CHAPTER 6

Recovery of nickel and gold through PIMs

6. Recovery of nickel and gold through PIMs

6.1 Solvent extraction (SX) of copper

ACORGA M5640 was found effective extracting agent for the recovery of Cu from the leach liquor as previously reported by our research group (Rao et al., 2021b). 99.97% of Cu was recovered from the leach liquor using ACORGA M5640. Moreover, the raffinate of this step was sent for the recovery of nickel by PIMs process. The pH modifications were done using ammonia solution and hydrochloric acid as per the experimental requirement during the transport studies. The concentration of metal ions in WPCBs leach liquor and SX raffinate has been shown in table-6.1.

Table-6.1 Concentration of various metals into the leach liquor and raffinate

Metals	Concentration of metals (x 10^{-3}mole L^{-1})	
	WPCBs leach liquor	Membrane Feed Phase (Raffinate after copper SX)
Copper	158.20 ± 0.32	0.0078 ± 0.005
Nickel	2.214 ± 0.20	1.92 ± 0.10
Zinc	1.33 ± 0.10	1.070 ± 0.05
Cadmium	0.44 ± 0.01	0.355 ± 0.01
Tin	0.344 ± 0.01	0.227 ± 0.01

6.2 PIMs process of nickel extraction

The applicability of a non-plasticized PVC-based PIMs incorporating 50 wt.% ACORGA M560 as the carrier for the selective extraction of nickel was explored in an PIMs extraction experiment. The elemental investigation of the raffinate liquor after copper recovery specified the presence of nickel (1.92 x 10^{-3} mole L^{-1}) as major elements, zinc (1.070 x 10^{-3} mole L^{-1}), cadmium (0.355 x 10^{-3} mole L^{-1}), tin (0.227 x 10^{-3} mole L^{-1}). The performance of PIMs to recover nickel was explored by varying the carrier concentrations, pH of feed phase, concentration of strip phase, and the stirring speed during the membrane transport experiments.

In the current work, nickel-oxime complex formation took place at pH 7.5. The extracting agent is regenerated after releasing the nickel ions into the strip phase and return back to the feed interface for coupled-counter transport. Nickel ions and H^+ transfer by diffusion in reverse orders through the PIMs, transported by the ligand within the ACORGA M5640 as expected in coupled-counter mechanism. The three main steps involving the transportation of nickel from feed to strip solution through PIMs containing ACORGA M5640 as carrier is: complexation between nickel ions and the oxime at the feed and PIMs interface, diffusion of nickel-oxime complex through the PIMs and the de-complexation on the membrane –strip solution interface. The mechanism is similar to previously reported for the copper recovery using D2EHPA (Kavitha and Palanivelu, 2012b). The schematic representation of dual compartment transport cell has been shown in figure-6.1.

The removal efficiency of nickel was calculated as follows (Qiu et al., 2019):

$$E(\%) = \frac{C_i - C_t}{C_i} X100 \quad \text{.....(6.1)}$$

Where,

C_i is the initial concentration (ppm) of nickel ion in the feed solution

C_t is the concentration (ppm) of nickel ion in feed solution at time t.

The nickel flux (J) (mole/(m^2.sec) was calculated by the equation suggested by Arous et al., (2004)

$$J = \frac{V}{A} . \frac{dC}{dt} \quad \text{.....(6.2)}$$

Where, V= Volume (m^3) of strip phase contacting with PIMs

A= PIMs Area (m^2) contacting with the aqueous solution

dC/dt= Concentration gradient (mole/m^3.sec)

