

# Transportive Separation of Palladium, Gold and Platinum through Cellulose Fiber Supported Solid Membrane

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## Abstract

Transportive separation of palladium, gold and platinum were explored through cellulose fiber supported solid membrane from source to receiving phase in the mixed solvents. Cellulose fiber supported solid membrane technique based on the capillary action and ion exchange mechanisms was used to study the transportive separation of metal ions. Cellulose fiber supported solid membrane was prepared by chemically modification using the esterification reaction with citric acid. The experimental variables explored were concentration of palladium, gold and platinum metal ions ( $10^{-2}$  to  $10^{-4}$  M) in the source solution, mixed solvent composition (20 % v/v Aliquat-336 (tricapryl methyl ammonium chloride), acetone or tetrahydrofuran or 1, 4 dioxane or methanol or ethanol or 2-propanol 10 to 60 % and HCl 0.1 to 1 M) in the receiving phase and stirring speed (40-120 rpm) of the bulk phases. The enrichment of concentration of palladium, gold and platinum metal ions was carried out from the dilute solutions.

**Key words:** Cellulose fiber supported solid membrane, binary mixtures of metal ions, ion exchange, extraction, stripping, transportive separation

## Introduction

Separation of gases or organic or inorganic metal ions or anions is an important aspect in chemical research investigation to explore. The several techniques have been developed such as GC, TLC, HPLC, ion exchange, solvent extraction, membrane, etc., for the separation of chemical species. For

separation of platinum metal ions, membrane technique is an emerging technique. In mining processes, ores containing platinum, gold and palladium are leached under oxidizing and acidic conditions. Under these conditions, Dowex anion exchange resins were found to be tough and steady performers. The precious metals are used as heterogeneous or homogeneous catalysts. The quality and higher costs demand the recovery of these metals. During the reactions, part of the metal can be lost.

The ion exchange and solvent extraction of palladium [1-5], gold [6-10] and platinum [11-13] could be used for the recovery and separations. The resins are effective under basic to acidic conditions. Dowex anion exchange resins were also used in the recovery of platinum and palladium from spent plating bath solutions. Minataur Process was used for the production of high-purity gold. The commercial implementation of this process represents a significant advance in gold-refining technology [14-16]. The solvent extraction of gold and platinum had been studied [17-21]. Transports of manganese, cobalt and nickel were explored the through fiber supported solid membrane [22]. Thus, the fiber supported solid membrane has been emerged as unique technique for the transportive separation of metal ions. Therefore, it is worthwhile to explore the transportive separation of value added noble metal ions through fiber supported solid membrane for the demonstration and application.

GC the pressurized gas mobile phase chromatographic technique either with vertical or horizontal or coiled column based on the partition and movement of solute between gas and solid phase was used for the separation of chemical species. HPLC the pressurized liquid mobile phase chromatographic technique either vertical or horizontal column based on the partition and movement of solute between liquid and solid phase was used for the separation of chemical species. TLC the vertical plate (strip) based on the partition and movement of solute between liquid and solid phase technique uses the capillary mechanism for flow of liquid as mobile phase. The presently developed technique is the liquid chromatographic horizontal fiber column (based on the capillary mechanism) connects the source and receiving phases without flow of mobile phase. In this technique, the mechanisms involve the cation exchange and travel of solute (transport) through the fiber supported solid membrane column. In this technique, source, membrane and receiving phase are stationary phases and there is no mobile phase. The fiber plays the role of column and support. The travel of metal ion through the fiber supported solid membrane is the transport of metal ions through the fiber supported

solid membrane due to the driving force of the receiving phase (concentration gradients of chemical species).

