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Removal-concentration of pollutant metal-ions by water-soluble polymers in conjunction with double emulsion systems: A new hybrid method of membrane-based separation

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ABSTRACT

The effect of reverse emulsion globules stabilized by non-ionic surfactants on metal-ion retention properties of poly(acrylic acid) was studied by continuous enrichment of external aqueous phase in a dead-end filtration system. Double emulsion systems were made by two-steps method confining an acid solution at pH 1.0 in the inside of reverse emulsion. Continuous phase of second dispersion stage was a poly(acrylic acid) solution at pH 6.0. By application of pressure, a divalent metal-ion stream, Cu^{2+} and Cd^{2+} at pH 6.0 was continuously added from a reservoir. Results indicate that it is possible to increase the maximum retention capacity of retention system above maximum retention capacity of poly(acrylic acid). The increase in the metal-ion retention can be explained via the macromolecular transport of metal-ions through oil phase of double emulsion. In general, a sequence given by linking of metal-ions by the polymer, adsorption of polymer on liquid–liquid interface, transporting of metal-ion and functional group regeneration is suggested and associated to the increases of overall system retention. Combination of water-soluble polymer and double emulsion systems appears as a novel alternative to remove and concentrate pollutant metal-ions in aqueous solution.

1. Introduction

A reverse emulsion globule (REG) is the result of the dispersion of primary emulsion (water-in-oil or *w*/*o*) in a continuous aqueous phase in presence of some surfactant agent or mixture of these; this kind of systems are denominated double emulsions (DEMs) and these can be water/oil/water (*w*/*o*/*w*), or oil/water/oil (*o*/*w*/*o*). DEMs have promising applications in the food, cosmetic and pharmaceutical industries, also in other fields like agriculture in the production of multicompartment microspheres for the release of bioactive substances or fertilizers [1–3]. DESs are used in the recovery of inorganic and organic species from aqueous effluents in separation-concentration processes known as extraction by emulsion liquid membranes or surfactant liquid membranes [4–7].

Usually DESs are prepared by a two-steps emulsification process using two surfactants; a hydrophobic designed to stabilize the interface of the internal emulsion (emulsion type *w*/*o*) and a hydrophilic one to stabilize the external interface of REGs (emulsion type *w*/*o*/*w*) [1,2].

In general, DEMs are compartmented systems formed by an internal aqueous phase (w_{int}) separated of external aqueous phase (w_{ext}) by an oil phase. Composition of w_{int} can be determined in the emulsion preparation and modified by transport process though oil phase which acts as liquid membrane between the aqueous phases; whereas w_{ext} can be established during preparation and this can be easily modified by addition of some component (solute, solvent or particles) [3].

In the metal-ion separation, by DEMs type *w*/*o*/*w*, are commonly used low molecular weight species as carriers of metal-ions from w_{ext} to w_{int} by coupled transport mechanism. In this mechanism, driven force is the acidity gradient generated as consequence of acid solution confined in the interior of REG [4–8].

On the other hand, metal-ion retention properties of water-soluble polymers (WSPs) have been studied by diafiltration experiments in order to determine retention capacity of polymer as function of pH, ionic strength or in presence of interfering species. The most common investigated ligands present in these polymers are: amines, carboxylic acids, amides, alcohols, amino acids, pyridines, thioureas, imines, etc. [9,10].

Polymers with carboxylic acid groups acquires an important role in the study of environmental systems in areas as soil science where poly(acrylic acid) (PAA) is commonly used as model to describe the humic substances; besides, PAA and related polymers (polymer and copolymer with carboxylic acid groups) have a wide varied of technological applications [11,12]. In the context of me-

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Abbreviations

α	Dissociation grade (dimensionless)
ΔC_p	Concentration of permeate for each collected fraction (mmol/L)
r_0	Added amount of metal-ion (mmol/L)
r_g	Radius of gyration (m)
r_{max}	Maximum polymer-metal ratio (dimensionless)
V_c	Volume of solution in the filtration cell (L)
V_p	Total volume of permeate (L)

Acronyms

CMC	Critical micelar concentration
CMR	Maximum retention capacity
DEM	Double emulsion
HLB	Hydrophilic-lipophilic balance
o/w/o	Oil-in-water-in-oil emulsion
LPR	Liquid-phase polymer-based retention
PAA	Poly(acrylic acid)
PEG	Polyethylene glycol
PEUF	Polymer enhanced ultrafiltration
REG	Reverse emulsion globule
w_{ext}	External aqueous phase
w_{int}	Internal aqueous phase
w/o	Water-in-oil emulsion
w/o/w	Water-in-oil-in-water emulsion

tal-ion removal, the interaction of carboxylate groups with cations permits to retain, concentrate and recover heavy metal-ions and other ionic species in polymer-based separation processes. Examples of these processes are: liquid-phase polymer-based retention (LPR, this technique is also named polymer-enhanced ultrafiltration, PEUF), resins, filtration by polymeric membrane, and others.

