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Water-Soluble Polymer-Metal Complexes for Liquid-Phase Retention Separation

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SUMMARY: The concept and the major features of the Liquid-Phase Polymer-Based Retention (LPR) separation are outlined. The fundamentals of the metal ion interaction with respect to enrichment and separation procedures are developed and the role of complex-forming polymeric agents is discussed. The scope, major advancements, and typical application examples based on metal complexes are highlighted.

Introduction

Metal ion complexation and separation in aqueous solutions play an important role for metal removal in municipal and industrial wastewater. Heterogeneous methods such as solvent extraction, sorption, ion-exchange, precipitation, and other methods have been used for the separation of inorganic ions contained in natural waters, industrial fluids, or dissolved solid materials. However, in contrast with homogeneous reactions, techniques based on a two-phase distribution or on heterogeneous reactions, frequently cause problems because diffusion-controlled processes must be used. Two-phase systems can be avoided by using separation methods based on pressure-driven membrane processes in the homogeneous aqueous phase.

Fundamentals

A semipermeable membrane is the main element of any membrane separation process. Certain solution components will pass through the membrane, forming the permeate or filtrate, whereas others will be retained by the membrane, forming the retentate or

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concentrate. The most important parameter of membrane separation is the retention R of a component. The retention of a metal ion (R_M) is defined in Eq. 1:

$$R_M = 1 - (c_{M,P} \bullet c_{M,F}^{-1}) \quad (1)$$

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

When the target metal ion (M) and non-target metal ions (N) are separated through the membrane, the separation factor ($S_{M/N}$) can be expressed as:

$$S_{M/N} = (c_{M,P} \bullet c_{M,F}^{-1}) \bullet (c_{N,P} \bullet c_{N,F}^{-1})^{-1} \quad (2)$$

where $c_{N,P}$ and $c_{N,F}$ are the concentrations of the non-target metal ions in the permeate and in the feed solution; R_N is the retention of N.

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

$$S_{M/N} = 1 - R_M \quad (3)$$

Many parameters influence the retention of metal ions by membranes, depending on their type, solution composition, pH, temperature, membrane material, pore size, hydrodynamics, etc.1-3). However, mostly the size of a dissolved species (hydrated ion, hydrated molecule, colloidal particle, etc.) is the crucial factor for the retention by membranes.

Liquid-Phase Retention Separation

The general principle of liquid-phase retention separation 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 non-target 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 non-target species.

In the liquid-phase separation process, the membrane represents a barrier which has to retain all ions bound to the polymer agent 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 liquid-phase retention separation procedure is illustrated in Fig. 1.

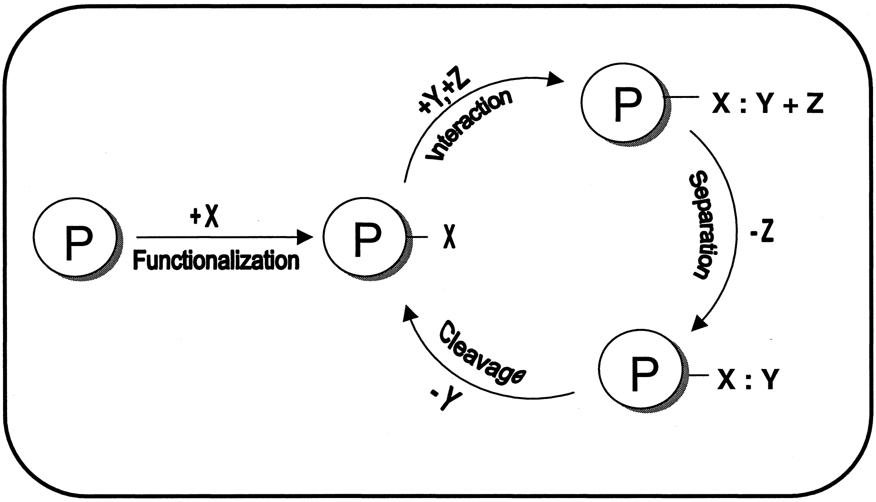

Fig. 1: Functionalization, interaction with metal ions, separation, and cleavage from water-soluble polymers using the liquid-phase retention (LPR) separation.
P = Polymer, X = Functional molecule or group, P-X = Polymer ligand, Y = Target metal ion, Z = Non-target metal ion, P-X:Y = Polymer-metal complex.

