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Abstract: The metal recovery from red mud solution containing chelating agents such as nitriloacetic acid (NTA), ethylenediaminetetraacetic acid (EDTA), citric acid, and phosphoric acid were studied by using the Neosepta CMX and CMB cation exchange membranes in Donnan dialysis process. The stripping solution was 1.0 M HCl solution and no external potential field is applied. The efficiency of chelating agents on the recovery of metal ions through membranes was correlated with the flux data. It was observed that the removal and fluxes of metals were enhanced with citrate, EDTA and NTA chelating agents in contrast were decreased with phosphate complexing agent.

Keywords: Donnan dialysis, chelating agents, red mud, cation exchange membranes, metal recovery

INTRODUCTION

Recently, great attention has been paid to develop an efficient technique for separation and recovery of toxic metal ions. One of these methods, the

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Donnan dialysis which is a membrane-based equilibrium process and different from the classical dialysis technique, is used for purification and concentration of diluted solutions, particularly for recovery of valuable ions and removal of undesired ions from waste effluents (1). The main advantage of this process is economical, simple, and especially energy saving. In spite of these advantages, the process is not applied mainly in industry. However, some potential applications at laboratory scale for treatment of metals (alkali, alkali earth, transition, and rare earth) have been conducted (2–4).

Concerning the chelating agents, few studies were carried out (4, 5). Strong chelating agents such as EDTA, NTA, and citric acid are commonly used in metal plating, water softening, photography, textile and paper processing, and industrial cleaning industries (6–9). Particularly these agents are applied for complicated treatment of industrial polluted effluents and used by reducing the efficiency of metal removal using of chemical precipitation (e.g. OH^-, S^{2-}), ion exchange or other analytical processes (10). They definetely alter by complexation of the migration behavior of metals. On the other hand, the removal of heavy metals by reaction with complexing agents including EDTA, NTA, and citric acid is quite often used and it is pointed out that the complexing agents are an efficient method (11–13), but also the main disadvantages is the high cost of these agents. Also, the migration behavior of metals in aqueous solution can be altered significantly due to complexation. Therefore, the treatment methods and particular complexing agents for metal recovery must be confirmed.

Red mud (bauxite wastes of alumina manufacture) emerges as unwanted by-products during the alkaline-leaching of bauxite in the Bayer process. About 500.000 m^3 of strongly alkaline (pH $\approx$ 12–13) red mud-water pump is dumped annually into specially constructed dams around Seydisehir Aluminium Plant. Since the plant began to process, red mud accumulated over time, therefore, causing serious environmental problems. Today, its disposal and utilization is one of the main problems for all alumina industries in the world. Red mud has been used as absorbents, building materials, catalysts, fillers, and pigments (14–16), and considered as a secondary raw material for the recovery of valuable substances. The recovery of alkali, iron, aluminium, and titanium from red mud has been studied (17–19).

The recovery of metals particularly titanium from aqueous red mud solution was examined by using both charged polysulfone membrane (20) (homogeneous composition) and CMX CMB membranes (21), as well as the separation of Fe(III) and Ti(IV) from binary mixture solution including EDTA (22) in terms of the Donnan dialysis conditions. However the work reported here was conducted to give better knowledge about metal recovery in the presence of various chelating agents which differentiate the equilibrium uptake of metals and affects the selectivity of membranes towards metal ions. These data would be useful and critical because of the further investigation of the process for electrodialysis treatment. The recovery of metals across Neosepta CMX and CMB cation exchange membranes was studied in a batch cell.

EXPERIMENTAL

H_3PO_4, HCl, $C_{10}H_{14}N_2Na_2O_8 \cdot 2H_2O$ (EDTA), and $C_6H_8O_7$ (citric acid) from Merck Co., and $C_6H_6Na_3O_6 \cdot H_2O$ (NTA) were supplied from Fluka and all chemicals were analyzed to be of reagent grade. The cation exchange membranes Neosepta CMX and CMB were supplied by Eurodia Ltd., the membranes are homegeneous films, strongly acidic cation exchange membranes. Details of their chemical structure cannot be known but they contain sulfonated functional groups and their properties are listed in Table 1. To remove impurities, the membrane was conditioned by a cycle of equilibrations with H_2SO_4, distilled water, NaOH, distilled water again, and then the resulting membrane was immersed in 1 M HCl before use.