In general, metal-ion retention by PAA decreases as pH is decreased and ionic strength is increased [9,10]. Besides, retention decreases as polymer-metal ratio is increased since added number of metal-ions are in excess with respect to number of "active" functional groups on polymer chain. As result of polymer-metal interaction, polymer chains in solution experiment conformational changes and a marked decreasing of the surface charge. These changes have been associated to the polymer adsorption from aqueous solution under a regimen of high metal-ion concentration [13]. In researches reported so far only two retainer elements have been considered by LPR technique and filtration by membrane: (1) membrane and (2) macromolecular species as linear WSP, micelles or polymeric dendrimers [9,13–15].

It is clear that if REGs are added to inside of filtration cell then these can be considered additional retainer elements in the retention process which additionally produce the compartmentation of solution. In consequence, a DEM can be produced whereas system is stirred to low stirring rate in order to avoid the rupture of REGs. Whether a WSP is added to the w_{ext} of the DEM a new system is formed. For the specific case of PAA, this kind of the system which combines REG and soluble PAA can be denoted as *w/o*/PAA.

On the other hand, to achieve the stabilization of REGs a hydrophilic surfactant (a surfactant with hydrophilic–lipophilic balance, HLB, larger than 15.0) must be added and distributed mainly in the external interphase [1,2]. In a *w/o*/PAA, if hydrophilic surfactant is an anionic surfactant, then PAA is not absorbed on the REGs as result of electrostatic repulsion between carboxylate groups of PAA and negative electrostatic charges of surfactant molecules. However, in these circumstances, surfactant molecules can strongly interact and retain positively charged species competing with polymer during retention experiment. If a cationic hydrophilic surfactant is used then PAA can be adsorbed on the emulsion and, negative effects on retention properties and stability REG are expected. And if a non-ionic hydrophilic surfactant is used then REGs could be stabilized without to affect significantly the retention properties of PAA. Many *w/o*/polymer systems have been studied and reported [16–18], but in the vast majority of cases, these are surfactant polymers which have been added only in order to increase the stability of DEM.

For weak polyelectrolytes as PAA, the degree of dissociation (α) depends on the pH. Thus, for polyacids, at low pH whether $\alpha = 0$ then the situation is similar to that for the adsorption of neutral polymers. In the limit of high pH, where $\alpha = 1$ then adsorption behavior is like that of strong polyelectrolytes. For intermediate values of pH, the situation is complex because α might be a function of the distance from the surface [18].

In a *w/o*/PAA system, if metal-ion concentration is increased continuously then it is expected that PAA achieves its maximum retention capacity as added metal-ion concentration (r_0) is increased as well as also it is expected that polymer molecules in solution decrease their surface charge density by elimination of net charge and consequently the electrostatic repulsion between polymer and emulsion globules should be also decreased.

As it was previously indicated, divalent metal-ion retention properties of PAA have been studied by resins (experiments in solid phase) [19,20] and filtration experiments assisted by WSPs (experiments in liquid phase) [9,10]. Besides, stabilization of DEMs by hydrophobically modified PAA and the adsorption of PAA in the liquid–liquid interface also have been reported [21,22]. However, from the literature review carried out by us, we have not information of reported studies on the effect of REGs on retention properties of WSPs neither its simultaneous application to remove pollutant metal-ions. In consequence, in this work we studied the effect of REGs stabilized by non-ionic surfactants on divalent metal-ion retention properties of PAA in presence of a pH gradient in a *w/o*/PAA system during continuous diafiltration experiments in order to determine its possible application to remove and concentrate pollutant metal-ions by membrane-based processes.

2. Material and methods

2.1. Reagents

Decane (Sigma-Aldrich) was used as oil phase of emulsion, sorbitan monooleate (span 80, Sigma-Aldrich) and polyoxyethylene sorbitan monooleate (tween 80, Sigma-Aldrich) were used to stabilize the reverse emulsion and double emulsion, respectively. Additional information of surfactants is shown in the Table 1. Nitric acid solution at 70% (HNO_3, Aldrich) was used as disperse phase in the reverse emulsion. Poly(acrylic acid) (PAA, solution at 25%, Sigma-Aldrich, 250 kDa) was used as WSP and, copper and cadmium nitrates (analytical grade, Merck) were used to prepare metal-ion solutions.

Table 1
Hydrophobic and hydrophilic surfactants data. CMC = Critical micelar concentration.

Surfactant	Molecular weight (g/mol)	CMC (mg/L)	HLB	Ref.
Span 80	428	0.135	4.4 ± 0.1	[23]
Tween 80	1308	10.0	15.5 ± 0.5	[24]