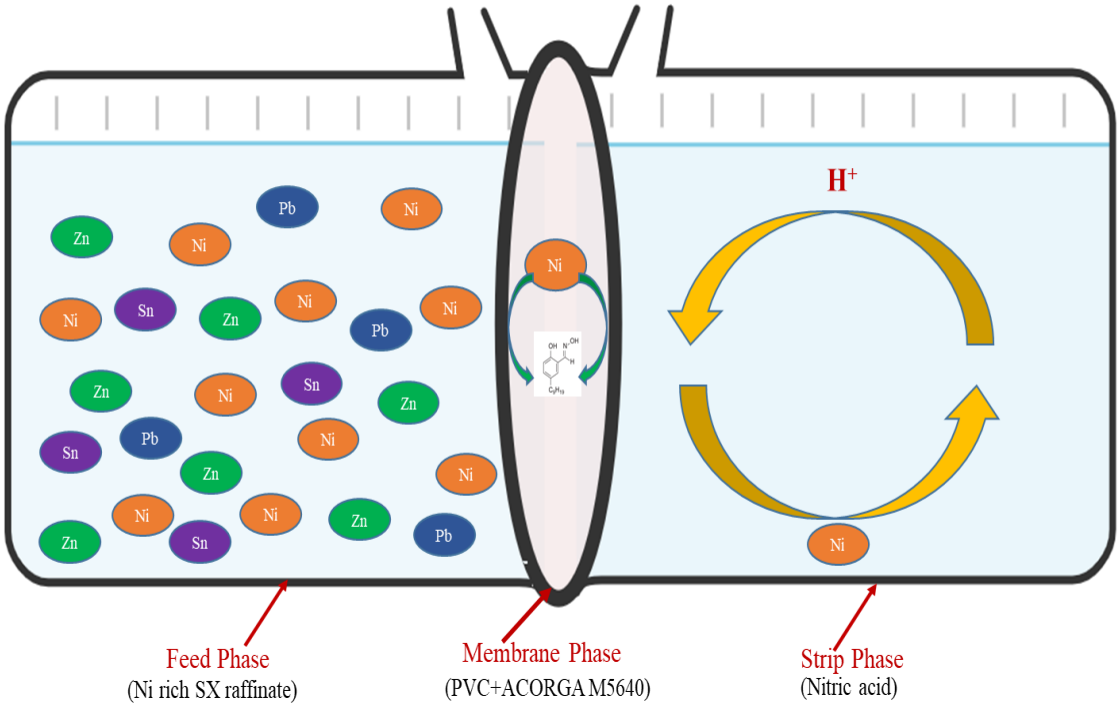

Figure 6.1-Schematic representation of nickel transportation through two compartment membrane transport cell.

6.2.1 Effect of carrier concentration

The carrier concentration was varied in the range of 0-70% by weight to check the nickel extraction capacity of ACORGA M5640. There was no nickel transportation from feed phase to strip phase seen without carrier (100% polymeric membrane), which stipulates that the adding carrier during PIMs synthesis had a noteworthy consequence on the nickel ion transport across the PIMs system. The effect of amount of ACORGA M5640 on the transport of nickel ions from feed phase encompassing 19.2 x 10^{-4} mole/L nickel to the strip solution of 1M HNO_3 was investigated and shown in figure-6.2. It could be observed at optimum conditions that the nickel flux increases with increasing the carrier concentration till 50% and after that constant till 60% carrier. The possible reason behind the increment of nickel flux could be the formation of more nickel oxime complex at membrane phase by increasing the carrier concentrations in PIMs. Moreover, the rise in carrier concentration also increases the thickness of the membrane and concentration gradient. The diffusion of nickel complex

through the PIMs is the rate determining step at the lower concentration of ACORGA M5640. However, the diffusion of metal cations through the aqueous edge film is the rate-determining step in case of higher ACORGA M5640 concentration. The further increase of carrier concentration after a certain limit leads to decrease the strength of PIMs and it could not be possible to sandwich this PIMs in membrane transport cell. Therefore, the optimum membrane component was chosen for further experiments was 50-50% base polymer and carrier as PIMs components.

