

Polymer–metal complexes for environmental protection. Chemoremediation in the aqueous homogeneous phase*

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Abstract: The concept of chemoremediation in the liquid homogeneous phase using polymer reagents as a green technology is presented and outlined. It is based on the retention of polymer–metal complexes in aqueous solution according to their molecular size by using membrane filtration. The fundamentals of the metal ion interaction with respect to enrichment and separation procedures are discussed, and the role of polymer–metal complexes is assessed. The formation conditions of these polymer–metal complexes as well as major factors influencing the process are investigated. In addition, recent developments using this method are evaluated, and several application examples are highlighted.

INTRODUCTION

Removal, separation, and enrichment of hazardous metal ions in aqueous solutions play an important role for environmental remediation of municipal and industrial wastewater. Among many separation techniques, membrane separation is an efficient and widely applied separation process that is comparable to other separation techniques in terms of technical and economical feasibility. Many commercial separation problems are being solved by membrane processes, which can be successfully used to treat industrial effluents. Liquid–liquid extraction, sorption, precipitation, ion exchange, and others are classic preconcentration and separation methods for elements in geological, biological, environmental, and industrial fluids.

Heterogeneous methods have been used for the separation of inorganic ions contained in natural waters, industrial fluids, or dissolved solid materials. In contrast to homogeneous reactions, these two-phase distributions or heterogeneous reactions with diffusion-controlled processes have disadvantages, such as long contact times. Two-phase systems can be avoided by using separation methods based on pressure-driven membrane processes in the aqueous homogeneous phase.

The efficient and selective separation of inorganic ions can be achieved by using water-soluble, polymeric reagents in combination with membrane filtration [1]. This technique, developed in our laboratory, termed liquid-phase polymer-based retention (LPR), is based on the separation of ions bound to water-soluble polymers with chelating groups (polychelators) from noncomplexed ions [2–4]. It has found application in the recovery of metals from diluted solutions both on an analytical and technical scale.

*Lecture presented at the International Symposium on Green Chemistry, Delhi, India, 10–13 January 2001. Other presentations are published in this issue, pp. 77–203.

FUNDAMENTALS

Membrane separation processes are based on semipermeable membranes, which separate certain solution components by passing them through the membrane, forming the permeate or filtrate, and retaining others, forming the retentate or concentrate. The most important parameter of membrane separation is the retention R of a component. The retention of a metal ion (R_Y) is defined in eq. 1:

$$R_Y = 1 - (c_{Y,P} \cdot c_{Y,F}^{-1}), \quad (1)$$

where $c_{Y,P}$ and $c_{Y,F}$ are the concentrations of the target metal ion in the permeate and in the feed solution.

When the target metal ion (Y) and nontarget metal ions (Z) are separated through the membrane, the separation factor ($S_{Y/Z}$) can be expressed as:

$$S_{Y/Z} = (c_{Y,P} \cdot c_{Y,F}^{-1}) (c_{Z,P} \cdot c_{Z,F}^{-1})^{-1}, \quad (2)$$

where $c_{Z,P}$ and $c_{Z,F}$ are the concentrations of the nontarget metal ions in the permeate and in the feed solution; R_Z is the retention of Z .

If Z passes through the membrane freely ($R_Z = 0$), the efficiency of the separation can be characterized by the retention of the target metal ion:

$$S_{Y/Z} = 1 - R_Y \quad (3)$$

The retention of metal ions by membranes is influenced by many parameters, depending on their type, solution composition, pH, temperature, membrane material, pore size, hydrodynamics, etc. However, mostly the size of a dissolved species (hydrated ions, hydrated molecules, colloidal particles, etc.) is essential for the retention by membranes.

LIQUID-PHASE RETENTION

The general principle of liquid-phase retention is to add water-soluble polymeric binding agents to a multicomponent solution, so that these agents will form macromolecular compounds with the target ions only. Thus, the size of the metal ion would be increased significantly whereas the size of the nontarget species would remain unchanged. If such a solution is then passed through an ultrafiltration membrane, the membrane would separate the target metal ions from the nontarget species.

