Transport of Metal Ions through Cellulose Fiber Supported Solid Membrane into Tributyl Phosphate Containing Mixed Solvents

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A novel cation exchange fiber supported solid membrane was developed for transport of cobalt, manganese and nickel metal ions. Fiber supported solid membrane was prepared by chemically modifying the cellulose fibers with citric acid. In the fiber supported solid membrane, the diffusion by capillary action by keeping the liquid phase in the porous solid fiber and ion exchange mechanism were used for the effective transport of metal ions. The experimental variables examined were concentration of metal ions (10^{-2} to 10^{-4} mol L^{-1}) in the source solution, mixed solvent composition ($\varphi = 20$ % TBP, acetone or tetrahydrofuran or 1,4-dioxane or methanol or ethanol or 2-propanol 10 to 60 % and HCl (1 to 2 mol L^{-1}) in the receiving phase and stirring speed (40–120 rpm) of the bulk source and receiving phase. The enrichment of concentration of cobalt, manganese and nickel metal ions was observed from the dilute solutions.

Key words:
Cobalt, manganese and nickel metal ions, fiber supported solid membrane, binary of mixtures of metal ions, ion exchange, extraction, stripping

Introduction

In the recent developments in ion exchange, solvent extraction and membrane techniques, the combination of tetrahydrofuran with nitric acid medium was reported for the separation and purification of uranyl ions from other metal ions in a single step on Dowex-50. The concept of combined ion exchange-solvent extraction (CIESE) was introduced by Korkisch and collaborators.[1] The combined liquid-liquid extraction and ion exchange of metal ions were explored in the mixed solvents.[2,3] The use of 2-thenoyltrifluoroacetone, tri-*n*-butyl phosphate, acetylacetone, methyl ethyl ketone, and methyl isobutyl ketone in conjunction with acetone, methanol, ethanol, 1,4-dioxane, 2-propanol and tetrahydrofuran and also hydrochloric or nitric acid has added advantage for the CIESE separation of many metal ion mixtures generally associated with ores and minerals.[4]

In the usages of cellulose fibers, the sodium chloride flux was investigated through the microbial cellulose membrane in concentration polarization.[5] The modified thiol cotton fiber (TCF) was explored for quantitative adsorption of traces of heavy metals from the aqueous solution.[6] The cellulose fiber had been explored for the chromatographic performance in the capillary electro-chromatography.[7]

Development in the techniques, the direct coupling of liquid-liquid extraction with liquid chromatography has been explored for the analysis of *n*-butylphthalate in wastewater. A review describes the micro-extraction technique developed over the last decade, and also presents the characteristics of various approaches in the drug analysis.[8] The different environmentally friendly and non–polluting agricultural residues such as wheat straw, bagasse, cotton stalks, and saw dust have been chemically modified to use as a cation exchanger. In addition to this, the solid phase extraction of metal ions is a versatile technique due to its simplicity, rapidity, low cost and higher recovery. Cellulose is an attractive support material due to good porosity, high hydrophilicity, low swelling, steady chemical resistance, wide availability and easy biodegradability. The cellulose sorbents containing iminodiacetic acid and quinoline groups or reagents had been investigated for pre-concentration of metal ions.[9] Oxime, sulphoxine and 2, 20-diamino-diethylamine cellulose based macromolecular chelators are good adsorbents for the removal of platinum metal ions. The functionalized acetoacetamide chelating groups over microcrystalline cellulose were explored for adsorption of Fe(III), Cu(II) and U(VI) metal ions. The sulphydryl cotton fiber (functionalized cellulose sorbent)[10] had also been used for the enrichment of methyl mercury, selenium and multi-metal ions mixtures. The modified cotton fiber porous structure permits the rapid entrance and diffusion of liquid phase.[10–12]

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In the literature, a charge transport by ion translocating membrane proteins on solid supported membranes had been reported.[13] A correlated dynamics of inclusions in a supported membrane had been discussed.[14] An environment-responsive paper-supported composite membrane had been used to switch between hydrophobic and hydrophilic states in a reversible manner by addition or removal of anti-chaotropic salts.[15] A research work on recent advances in supported liquid membrane technology had been discussed.[16] Separation had been explored of copper, cobalt, nickel, and manganese by adsorbing colloid flotation,[17] by redox leaching and solvent extraction[18] and from sulfate solutions by Cyanex 301.[20] Process had been developed for cobalt separation and recovery in the presence of nickel from sulphate solutions by Cyanex 272.[21,22] However, their aspects are different from the present research work.