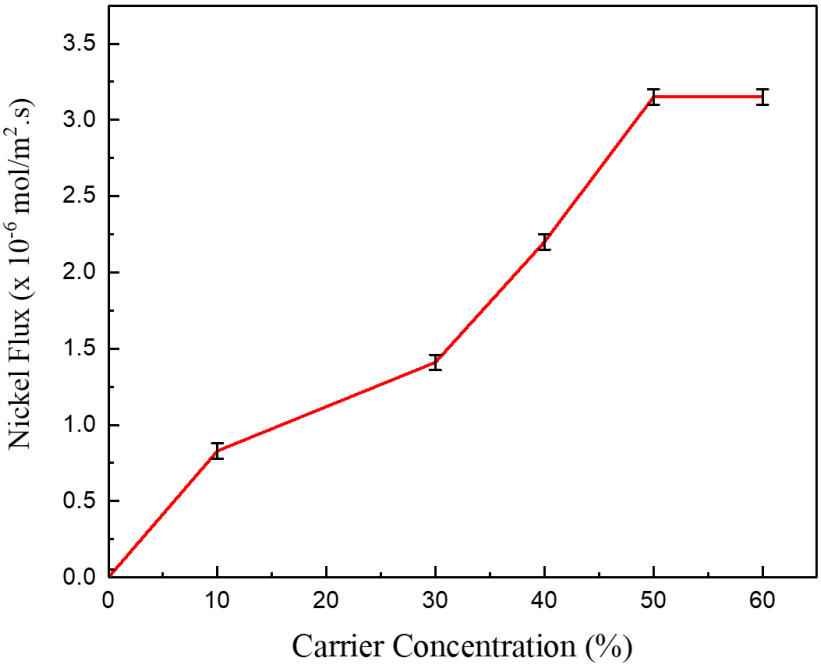

Figure 6.2-Effect of amount of carrier in membrane on nickel recovery (**Experimental conditions:** pH of feed phase: 7.5; strip phase: 1M HNO_3; stirring speed:550 rpm at room temperature)

6.2.2 Effect of pH of feed phase on nickel transport

pH of feed phase is one of significant driving forces for the transportation of metal ions through the PIMs (Bahrami et al., 2020; Tasaki et al., 2007). Therefore, we studied the effect of varying the pH of the raffinate received after SX process and the results has been shown in figure-6.3. In order to evaluate the nickel aqueous feed phase pH, on the transport of nickel ions, pH was varied in the range of 1.0–8.5. Hydrochloric acid and ammonia solutions were used to preserve the feed pH in the beyond range. There was no transport of nickel from feed

phase to strip phase observed below pH 4.5. The transport of Ni starts beyond pH 4.5 and improved with increasing pH up to 7.5 and then rests constant afterward up to pH 8.0 and then declines further. The development of stable nickel ammine complexes during the pH modification by ammonia solution is responsible for the reduction in the nickel recovery after pH 8.0 (Mubarok and Yunita, 2015; Sridhar et al., 2010). The transport of nickel ions depends on the released protons during the formation of complex at membrane phase. This is similar to the nickel oxime complex formation during the solvent extraction routes reported in previous researches (Dhanunjaya et al., 2022). The exchange of nickel ion in the feed for two protons and the exchange of two protons in the strip solution for one nickel ion as indicated by forward and backward reactions in PIMs system.