Process

In the liquid-phase polymer-based retention (LPR) process, the membrane represents a barrier that has to retain all ions bound to the polymer agents and to allow to permeate all unbound ions. Consequently, the membrane pore size, but not the material or its shape, is the most important feature. Nevertheless, the surface properties of the membrane material can influence the separation process, if an interaction between the soluble polymer and the membrane can occur.

The general function of the polymeric complexing agents in the LPR process is illustrated in Fig. 1. As shown there, several steps can be discerned when employing the LPR process:

- preparation of the polymer reagent from a monomeric precursor by polyreaction or by polymer-analogous functionalization from a preformed polymer;
- interaction with the metal ions in the homogenous phase (aqueous solution), predominantly based on complexation, with the formation of the interaction product with the target metal ions;
- separation of the polymer-metal complex from non-bound metal ions using membrane separation techniques; and
- cleavage and removal of the target metal ions yielding the polymer reagent.

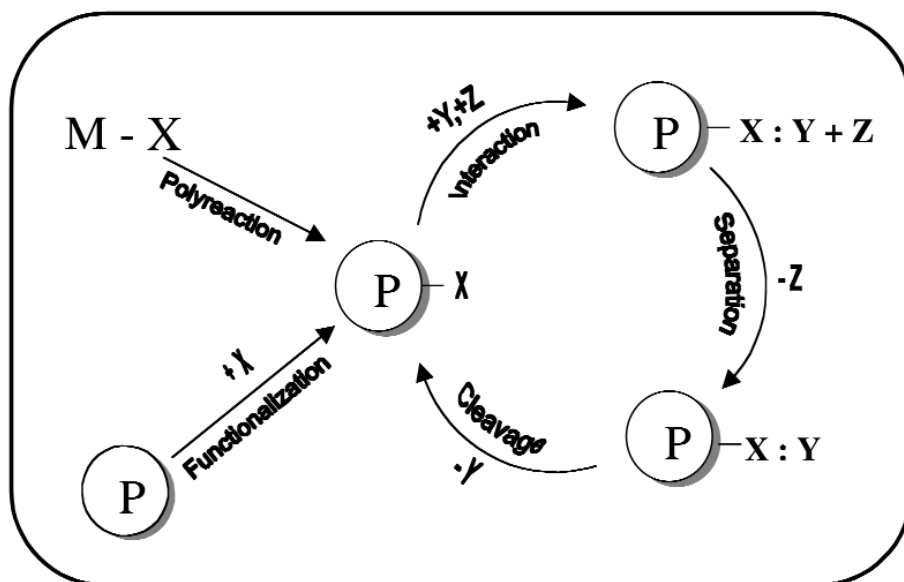


Fig. 1 Scheme for the liquid-phase polymer-based retention (LPR) processes. P = polymer, X = functional moiety, P–X = polymer ligand, Y = target metal ion, Z = nontarget metal ion, P–X:Y = polymer–metal complex.

Equipment

On a laboratory scale, conventional membrane filtration systems with stirred cells are used. A typical experimental set-up is depicted in Fig. 2. For large-scale applications, however, hollow-fiber systems with pumps have been shown to be more advantageous [5].

Mostly polysulfone, polyamide, or cellulose membranes with a molecular mass cut-off (MMCO) of 10 kg mol^{-1} in connection with polymeric reagents of molar masses in the range between 20 and 100 kg mol^{-1} are employed. Pressure differences are typically varying in the range from 0.1 to 1 MPa (ca. 15 to 150 psi). In our laboratory a standard pressure of 300 kPa is employed for stirred-cell systems. The experimental details have been described previously in detail [1–4,6].

Polymer reagents

The separation process will be successful, if the polymer reagents employed meet the following requirements [1,4]:

- high affinity towards the target metal ion,
- inactivity towards the nontarget metal ion,
- high molecular mass,
- possibility of regeneration,
- chemical and mechanical stability,
- low toxicity, and
- low cost.