In the fiber supported solid membrane technique, the mechanisms involved are ion exchange and diffusion of metal ion through the fiber supported solid membrane. Source, membrane and receiving phase are stationary phases and there is no mobile phase. The fiber plays the role of support. The driving force for transport of metal ion is a gradient in concentration of chemical species. An aim of this paper is to explore the chemically modified cellulose fiber for the transport of metal ions and thereby to increase the stability of supported membrane technique. Due to a large surface area and capillary action of fine fibers, micro fibers absorb liquid seven times its mass in fluids. The cellulose porous micro fibers are extremely durable and effective even after several washings. It is an exceptionally cost-effective product. From the design and development based on chemically modified fiber supported solid membrane emerges a versatile technique for the transport and separation of metal ions. It is a nonstop process. The advantages of fiber supported solid membranes are: no loss of solvent, flow rates of source and receiving phase could be controlled and desired solid membrane phase could be chemically attached to the fiber for the selective separations. Moreover, time consumption could be controlled by increasing or decreasing the membrane length. In addition to this, citric is environmentally friendly, non-polluting, and forms metal complexes with several metal ions. The mixed solvent system enhances the transport of metal ions through the fiber supported solid membrane. Bismuth, cadmium and lead metal ion transports had been explored through the fiber supported solid membrane system.[23] However, in the reported work, the combinations were used of organic solvents such as methanol, ethanol and acetone with hydrochloric acid. Although, an organic solvent acetone forms an oxonium salt with HCl, however, TBP (tributyl phosphate) is a strong solvent which also forms strong liquid anion exchanger with HCl, in other words, in the presence of TBP (tributyl phosphate) in mixed solvents has added advantages of decreasing the dielectric constant of aqueous phase and favored ion pair formation to enhance the metal ion transport through the fiber supported solid membrane. Therefore, it is worthwhile to explore the ion transport of metal ions through the fiber supported solid membrane in the presence of TBP in mixed solvents.

In this work, the transports of cobalt, manganese and nickel metal ions have been explored from aqueous source to receiving phase through fiber supported solid membrane in the mixed solvents of tributyl phosphate (TBP), acetone, tetrahydrofuran, 1,4-dioxane, methanol, ethanol, 2-propanol in hydrochloric acid.

Experimental

Materials and methods

Cellulose porous solid fibers (Aldrich Chemicals) were used. Tributyl phosphate (TBP), methanol, ethanol, 2-propanol, acetone, tetrahydrofuran and 1,4-dioxan (Aldrich Chemicals CO, USA) were used without further purification. The dilute acid solution was prepared from concentrated acid solutions (Merck, India Ltd.,) in distilled and de-ionized water. The stock solutions of cobalt, manganese and nickel and other metal ions were prepared from their chlorides or nitrates. The concentration of metal ion in the solution was analyzed by EDTA titrations or gravimetric or spectrophotometer determinations depending on the metal ion concentrations. The fiber solid supported membrane was synthesized as reported earlier.[23] Fibers of diameter 0.027 cm (270 μm), and porosity 30 to 50 % were used. The cross section area of porous fibers was $5.73 \cdot 10^{-4}$ cm^2. The membrane cell was used as described earlier.[23] The experiments were carried out at room temperature.