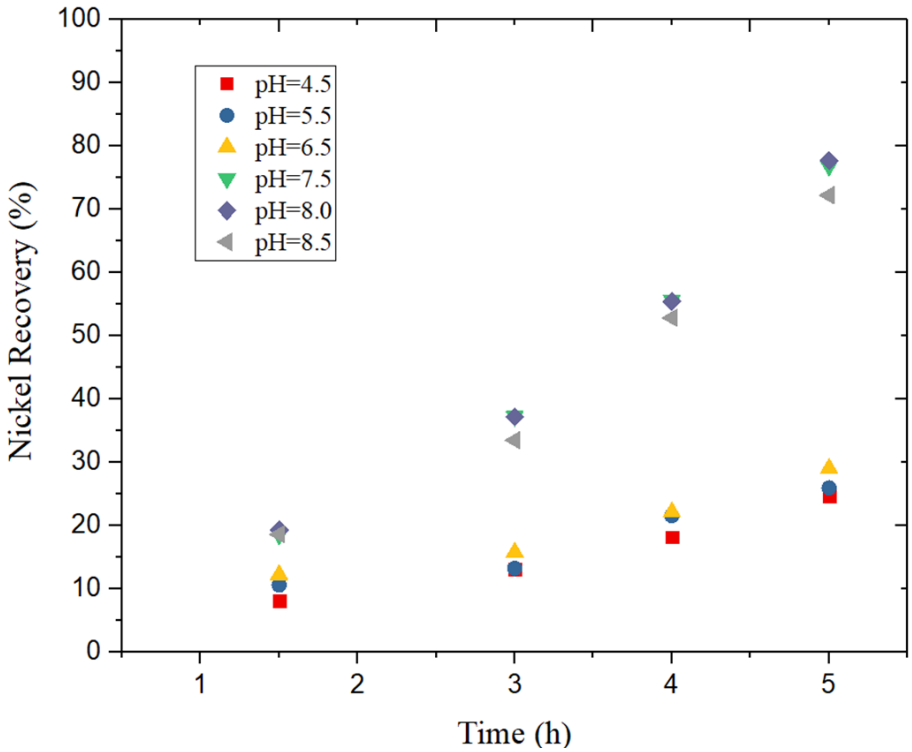

Figure 6.3-Effect of pH on nickel recovery from feed to strip phase **(Experimental conditions:** carrier concentration: 50%; strip phase: 1M HNO_3; stirring speed:550 rpm at room temperature)

6.2.3 Effect of stripping agent

In the PIMs system, the extraction and stripping take place simultaneously. Hence, as the extraction of nickel occurs at the interface of feed and PIMs phase, the concurrent stripping of

nickel requires and effective stripping agent at the another side of the PIMs. The regeneration of carrier takes place during the transportation and the metal is striped in the stripping step. The stripping of nickel from nickel oxime is a necessary step otherwise this may saturate the PIMs phase and the permeation rate may be hindered. Consequently, the transport efficiency of nickel is also affected by the stripping solutions (acids) and the concentration of acid used for stripping the metal from the nickel-oxime complex at the membrane phase. In the current study, nitric acid was chosen as stripping phase and its concentration was varied from 0.5-1.5M. The effect of nitric acid concentration on nickel recovery has been shown in figure-6.4. The flux of nickel increases as the concentration of nitric acid increases upto 1M and further increase in acid concentration doesn't show any effect on nickel transport. Moreover, the higher acid concentration (strip phase) may also weaken the membrane for further experiments. Therefore, 1M HNO_3 was preferred as the stripping solution for the further investigations.

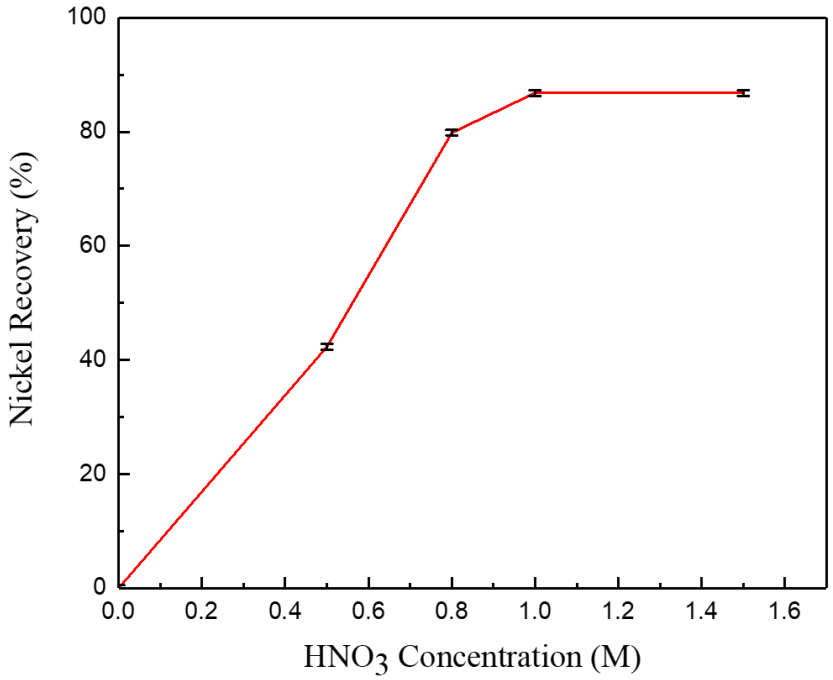

Figure 6.4-Effect of nitric acid (stripping solution) on nickel recovery from WPCBs solution **(Experimental conditions:** Carrier concentration: 50%; pH of feed phase: 7.5; strip phase: 1M HNO_3; stirring speed:550 rpm at room temperature)

6.2.4 Transport studies

The transportation of metals ions through PIMs take place by exchanging the ion species between two phases by membrane phase. One of the benefits of PIMs process is to combine the extraction and stripping into single step and hence the separation is not restricted by the equilibrium conditions. A surplus of protons in the strip phase is the driving force for the mass transfer. Therefore, the high acidity of strip phase enhances the sufficient strength of stripping liquor to break the bond between nickel ion and carrier anion. Consequently, the proportion of nickel back-extraction improved with increase of nitric acid concentration.

