

Characterization of Lithium Ion Transport Via Dialysis Process

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Abstract

Dialysis is a membrane based separation process in which the concentration gradient across the membrane is the driving force resulting in a flow of material from one side of the membrane to the other. In this study membranes (Accurel, Celgard, GVHP, PM30 and PTHK) with different pore sizes were employed to characterise the transport of lithium ion in various (0.01, 0.1, 0.5, 1 and 2.5 w/v percent) initial feed concentrations via the dialysis process. This may be considered as a basis for wastewater treatment containing metal ions. The results show that low initial feed concentration causes less passage of ions through the membrane due to low driving force i.e. concentration gradient across the membrane. The investigation of the effect of membrane pore size on ion transport revealed that large pore size membranes provide less penetration of the metal ions through the membrane. These reproducible results, which are not expected, have been explained by the transport mechanism. Two types of mechanisms (extensive versus intensive) have been suggested for metal ion transport through different membranes. If the mechanism of ion transport is intensive, more ions pass through the membrane. Extensive mechanism results in lower ion transport through the membrane.

Keywords: membrane, dialysis, lithium, wastewater, ion transport, mechanism

Introduction

Dialysis is a membrane based separation process in which the concentration gradient across the membrane is the driving force resulting in a flow of material from one side of the membrane to the other. The transport is due to the solution-diffusion mechanism [1]. Most researchers have employed an ion-exchange membrane indicating the process as diffusion [2] or Donnan dialysis [3-5]. The process is based on the Donnan equilibrium principle [6] with the usual aim being the separation of ions or charged species. The transport in the Donnan dialysis is a function

of two phenomena, i.e. diffusion due to the concentration gradient, and migration due to the potential gradient arising from the difference in ionic concentrations across the membrane [5]. Another important parameter affecting the permeation of ions is the membrane charge [7], which depends on the pH, and the electrolytes in the bulk solution [7].

Dialysis is able to solve two important industrial problems, i.e. recovery of valuable materials and removal of undesired ions from waste streams [8]. The process has been used to recover various acids including organic

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acids [2] from waste streams generated in steel, metal-refining, and electro-plating industries [2], and to remove Na^+ [9], Cu^{+2} [5], Ni^{+2} [10], ternary (Cu^{+2} - Ni^{+2} - Co^{+2}) ion system [11], nitrate [12] and fluoride [4]. In dialysis, the improvement of permeation and selectivity is the key point for industrial applications. For this purpose, ion-exchange membranes are combined with complexing agents (such as EDTA [10] or citric acid [3]) for the enrichment of metal ions [11].

Although numerous papers have dealt with the Donnan dialysis using ion-exchange membranes, the employment of other types of membranes is scarce. Marty et al [13] used an ultrafiltration polysulfone membrane with a molecular weight cut-off of around 10 KD for the dialysis of Ni^{+2} . They employed a hydrosoluble chelating polymer with carboxylate groups to enhance the performance [14], and suggested this system for concentrating high volumes of heavy metal diluted solutions.

In this study, a dialysis process using a wide range of porous membranes, excluding ion-exchange membranes, was employed for lithium ion transport to remove the metallic ion from the feed. This study may be considered as a basis for wastewater treatment containing metal ions.

Materials and Methods

Dialysis was carried out in a stirred cell represented in Fig 1. The cell consisted of two chambers. The membrane was sandwiched between the two half cells. The effective volume of each cell was 75 ml. The whole membrane disc was 4.7 cm in diameter and the effective part was 3.6 cm in diameter.

Lithium nitrate (from Merck) was used for the preparation of metal ion solutions. For each set of experiments, the solution containing a specified amount of lithium ion was introduced in the feed side of the cell. The strip side of the cell was filled with deionised water. The experiment was commenced immediately by starting the stirrers to move at a specified speed. A wide range of concentration in the feed side i.e. 0.01, 0.1, 0.5, 1 and 2.5 percent (w/v) was tested. Over time the concentration of the lithium ion in the strip side was measured using an atomic absorption analyser (Shimadzu Model AA-670).

A variety of membranes were used to elucidate the effect of membrane characteristics including pore sizes. The specifications of the membranes used are represented in Table 1.