Red mud was supplied from Etibank Seydisehir Aluminium Plant, and had the following average composition (% by wt): Al_2O_3: 18.71 ± 0.59, Fe_2O_3: 39.70 ± 0.67, TiO_2: 4.90 ± 0.54, Na_2O: 8.82 ± 0.96, CaO: 4.47 ± 0.56, SiO_2: 14.52 ± 0.37, loss on ignition: 8.15 ± 0.40. The preparation of red mud solution was described in a previous paper (20, 21). Experiments were performed on this solution which was diluted as 1/2 from the original stock solution that constis of Al(III): $1.73 \pm 0.04 \times 10^{-2}$, Fe(III): $2.51 \pm 0.06 \times 10^{-2}$, Ti(IV): $0.29 \pm 0.01 \times 10^{-2}$, and Na(I): $1.52 \pm 0.01 \times 10^{-2}$ M and chelating agents were added as an equimolar of Fe(III) ion. The same equimolar solution of chelating agents was added to compare their effectivenss.

For the measurement of the diffusional flux of metal ions, a two-compartment cell (made of Teflon) was used. The membrane was clamped tightly between two compartments of 40.0 ml capacity and the surface area of the membrane was 7.1 cm^2. The donor solutions were either red mud solution or containing the chelating agents, while the stripping solution consisted of 1.0 M HCl solutions. The sampling of the solution was carried out at certain time intervals and the amount of metal ions transported across the membrane was determined by use of an ICP-AES (Varian, vista\AX CCD

Table 1. Properties of the cation exchange membranes used in this study

Property	Neospeta CMX	Neosepta CMB
Type	Strongly acidic cation permeable	Strongly acidic cation permeable
Characteristics	High mechanical strength	High mechanical strength
Ion exchange groups	Sulfonate	Sulfonate
Thickness (mm)	0.18	0.22
Electrical resistance (Ω cm^{-2})	3.1	4.3
Ion exchange capacity (meq/g)	1.7	2.6
Water content (%)	25	30

Simultaneous ICP-AES). Both external solutions were stirred at 600 rpm with a magnetic stirrer. All the measurements were carried out at 25°C. All experiments were carried out in Donnan dialysis process and no electric current was applied.

RESULTS AND DISCUSSION

In order to compare the recovery of metals ions, the flux was evaluated for all of the experimental conditions. The metal flux, J_M, was obtained from the time profile of stripping phase concentration of metal by initial rate technique.

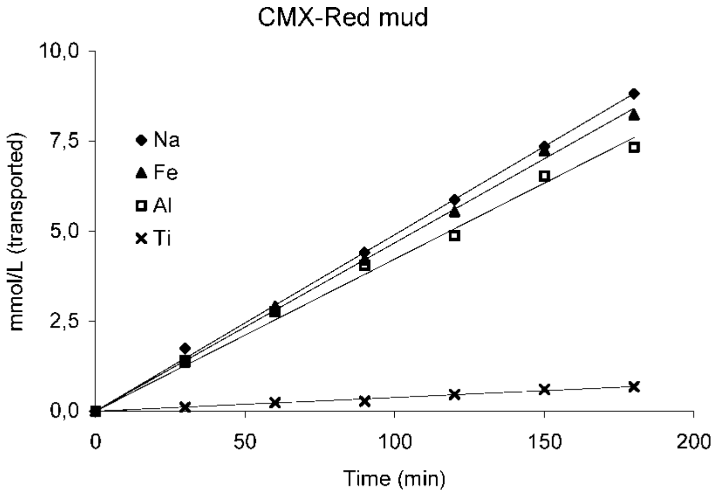
$$J_M = \left(\frac{V}{A}\right)\left(\frac{dM^{n+}}{dt}\right)_{t\to 0} \tag{1}$$

where V is the volume of stripping solution, A is the effective membrane area. In fact, J_M is calculated by differentiating the curve-fit polynomials of the time profiles up to 30 min. Each experiment was at least duplicated and reproducibility of flux measurements was mostly found within 5% and thus the calculated fluxes were given in Table 2.

First, the experiment was conducted to determine the recovery order of Al(III), Fe(III), Ti(IV), and Na(I) ions without any chelating agents added. The obtained example of typical curves on the stripping phase versus time is shown in Fig. 1 for both membranes. The transport order of metals from red mud was found to be in the order Na(I) > Fe(III) >Al(III) > Ti(IV) for CMX membrane and Na(I) > Al(III) > Fe(III) > Ti(IV) for CMB membrane.