The dissolved ACORGA M5640 in the membrane phase reacts at the donor phase-membrane interface with the nickel ions by exchanging the protons. Hence, the formation of complex takes place at the PIMs phase. Further this complex disperses across the membrane to react with the available protons at the membrane-back extractant interface. Thus, nickel ions are stripped from the membrane to the strip phase. The mechanism of nickel ion complexation with ACORGA M5640 has been shown by eq: 6.3

$$\boldsymbol{M^{2+}}\text{aq} + \boldsymbol{2(L)_2}\ \text{m} = \boldsymbol{ML_2}\ \boldsymbol{(L)_2}\text{m} + \boldsymbol{2H^{+}}\text{aq} \quad \text{.....(6.3)}$$

where aq and m is aqueous feed phase and membrane phase,
M and L is nickel and ligand in ACORGA M5640 respectively.

99.77% of nickel from the feed phase to strip phase is transported selectively through the transport cell experiment as the concentration profile shown in the *figure-6.5*. Moreover, no other trace metals were found in the strip solution in the current study. Hence, the method is confirming the selectivity of PIMs incorporating ACORGA M5640 for nickel ions.

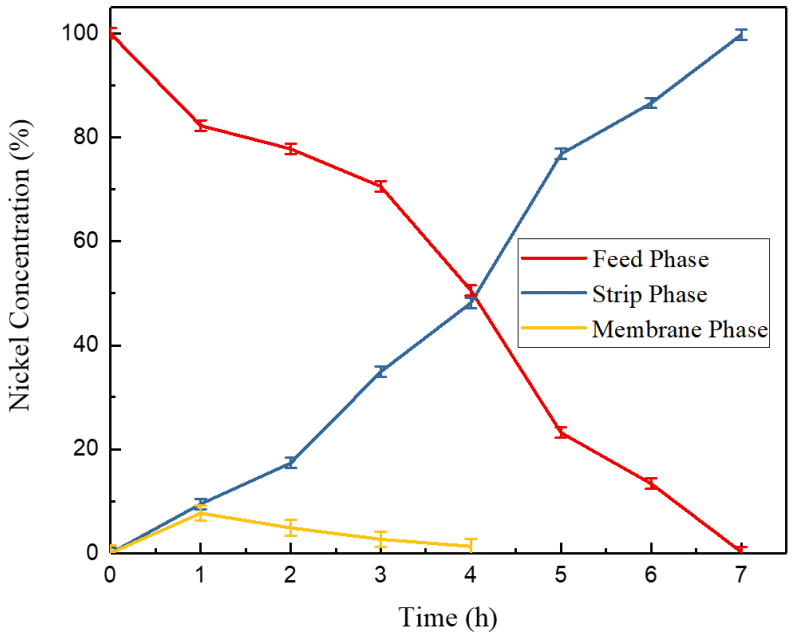

Figure 6.5-Concentration profile of nickel in the feed, strip and membrane phase as a function of time **(Experimental conditions:** Carrier concentration: 50%; pH of feed phase: 7.5; strip phase: 1M HNO_3; stirring speed:550 rpm at room temperature)

6.2.5 PIMs stability studies

The PIMs stability has been tested by reusing the same membranes for the multiple experiments. In each set of experiments, the feed phase and strip phase were replaced with the fresh solutions and the optimum parameters were used for all the eight experiments. The PIM stability for nickel transportation from the WPCBs leach liquor using ACORGA M5640 as carrier has been shown in figure-6.6. The flux of nickel was constant till seventh cycle and decreased slightly in eighth cycle signifying the constancy of PIM for eight duplicate experiments. Each experiments (each one lasting for 7 h) were conducted with 19.2 x 10^{-4} mole/L nickel containing in feed phase and 1M nitric acid as strip phase. The result of current study validates the high stability of PIMs as observed in previous researches.