In the separation technique, the movement of solute or transport of solute is carried out by using an extraction, adsorption, sorption and/or then or simultaneously the stripping, desorption, elution in the two phases solid-gas or solid-liquid or liquid-gas or liquid-liquid media by consecutive or simultaneous operations. In addition to this, in ion exchange chromatography, sorption and elution both processes are carried out by using two phases solid-liquid media one after the other. In solvent extraction, extraction and stripping both processes are carried out by using two phases liquid-liquid media one after the other. In TLC, GC and HPLC, adsorption (sorption, extraction) and desorption (elution, stripping) both processes are carried out using two phases solid-liquid (for HPLC, TLC) and solid-gas (for GC) media simultaneously. Moreover, in the separation technique, the movement or transport of solute is carried out in two phases media by two mechanisms, first is adsorption and de-sorption of solute by moving a liquid or gas or solid phase, and second is diffusion of solute by the stirring of phases. In the proposed fiber supported solid membrane technique, ion exchange and diffusion both mechanisms are involved, however, there is no mobile phase but involves the diffusion of solute by capillary action including ion exchange.

The aim of this paper is to explore the transportive separation of metal ions with maintaining the stability and efficiency of supported solid membrane system. The first idea is to use the porous solid fiber as support for membrane phase. The second idea is to chemically fix the solid membrane phase in the fiber. In this technique, the mechanisms involve the cation exchange and travel of solute (transport) through the fiber supported solid membrane. The transportive separation of palladium, gold and platinum metal ions have been explored from the aqueous source to receiving phase through fiber supported solid membrane in the mixed solvents of tricapryl methyl ammonium chloride (Aliquat-336), acetone, tetrahydrofuran, 1, 4 dioxane, methanol, ethanol, 2-propanol in hydrochloric acid.

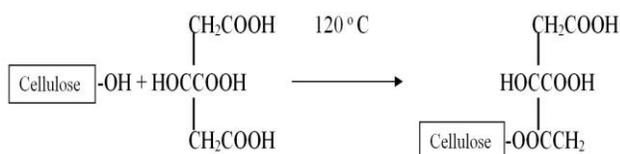
## Materials and Methods

### Chemicals

The dilute acid solution was prepared from concentrated acid solutions (Merck, India Ltd.) in distilled and de-ionized water. The cellulose porous solid fibers (Aldrich Chemicals) were used. Tricapryl methyl ammonium chloride (Aliquat-336), methanol, ethanol, 2-propanol, acetone, tetrahydrofuran and 1, 4 dioxan (Aldrich Chemicals CO, USA) were used without further purifications. The stock solutions of palladium, gold and platinum and other metal ions were prepared from their chlorides or nitrates or ammonium containing salts. The concentration of metal ion in the solution was analyzed by EDTA titrations or gravimetric or spectrophotometer determinations depending on the metal ion concentrations.

### Synthesis of Fiber Supported Solid Membrane

The experimental procedures and chemical modifications of cellulose fibers are done as described earlier [22]. The fibers were used with dimensions, the diameter 0.027 cm (270  $\mu\text{m}$ ) and porosity 30 to 50 %. The cross section area of porous fibers was  $5.73 \times 10^{-4} \text{ cm}^2$ . The amount of aqueous solution in the porous fiber was calculated by weighing the porous solid fibers before and after soaking in the aqueous solution. The cellulose fibers were modified by the scheme.

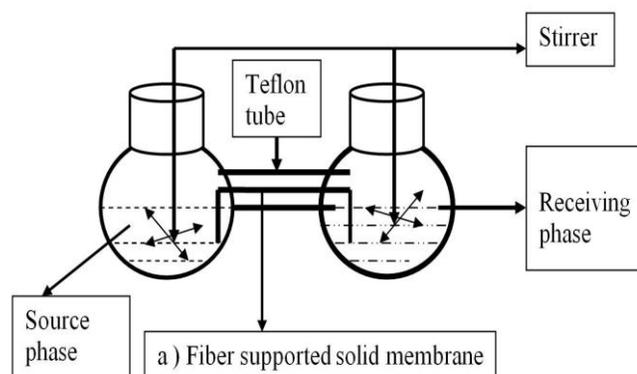


The pre-treated cellulose fiber was treated with 0.5M citric acid at the ratio of 1:12 (cellulose fiber: acid, w/v) and stirred for 30 min. The acid/cellulose fiber slurry was placed in a stainless steel reactor and dried at 50 °C in a forced air oven. After 24 h, the thermochemical esterification between acid and cellulose fiber was carried out by raising the oven temperature to 120 °C for 90 min. After cooling, the esterified cellulose fibers were washed with distilled water until the filtrate is free from citric acid (Tested

