Recent developments of microcapsules and polymer particles for separation medium

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Abstract. Microcapsules and porous polymer particles containing extractants, which are functional molecules to extract target ions or molecules by specific interaction using in solvent extraction process, are expected to be an effective separation medium of various substances from aqueous solution in hydrometallurgical process of harmful or valuable metals and in environmental protection processes from various pollutants. The preparation method, encapsulating materials and application area of these materials has been developed and extended in recent years. Recent topics of this field was been presented. The research on the polymeric particles for separation medium investigated by authors was introduced and showed the structural effect of the polymeric particles containing extractant on the separation performance of metal ion and chiral separation of amino acids by porous particles impregnated with phospholipids.

1. Introduction

Separation process is quite important in the production of various chemicals, removal of pollutants from environment, and recovery and recycle of valuable resources. Distillation, adsorption, extraction, precipitation filtration is well established in the manufacturing processes of chemicals and materials and in the waste treatment process. However, separation in environmental protection, recycling of valuable materials, and biological processes requires highly selectivity and economical effectivity due to large amounts of contaminants, highly diluted state in the solution, and also large treatment amount, so research and development of new separation methods, processes and materials are still ongoing.

Polymeric materials play an important role in separation processes [1]. Polymeric particles as separation media have several advantages: (1) large specific interfacial area, (2) the core and semipermeable membranes of the polymeric particle can be used as independent phases which can then support the different ligands, (3) easy separation of the two phases [2].

Solvent extraction has been used for separation and recovery of various substances such as metal ions, organic acids, antibiotics, amino acids and proteins, due to its relatively high selectivity for target substances, simplicity of equipment and operation, and facility of scale-up and application [3]. However, it uses large amounts of organic solvents which may adversely affect the environment and the human body. Solvent extraction also has some problems in that the phase separation of organic and aqueous
phases is difficult and extractants and/or organic solvents are lost by being dissolved in the aqueous phase. To solve these problems, the immobilization of the extractant [4-6] and microencapsulation [1, 7] of the extractant have been investigated as like as a fusion of extraction and adsorption. Liquid extractant is changed to solid state through these processes. In the microencapsulation of extractant, entrapment of extractant is carried out at the same time as the wall forming of microcapsules by polymerization of monomer or cross-linking of polymer chain [7]. The immobilization of the extractant is achieved using porous polymer particles [4-6] and in some cases using fibers [8]. Porous polymer prepared particles impregnated with the extractant are called solvent impregnated resins (SIRs). Solvent impregnated resins are simply prepared by immobilization of the extractants within the matrix structure of the polymer particles by physical contact. Hence, SIRs containing various extractants have been prepared and investigated for a variety of applications [4].

Recent applications of microcapsules and polymer particles containing extractant were reviewed and our application were presented in this paper.

2. Recent research on microcapsules and polymer particles containing extractants

Recent topics on the research related with separation using microcapsules or polymer particles containing extractants in literatures are summarized in Table 1 in which that is mutual and selective separation of various metal ions, removal of CO\textsubscript{2} in gas mixture, and removal of pollutants in aquatic environment.

Mutual and selective separation of valuable metals are also hot topic as well as adsorption and solvent extraction systems. The first approaches are application of new extractants including recognition molecules to target ones. New extractants having different steric structure [9] and cyclic structure [10] were impregnated into polymer particles with different wall materials and different pore structures. Selective extraction of target metal ions was achieved by considering the stability of the extraction complex in the particles. Selective effluent of Am(III) was also achieved by using citrate ion as complexing eluent in the column separation [9].

The second one is the application of shell layer of the microcapsules [11] or coating polymer layer on the porous particles [12, 13] to improve selectivity of metal extraction. Shell layer forming the wall of microcapsules selectively adsorbed MoO\textsubscript{4}\textsuperscript{2-} and the extractant entrapped in the center of the microcapsules as a core material selectively extracted ReO\textsubscript{4}\textsuperscript{2-} [11]. The porous particles coated with PVA membrane containing Alain 336 extractant was observed excellent stability and excellent selectivity of ReO\textsubscript{4}\textsuperscript{2-} adsorption from the mixed aqueous solutions [12, 13]. However, the mechanism of selective permeation of ReO\textsubscript{4} through PAV membrane is still unclear.