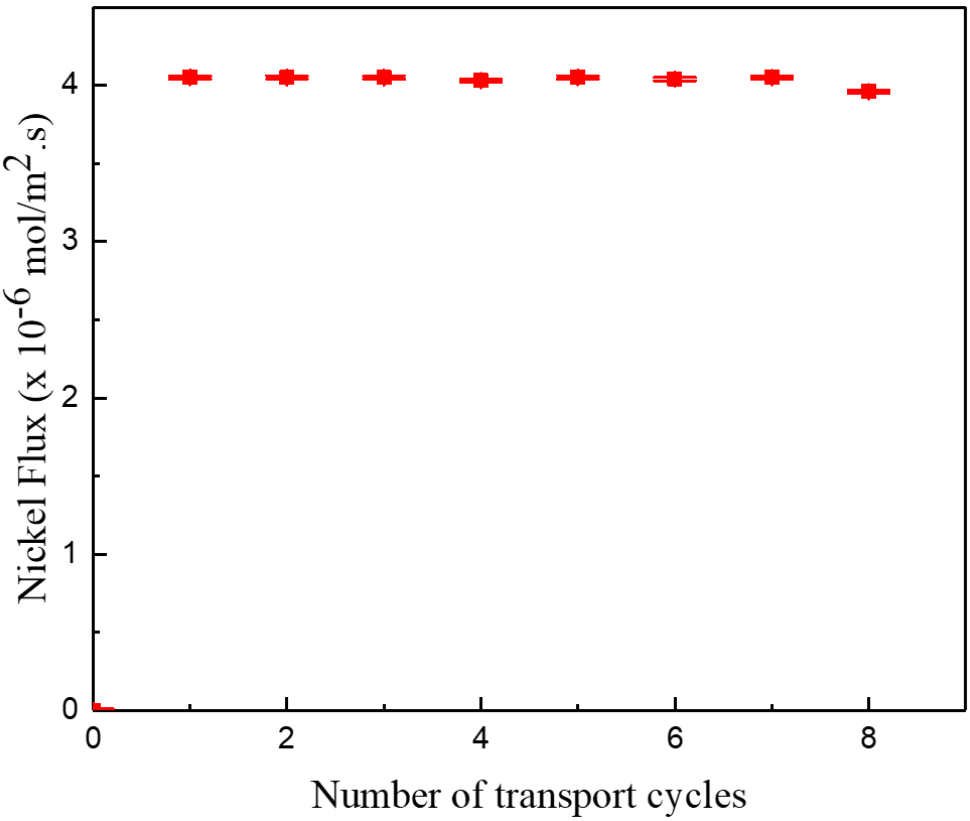

Figure 6.6-Stability of non-plasticized ACORGA M5640 carrier based PIMs for nickel transport (**Experimental conditions:** Carrier concentration: 50%; pH of feed phase: 7.5; strip phase: 1M HNO_3; stirring speed:550 rpm at room temperature)

6.3 PIMs process of gold extraction

CTA-TBAN based non plasticized PIMs were applied for the selective transportation of gold from the stage-2 multi metallic leach liquor. The feed phase contains gold (0.0506 x 10^{-3} mole L^{-1}), silver (0.0300 x 10^{-3} mole L^{-1}), tin (0.627 x 10^{-3} mole L^{-1}). The applicability and performance of PIMs to recover gold was explored with the different carrier concentrations (5-60% TBAN), concentration of strip phase, and at the fixed stirring speed (550 rpm) during the membrane transport experiments. In the gold extraction of PIMs, anionic bromo-complexes of gold easily form complexes with TBAN at the feed and membrane interface. The anionic metal bromocomplexes of gold are extracted from the aqueous solution to the membrane phase by an anion-exchange mechanism. In the current work, gold-TBAN complex formation took place at pH 0.75.