as no turbidity with 0.1M lead (II) nitrate solution). After filtration, the esterified cellulose fibers product was suspended in 0.1M NaOH at suitable ratio and stirred for 60 min, followed by washing thoroughly with distilled water to remove residual alkali, and then the wet modified cellulose fibers were dried at 50 °C for 24 h and preserved in desiccators for use. Before use, if necessary, the cellulose fiber product was converted into acidic form with the acid treatment [23-27]. The chemically modified fibers are termed as the fibers supported solid membrane. The metal ion transport studies were carried out through the fibers supported solid membrane. The teflon tube with od 0.4 and id 0.2 cm was used as support for the fibers supported solid membrane.

### Procedure for Determination of Metal Ion Transportive Rate

The solutions were used of a source solution with a suitable palladium or gold or platinum metal ions concentration in 15 ml in the source compartment of the cell, and the receiving phase 15 ml with appropriate concentration of acid or mixed solvents of acid, Aliquat-336 and organic solvents in the receiving compartment of the cell. The pH of source solution was adjusted with dilute hydrochloric acid and sodium hydroxide solutions. The source and receiving solutions were connected with fiber supported solid membrane (supported in teflon tube with 0.4 cm diameter od, id 0.2 cm) (Figure 1). The samples of the source and receiving solutions were withdrawn and analyzed. The permeability coefficients were determined for the analysis of data.

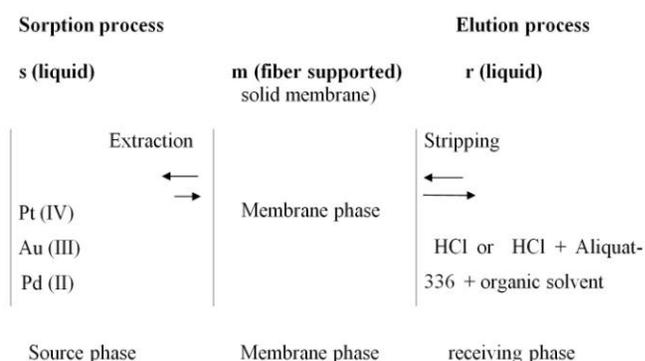


**Fig. 1.** The schematic presentation of fiber supported solid membrane cell.

## Results and Discussion

### Mechanism of Transportive Separation of Metal Ions

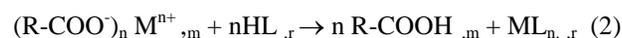
Figure 2 illustrates the transportive separation of palladium, gold and platinum metal ions from source to receiving through fiber supported solid membrane. There is no continuous flow of mobile phase either from source or receiving phase through the fiber supported solid membrane. However, there is a transportive separation of metal ions from the source phase through the membrane phase to receiving phase due the driving force of receiving phase. However, the ion exchange mechanism was used during the process of ion transportive separation through the fiber supported solid membrane. The capillary action mechanism in the porous fiber is assisting to maintain the liquid in the fiber during the transportive separation of metal ions. In the fiber, supported solid membrane phase (chemically bonded is citric acid) is used as the membrane barrier in between source and receiving phases. The transportive separation of metal ions are occurred through the fiber supported solid membrane phase because of the difference in gradient concentrations in between source and receiving phase, and also the driving forces of the acid and mixed solvents compositions in the receiving phase (Figure 2). The transportive separation of metal ion from source to receiving phase through membrane phase depends on the diffusion of metal ions and also the tendency of the metal ion complex formation, such as citrate, chloro, etc.



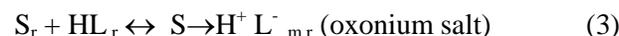
**Fig. 2. The metal ion transport through fiber supported solid membrane.**

### Reactions Involved in the Membrane Transportive Separation of Metal Ion

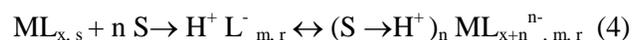
The fibers supported solid membrane cation exchanger transport metal ions from source solution through membrane phase to receiving phase as presented by following equation.