Table 2. The obtained flux values of the membranes for Al(III), Fe(III), Ti(IV) and Na(I) ions with the chelating agents

	$J \times 10^{11}$, (mol cm^{-2} s^{-1})			
Experiment	Al	Fe	Ti	Na
	CMX membrane			
Red mud	404.53 (±0.22)	440.17 (±0.02)	34.00 (±0.05)	462.24 (±0.12)
EDTA	528.43 (±0.18)	93.35 (±0.02)	42.66 (±0.06)	1154.17 (±0.24)
Citrate	454.89 (±0.29)	462.80 (±0.07)	40.90 (±0.06)	517.68 (±0.33)
NTA	443.56 (±0.04)	371.71 (±0.344)	43.45 (±0.34)	1471.00 (±0.72)
Phospate	56.58 (±0.24)	34.29 (±0.03)	33.83 (±0.07)	331.54 (±0.17)
	CMB membrane			
Red mud	177.09 (±0.45)	151.06 (±0.09)	10.41 (< ±0.01)	342.29 (±0.36)
EDTA	323.62 (±0.56)	98.44 (±0.08)	25.80 (±0.01)	1007.07 (±0.34)
Citrate	315.70 (±0.39)	205.38 (±0.14)	36.55 (< ±0.01)	434.51 (±0.05)
NTA	316.27 (±0.20)	230.83 (±0.05)	32.87 (±0.01)	1357.85 (±0.07)
Phospate	38.76 (±0.03)	35.47 (±0.20)	16.35 (±0.01)	248.94 (±0.07)



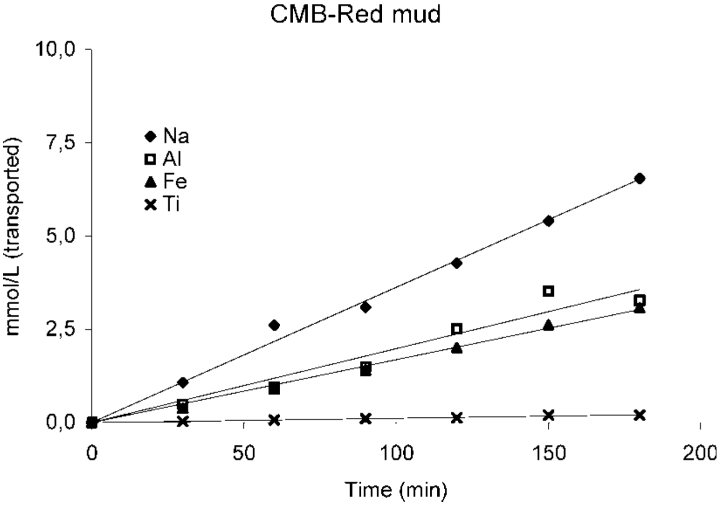


Figure 1. Time profiles of recovered metals without chelating agents across the membranes.

This order was in agreement with Hofmeister series which was performed in terms of membrane chemistry (23). It can be seen that over time, Na(I), Al(III), and Fe(III) together increases almost linearly and gradually Ti(IV) for CMX membrane. In case of CMB membrane, the increasing was observed as separately for all metals.

Second, the main experiment was conducted by adding of chelating agents into the feed phase. Time profile of recovered metals with NTA chelating agent is illustrated in Fig. 2. It is seen that the the recovery of metals strongly depends on the NTA chelating agent which is affected significantly by the recovery of Al(III) and Fe(III) and that order was changed from the original state. This difference was opposite to that of the formation constants of Al(III) and Fe(III) metals with this chelating agent. However, the transport of Na(I) ion was significantly increased. This result is due to the structure of the chelating agents which contains already 3 mol Na in its structure.