Three main groups of polymer reagents can be classified:

- basic polymers, such as poly(ethylenimine), poly(vinylamine), poly(allylamine), and other amino or imino group-containing polymers;

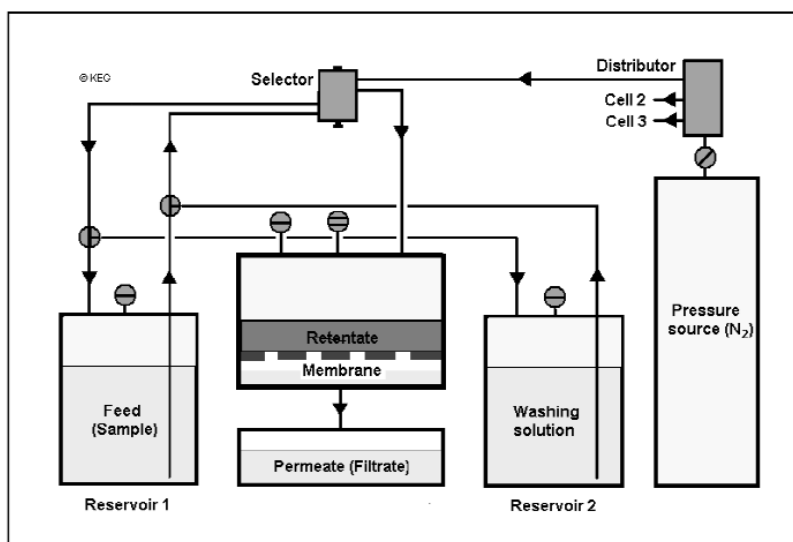


Fig. 2 Schematic representation of the experimental set-up for the liquid-phase polymer-based retention (LPR) method.

- neutral polymers, such as polyglycols, polyalcohols, polyethers, etc.; and
- acidic polymers, such as (poly(acrylic acid), poly(vinylsulfonic acid), poly(styrene-sulfonic acid), and others.

The soluble, non-crosslinked, hydrophilic polymers with complex-forming moieties, capable to bind, enrich, and separate metal ions from aqueous solutions, were termed “polychelators” [2–4].

A variety of polychelators have been prepared and investigated in conjunction with LPR. They include derivatives of poly(ethylenimine), poly(vinylamine), and polychelators based on polyurethanes, poly(vinyl alcohol), as well as different other copolymers [4,8,10–18]. Poly(ethylenimine) is one of the binding agents most commonly used and studied in the LPR process [3,4,7–9,19–21]. This basic polymer was applied to remove heavy metals from industrial wastes and natural waters.

The selectivity of the polychelators can be significantly enhanced by introducing special ligands [4,7,9,12–16]. The criteria for selecting the appropriate polymeric ligands, the binding conditions, and several factors influencing the separation of the target metal ions have been studied and discussed in detail [4,8,10]. Hydroxy-functional polymers based on aziridine such as poly[1-(2-hydroxyethyl) aziridine] containing hydroxyl groups in the side chain have been shown to be able to bind a number of metal ions [20].

Recent studies in our laboratory include the synthesis of environmentally degradable chelating polymers based on ethylenediaminetetraacetic acid (EDTA) and others [22,23]. Generally, the large number of the metal ions investigated include many transition metals, alkali and alkaline earth metals, and elements from the lanthanide and actinide series [3,4,8,10,17].

Interaction and profiles

Generally, low-molecular substances can be bound to macromolecules by all intermolecular forces, predominantly by ionic or complex bonds or the combination of both. Complex bonds are significantly more selective than ionic interactions. The formation of complexes with water-soluble polymers occurs

in the same manner as in the case of chelating resins [7]. For example, it is well known that resins containing amino and imino groups form stable complexes with copper, nickel, and other transition metals.

Evidently, a number of factors influence the interactions and binding conditions [4,5]:

- binding degree,
- pH value,
- solution composition, and
- synergism.

The interaction pattern of polymeric ligands with metal ions are documented in LPR profiles, which are plots of the retention R vs. the filtration factor Z .