The solvents as methanol, ethanol, 2-propanol, acetone, tetrahydrofuran and 1, 4 dioxan in the receiving phase form oxonium salt with acids such as HCl, HNO<sub>3</sub>, etc., and acts as liquid anion exchangers [28-30]. The interface formed in the pores of the fibers in between source solution and receiving phase due to the capillary action was used as the membrane barrier for the transport of metal ions through fiber supported solid membrane. The formed liquid anion exchangers are used at the interface to carry the formed anions or anionic complexes from the interface towards the receiving phase. The use of mixed solvents in receiving solution enhances the metal anionic complex formation at the interface and consequently transport of metal ions from source to receiving phase. The formation of liquid anion exchangers of the solvent (S) with acid (HL) are given by the following equations.



The formed liquid anion exchangers transport the metal ions from interface to receiving phase as presented by following equation.



The role of Aliquat-336 (liquid anion exchanger) is to transport the negatively charged metal ion complexes from solid membrane to receiving phase as given below.



The metal ion concentration was determined with respect to time. The plots of  $\log C_t/C_0$  vs time (t) were presented in the Figure 3. The  $\log P$  values were calculated using the slope of the straight line, cross section area (A,  $5.73 \times 10^{-4} \text{ cm}^2$ ), and (l, 4 cm) length of fiber.

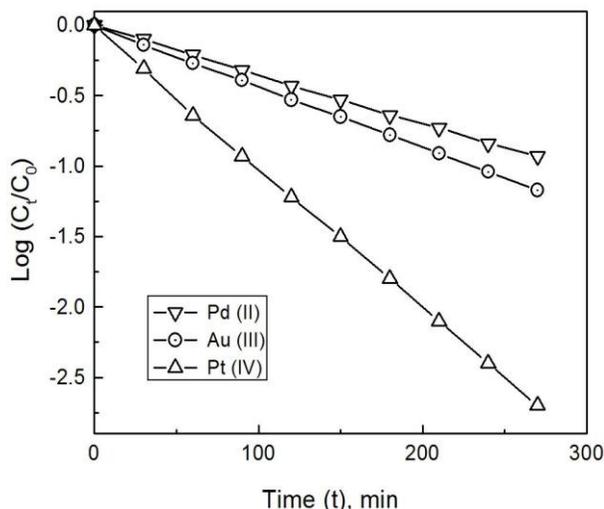


Fig. 3. The plot of  $\log C_t/C_0$  vs. time, Metal ion = 0.001 M, HCl = 0.1 M, Aliquat-336 = 20 % v/v and acetone = 60 v/v %.

### Estimation of Transportive Rate of Metal Ion

The transportive rate of metal ion is estimated as described earlier<sup>22</sup>. In the fiber supported solid membrane cell, the rate of change of concentration of metal ion ( $C^s$ ) 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 the Equation (7), where, k is a rate constant.

$$-dC^s/dt = k \cdot A/(V_s \cdot l) \cdot C_0^s \quad (6)$$

After integrating the equation (6), the permeability coefficient (P) of transport of metal ions is obtained by the equation (7). In the fibers supported solid membrane system, membrane supports can be used with the design of cross section area to length ratio (A/l), where length, l, is increased, while the cross section area, A, is decreased. Therefore, in the proposed fibers supported solid membrane system, by increasing the length, l, and decreasing the cross

section area, A, the membrane support becomes a fiber with a long length, l, and small cross section area, A, (As a fiber with long length and low cross section area A). The permeability coefficient of transport of metal ion is expressed by equation (7).

$$\ln(C_t^s/C_0^s) = -(A/V_s) \cdot (P/l) \cdot t \quad (7)$$

Where,  $C_0$  is the value of  $C_t$  at time zero. The permeability coefficient (P) is calculated from the plots of  $\log(C_t/C_0)$  vs t (time) by using membrane cross section area (A), length of fibers (l) and source phase volume ( $V_s$ ). The calculated permeability coefficient (P) is used to interpret the data of transportive separation of metal ions through porous solid fiber supported solid membrane at different experimental conditions.

### Effect of Fiber Length on Transportive Separation of Metal Ion

The plot of  $\log P$  against the length of porous solid fiber supported solid membrane is given in the Figure 4. 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 for the transportive separation of metal ion through the fiber supported solid membrane.