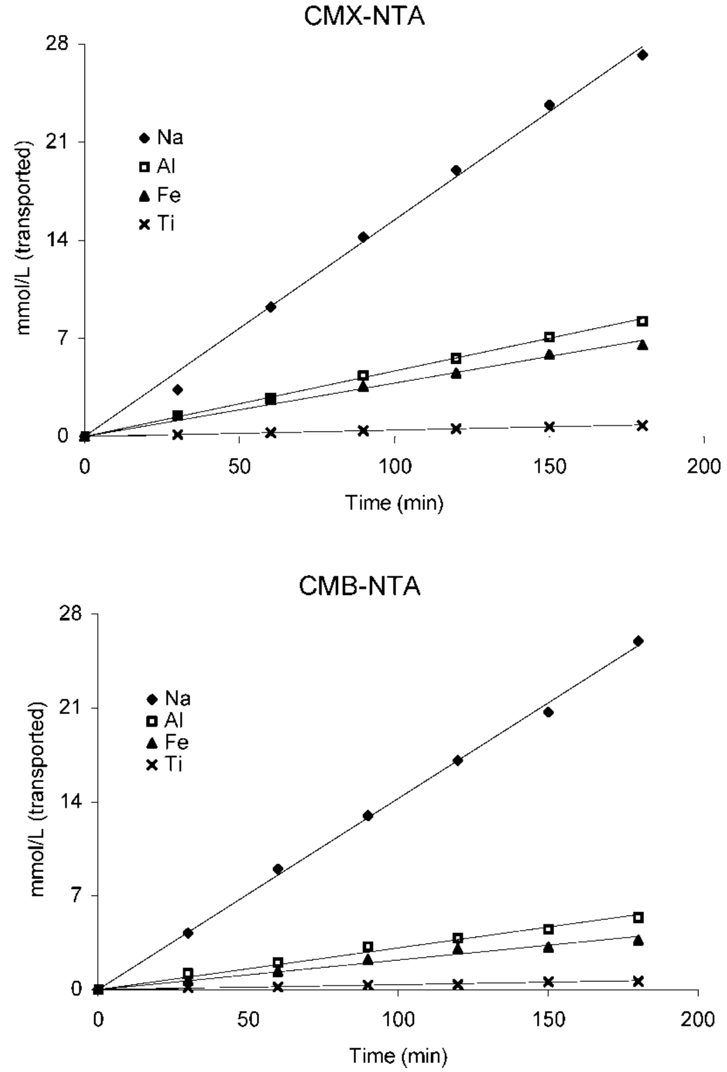


Figure 2. Time profiles of recovered metals with NTA chelating agents across the membranes.

Time profile of recovered metals with EDTA chelating agent was illustrated in Fig. 3. It is seen that the metal recovery was found to be in the order Na(I) > Al(III) > Fe(III) > Ti(IV) for both membranes. As expected, in this experiment that the significant difference was observed with EDTA-Fe complex. As seen in Fig. 3 the recovery of Al was somewhat increased by adding of EDTA while it was in the reverse with respect to the original

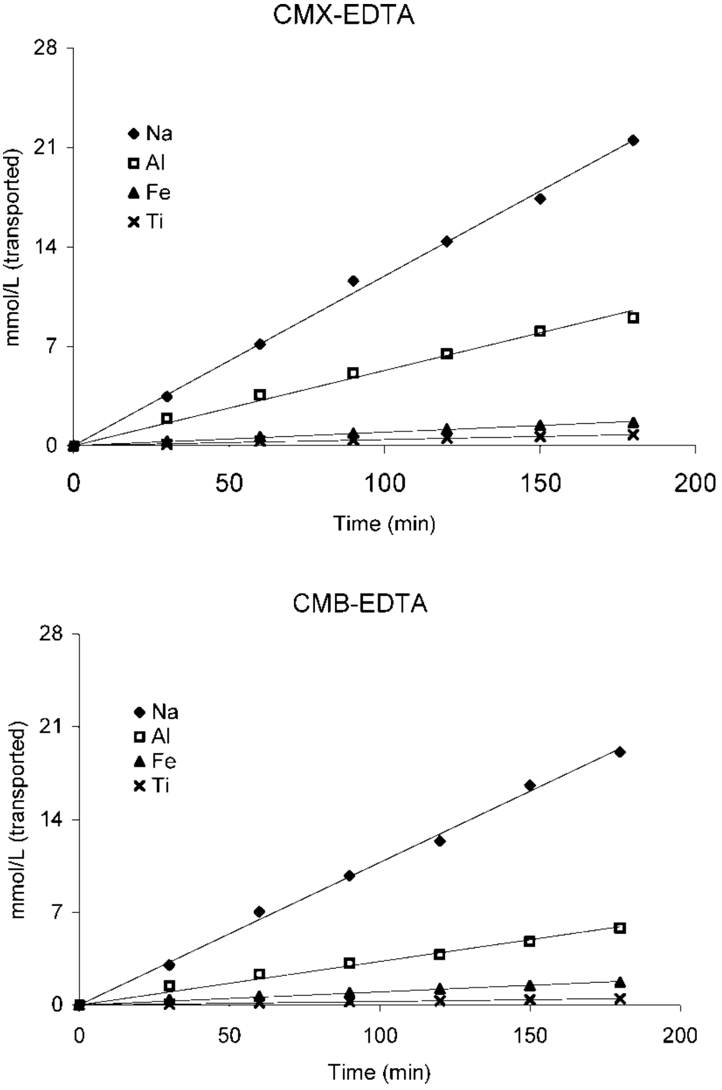


Figure 3. Time profiles of recovered metals with EDTA chelating agents across the membranes.

solution for CMX membrane. The fluxes of Ti(IV) was also increased with the EDTA chelating agents. On the other hand, Na(I) maintains nearly constant and increases somewhat. The complexing agents we examined have a higher affinity and act as a masking to cationic metals than to the Na.

