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Polymer inclusion membranes as a new tool for Zn speciation: influence of the membrane composition in diffusional fluxes

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Abstract

In this work we evaluate different polymer inclusion membranes (PIMs) based on cellulose triacetate (CTA) as polymer, to be applied for Zn speciation measurements in waters. Different extractants, for example D2EHPA, an ionic liquid Cyphos IL 104, or a macrocycle Kryptofix 22DD, have been tested as carriers. Important parameters such as preconcentration and membrane stability were considered to determine the optimal membrane composition for Zn transport. Diffusional fluxes were measured and the correlation with free metal concentration was evaluated. The influence of the presence of EDTA in the water sample has also been studied as a mean to get information about speciation of Zn.

Keywords: zinc, polymer inclusion membranes, speciation

1. Introduction

Determination of free metal and labile metal concentration in river waters is of paramount importance in environmental studies. Several techniques have been developed for that purpose such as ion-selective electrodes, absence of gradients and Nerstian equilibrium stripping (AGNES), diffusive gradients in thin-films (DGT) and permeation liquid membranes (PLM). In PLMs a solid support is impregnated with an organic solution containing an extractant. The membrane is placed between two aqueous phases, the test sample and the strip (or acceptor solution). Under specific working conditions, the initial flux under steady-state regime is proportional to the free metal in the source solution (Buffle *et al*. 2000). Consequently, flux measurements afford to obtain information about metal speciation.

Stability is one of the most important factors limiting the use of PLM. Thus, a new type of functionalized membranes has emerged, called polymer inclusion membranes (PIMs) (Almeida *et al*. 2012). PIMs are made of a polymer, responsible of the mechanical strength, a plasticizer and an extractant responsible of the transport of the selected species. PIMs containing an organic derivative of the phosphoric acid (di-2-ethylhexyl phosphoric acid, D2EHPA) have been incorporated in a passive sampling device for Zn determination in waters (Almeida *et al*. 2014). Our group has also been involved in the preparation of a PIM based device for availability measurements of Zn in hydroponic solution. The technique has been compared with AGNES, DGT and ASV (anodic stripping voltammetry) measurements and good correlation was obtained.

Since membrane composition is a crucial issue that should be optimized to allow the desired stability and suitable conditions for speciation measurements, we have prepared different PIMs containing an organic derivative of the phosphoric acid (D2EHPA), an ionic liquid Cyphos IL 104, or a macrocycle Kryptofix 22DD (Gramlich *et al*. 2012). Membranes have been tested, and the influence of different experimental parameters is discussed to apply the system to Zn speciation measurements in waters.

2. Experimental

2.1. Reagents and solution

All reagents and solvents used in this study were of analytical grade. Celullose triacetate (CTA), nitrophenyl octyl ether (NPOE), 2-(N-morpholino) ethanesulfonic acid (MES), and dodecanoic acid (lauric acid) were obtained from Fluka (Switzerland). Trichlormethane was purchased from Panreac (Spain). D2EHPA was provided by Sigma-Aldrich (USA) and Kryptofix® 22DD from Merck. Cyphos IL 104 phosphonium salt was kindly donated from Cytec. For the preparation of the synthetic water solution the following reagents were used: calcium chloride 6-hydrate ($CaCl_2 \cdot 6H_2O$), sodium bicarbonate ($NaHCO_3$) and sodium sulphate (Na_2SO_4); they were all purchased from Panreac (Spain). The synthetic water was prepared at the following concentration: 2 mM $NaHCO_3$, 0.25 mM Na_2SO_4, 0.75 mM $CaCl_2$. The organic ligands ethylenediaminetetraacetic acid (EDTA) and trans-1,2-diaminocyclohexane-N,N,N',N'-tetraacetic acid monohydrate (CDTA) were provided by Sigma-Aldrich (USA).

Calibration standards of Zn were prepared using the 1000 mg L^{-1} zinc stock solution for atomic spectroscopy (Sigma-Aldrich). The concentration range was, from 0.05 mg L^{-1} to 1 mg L^{-1} for synthetic water solution measurements and from 1 mg L^{-1} to 40 mg L^{-1} in 0.5 % nitric acid for receiving solution measurements.

Ultrapure water from a MilliQ Plus water purification system (Millipore Ibérica S.A., Spain) was used to prepare all solutions.