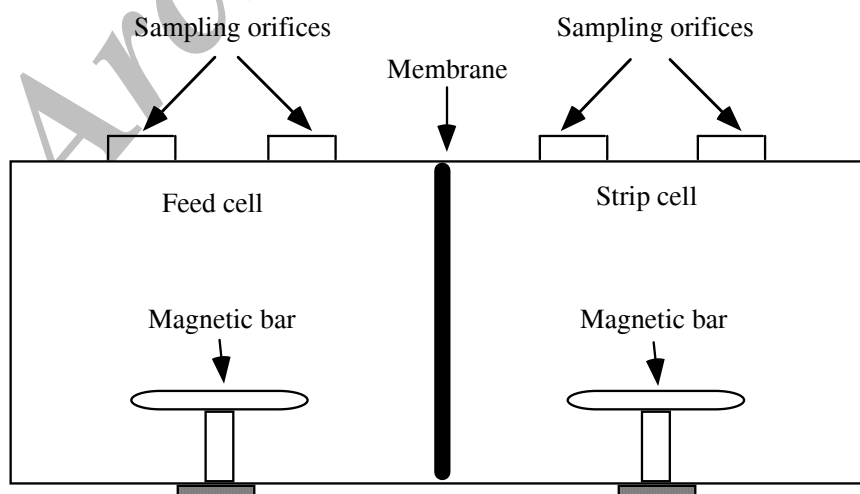


Figure 1. Experimental set-up.

Table 1. Specifications of membranes.

	PM30	PTHK	Celgard	Accurel	GVHP
Manufacturer	Amicon	Millipore	Hoechst	Akzo Nobel	Millipore
Material	PS ⁽¹⁾	PS ⁽¹⁾	PP ⁽²⁾	PP ⁽²⁾	PVDF ⁽²⁾
Hydrophobicity	hydrophobic	hydrophobic	hydrophobic	hydrophobic	hydrophobic
MW Cut-Off (Da)	30,000	100,000	[-]	[-]	[-]
Mean Pore Size (μm)	0.004	[-]	0.05	0.1	0.22
Porosity (%)	5.9	[-]	38	45	60
Thickness (μm)	100	130	40	90	120

(1) polysulphone

(2) polypropylene

(3) polyvinylidene fluoride

Results and Discussions

Lithium ion transport through various membranes with different feed concentrations based on a dialysis process was measured. The results of the ion transport through

different membranes are shown in Figures 2 to 6 for various initial feed concentrations. A summary of the results is presented in Table 2.

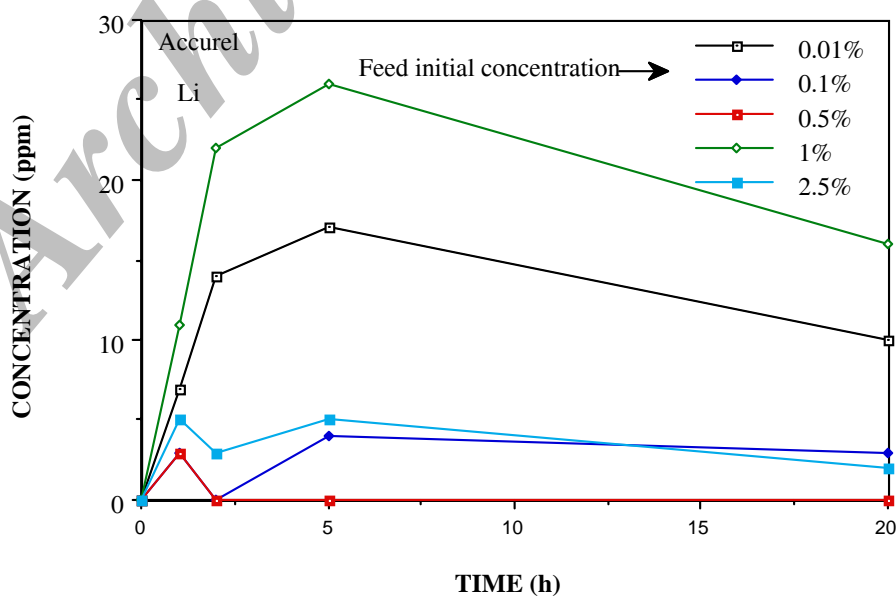


Figure 2. Concentration of lithium ion in the strip side versus time for different feed concentrations (Accurel membrane).

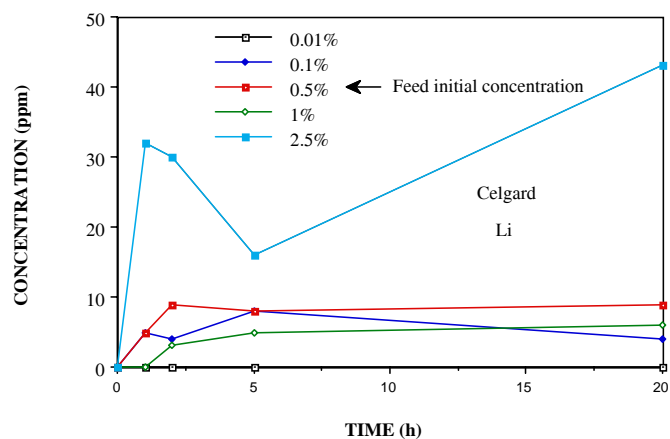


Figure 3. Concentration of lithium ion in the strip side versus time for different feed concentrations (Celgard membrane).