Transport of metals by adding of citric acid and phosphoric acid chelating agents were plotted as function of time in Figs. 4 and 5, respectively. The presence of citrate complexing agents affect the recovery process significantly and the recovery order for metals was found to be same order as Na(I) >

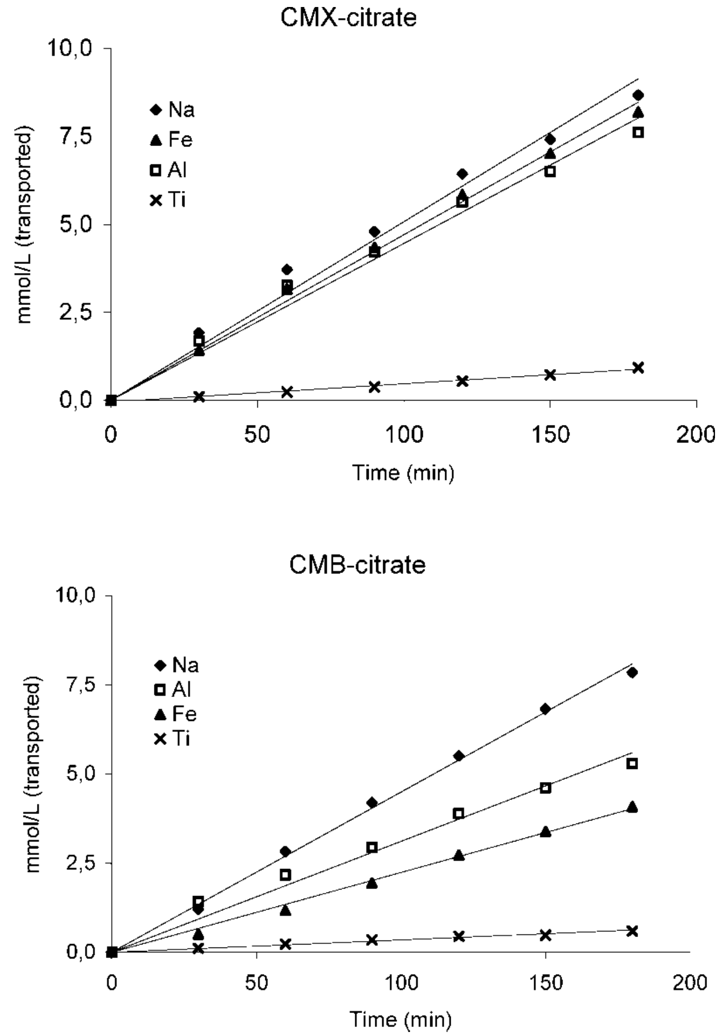


Figure 4. Time profiles of recovered metals with citrate chelating agents across the membranes.

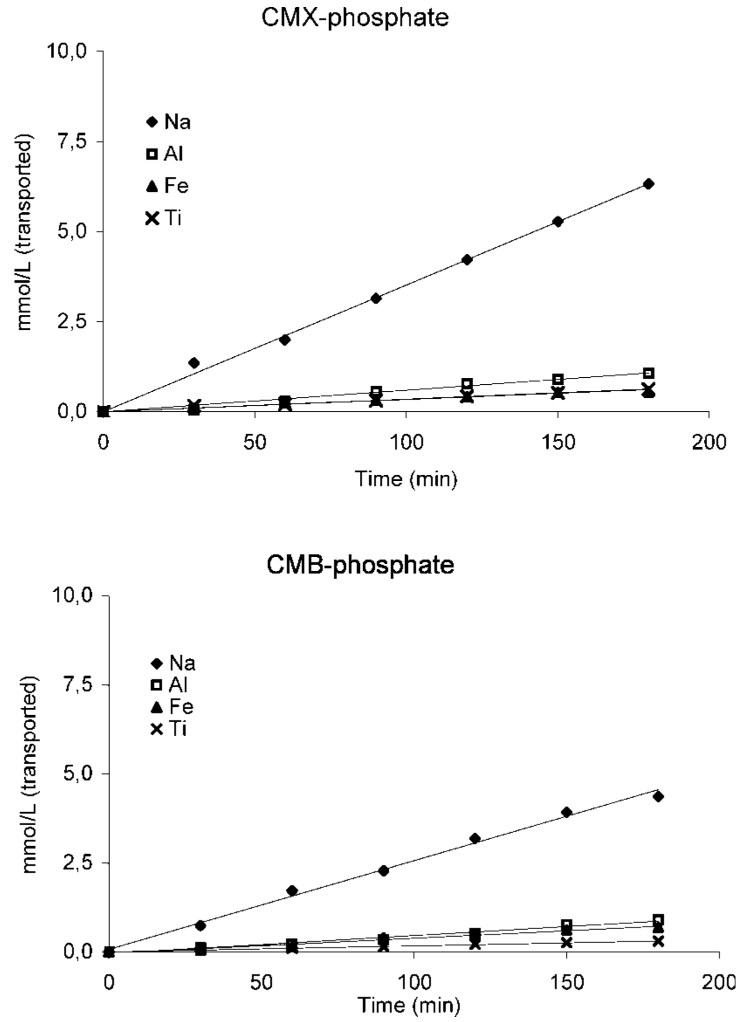


Figure 5. Time profiles of recovered metals with phosphate chelating agents across the membranes.