2.2 Instrument and apparatus

A sequential inductively coupled plasma atomic emission spectrometer (Liberty RL, Varian, Mulgrave, Vic., Australia) was used to determine the total concentration of

Zn (λ=213.81 nm) in aqueous solutions. The pH values of the water samples were determined with a Crison Model GLP 22 pH meter.

2.3 Membrane preparation

PIMs were prepared using the following procedure: 200 mg of CTA were dissolved in 20 mL of trichloromethane and maintained under stirring for 5 hours. Afterwards, the desired amount of plasticizer was added, followed by 1 more hour stirring. Later, the appropriate amount of carrier: D2EHPA, Cyphos IL 104 or a mixture 22DD/lauric acid (mole ratio 1:1) was added to the mixture and stirred for 1 hour in order to obtain the final membrane compositions as shown in Table 1. Finally, the resulting solution was poured into a 9.0 cm diameter flat bottom glass petri dish, which was set horizontally and covered loosely. The organic solvent was allowed to evaporate over 24 h at room temperature, and the resulting film was afterward carefully peeled off from the bottom of the petri dish.

Table 1. Composition of different PIMs tested

PIM	Composition (weight fraction in %)
M1	55% CTA+45% D2EHPA
M2	70% CTA+30% Cyphos
M3	76% CTA+18% 22DD+ 6% lauric acid
M4	50% CTA+30% D2EHPA+20% NPOE
M5	50% CTA+50% Cyphos
M6	50% CTA+30% Cyphos+20% NPOE

2.4 Measurement of diffusional fluxes

The device designed (PIM device) consists of a glass tube with two openings, one at the top (0.9-cm diameter) and another one at the bottom (1.8-cm diameter). The PIM was placed at the bottom opening and fixed with a screw cap specially designed to expose the maximum membrane area to the sample solution (1.55 cm^2). The opening at the top was closed with a standard screw cap and was used to fill the device with the appropriate receiving solution (2.5 mL). To carry out the experiments using this device, 650 or 250 mL of synthetic water solution with Zn (II) added were poured into a glass beaker placed on a magnetic stirrer. The PIM device was immersed 1 cm in the sample solution in a vertical position under stirring conditions. After a predetermined contact time, the device was removed from the solution and Zn concentration in both phases, pH and membrane weight were measured.

The preconcentration factor, F(t), was measured as in eq. (1):

$$F(t) = \frac{[Zn]_t}{[Zn]_o} \qquad \text{(eq. 1)}$$

where $[Zn]_t$ is the concentration measured in the receiving solution after the fixed exposure time t, and $[Zn]_o$ is the initial Zn concentration in the synthetic water sample.

Diffusional flux, J_{PIM}, was calculated as shown in eq. (2), where n is the number of mol of Zn accumulated in the receiving phase, t is the exposure time and A represents the membrane surface.

$$J_{PIM} = \frac{n}{(tA)} \qquad \text{(eq. 2)}$$

3. Results and discussion

In a previous work we have used a PIM based on PVC:D2EHPA to measure Zn availability in hydroponic media. The fluxes in PIMs measured under a dynamic regime have been compared with other techniques such as DGT and ASV. The comparison with AGNES concentration in the presence of different ligands (humic acids and EDTA) has shown good correlation, which means that PIM fluxes are mainly due to the free Zn in this particular medium. In view to extending the application of PIM for metal speciation in surface waters, we have carried out new investigations, using PIMs made of CTA and trying to improve preconcentration factors while reducing the exposure time.

Preliminary experiments were designed with different PIM composition and the PIM device was contacted with synthetic water for 6 h. The initial Zn added was 100 μg L^{-1} and the measured pH was 8.3. Also, two different stripping phase composition were evaluated, 0.01 M HNO_3 and 0.5 mM CDTA. The obtained results have been collected in Table 2. It can be seen that the different systems allow Zn transport but preconcentration factors around 1 were obtained in most of the cases. Better results in terms of preconcentration factor were attained for M4. It is worth mentioning the positive effect of NPOE addition (comparing for example M1 and M4) which can be attributed to changes in membrane viscosity and solubility properties. Also, when 0.01 M HNO_3 is used as stripping phase better results were obtained compared to 0.5 mM CDTA, irrespectively of the membrane composition.