The retention of metal ions in solution by polymeric reagents can be calculated as follows [3,4]:

$$R (\%) = c_r \cdot c_o^{-1} \cdot 100,$$

where c_r is the metal concentration in the retentate after a filtrate volume of V_f has been passed, and c_o is the initial metal concentration.

The filtration factor Z is defined as the ratio of the volume of filtrate V_f and the volume of cell solution V_o :

$$Z = V_f \cdot V_o^{-1}$$

Typical examples of retention profiles are shown in Fig. 3.

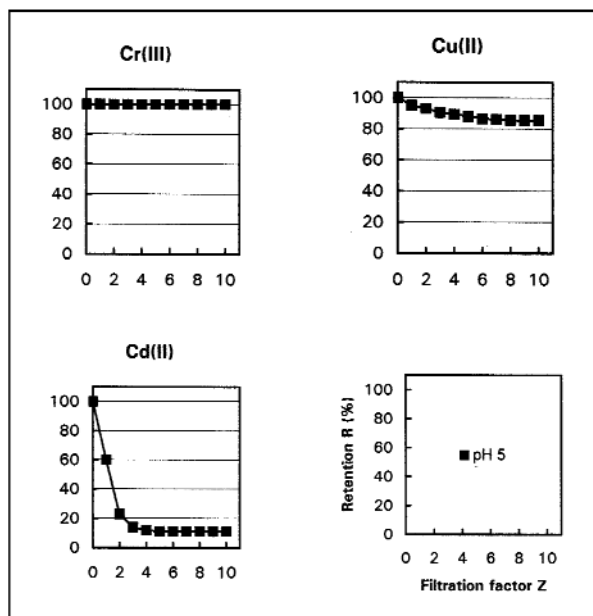


Fig. 3 Typical retention profiles for some metal ions obtained by using the liquid-phase polymer-based retention (LPR) method: 100% retention for Cr(III), 85% for Cu(II), and 10% for Cd(II) (1 wt% polymer solution, pH 5, $Z = 10$).

Polymer regeneration

The LPR process appears to be economically more feasible, if the polymer could be regenerated and re-used. Three major methods for regeneration of the polymeric agent are known:

Chemical regeneration

Protolysis. By changing the pH of the retentate, the polymer–metal complex bond is cleaved. The retentate is then membrane-filtered again. This time, only the polymer will be retained by the membrane, whereas the target metal ions will pass into the permeate.

Transcomplexation. Another method is the competitive binding process using an agent with a stronger binding affinity. In this case, a reagent with a higher stability constant for the target metal ions is used, e.g., ethylenediaminetetraacetic acid (EDTA) for some transition metals.

Redox reactions. In certain cases, redox reactions can be applied, when the metal ions can be reduced, thus facilitating the subsequent separation step. For example, hexavalent chromium can be reduced with sodium sulphide to Cr(III), which then precipitates as Cr(OH)₃, whereas the polymer remains in solution.

Electrochemical regeneration

The electrolysis of the retentate results in a deposition of the metal on an electrode, whereas the polymer reagent remains in the solution. No further separation of the polymer from metal ions is necessary, and the metals are recovered in a very pure form. However, electrochemical regeneration appears to be more energy-consuming than the chemical one.

Thermal regeneration

If the polymer–metal bond can be cleaved by heating the retentate, thermal regeneration is also an alternative. However, this method seems to be restricted to few cases.

APPLICATIONS

Major applications in the LPR separation research field are listed in Table 1.

Table 1. Major applications in liquid-phase retention technology.