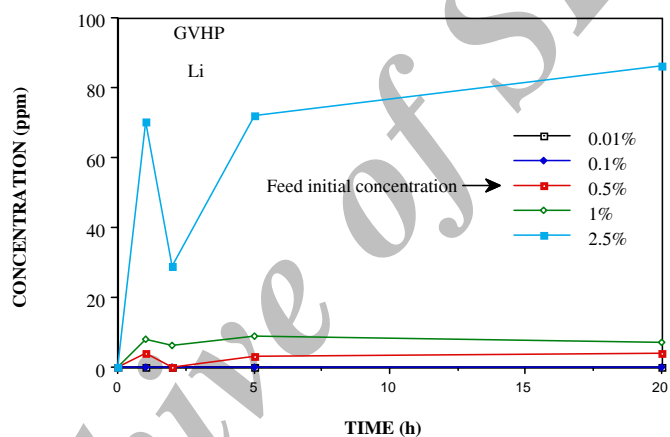


Figure 4. Concentration of lithium ion in the strip side versus time for different feed concentrations (GVHP membrane).

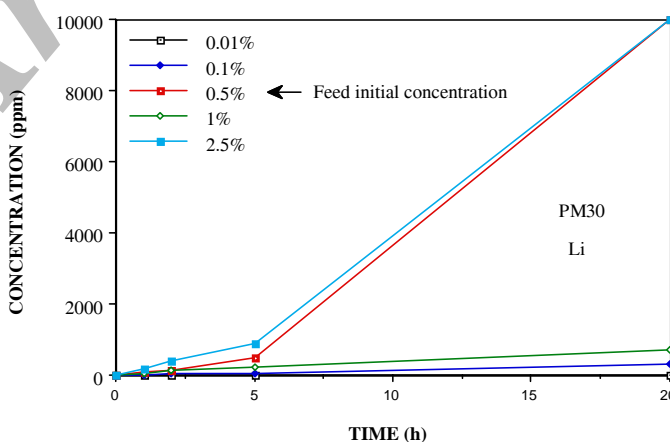


Figure 5. Concentration of lithium ion in the strip side versus time for different feed concentrations (PM30 membrane).

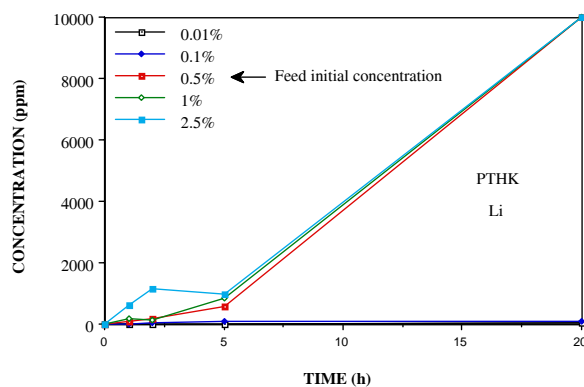


Figure 6. Concentration of lithium ion in the strip side versus time for different feed concentrations (PTHK membrane).

Table 2. Concentration (ppm) of lithium ion in the strip side versus time for different membranes and various initial feed concentrations.

TIME (h)	IFC* 0.01%	IFC 0.1%	IFC 0.5%	IFC 1%	IFC 2.5%	Membrane
0	0	0	0	0	0	PM30
1	0	5	91	56	180	“
2	3	32	150	117	416	“
5	5	28	495	225	902	“
20	10	295	10000	695	10000	“
0	0	0	0	0	0	PTHK
1	0	14	84	159	632	“
2	0	35	192	127	1175	“
5	7	87	582	862	8000	“
20	28	84	10000	10000	10000	“
0	0	0	0	0	0	Celegard
1	0	5	5	0	32	“
2	0	4	9	3	30	“
5	0	8	8	5	16	“
20	0	4	9	6	43	“
0	0	0	0	0	0	Accurel
1	7	3	3	11	5	“
2	14	0	0	22	3	“
5	17	4	0	26	5	“
20	10	3	0	16	2	“
0	0	0	0	0	0	GVHP
1	0	0	4	8	70	“
2	0	0	0	6	29	“
5	0	0	3	9	72	“
20	0	0	4	7	86	“