The third one is the application of ionic liquid which was impregnated into porous polymer particles [14], was encapsulated [15], and was covalently linked on the porous polymer particles [16]. Ionic liquid has unique properties such as low vapor pressure, no freezing point and specific extraction ability for various substances. Although ionic liquids are expected to be good solvent in solvent extraction fields, ionic liquids have a high viscosity which may cause a disadvantage on the operation and process design of the solvent extraction. Therefore, in order to solve these problem, microencapsulation and impregnation of ionic liquids into the polymer particles are expected to be effective methods and widely investigated [7, 23].

The fourth one is the separation of CO\textsubscript{2} from mixed gas using porous particles impregnating polyamines as adsorbent of CO\textsubscript{2} [17, 19, 24, 25]. Selective removal of CO\textsubscript{2} using fixed bed column and regeneration of adsorbent were successfully achieved by investigation of the effects of porous properties and materials of particles, adsorbent type, and operation condition of flow separation [17, 18].

The last part is the environmental application, especially for the removal of pollutants, such as phenol from waste water with microencapsulated extractant [19], pharmaceuticals from hospital waste water with microencapsulated solvents [20], heavy metals from waste water with microencapsulated new extractant [21], and pyridine derivatives from an aqueous waste stream with impregnated new solvent [22]. All are successfully observed enough removal efficiency of pollutants from waste water with
simple and easy operation using solid polymer particles. Simple and easy operation using polymer particles would be expected as an effective separation process in the environmental field.

**Table 1** Recent research on microcapsules and polymeric particles containing extractant

| Research topic                                      | Structure          | Wall material      | Active chemicals (extractant) | Preparation method | Target     | Ref |
|----------------------------------------------------|--------------------|--------------------|-------------------------------|--------------------|------------|-----|
| Selective and Mutual Separation of metal ions: application of new extractant | Matrix             | PS-DVB, PMA       | Et(p)TDPA, Et(o)TDPA          | SI                 | Am, Eu     | 9   |
| Selective and Mutual Separation of metal ions: application of new extractant | Matrix             | acrylic ester     | C8-Cyclen                     | SI                 | Pd(II)     | 10  |
| Selective and Mutual Separation of metal ions: selective separation by shell layer | Single core        | crosslinked chitosan with TPP | N263 | MC | ReO4+ over MoO32- | 11 |
| Selective and Mutual Separation of metal ions: selective separation by coating layer | Matrix             | LS-300 coated with PVA | Alamin 336                  | SI                 | ReO4+      | 12   |
| Selective and Mutual Separation of metal ions: application of ionic liquid | Matrix             | XAD resins        | Cyphos IL101                  | SI                 | Au(III)    | 14 |
| Selective and Mutual Separation of metal ions: application of ionic liquid | Single core        | polystyrene       | ionic liquid (IL) ([Bmin][NTf2]) | MC                 | Li         | 15 |
| Selective and Mutual Separation of metal ions: application of ionic liquid | Matrix and covalently bonded on the resin. | PS-DVB-Sulfonyl chloride resin | Hbet-STFS | Hbet-STFS was attached on PS-DVB | Sc(III) | 16 |
| Separation of CO2                               | Matrix             | MR10              | PEI                           | SI                 | CO2        | 17 |
| Separation of CO2                               | Matrix             | D101, X-5 ADS-17  | PEI                           | SI                 | CO2        | 18 |
| Removal of pollutants                           | Single core        | cellulose acetate | Cyanex 923                   | MC                 | phenol     | 19 |
| Removal of pharmaceuticals from water           | Single core        | Alginate           | dibutyl sebacate and oleic acid | MC                 | Pharma-ceuticals | 20 |
| wastewater treatment: application of new extractants | Matrix             | C4C/PIP           | C4C and PIP                   | MC                 | Pb(II), Zn(II), Cu(II), Ce(II) | 21 |
| wastewater treatment: application of new solvent | Matrix             | Amberlite XAD4    | PhOHs                         | SI                 | 4-CNPy     | 22 |