In terms of practical aspects, mostly polysulfone, polyamide, or cellulose membranes with a nominal molecular mass cut-off of 10,000 g mol^{-1} in connection with polymers of molar masses in the range of 20,000 - 100,000 g mol^{-1} have been used. The experimental details have been described previously in detail[1-6].

Water-Soluble Complexing Polymers

Hydrophilic polymers are available in a great number[7,8], however, the number is considerably reduced when considering them for use with liquid-phase separation. The reason is that the separation process will only be successful if the polymer used meets the following requirements[4]:

- water-solubility,
- high molecular mass,
- high affinity towards the target metal ion,
- inactivity towards the non-target metal ion,
- chemical and mechanical stability.

Three main classes of metal complexing polymers can be discerned in this context:

a) Basic polymers, like poly(ethylenimine), poly(vinylamine), poly(allylamine), and other amino or imino group-containing polymers.

b) Neutral polymers such as polyglycols, polyalcohols, polyethers, etc. They are primarily less suitable for LPR, if not functionalized specifically.

c) Acidic polymers, e.g., poly(acrylic acid), poly(vinylsulfonic acid), poly(styrenesulfonic acid), and others. These polymers suffer frequently from a low selectivity, when it is necessary to separate metal ions from multicomponent solutions.

The soluble, non-crosslinked, hydrophilic polymers with complex-forming moieties, capable to bind, enrich, and separate metal ions from aqueous solutions, were termed ‘polychelatogens’ and the method using these reagents was called ‘Liquid-Phase Polymer-Based Retention’ (LPR)[1-3].

A series of polychelatogens have been prepared and investigated in conjunction with liquid-phase retention separation[3,4,9,10]. Clearly, the selectivity of the polymeric reagents can be significantly enhanced by introducing special ligands[4,9,11-16].

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[3,4,10]. The large number of metal ions investigated include many transition metals, alkali and alkaline earth metals, and elements from the lanthanide and actinide series[4,17].

Scope and Developments

Membrane-based approaches have been extensively employed to the enrichment and separation of various metal ions[3,4,9,10]. Also ion-exchange in the liquid phase has been performed under these conditions[18] and mathematical modeling of the LPR method was reported[19].

Significant achievements in the LPR separation research field are compiled in Table 1.

Table 1. Major advances in liquid-phase retention separation in conjunction with functional polymers

Advancement	Year	Citation
Polypeptide synthesis	1972	Nature **237**, 512
Soluble polymer supports	1974	Liebigs Ann. Chem. 1671
Water-soluble polymer-metal complexes	1980	Pure Appl. Chem. **52**, 1883
Liquid-phase Polymer-based Retention (LPR) method	1985	Nature **315**, 313
Anion exchange	1988	Naturwissenschaften **75**, 198
First review on LPR	1988	Sep. Purif. Methods **17**, 105
Selective polymer ligands	1990	Anal. Chim. Acta **230**, 171
System design for analysis	1992	Internat. Lab. **17**, 47
Actinide separation	1993	Chem. Tech. **45**, 464
Approval of LPR for analysis by IUPAC	1994	Pure Appl. Chem. **66**, 631
Environmental applications	1996	Env. Sci. Technol. **30**, 725
Mathematical modeling	1996	Macromol. Theory Simul. **5**, 357
Interpolymer complexes	1998	Macromol. Chem. Phys. **199**, 1153
Environmentally degradable polymers	1999	Polym. Internat., in press

The appropriate use of the LPR technique allows to significantly increase the sensitivity and to considerably decrease the time required for analytical determinations. Thus, a number of hyphenated techniques in conjunction with the LPR method have been developed[20-22)]. To enhance the performance in analytical applications, special membrane systems for this method have been designed and commercialized[23)].

Recent 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[24-26)].