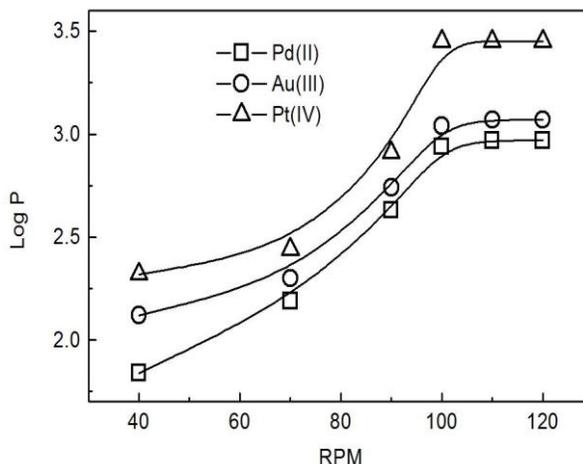


Fig. 4. Variability of  $\log P$  with respect to rpm of source and receiving phases, Metal ion = 0.001 M, HCl = 0.1 M, Aliquat-336 = 20 % v/v and acetone = 60 v/v %.

### Effect of Stirring Speed on Transportive Separation of Metal Ion

The stirring of source and receiving bulk solutions is essential in order to achieve the effective diffusion of 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. The increased in the P value was observed for the 40 to 100 rpm. This shows that 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.

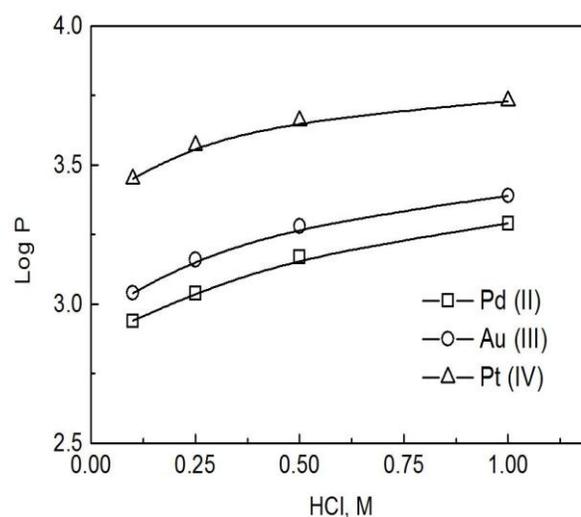
**Table 1. Log P values for platinum metal ions in HCl and mixed solvents for the variation of fiber supported solid membrane length.**

Fiber length	Metal ion, Pt(IV)	
	HCl	HCl-Aliquat-336
		-Acetone
1	0.92	3.69
2	0.89	3.62
3	0.77	3.56
4	0.67	3.45
5	0.62	3.41
6	0.58	3.3
7	0.54	3.2
8	0.52	3.11
9	0.49	3.01
10	0.47	2.91
15	0.46	2.82

### Effect of pH on Transportive Separation of Metal Ion

The effect of pH of source solution was explored for the transportive separation of metal ion from source to receiving phase through porous solid fiber supported solid membrane. The pH of source phase is varied from the 1 to 5. The variation of pH of source solution is an essential in order to dissociate the carboxylic acid group in the fiber solid membrane in presence of aqueous 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. The log P values were increased with the increased in the pH of 1 to 5 (Figure 5).



**Fig. 5. Dependency of P with HCl concentration in the receiving phase, Metal ion = 0.001 M, Aliquat-336 = 20 % v/v and acetone = 60 v/v %.**