Results and discussions

Metal ion transport mechanism

In the metal ion transport mechanisms, the transport of cobalt, manganese and nickel metal ions from source to receiving phase through fiber supported solid membrane is illustrated in Fig. 1. There is no continuous flow of mobile phase either from source or receiving phase through the fiber supported solid membrane. The capillary action mechanism in the porous fiber helps to maintain the

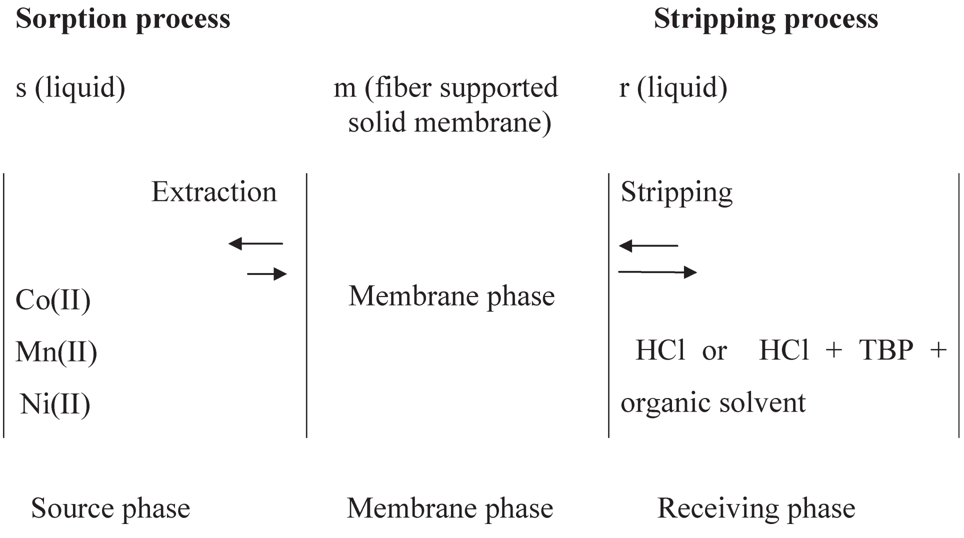

Fig. 1 – *Metal ion transport through fiber supported solid membrane*

liquid in the fiber during the transport of metal ions. However, there is a transport of metal ions from the source through the membrane to receiving phase due to the driving forces of receiving phase. Moreover, the ion exchange and diffusion of chemical species through the fiber supported solid membrane are the important aspects responsible for the transport of metal ions. In the fiber, the supported solid membrane phase (chemically bonded is citric acid) is used as the membrane barrier between the source and receiving phases. The driving forces of the acid and mixed solvents compositions in the receiving phase enhance the metal ion transport. As described earlier,[23] a fiber supported solid membrane cell was used.

For calculation of the permeability coefficient (*P*), the metal ion concentration change rate (C^s) in the source phase with respect to time (*t*) through a cross section area (*A*), volume of source phase (V_s) and fibers column membrane phase length (*l*) can be given by eq. (2), where, *k* is a rate constant.

$$-dC^s/dt = k \cdot A/(V_s \cdot l) \cdot C^s_0 \qquad (1)$$

After integrating eq. (1), the permeability coefficient (*P*) of transport of metal ions is obtained by eq. (2).

$$\mathrm{Ln}(C_t^s/C_0^s) = -(A/V_s) \cdot (P/l) \cdot t \qquad (2)$$

The calculated permeability coefficient (*P*) is used to interpret the data of transport of metal ions through porous solid fiber supported solid membrane at different experimental conditions.

Reactions occurred in the fiber supported solid membrane system, the cation exchange transport of metal ions (M) from source solution through membrane (R-COOH, citric acid bonded to cellulose) to receiving phase (HL, complexing reagents, HCl), given by following equations.

$$M^{n+}_s + n\ \mathrm{R\text{-}COOH}_m \rightarrow (\mathrm{R\text{-}COO}^-)_n\ M^{n+}_m + n\ H^+_s \qquad (3)$$

$$(\mathrm{R\text{-}COO}^-)_n\ M^{n+}_m + n\mathrm{HL}_r \rightarrow n\ \mathrm{R\text{-}COOH}_m + \mathrm{ML}_{n,r} \qquad (4)$$

Solvents such as tributyl phosphate, methanol, ethanol, 2-propanol, acetone, tetrahydrofuran and 1,4-dioxan form oxonium salt with acids such as HCl, HNO_3, etc. The oxonium salts act as liquid anion exchangers. The formation of liquid anion exchangers of the solvent (S) with acid (HL) are given by the following equations.

$$S_r + \mathrm{HL}_r \Leftrightarrow S \rightarrow H^+\ L^-_{m,r}\ \text{(oxonium salt)} \qquad (5)$$