Conclusion

The typical features and a lot of examples of the liquid-phase retention separation of metal ions presented here demonstrate that the LPR technique is an effective and powerful method for the metal ion separation and enrichment in aqueous solutions. To utilize the full potential of the method, further interdisciplinary studies in fundamental and applied research are required.

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References

1. B.Ya. Spivakov, K. Geckeler, E. Bayer, *Nature* **315**, 313 (1985)
2. K.E. Geckeler, E. Bayer, B.Ya. Spivakov, V.M. Shkinev, G.A. Vorobeva, *Anal. Chim. Acta* **189**, 285 (1986)
3. K.E. Geckeler, V.M. Shkinev, B.Ya Spivakov, *Sep. Purif. Methods* **17**, 105 (1988)
4. K.E. Geckeler, G. Lange, H. Eberhardt, E. Bayer, *Pure Appl. Chem.* **52**, 1883 (1980)
5. K.E. Geckeler, V.M. Shkinev, B.Ya. Spivakov, *Angew. Makromol. Chem.* **155**, 151 (1987)
6. K.E. Geckeler, H. Eckstein, *Analytische und präparative Labormethoden*, Vieweg, Wiesbaden, 1987
7. P. Molyneaux, in: *Chemistry and Technology of Water-Soluble Polymers,* C.A. Finch (Ed.), Plenum Press, New York, 1983
8. K. Geckeler, V.N.R. Pillai, M. Mutter, *Adv. Polym. Sci.* **39**, 65 (1981)
9. B.L. Rivas, K.E.. Geckeler, *Adv. Polym. Sci.* **102,** 171 (1992)

10. K.E. Geckeler, *Metal Complexation Polymers*, in: *The Polymeric Materials Encyclopedia*, CRC Press, Boca Raton, New York, London, Tokyo, 1996, Vol. **6**, p. 4101
11. K.E. Geckeler, E. Bayer, G.A. Vorobeva, B.YA. Spivakov, *Anal. Chim. Acta* **230**, 171 (1990)
12. K.E. Geckeler, B.L. Rivas, R. Zhou, *Angew. Makromol. Chem.* **193**, 195 (1991)
13. K.E. Geckeler, R. Zhou, B.L. Rivas, *Angew. Makromol. Chem.* **197**, 107 (1992)
14. R. Zhou, K.E. Geckeler, *Z. Naturforsch.* **47b**, 1300 (1992)
15. K.E. Geckeler, *Polym. J.* **25**, 115 (1993)
16. V. Palmer, R. Zhou, K.E. Geckeler, *Angew. Makromol. Chem.* **215**, 175 (1994)
17. A. Novikov, S. Korpusov, R. Zhou, K.E. Geckeler, *Chem. Tech.* **45**, 464 (1993)
18. K.E. Geckeler, E. Bayer, V.M. Shkinev, B.Ya. Spivakov, *Naturwissenschaften* **75**, 198 (1988)
19. B.Ya. Spivakov, V.M. Shkinev, V.I. Golovanov, E. Bayer, K.E. Geckeler, *Macromol. Theory Simul.* **5**, 357 (1996)
20. K.Geckeler, E. Bayer, V.M. Shkinev, B.Ya. Spivakov, *Fresenius Z. Anal. Chem.* **333**, 763 (1989)
21. I.V. Markova, V.M. Shkinev, G.A. Vorobeva, K.E. Geckeler, *Zh. Anal. Khim.* **46**, 182 (1991)
22. O.D. Prasolova, L.V. Borisova, V.M. Shkinev, K.E. Geckeler, *Zh. Anal. Khim.* **48**, 85 (1993)
23. K.E. Geckeler, E. Bayer, V.M. Shkinev, N. Gomolitski, B.Ya. Spivakov, Internat. Lab. **17**, 47 (1992)
24. S.J. Choi, K.E. Geckeler, *The Polymer Society of Korea*, Seoul, April 16-17, 1999, Abstr. Vol. 22, No. 1, p. 216
25. M. Tuelue, K.E. Geckeler, *Polym. Internat.,* in press (1999)
26. K.E. Geckeler, K. Volchek, *Env. Sci. Technol.* **30**, 725 (1996)