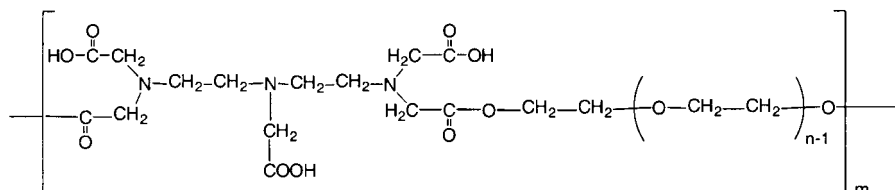
Application	Year	Reference
Water-soluble polymer-metal complexes	1980	<i>Pure Appl. Chem.</i> 52 , 1883
Liquid-phase Polymer-based Retention (LPR)	1985	<i>Nature</i> 315 , 313
Anion exchange in homogeneous liquid-phase	1988	<i>Naturwissenschaften</i> 75 , 198
First review on LPR	1988	<i>Sep. Purif. Methods</i> 17 , 105
Selective polymer ligands	1990	<i>Anal. Chim. Acta</i> 230 , 171
System design for analysis	1992	<i>Internat. Lab.</i> 17 , 47
Actinide separation	1993	<i>Chem. Tech.</i> 45 , 464
LPR for analysis	1994	<i>Pure Appl. Chem.</i> 66 , 631
Environmental applications	1996	<i>Env. Sci. Technol.</i> 30 , 725
Mathematical modeling	1996	<i>Macromol. Theor. Simul.</i> 5 , 357
Environmentally degradable polymers	1999	<i>Polym. Internat.</i> 48 , 909
Renewable resource-based polycondensates	2000	<i>Polym. Internat.</i> 49 , 1519

Preparative applications

Most of the applications to date are related to the removal of heavy metals from liquid wastes or spiked solutions. For example, metals such as copper, nickel, lead, chromium, mercury, and arsenic, among others, can be selectively removed from multi-component solutions of different origins such as electroplating wastewaters, mining and chemical effluents, and wastes from soil washing processes [5]. Also, metals were removed from natural waters, e.g., groundwater and seawater. It was demonstrated that the selectivity of the process is high, so that target transition metal ions can be separated from each other or from alkali and alkaline-earth metals ions, even if the latter are present in much higher concentrations.

Novel approaches include the employment of environmentally degradable polymers as functional reagents in conjunction with the liquid-phase separation procedure and also the general extension to environmentally relevant applications [5,22–24]. Thus, polymer reagents based on water-soluble polyesters with pendant carboxylic groups were synthesized by polycondensation of ethylenediaminetetraacetic acid (EDTA) dianhydride and diethylenetriaminepentaacetic acid (DTPA) dianhydride with poly(ethylene glycol)s of different chain-lengths [22].

The structure of the DTPA-polyester is given below:



Both experimental approaches, polycondensation using different solvents and in the melt were studied, and melt condensation was found to give higher yields of polyesters. The maximum complexing capacity of the functional polyesters was determined for copper in aqueous solution using the LPR technique and found to be 257 mg g^{-1} for the EDTA-polyester and 230 mg g^{-1} for the DTPA-based copolymer at $\text{pH} = 5$ [22].

Other polymers recently designed for LPR include the poly[(2-hydroxyethyl)-DL-aspartamide], synthesized by polyreaction of aspartic acid and subsequent polymer-analogous functionalization with ethanolamine [24]. The metal complexing properties of the polymer were studied for Cr(III), Fe(III), Co(II), Ni(II), Cu(II), Zn(II), Sr(II), Cd(II), and Pb(II) ions in aqueous solution. According to the retention profiles of LPR, Cr(III), Fe(III), Cu(II), and Pb(II) showed a strong interaction with this polymer under the conditions studied indicated by retention values of >85 at $\text{pH} 5$. In addition, general mathematical modeling studies were performed [25].

Analytical applications

The LPR technique allows a significant increase in the sensitivity and a considerable decrease in the time required for analytical determinations. A number of analytical and hyphenated techniques in conjunction with the LPR method have been developed [26–30]. Also, special membrane systems for this method have been designed and commercialized to enhance the performance in analytical applications [27].

Recently, a technique combining inductively coupled plasma spectrometry and LPR for the environmental monitoring and assessment of drinking water has been developed [29]. The determination of some trace elements has been made possible, and the analytical accuracy of other elements has been shown to be significantly enhanced.

CONCLUSION

Liquid-phase polymer-based retention (LPR) has been shown to be an effective and powerful technology for metal ion separation and enrichment in the homogeneous phase using the environmentally benign solvent water. Thus, this method can be an alternative for conventional chemoremediation methods.

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