The formed liquid anion exchangers transport the metal ion complexes from the interface of membrane to receiving phase as presented by the following equation.

$$\mathrm{ML}_{x,s} + n\ S \rightarrow H^+\ L^-_{m,r} \Leftrightarrow (S \rightarrow H^+)_n\ \mathrm{ML}_{x+n}{}^{n-}{}_{,m,r} \qquad (6)$$
$$\text{(ion pair)}$$

In the experimental variables, the metal ion concentration was determined with respect to time as described earlier.[23] The log *P* values were calculated using the slope of the straight line, cross section area (*A*, $5.73 \cdot 10^{-4}$ cm^2), and (l, 4 cm) length of fiber. The plots of log *P* against the length of porous solid fiber supported solid membrane were plotted as described earlier[23] for the transport of cobalt, manganese and nickel metal ions. The log *P* value decreases with the increase in the length of the porous solid fiber supported solid membrane. The cause is the increased path length of the metal ion transport through the fiber supported solid membrane.

Effect of stirring speed

The stirring of bulk phases diffuses the chemical species by capillary action with ion exchange mechanism from source to receiving through fiber supported solid membrane phase. The stirrings of bulk source and receiving phases were carried out to increase the diffusion by capillary action of chemical species in order to achieve the equilibrium between the rate of diffusion of chemical species and rate of ion exchange chemical reaction. The stirrings of source and receiving bulk solutions effectively diffuse metal ions through bulk solution as well as fiber supported solid membrane. The source and receiving phases were independently stirred for the 40 to 120 rpm. An increase in the *P* value was observed for the 40 to 100 rpm. This shows the decrease in the thickness of diffusion layer at the bulk liquid solution and also at the interface of liquid in the porous solid fiber supported solid membrane. The *P* value nearly remains the same for 100 to 120 rpm (Table 1). The stirring range represents the achievement of minimum diffusion layer thickness at the interface of liquids in the fiber supported solid membrane. Further, research studies were carried out at 110 rpm for the cobalt, manganese and nickel metal ions.

Table 1 – *Log P values for cobalt, manganese and nickel metal ions in mixed solvents for the variation of stirring speed*

rpm	Metal ion		
	Ni(II)	Mn(II)	Co(II)
40	1.85	2.11	2.33
70	2.2	2.32	2.45
90	2.64	2.77	2.93
100	2.95	3.06	3.46
110	2.98	3.09	3.46
120	2.98	3.08	3.46

Effect of pH of source phase

The transport of metal ion through the fiber supported solid membrane is controlled by diffusion by capillary action and ion exchange mechanisms. The pH variation of source phase was done in order to enhance the complex formation between metal ion and fiber solid membrane to promote the extraction of metal ion in the membrane phase. The pH of source phase is varied from 1 to 5 for the cobalt, manganese and nickel metal ions. The variation of pH of source solution is essential in order to dissociate the carboxylic acid group in the fiber solid membrane in the presence of aqueous phase at the interface of source and membrane phase. The dissociation of carboxylic acid groups depends on the pH of source solution. In order to chemically exchange the metal ions with hydrogen ions from carboxylic acid groups in the fibers solid membrane phase, the pH of the source solution was varied. This effect can be seen from eq. (3) of pH of source solution on the metal ion exchange on the solid ion exchangers. The log *P* value increases with the increase in pH from 1 to 5 (Fig. 2).

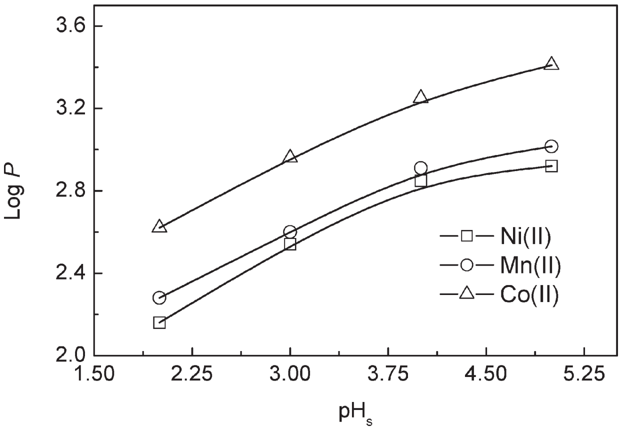

Fig. 2 – *Dependency of P on pH of source solution, metal ion = 0.001 mol L^{-1}, HCl = 1 mol L^{-1}, TBP (φ = 20 %) and acetone (φ = 60 %)*