Fe(III) > Al(III) > Ti(IV). It is indicated from Fig. 4 that a significant difference was found for Ti(IV) which dramatically increased more than two-fold with respect to other chelating agents. An interesting result was obtained with phosphate chelating agents which has an influence on process affectiveness as masking. Thus, the recovery of metals dramatically deteriorated. For all metals the results showed a decrease of metal recovery with phosphoric acid and it might be explained by a higher degree of dissociation of acidic groups as phosphate, involved in metal binding.

Basically, the chosen complexing agents, citric acid, NTA, EDTA, and H_3PO_4 are all polyprotic acid (H_xL) which can exist in a number of many protonated forms in aqueous solution and readily form stable chelates with most heavy metals in 1 : 1 molar ratio over a wide pH ranges (24). The transported quantities of metals were compared and the transport for chelated forms for Al(III), Ti(IV), and Na(I) ions except Fe(III) is seen to be higher than that of the original red mud solution as reported in Table 2. The transport of metal ions can be explained by means of the Donnan dialysis process which was described in our previous work (20, 21). In this process, transport of metal ions is balanced by the pumping ion, in this case H^+ ions moving in counterbalance. The results show that an increase of metals with NTA, EDTA, and citric acid chelating agents are observed in contrast, decreased with phosphoric acid when both membranes were used. Comparing of the flux values, the CMX membrane is somewhat higher than that of the CMB membrane. All separations are improved when chelating agents, particularly citrate, NTA, and EDTA were used. Compared to citrate, the enhancement is more significant while using NTA and EDTA as a complexing agent.

The formation of chelated complex depends strongly on the pH of the solution. Essentially, the distribution of species at different pH values can be obtained from a set of mass balance equations by taking into account the formation constants (7). The complex formation constant of Fe with EDTA, NTA, phospate, and citrate chelating agents is as log K_f 27.7, 17.9, 22.5, and 13.5 respectively. In addition to the complex formation constant of Fe, Al, and Ti with EDTA chelating agents is as log K_f 27.7, 18.9, and 17 respectively. In this case, the most favorable complex formation is Fe with respect to others (24). In other words, chelated forms cannot pass through the membrane. When the flux values of Fe with and without EDTA chelating agents was compared, the flux values were significantly decreased about 4.5 fold for the CMX membrane and 1.5 fold for the CMB membrane. On the other hand, the meaning of chelating agents is to mask the Fe metals in the feed phase while the other was transported. It was reported that the divalent chelated anions CuL^{2-} absolutely dominates at pH 3–12 for an equimolar diluted solution of Cu(II) and EDTA at $10\,\mathrm{mol\,m^3}$ and the univalent chelated anions $CuHL^-$ at pH <3 (7). In case of Cu(II) and NTA, the univalent chelated anions CuL^- dominate very broad ranges as 1.5–11 (8).

The adding of chelating agents increased the transport of metal ions from feed phase to stripping phase by Donnan dialysis which was discussed in detail in the literature (3, 25). Of course the fluxes of Ti(IV), Al(III), and Na(I) ions with chelating agents resulted in increased counterbalance with H^+ ions which is the driving force. In other words, the Fe(III) ions forms complexes, and its transport was prevented, so the transport of other metals is accelerated in terms of the driving force. During the Donnan dialysis process, the transported flux of metals from feed to stripping phase is equal to that of the pumping ion. The flux is expected to depend on the chelating agents and other cation. To make additional possible explanation, further work may be studied with single salt and chelate systems, and cation influences to the transport of metals in several ways, both direct and indirect. The same rotational speed was kept constant with a magnetic stirrer in order to prevent the formation of significant boundary layers and to ensure that the concentration of metals was uniform throughout in both of the solutions. Application of the Donnan equilibrium expression to the experimental data leads to the transport of metals across the membrane. As expected, the pH of feed solution plays an important role on selective transport of metals by cation exchange membranes when the complexing agents were added to the feed solution (26, 27) because the extent of complexation between metal and complexing agents changes with the pH of solution (25). Thus the feed solution pH was adjusted as 1.5 for all experiments. At pH 1.5, if EDTA chelating agents are added into the solution by taking equivalent quantity of Fe(III), then all of the Fe(III) ions form complex, only the estimated free Fe(III) concentration is about 10^{-6} M (28).

To compare the results of Donnan dialysis for recovery of metals, particularly the Ti^{4+}, the quasi-steady state fluxes were calculated from the amount of transported versus time plots as given in Table 2 and its transport was particularly increased with citrate. The fluxes of Al^{3+} are roughly 10 times higher than Ti^{4+} and somewhat higher than that of Fe^{3+}, except EDTA complex.