MC: microencapsulation; SI: solvent impregnation; St-DVB: styrene-divinylbenzene; PMA: polymethyl methacrylate; Et(p)TDPA: para-dialkyl-diarylpyridine-2,6-dicarboxyamide; Et(o)TDPA: ortho-diarylpyridine-2,6-dicarboxyamide; C8-Cyclen: tetracetyl-substituted 1,4,7,10-tetraazacyclododecane; PEI: polyethyleneimine; TPP: sodium tripolyphosphate; N263: methyl trioctyl ammonium chloride; LS-300, XAD, MR10, D101, X-5, ADS-17 and XAD-4: commercial porous resin; C4C: 5,11,17,23-tetra-t-butyl-25,26,27,28-tetrakis(chlorocarbonyl-methoxy) calix[4]arene; PIP: piperazine; PhOHs: 1:1 mixture (mole basis) of 3,5-dibromo-4-(4,6,6-trimethylheptyl)phenol and 3,5,-dibromo-4-(4,8-di-methylphenyl)phenol; 4-CNPy: 4-cyanopyridine

3. Development of microcapsules and polymeric particles for separation medium

Our group was started a research on the research and development of microcapsules and microparticles from around 1990 and applications for separation medium from 1995, and has been continuing them yet. The basic preparation method is preparation from an emulsified state, which is a dispersed state of the liquid phase. Our investigations on microcapsules and polymer particles for separation medium are summarized in Table 2 which contains structure, initial state in the preparation, preparation method, particles size, wall material, extractant or active substances in the particles, their immobilization method, target chemicals and substances of separation, and references. The structure of the particles is divided into four types, single core, matrix, interconnected spherical pore, and multiple core as shown in Table 2. In single core structure, shell layer forms outer wall of the particles and the extractants and the active agents for separation are entrapped at central part as a core of the particles. In the matrix type,
small pore of the particles and gap space between the polymer chain is filled with the active agents. In the interconnected spherical pore type, the active agents are entrapped in a wall part of the particles. In the multiple core type, the active agents are entrapped as small dispersed droplets in the particles. These structures are controlled by the initial state of the emulsion and the preparation method.

### Table 2 Microcapsules and polymeric particles for separation medium developed

| Structure | Initial dispersion state & preparation method | Diameter | Wall material | Extractant | Immobil. method | Target | Ref. |
|-----------|---------------------------------------------|----------|---------------|------------|----------------|--------|------|
| O/W emulsion in situ polym. | av. 160-200 µm | St-DVB | TOA | MC | Pd, Pt, Au | 26,27 |
| O/W gel entrapped in situ polym. | av. 1.8-2.3 mm | St-DVB | TOA | MC | acetic acid | 28 |
| O/W emulsion in situ polym. | av. 160-200 µm | pDVB | TOA | MC | Pd, Pt, Au | 29,30 |
| Bulk polym. & grinding | av. 250 µm | TRIM | LIX84-I + IL | MC | Cu | 36 |
| Commercial XAD4 | 250-850 µm | St-DVB | LIX84-I | SI | Cu | 37 |
| W/O/W emulsion in situ polym. | 210-420 µm | pDVB | TOA | MC | Pd | 38 |
| O/W emulsion gelation & cross-link | av. 3 mm | ArgNa+PVA | PC-88A | MC | Co, Ni | 42 |
| S/O/W emulsion in situ polym. | av. ≥ 200 µm | TRIM | DNA | MC | HOC | 43 |
| W/O/W emulsion in situ polym. | 150-300 µm | pDVB | PAA | MC | H2O vapor | 45 |