In relation to membrane stability, it is remarkable the extremely low values of mass loss obtained with PIMs containing the Cyphos IL 104 (M2 and M5). This issue is very important when long exposure times are envisaged.

Table 2. Results obtained for different PIMs after 6 h exposure time. [Zn]total = 100 μg L^{-1}.

PIM	Stripping	Mass loss	F(t)
M1	HNO_3	14%	3.5
	CDTA	14%	1
M2	HNO_3	2%	1.5
	CDTA	1%	0.6
M3	HNO_3	15%	0.5
	CDTA	11%	0.8
M4	HNO_3	13%	10
	CDTA	14%	3.7
M5	HNO_3	2%	3.8
	CDTA	3%	1.5

Taking into account these results we decided to continue our investigation with membrane M4, and also, a new membrane containing Cyphos IL 104 was prepared but with NPOE added in the membrane formulation (M6). Moreover, to avoid undesirable precipitation reactions, further experiments were undertaken in synthetic water buffered with MES (pH 6.3). Fluxes were measured at different metal concentration and the deployment time was 24 h. The results obtained are depicted in Table 3. We observed that the flux increased as the total metal concentration increases from 0.1 to 2.2 mg L^{-1}.

Table 3. Diffusional fluxes measured for M4 and M6 at different total metal concentration. Conditions: sample volume 250 mL, stripping 0.01 M HNO_3 and exposure time 24 h.

Name	**[Zn]total µg L^{-1}**	**Mass loss**	**J_{PIM} nmol cm^{-2} h^{-1}**
M4	98	16%	2.2
	512	13%	7.1
	1970	17%	29.1
M6	1970	3.5%	34.8

It can also be seen in Table 3 that M6 with Cyphos IL 104 and NPOE give higher flux than M4. The positive role of the plasticizer is again emphasised. Moreover, the mass loss of M6 remains very low in concordance with the results shown in Table 2.

According to the theory developed for PLM, the flux measured under dynamic regime is proportional to the free concentration of the metal or free metal plus labile complexes. For that, the diffusional fluxes obtained at different total metal concentration were plotted against the free metal obtained with Visual-MINTEQ. As can be seen in Fig 1, good correlation is obtained (R^2=0.9984).

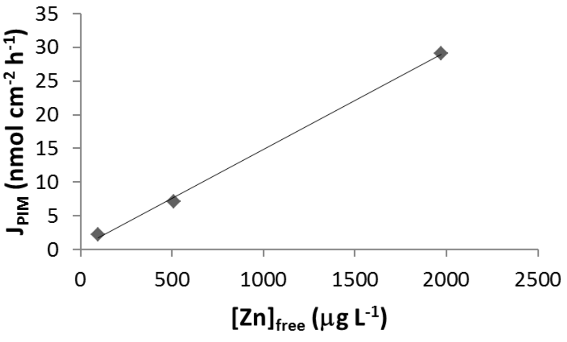

Figure 1. Fluxes measured with M4 for different Zn concentration in synthetic waters.

We have also tested the influence of the presence of organic ligands in fluxes measured with PIM, to check the speciation ability of the technique. For this purpose EDTA was added to the synthetic water at a concentration of 20 µM. EDTA forms with Zn(II) stable complexes and its lability has been studied by AGNES, DGT and PLM techniques (Gramlich *et al*. 2014). Table 4 shows that in the presence of EDTA the flux is reduced from 29.1 to 14.9 nmol cm^{-2} h^{-1}. This decrease correlates with free zinc concentration also calculated using Visual-MINTEQ. The effect of other ligands forming complexes with Zn(II) is currently under investigation.

Table 4. Effect of the presence of EDTA in PIM fluxes. Experimental conditions: sample volume 250 mL, stripping 0.01 M HNO_3 and exposure time 24 h.

PIM	**[Zn]total µg L^{-1}**	**[Zn]free µg L^{-1}**	**J_{PIM} nmol cm^{-2} h^{-1}**
M4	1970	1869	29.1
	1970	628,3	14.9

4. Conclusions

We have prepared and tested different polymer inclusion membranes for Zn speciation measurements. PIMs containing either D2EHPA or the liquid ionic Cyphos IL 104 have shown higher fluxes when NPOE is incorporated in their formulations. The effect of different metal concentrations as well as the addition of EDTA has been studied, and measured fluxes agree with the free metal in the aqueous solution.

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