively. A maximum enrichment of >60 times was reached for Cd after 16 hours when the membrane was impregnated with 20% Cyanex-302 in kerosene.

(iii) Transfer of Cu in the Presence of Cd and Zn

The results for the transfer of Cu from the above feed containing Cd and Zn in the same concentrations as in Section (ii) and represented as a semilog relation between log C/C_o vs t indicate that the transfer rate of Cu increases with the increase in the extractant concentration in kerosene from 1 to 20% (Fig. 8). The enrichment factor Y of Cu evaluated at different contact times is given in Table 3. The tabulated data show that a maximum

TABLE 2
Enrichment Factor (Y) of Cd in the Presence of a Mixture Containing Cu and Zn in the Investigated SLM at Different Cyanex-302 Concentrations

	$Y = [Cd_s]/Cd_f]$		
Time, s × 10^{-3}	[Cyanex-302] = 1%	[Cyanex-302] = 10%	[Cyanex-302] = 20%
3.6	0.14	0.13	0.42
7.2	0.46	0.46	1.20
10.8	0.73	0.74	1.62
18.0	1.25	1.93	3.94
25.2	1.80	4.75	
36.0			21.65
39.6	2.84	>17	
46.8			23.98
54.0	4.05	>18	
57.6			61.53
72.0	5.44	>18	>61

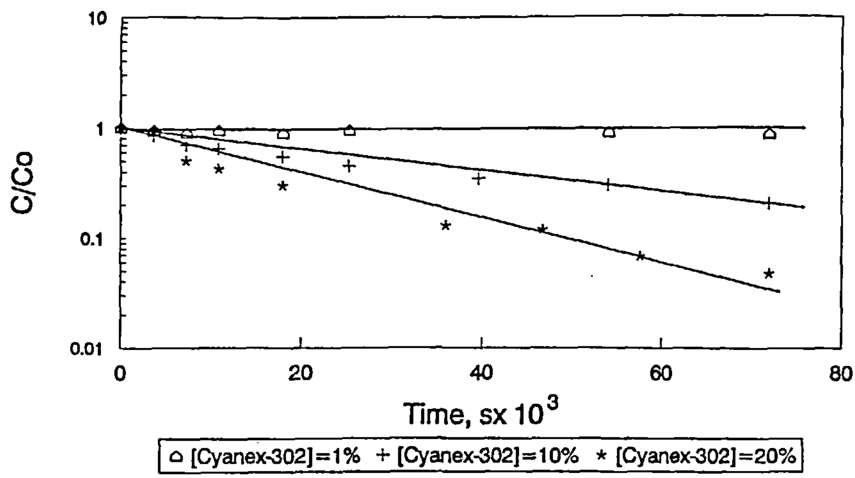

FIG. 8 Effect of Cyanex-302 on the transfer of Cu through SLM in the presence of Cd and Zn in aqueous phosphate medium of pH 2.

enrichment of 18 times could be reached after 20 hours when the membrane is impregnated with 20% Cyanex-302 in kerosene.

Although batch experiments under equilibrium conditions indicated that about 90% of Zn(II) is extracted by 20% Cyanex-302 in kerosene and

TABLE 3
Enrichment Factor (Y) of Cu in the Presence of a Mixture Containing Cd and Zn in the Investigated SLM at Different Cyanex-302 Concentrations

	$Y = [Cu_s]/Cu_f]$		
Time, s × 10^{-3}	[Cyanex-302] = 1%	[Cyanex-302] = 10%	[Cyanex-302] = 20%
3.6	0.053	0.1777	0.0999
7.2	0.111	0.286	0.751
10.8	0.105	0.615	1.216
18.0	0.111	0.909	1.898
25.2	0.105	1.333	
36.0			6.543
39.6	0.118	1.999	
46.8			5.849
54.0	0.111	2.333	
57.6			12.282
72.0	0.118	3.501	17.701

TABLE 4
Selectivity of Cd–Cu Separation (S) in the Used SLM at Different Cyanex-302 Concentrations

[Cyanex-302], %	$S = Y_{Cd}/Y_{Cu}$
1	17.1
10	3.6
20	2.7

93% of the extracted species could be stripped by 2–4 M HCl, kinetic experiments for a period of 20 hours in the investigated SLM system when the Cyanex-302 concentration was 1, 10, or 20% did not show any transfer of the Zn(II) ions.

According to Cox et al. (11), the reduced interfacial area in SLM operation can affect the nature of the metal–extractant interactions which indicates that the results of the liquid–liquid extraction may not be directly transferable to SLM operations. This could explain the discrepancy between the results of the equilibrium and those of the permeation experiments in the present work. Recently, Eschrafizadeh et al. (12) observed a difference in behavior between liquid–liquid extraction and SLM operation for Rh(III).

Selectivity of the SLM System

The difference in the kinetic behavior of Cd and Cu in the investigated system could be used to favor selectivity in the investigated system for the removal of Cd in presence of Cu. As the selectivity of one ion over the other is defined as the ratio of their respective enrichment factors (8), the selectivity of Cd–Cu separation evaluated from the ratio of their enrichment factors calculated after a fixed time of 7 hours decreases from 17.1 to 2.7 with an increase in Cyanex-302 concentration in the SLM from 1 to 20% (Table 4). However, the use of high extractant concentration is favored in cases where complete removal of Cd is more important than the selectivity of Cd–Cu separation. The use of 10% or more of Cyanex-302 could completely remove 4.45×10^{-4} M Cd after 11 hours from aqueous 0.097 M phosphate solution.

CONCLUSIONS

- The individual transfer experiments of Cd through a cellulose nitrate membrane impregnated with Cyanex-302 in kerosene increased with an increase in stirring rate, phosphate concentration in the feed, and molarity of HCl used as the stripping solution.

- The transfer experiments of Cd in the presence of a mixture containing Cu and Zn showed that Cd and Cu could be extracted by Cyanex-302. The transfer rate increased with an increase in Cyanex-302 concentration from 1 to 20%.
- In the investigated SLM system the extracted Cu could be stripped by 4 M HCl which did not strip the extracted Cu in batch experiments.
- Although Zn was highly extracted by 20% Cyanex-302 and stripped by 4 M HCl in batch experiments, mass transfer experiments through SLM did not show any transfer of Zn ions over a period of 20 hours.
- The investigated SLM system could be used for complete removal of 4.45×10^{-4} Cd from an aqueous phosphate medium of pH 2. In addition, the present system is selective for Cd–Cu separation from aqueous phosphate medium, and this selectivity increases from 2.7 to 17.1 by decreasing the extractant concentration from 20 to 1%.

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