The concentrations of metals in the solution are different so the fluxes were given to compare their removal efficiency. There was a distinguishable increase in Al(III), Fe(III), and Ti(IV) removal in the presence of citrate chelating agents, but in the presence of phosphate the efficiency of metals removal deteriorated significantly. In the presence of NTA and EDTA there is only a moderate effect on the removal of Al and Ti. The results obtained show removal of metal ions from red mud solution can be achieved in the presence of citrate, NTA, and EDTA chelating agents as complexing agents.

The function of the chelating agents in the methodology is to achieve the removal of metal complex ions by masking some of the metals in the feed phase. Particularly, the affected ions are Fe(III) and Al(III). Therefore, the recovery factor values of these metals were given to compare the affect of the chelating agents as illustrated in Figs. 6 and 7. The recovery factor (RF) for Donnan dialysis process was defined as follows:

$$RF = 1 - C_{Me,f}/C^{o}_{Me,f} \tag{2}$$

Al(III), Fe(III) and Ti(IV) are believed to form strong, non-labile complexes with chelating agents. It was reported that Ti(IV) chelated complex in aqueous solution was synthesized, especially the chelated complex with NTA was found to be very stable (29); even it was no precipitate over pH 10. It is seen in Fig. 6 as opposed to Fig. 7 that the RF values of Al(III) were found to be in the order as EDTA > citrate > red mud for both membrane. The RF values of Al(III) in the chelating forms is somewhat higher with respect to the red mud solutions. This increase could be due to complex formation of chelating agents with Fe(III).

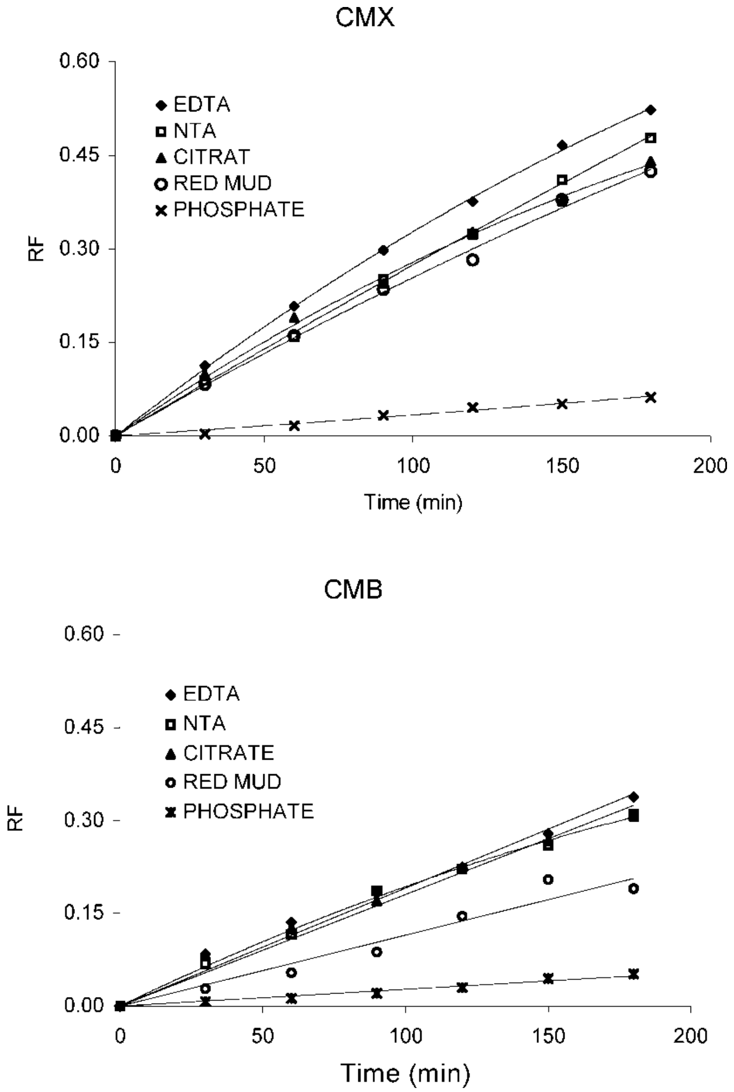


Figure 6. The affect of chelate complexing agents on the recovery factor values of Al(III) with time across membranes.