* initial feed concentration

These Figures indicate that the concentration of ions in the strip side is initially increased. The concentration reaches a plateau and increases or decreases during the time after the initial increment. The plateau curves indicate the equilibrium between passing the ions through the membrane and the back diffusion of the ions from the strip side towards the feed side. The increasing graphs represent the ongoing transport of ions from the feed side. If back diffusion is prevailing, the concentration of ions in the strip side is declined. In the dialysis process, the driving force is the differences between the concentrations in the two sides of the membrane. In general, the ion transport depends on molecular diffusion and bulk transport. In our experiments, bulk transport has no effect on ion movement due to the hydrophobicity of the membranes. In other words, water is a media that does not pass through the membrane, so it is not a factor for ion transport. Ion diffusivity depends on interactions between ions and membrane pores, as well as ions themselves. If the number of ions is limited (e.g. low ion concentration), the ion fluctuation occurs in a large distance, i.e. the fluctuation range is high. The low number of ions causes a lower collision of ions, resulting in a higher fluctuation range. If the number of ions is high (e.g. high concentration), the ions collide more frequently, resulting in less movement of the ions or a low fluctuation range. We call the ion movement based on the first state "extensive mechanism", and the second, "intensive mechanism". In the extensive mechanism it is probable that the ions energy is compared with the intensive mechanism.

If the mechanism of ion transport is in-

tensive, more ions pass through the membrane. Extensive mechanism results in lower ion transport through the membrane.

Now consider the same concentration of the feeds challenged with small and large pore-size membranes. For small pore size membranes, initially there is a greater accumulation of ions in the feed side due to less chance of ion passage through the membrane. Greater accumulation of the ions results in a higher concentration, corresponding to the intensive mechanism and higher transport of the ions through the membrane. In the case of large pore size membranes, the initial lower accumulation of the ions in the feed side causes less concentration and extensive mechanism results in a lower passage of ions.

Our results (Figures 7 to 11) show that for large pore size membranes (GVHP), with extensive mechanism there is less passage of the ions through the membrane compared with small pore size membranes (PTHK, PM30). Intensive mechanism for the latter membranes causes greater passage of the ions. For membranes with pore sizes between these two categories (Celgard, Accurel), a mixed mechanism occurs. This results in less passage of the ions compared with small and large pore size membranes. For a mixed mechanism there is no high energy like the intensive mechanism, nor freedom such as extensive mechanism, so the passage is less compared with the other mechanisms. Mixed mechanism is the transition from intensive to extensive mechanism.

In summary we suggest that, for different pore size membranes tested in this study, the mechanisms are as follows:

20 nm - 100 nm	0.05 μm - 0.1 μm	0.1 μm - 0.2 μm
intensive mechanism	mixed mechanism	extensive mechanism
high number of ions	medium number of ions	low number of ions

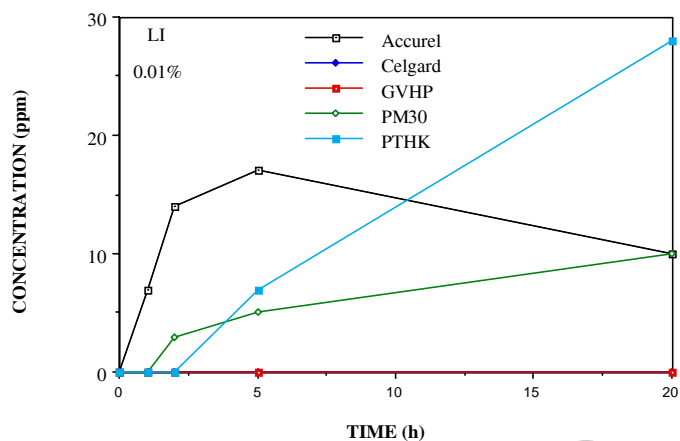


Figure 7. Concentration of lithium ion in the strip side versus time for different membranes (initial feed concentrations = 0.01%).

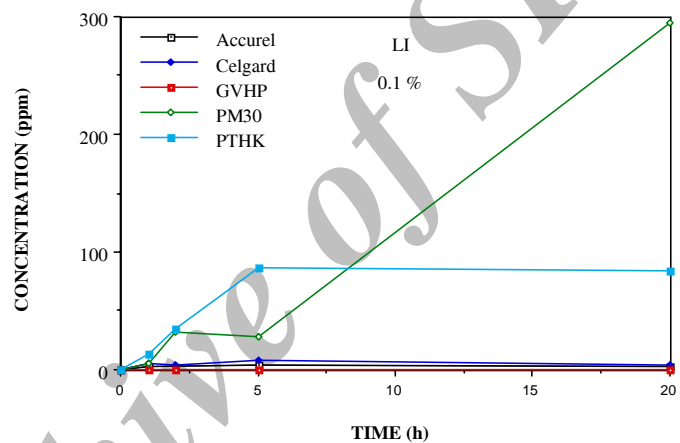


Figure 8. Concentration of lithium ion in the strip side versus time for different membranes (initial feed concentrations = 0.1%).