Polym.: polymerization; MC: microencapsulation; SI: solvent impregnation; St-DVB: styrene-divinylbenzene; pDVB: poly divinylbenzene; ArgNa: Sodium alginate; PVA: poly vinyl alcohol; TRIM: Trimethylolpropanediol; HOC: hazardous organic compounds; TOA: tri-n-octylamine; PC-88A: 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester; LIX84-I: 1-(2-hydroxy-5-nonyphenyl)ethanone oxime; IL: ionic liquid; DPPC: 1,2-dipalmitoyl-sn-glycero-3-phosphocholine; cells: nitrifying bacteria; co-cult.: co-cultivation; PAA: poly acrylic acid; #: not published

#### 3.1. Morphology characterization

The typical SEM images of the polymeric particles with the structure of interconnected spherical pore, shown by PDVB, matrix type, shown by XAD-4, and multiple core, sown by PVA/alg-GA containing phenolic oxime extractant, LIX84-I, which have an ability to extract various metal ions, especially Cu(II), from the aqueous solution is show in Figure 1. PDVB has a rough surface and inner
aqueous droplets are observed on the surface of the particles and in the cross section. The inner aqueous droplets of W/O/W emulsion in the initial state formed large spherical pores which are interconnected. XAD-4 has a dense structure observed on the surface and in the cross section. Because of the long contact time of LIX84-I and the polymeric particles in hexane for PDVB and XAD-4, we assume that the LIX84-I would exist in the wall of the polymeric particles and on the surface of interconnected pores. On the other hand, PVA/alg-GA has a dense surface and some small depressions can be seen on the surface of SEM image. It is considered the depressions were caused by the droplets of LIX84-I which were released from the surface of the particle during the crosslinking of the alginate. The cross-section image shows the rough structure which contains a lot of round shaped particles, empty spaces between the particles and many isolated spherical pores with dense shells surrounded by the particles. The particles and the shell wall are considered to be the hydrophilic polymer of PVA/alg-GA. The spherical pores were considered to be the traces of the droplets of LIX84-I which were released during the sample preparation under SEM observation. These droplets of LIX84-I in the spherical pores would act as an organic extraction media in the PVA/alg-GA polymeric particles.

![Figure 1](Typical SEM images of the polymer particles containing LIX84-I with various structure; interconnected spherical pore (PDVB), matrix (XAD-4), and multiple core types (PVA/arg-Na))

### 3.2. Characterization of extraction rate with polymeric particles with different structures

The extraction rate of Cu(II) form the ammonium sulphate solution using various types of polymeric particles was different as shown in Figure 2. For polymeric particles with interconnected spherical pore (PDVB), the extraction rate was extremely rapid at the initial stage, slowed down as the extraction proceeds and reached an almost constant value after 60 minutes of contact time. Otherwise, for matrix type polymeric particles (XAD-4), the extraction amount of Cu(II) slowly increased in initial stage and reached an almost constant value after 360 minutes. On the other hand, for multiple core type (PVA/alg-GA) the Cu(II) extraction was also slow in the initial stage and slowly reached an almost constant value after 120 minutes.

According to our previous study [32], a small particle size lower than around 20 µm presents a larger surface for extraction and leads to a rapidly increase in the extraction amount at the initial stages. Despite of their relatively large size, the PDVB polymeric particles present a larger surface area for the extraction due to the existence of interconnected spherical pores, which tend to rapidly increase the initial Cu(II) extraction. For the XAD-4 polymeric particles, a slow extraction of Cu(II) was observed. This slow extraction rate frequently observed on the extraction using commercially available porous resin impregnated with extractants. The dense structure and small pores of the matrix type particle systems would prevent the diffusion of Cu(II) onto the active sites of the polymeric particles, extractant to an interface where proceed the extraction, and the extraction complex between Cu(II) and extractant from the interface. The extraction of Cu(II) into the PVA/alg-GA polymeric particles also slowly increased...
at the initial stages due to large particle size, however, the extraction was faster than that of the matrix type. The overall extraction kinetics of Cu(II) with all particle systems were well followed a pseud-second order kinetic model. The analysis based on the diffusion model was also conducted for extraction kinetic results with all particle systems. Based on the analysis, in the PDVB polymeric particles, complex formation is the predominant rate-determining step in the initial stage of the extraction of copper(II), film and intraparticle diffusion become the rate-determining step in the later stage of the extraction. In the XAD-4 and PVA/alg-GA polymeric particles, film diffusion is the rate-determining step in the initial stage of the Cu(II) extraction.