Effect of hydrochloric acid concentration in receiving phase

The bulk phase source and receiving are continuously stirred. Therefore, the chemical species are continuously diffused in the bulk phase. In addition to this, the chemical species are constantly diffused in the fiber supported solid membrane by capillary action. Transport of metal ion through the fiber supported solid membrane is controlled by diffusion of chemical species by capillary action and ion exchange mechanism. Therefore, the stirring of bulk phase and composition of receiving phase are also the important factors for the transport of metal ions. The hydrochloric acid and mixed solvents in receiving phase were used to enhance the stripping process at the interface of solid membrane and receiving phase. The oxonium salt and ion pair formations also depend on the hydrochloric acid concentration and organic solvent in the receiving phase. The transport of metal ion through the porous solid fiber supported solid membrane is also controlled by the difference in the gradient concentration in source and receiving phase. The effect of driving force of hydrochloric acid is explored on the transport of metal ions from source to receiving phase through the fiber supported solid membrane. The hydrochloric acid in the receiving solution strips out the metal ion from the carboxylic acid groups from the fiber supported solid membrane (eq. (4)). The hydrochloric acid concentration in the receiving solution was varied from 1 to 2 mol L^{-1} for the transport of cobalt, manganese and nickel metal ions (Table 2). The increased hydrochloric acid concentration increases the log *P* values for the concentration range 1 to 2 mol L^{-1}.

Table 2 – *Log P values for cobalt, manganese and nickel metal ions in mixed solvents for the variation of HCl concentration*

HCl (mol L^{-1})	Metal ion		
	Ni(II)	Mn(II)	Co(II)
1.0	2.95	3.05	3.47
1.25	3.05	3.17	3.58
1.5	3.18	3.27	3.67
2.0	3.27	3.39	3.74

Effect of organic solvents in receiving phase

The presence of organic solvent in hydrochloric acid in receiving phase decreases the dielectric constant of the medium and also enhances the oxonium salt and ion-pair formations. The ion transport of metal ion from source to receiving through membrane phase can be enhanced by the increased rates of ion exchange reaction, oxonium salt and ion pair formation. In order to increase the rate of metal ion transport, the receiving phase consisting of hydrochloric acid, organic solvent (acetone, etc.) and tributyl phosphate was used; this enhances the ion exchange reaction at the interface of membrane to receiving phase. The ion exchange reaction at the interface of source to membrane phase is to be dominated by the ion exchange reaction at the interface of membrane and receiving phase in order to achieve an effective transport of metal ions. The transports of cobalt, manganese and nickel metal ions through the porous solid fibers supported solid membrane also depend on the concentrations of organic solvents such as tributyl phosphate, methanol, ethanol, 2-propanol, acetone, 1,4-dioxan and tetrahydrofuran in hydrochloric acid in receiving phase. The elution or stripping out the cobalt, manganese and nickel metal ions from the fiber supported solid exchanger membrane can be enhanced by the formation of ion pairs of negatively charged metal ion complexes with liquid anion exchangers in the mixed solvents (eqs. 5–6). The tributyl phosphate (TBP) and acetone percentage in the receiving solution was used φ = 20 %, and from φ = 10 to 60 % (Fig. 3), respectively. The increased acetone percentage (φ/%) from the 20 to 60 in the receiving phase increases the *P* values.