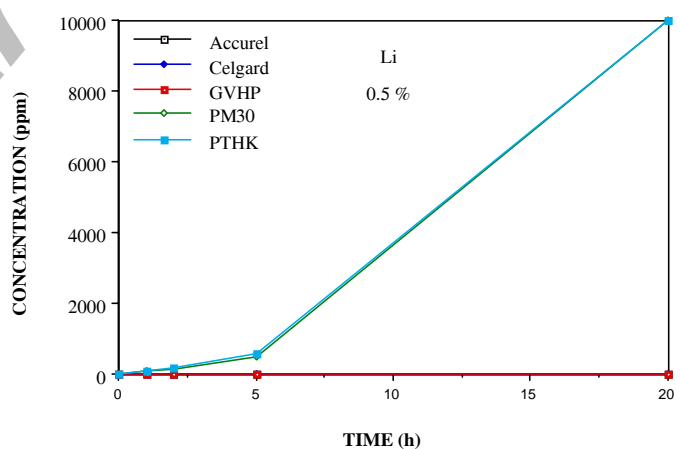


Figure 9. Concentration of lithium ion in the strip side versus time for different membranes (initial feed concentrations = 0.5%)

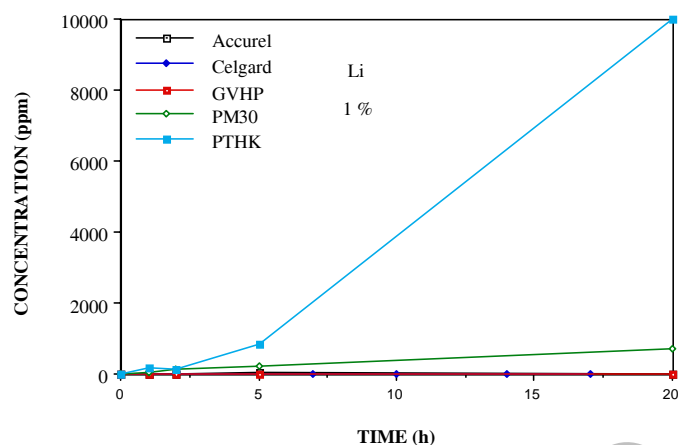


Figure 10. Concentration of lithium ion in the strip side versus time for different membranes (initial feed concentrations = 1%)

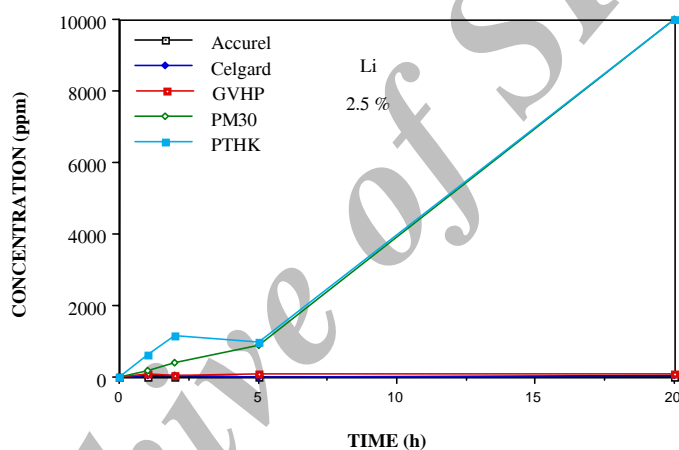


Figure 11. Concentration of lithium ion in the strip side versus time for different membranes (initial feed concentrations = 2.5%)

The range of mechanism change depends on many factors including the type of feed and membrane. However for the feed and membranes tested in this work, it seems that the above chart is more convenient.

Conclusions

The results of this study show that for large pore size membranes there is less passage of the ions through the membrane compared with small pore size membranes. Different mechanisms of metal ion transport are responsible for this unexpected observation. Extensive mechanism for the first category

and intensive mechanism for the latter membranes cause greater passage of the ions. For membranes with pore sizes between these two categories, a mixed mechanism occurs. This results in less passage of the ions compared with small and large pore size membranes.

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