Figure 2 Time course of the Cu(II) extraction with the polymeric particles containing LIX84-I with various structures; interconnected spherical pore (PDVB), matrix (XAD-4), and multiple core types (PVA/alg-Na)

3.3. Chiral Separation of amino acids with polymeric particles impregnated with phospholipids [39] Phospholipids form unique molecular assemblies, in which liposome is one of examples. Liposome and its bilayer membrane have been investigated as drug carrier, micro-reaction vessel, microcapsules, molecular recognition membrane and biomimetic membrane and sensors. In order to construct lipid bilayer on the polymeric particles, phospholipid, 1,2-dipalmitoyl-sn-glycero-3-phosphocholine (DPPC), was impregnated and supported on the walls of the polymeric particles with interconnected spherical pores. The PDVB particles with interconnected spherical pores containing an extractant, TOA, were prepared in advance, and the extractant was removed by washing with ethanol. DPPC molecules were impregnated into the PDVB polymeric particles by impregnation and solvent evaporation method.

The DPPC molecules impregnated into the polymeric particles exhibited liposomal membrane-like properties observed by Raman spectra and fluorescent molecular probes [39]. The membrane-like properties were changed around 41°C, which is almost same as the phase change temperature of DPPC [47]. The adsorption of L- and D-tryptophan (Trp) was carried out using the particles containing DPPC (DPPC-PP) at 30°C and 45°C for 72h as shown in Figure 3. L-tryptophan was adsorbed on DPP-PP at 30°C that is lower than the phase transition temperature and showed liposomal membrane-like properties. On the other hand, the adsorbed amount of D-tryptophan was surprisingly very low at 30°C. The adsorption amount of L-type was drastically decreased at 45°C and also those using the particles without DPPC. Furthermore, the adsorption amounts of D-tryptophan was quite low regardless of the temperature and the impregnation of DPPC. Furthermore, L-tryptophan was preferentially adsorbed from the racemic solution. In the cases of other amino acids, the adsorption amount of L-form was higher than that of D-form. From these results, it was suggested that the DPPC molecules impregnated into the porous particles with interconnected spherical pores reconstruct a bilayer membrane structure similar to liposomes and express chiral recognition ability for L-form of amino acids. The impregnation of DPPC
into the particles with interconnected spherical pores is quite simple and easy. Therefore, it would be expected to be applied as an immobilized bimolecular membrane, for example, as a molecular recognition, a membrane protein fixation, a molecular probe sensing, and a fixed-catalysis reaction fields.

4. Conclusion
Recent topics and our researches on microcapsules and porous polymer particles containing extractants, which are functional molecules to extract target ions or molecules by specific interaction using in solvent extraction process, were summarized and introduced. The structural characteristics of the particles with interconnected spherical pores, matrix and multiple core types and their influences on the extraction kinetics were described. The interconnected spherical pore type particles containing the extractant provided a quite fast extraction rate regardless of the relatively large particle size. Furthermore, the multiple core type gel-particles provided a relatively fast extraction rate despite the very large particle size. Also, the interconnected spherical pore-type particles impregnated with phospholipid DPPC reconstructed the phospholipid bilayer membrane and exhibit the chiral recognition ability for L-form of amino acids.

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