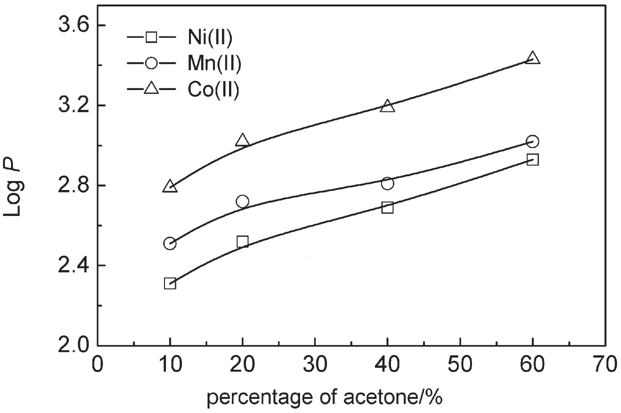

Fig. 3 – *Relation between P and percentage of organic solvent, metal ion = 0.001 mol L^{-1}, TBP (φ = 20 %) and HCl = 1 mol L^{-1}*

The transport of cobalt ions through the porous solid fiber supported in hydrophobic surface of Teflon tube (id 0.2 cm) and hydrophilic surface of glass tube (id 0.2 cm) was explored in mixed solvent systems. The results show that the transports of metal ions through the fiber supported solid membrane in Teflon tube are higher than that of glass tube fiber supported solid membrane.

The initial concentration of cobalt, manganese and nickel metal ion in the source solution was varied in the range 10^{-4} to 10^{-2} mol L^{-1}. The observed enrichment factor (EF is a ratio of metal ion concentrations at time in the receiving to source phase) with respect to initial metal ion concentration in source solution is shown in Table 3. The enrichment factor (EF) decreases with the increase in initial metal ion concentration in the source phase. Thus, the pre-concentration of metal ion is more effective from its low concentration solution.

Table 3 – *EF values for cobalt, manganese and nickel metal ions in mixed solvents for the variation of metal ion concentration*

Metal ion, log [M]	Metal ion		
	Ni(II)	Mn(II)	Co(II)
–2	2.49	2.74	2.94
–3	2.72	3.08	3.26
–4	3.51	3.76	3.94
–5	4.32	4.57	4.77

Log *P* for different mixed solvents

Taking into account the aspects of metal ion separations as described above, the role of hydrochloric acid concentration in conjunction with an organic solvent such as acetone and tributyl phosphate (TBP) in receiving phase was explored. The P values were determined for the different compositions of hydrochloric acid and an organic solvent such as acetone etc., and φ = 20 % TBP. The metal ion transports of cobalt, manganese and nickel were studied by using hydrochloric acid and organic solvents in mixed systems including TBP. The chemical properties, the chloro-complexes formation, solvation and ion exchange were important factors for the separation of cobalt, manganese and nickel metal ions. The different combinations of hydrochloric acid and organic solvents at φ = 20 % TBP were used for the determination of log *P* values. The combinations of hydrochloric acid and organic solvent are useful for the selective transports of metal ions from source to receiving phase (Table 4). The transports of cobalt, manganese and nickel metal ions through fiber supported solid membrane were observed in the sequence of decreasing efficiency as: fiber chemically modified (mixed solvents HCl + organic solvent + TBP as stripping agent in the receiving phase) > fiber chemically modified (mixed solvents HCl + organic solvent as the stripping agent in the receiving phase) > fiber chemically modified (mineral acids as stripping agent in the receiving phase). The efficiency of the organic solvent in the mixed solvents can be arranged in decreasing order as: TBP + tetrahydrofuran > TBP +1,4-dioxane > TBP + acetone > TBP + 2-propanol > TBP + ethanol > TBP + methanol > TBP.

Table 4 – *Log P values for some metal ions for 1 mol L^{-1} HCl in TBP φ = 20 % in mixed solvents*

Metal ion	Methanol			
	10 %	20 %	40 %	60 %
Co(II)	2.92	3.03	3.12	3.14
Mn(II)	2.73	2.83	2.94	3.05
Ni(II)	2.63	2.74	2.84	2.95
	Ethanol			
Co(II)	3.12	3.23	3.34	3.45
Mn(II)	2.77	2.92	3.13	3.27
Ni(II)	2.68	2.81	2.92	3.15
	2-Propanol			
Co(II)	3.15	3.29	3.52	3.72
Mn(II)	2.84	3.02	3.24	3.45
Ni(II)	2.72	2.94	3.14	3.35
	Acetone			
Co(II)	2.81	3.04	3.22	3.45
Mn(II)	2.53	2.74	2.83	3.04
Ni(II)	2.33	2.55	2.72	2.95
	1,4-Dioxane			
Co(II)	2.85	3.13	3.27	3.63
Mn(II)	2.58	2.78	3.06	3.35
Ni(II)	2.44	2.72	2.92	3.18
	Tetrahydrofuran			
Co(II)	2.87	3.18	3.47	3.85
Mn(II)	2.63	2.86	3.17	3.48
Ni(II)	2.51	2.82	3.13	3.42