However, a larger number of measurements may be necessary to draw proper conclusions on the precision of chelating agents. Overall, the variance of the Al and Fe results were different for both membranes due to their interaction with chelates. Generally, the convenient economic method for treatment of metal bearing effluents is chemical precipitation. However, the presence of strong chelating agents such as EDTA, NTA, citric acid, and tartarate may make the precipitation process ineffective,

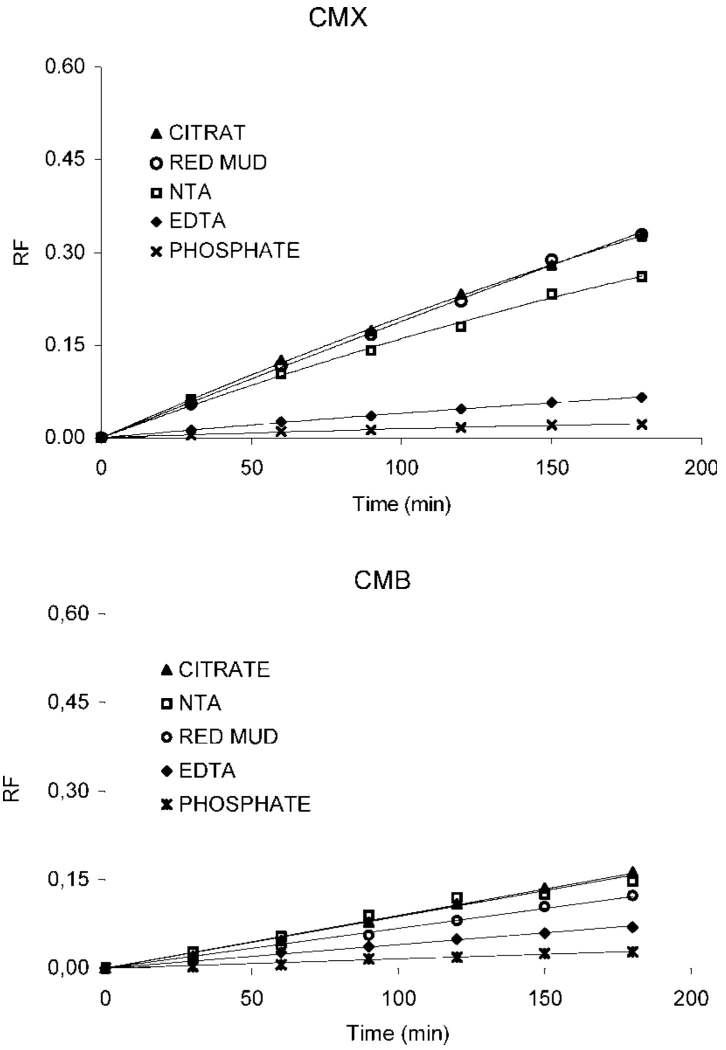


Figure 7. The affect of chelate complexing agents on the recovery factor values of Fe(III) with time across membranes.

even when treating streams with high metal concentrations (30). The main concern is recovery and reuse of the complexing agents. For this aspect, ion exchange (31–33), adsorption (34), inorganic materials such as TiO_2 (35) and goethite (36) and functional polymers (37) have been tried. Regardless of the used recovery method, in which, the final step to recover metals must be aided by an electrolysis process (38) Juang and Li (7) pointed out that the simultaneous recovery of metals and chelating agents is not possible using common electrolytic methods. It was reported that the separation of nickel ions from cobalt sulphate solution can be achieved in the presence of an EDTA as a complexing agent using a three compartment electrodialysis cell (39). In the other study, the effect of the chelating agent (EDTA) was investigated by electrodialysis (40). So, in this study, only the effect of chelating agents was investigated and no electrolytic method was applied. In previous studies, especially the selective transport of metals through cation exchange membranes can be improved by adding of anionic ligands as masking reagents to the feed solution (41, 42). The studies have shown that selective transport of metals is achieved by adding anionic ligands as masking reagents to the feed phase in membrane dialysis (26, 43). The complexing agents can differentiate the equilibrium uptake of metals on the membrane, so this results in the increase of the membrane selectivity. The complexing agents mainly used are EDTA, NTA, and citric acid. This concept has also been applied to other separation methods (44, 45). In the reported works, the chelated metal cannot be destreyod regardless of which concentration and which removal method is being used. The other point to take into account is higher by the fact that the composition of the solution can vary in the course of the experiment.

CONCLUSION

The results of our experiments demonstrated that the chelating agents differentiate the uptake of metals by masking. Thus an interesting perspective is offered for the recovery of metals in the presence of chelating agents by means of Donnan dialysis and is very interesting in the point of hydrometallurgical applications, particularly, citrate, NTA, and EDTA chelating agent is the usual reagent for metal recovery. The difficulty here is the application of the mathematical model to a system where several or more complex species are in solution. We are further suggesting that the Donnan dialysis can be an efficient technique for the recovery of metals from red mud by the addition of chelating agents when parameters such as electrolytic application, cation exchange membrane, and process parameters are optimized. The electrical application seems to be a valuable method, and furthermore, we think that it can be undoubtedly improved by considering of electrochemical cell by applying of electric current, so, further studies are under investigation with single component and multicomponent membrane systems. It can also be optimized by the research of the number of compartments as it determines the number of theoretical trays necessary for recovery.

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