### Effect of Acid Concentration on Transportive Separation of Metal Ion

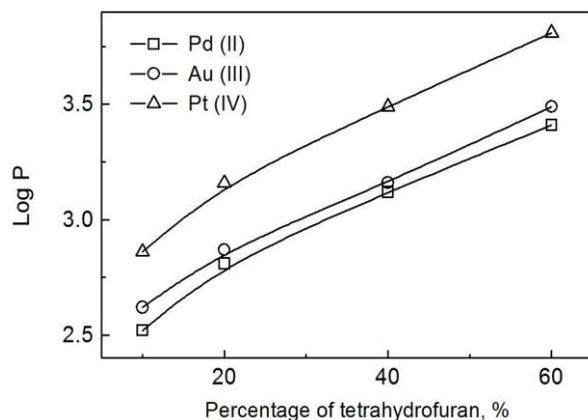
The transportive separation of metal ion through the porous solid fiber supported solid membrane depends on the difference in the gradient concentration in source and receiving phases. The effectiveness of driving forces of acid is explored for the transportive separation of metal ions from source to receiving phase through the fiber supported liquid membrane. The acid concentration in the receiving solution strip out the metal ion from the carboxylic acid groups from the fiber supported liquid membrane. The acid concentration in the receiving solution was varied for 0.1 to 1 M (Table 2). The increased acid concentration increases the log P values for the concentration range 0.1 to 1 M.

**Table 2. Log P values for palladium, gold and platinum metal ions in mixed solvents for the variation of pH of source solution.**

pH	Metal ion		
	Pd (II)	Au (III)	Pt (IV)
2	2.16	2.28	3.41
3	2.54	2.6	3.25
4	2.85	2.91	2.96
5	2.92	3.015	3.41

### Effect of Mixed Solvent on Transportive Separation of Metal Ion

The transportive separation of metal ions through the porous solid fibers supported solid membrane depend on the concentrations of organic solvents such as Aliquat-336, methanol, ethanol, 2-propanol, acetone, 1, 4 dioxan and tetrahydrofuran containing hydrochloric acid in receiving phase. The presence of organic solvents in the receiving solution enhances the transportive separation of metal ions from the source to receiving phase. The elution or stripping out the metal ions from the solid exchanger can be enhanced by the formation of ion pairs of negatively charged metal ion complexes with liquid anion exchangers in the mixed solvents. The Aliquat-336 and tetrahydrofuran percentage in the receiving solution was used 20 % v/v, and from 10 to 60 % v/v (Figure 6), respectively. The increased tetrahydrofuran percentage in the receiving phase increases the P values from the 20 to 60 % v/v.



**Fig. 6. The relation between P and percentage of organic solvent, Metal ion = 0.001 M, Aliquat-336 = 20 % v/v and HCl = 0.1 M.**

### Enrichment of Metal Ion Concentration

The initial concentration of metal ion in the source solution was varied in the range  $10^{-4}$  to  $10^{-2}$  M. 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 increase in the 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 palladium, gold and platinum metal ions in mixed solvents for the variation of metal ion concentration.**

Metal ion, log [M]	Metal ion		
	Pd (II)	Au (III)	Pt (IV)
-2	2.48	2.73	2.95
-3	2.74	3.09	3.27
-4	3.50	3.77	3.95
-5	4.33	4.59	4.78

### Log P Value in Different Mixed Solvent

The metal ion transport was carried out by using hydrochloric acid and organic solvents in mixed systems. The different combinations of acid and organic solvents are 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 metal ions through fiber supported solid membrane are observed in the sequence of decreasing efficiency as, fiber without modifications (mixed solvent as stripping agent in the receiving phase) > fiber chemically modified (mixed solvents 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 the decreasing efficiency of the organic solvents, Aliquat-336 + tetrahydrofuran > Aliquat-336 + 1, 4 dioxane > Aliquat-336 + acetone > Aliquat-336 + 2-propanol > Aliquat-336 + ethanol > Aliquat-336 + methanol > Aliquat-336.

**Table 4. Log P values for some metal ions for 0.10 M HCl in 20 % v/v Aliquat-336 in mixed solvents**

Metal ion	Methanol			
	10 %	20 %	40 %	60 %
Pt (IV)	2.91	3.01	3.11	3.12
Au (III)	2.72	2.82	2.93	3.03
Pd (II)	2.62	2.72	2.83	2.93
	Ethanol			
Pt (IV)	3.11	3.24	3.33	3.44
Au (III)	2.79	2.90	3.12	3.29
Pd (II)	2.69	2.80	2.91	3.13
	2-propanol			
Pt (IV)	3.14	3.28	3.50	3.70
Au (III)	2.83	3.01	3.23	3.44
Pd (II)	2.70	2.93	3.15	3.34
	Acetone			
Pt (IV)	2.80	3.03	3.21	3.44
Au (III)	2.52	2.73	2.82	3.03
Pd (II)	2.32	2.53	2.70	2.94
	1, 4 dioxane			
Pt (IV)	2.84	3.11	3.26	3.62
Au (III)	2.57	2.79	3.05	3.33
Pd (II)	2.45	2.71	2.90	3.16
	Tetrahydrofuran			
Pt (IV)	2.86	3.16	3.49	3.81
Au (III)	2.62	2.87	3.16	3.49
Pd (II)	2.52	2.81	3.12	3.41