In the separation of metal ions, the path travelled by metal ion through the fiber supported solid membrane depends on the diffusion of chemical species by capillary action and ion exchange reactions. Therefore, the separation factor[24] α, $\alpha = P_1/P_2$, for the two metal ions can be used to carry out the separation from the source phase through the fiber supported solid membrane. Where, P_1 is the permeability coefficient of a metal ion, which is weakly bound and selectively favorable to chloride ion complex formation. P_2 is the permeability coefficient of a strongly bound metal ion and less selectively favorable to chloride ion complex formation. For example, cobalt is relatively weakly bound and favorable to the formation of strong chloride complex in comparison with those properties of nickel. Therefore, cobalt is transported first.

The metal ions transports were studied in the binary mixtures using hydrochloric acid and organic solvents. The taken amount of metal ions in the source solution is given in Table 5. The separation of cobalt, manganese and nickel metal ion from beryllium, titanium, aluminum, calcium, magnesium, potassium, lanthanum and yttrium metal ions was carried out from the source through fiber supported solid membrane by using 1 mol L^{-1} HCl in 20 % TBP and 60 % tetrahydrofuran in receiving phase while beryllium, titanium, aluminum, calcium, magnesium, potassium, lanthanum and yttrium metal ions remained in the source solution and membrane phase. The scope for future work, precipitating agents such as sulfate, chloride, carbonate, oxalic acid, etc. could be used in the receiving phase. By using complexing agents as ethylenediamine tetra-acetic acid, D$_2$EHPA (organo phosphoric acid), amines, etc., either alone or together in receiving phase have an added advantage for the selective transport of metal ions.

The fiber supported solid membrane is a versatile unique technique for the transport of metal ions. A solid membrane is chemically attached to the porous solid fibers therefore the fibers supported solid membrane system continuously runs several hours together. The time required for each operation var-

Table 5 – *Separation of Co(II) = 0.15 mmol from binary mixtures in mixed solvent system*

Foreign ions	Foreign ions amount added mmol	Cobalt(II) found, mmol	Recovery (%)	Mixed solvents for cobalt metal ion
Be(II)	0.15	0.149	99.3	1 mol L^{-1} HCl in 20 % TBP in 60 % Tetrahydrofuran
Ti(IV)	0.20	0.15	100	
Al(III)	0.20	0.15	100	
Ca(II)	0.15	0.148	98.7	
Mg(II)	0.20	0.15	100	
K	0.15	0.149	99.3	
La(III)	0.20	0.20	100	
Y(III)	0.20	0.15	100	

ies from 5–6 h. However, the efficiency of fiber supported solid membrane depends on the pH of source solution, solid membrane and composition of mixed solvent in the receiving phase. The presented results are within the limits of analytical error ± 2.5 %.

Conclusions

The transports of metal ions were investigated from source to receiving through fiber supported solid membrane phase by using acidic mixed solvents. The transports of metal ions depend on the acid and organic solvent concentrations in the receiving phase and also stirring of the bulk source and receiving phases. The ion exchange and capillary action phenomenon are important aspects involved in the fiber supported solid membrane systems for the transport of metal ions. The design and development of chemically modified fiber supported solid membrane system is a versatile technique, which has various advantages over solvent extraction and ion exchange techniques, such as no dispersion of solvent phase, no loss of extracting phase or costly extractants, no pollution problem, and no limitation of small and large volumes. The scope for future work, the selective transport of metal ion could be achieved by using different either precipitating or complexing reagents in the receiving phase.

Nomenclature

C – concentration, molar, mol L^{-1}
aq – aqueous phase, mL
s – source phase, mL
m – membrane phase, mL
r – receiving phase, mL
t – time, min
P – permeability coefficient, cm min^{-1}
A – cross-section area, cm^2
V – volume, cm^3
φ – volume fraction, %

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