### Separation of Metal Ions in Mixed Solvents

The separation factor  $\alpha$  ( $\alpha = P_1/P_2$ ) for the transportive separation of mixtures of metal ions through supported liquid membrane [31] had been explained. Where,  $P_1$  is the permeability coefficient of metal ion which is weakly bound and selectively favorable to chloride ion complex formation.  $P_2$  is the permeability coefficient of strongly bound and less selective favorable to chloride ion complex formation. Example, platinum is relatively weakly bound and favorable to form the chloride complex in comparison with those of properties of gold. Therefore, platinum is transported first.

The transportive separation of metal ions from binary mixtures was done by using hydrochloric acid and organic solvents. The used amount of metal ions in the source solution is given in the Table 5. Platinum, gold and palladium metal ions separations from the metal ions of magnesium, nickel, aluminum,

calcium, manganese, potassium, europium and lanthanum were carried out from the source solution through the fiber supported solid membrane by using 0.1 M HCl in 20 % Aliquat-336 and 60 % 1,4 dioxane in receiving phase. Magnesium, nickel, aluminum, calcium, manganese, potassium, europium and lanthanum metal ion were remained in the source solution and membrane phase.

The fiber supported solid membrane system is a versatile membrane technique for separation of metal ions. The supported solid membrane is chemically attached in the porous solid fibers therefore the fibers supported solid membrane system continuously runs several hours together. The time required for each operation varies from 3 - 4 h. However, the efficiency of fibers supported solid membrane depends on the pH of source solution, solid membrane and composition of mixed solvent in the receiving phase.

**Table 5. The separation of platinum (Pt (IV) = 0.15 mmol) from binary mixtures in mixed solvent system**

Foreign ions	Foreign ions amount added mmol	Platinum (IV) found, mmol	Recovery(%)	Mixed solvents for platinum metal ion
Mg (II)	0.15	0.149	99.3	0.10 M HCl in 20 % v/v Aliquat-336 in 60 % 1, 4 dioxane
Ni (ii)	0.20	0.15	100	
Al (III)	0.20	0.15	100	
Ca (II)	0.15	0.148	98.7	
Mn (II)	0.20	0.15	100	
K	0.15	0.149	99.3	
Eu (III)	0.20	0.20	100	
La (III)	0.20	0.15	100	

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The fiber supported solid membrane system is a versatile membrane technique for separation of metal ions. The supported solid membrane is chemically attached in the porous solid fibers therefore the fibers supported solid membrane system continuously runs several hours together. The time required for each operation varies from 3 - 4 h. However, the no pollution problem and no limitation of small and

efficiency of fibers supported solid membrane depends on the pH of source solution, solid membrane and composition of mixed solvent in the receiving phase.

## Conclusions

The aim of this paper was to explore the transportive separation of metal ions with maintaining the stability and efficiency of supported membrane system. The first idea was to use the porous solid fiber as support for the membrane phase. The second idea was to chemically fix the solid membrane phase to the fiber. Therefore, an idea was to demonstrate the esterified citric acid over cellulose fiber as solid membrane phase and its practical application. The transportive separation of metal ions was investigated from source to receiving phase through fiber supported solid membrane in acidic and mixed solvents system by using in the receiving phase. The transportive separation of metal ions depends 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 useful in the fiber supported solid membrane system. The design and development of chemically modified fiber supported solid membrane system is a versatile technique. It overcomes the different disadvantages of the solvent extraction and ion exchange techniques such as no dispersion of solvent phase, no need of loss of extracting phase or costly extractants, large volumes.

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