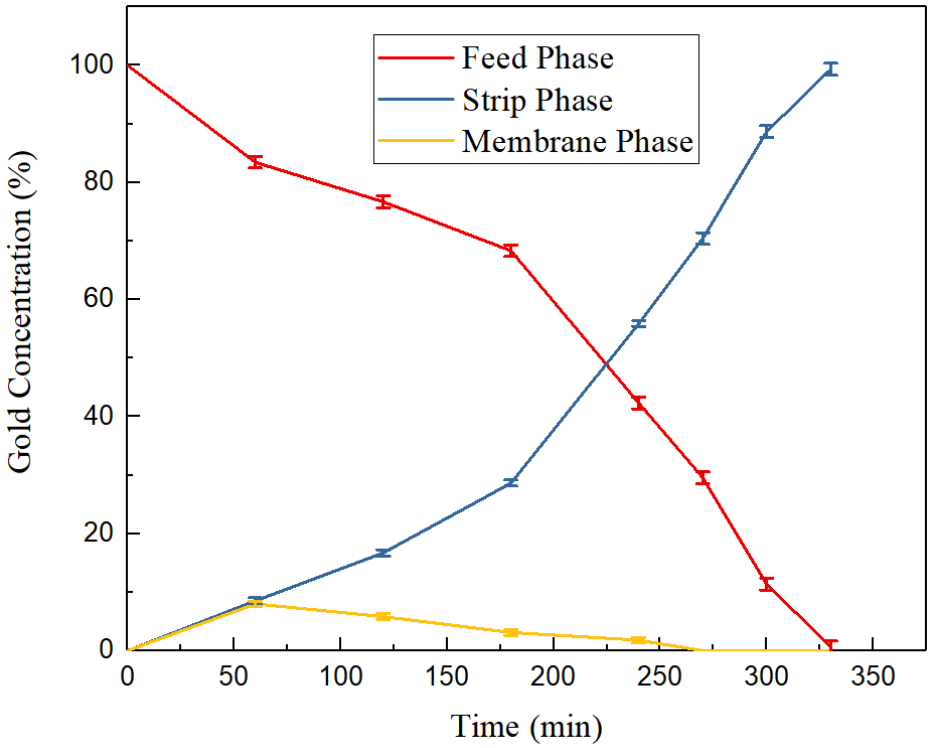

Figure 6.7-Concentration profile of gold in the feed, strip and membrane phase as a function of time (Experimental conditions: Carrier concentration: 50%; pH of feed phase: 0.75; strip phase: 1M NaOH; stirring speed:550 rpm at room temperature)

The carrier is regenerated after releasing the gold ions into the strip phase and return back to the feed interface for coupled-counter transport similar to the previous work. It is important to note that the gold extraction through PIMs involve several steps as discussed below; gold ions forms complex with TBAN at the source solution/interface of PIM to form metal carrier complexes. Further, Metal–carrier complexes diffuse through the membrane towards the stripping solution. The dissociation of the metal–carrier complexes occurs at the interface of the PIM/stripping phase and gold ions are released into the receiving phase. It is also suggested the extraction and back extraction occurs simultaneously. The possible extraction and back extraction reactions has been shown by the eq- 6.4 and 6.5

$AuBr_4$ + TBA-NO3 $\longrightarrow$ TBA-$AuBr_4$-NO_3 *(Extraction)……..(6.4)*

TBA-$AuBr_4$-NO_3 + NaOH $\longrightarrow$ $Na^+ Au(OH)_4^-$ + TBA-NO_3 +2Br_2 *(Stripping)……..(6.5)*

99.35% of gold from the feed phase to strip phase has been transported selectively through the transport cell experiment as the concentration profile shown in the *figure-6.7*. Moreover, no other trace metals were found in the strip solution in the current study. Hence, the method is confirming the selectivity of PIMs incorporating TBAN for gold ions.

6.3.1 Effect of carrier concentration

There was no gold extraction seen without carrier; TBAN in the PIMs system. However, introduction of 5% carrier into membrane phase shows smaller quantity of gold extraction (gold flux; 0.00275 x 10^{-6} mole/L) at optimized parameters. Hence, it is confirmed that introduction of carrier into PIMs components shows some significant impact on gold extractions in PIMs system. In the current work, TBAN concentration was varied in the range of 0-70% by weight to check the gold extraction capacity. The effect of amount of TBAN on the transport of gold ions from feed phase encompassing 0.506 x 10^{-4} mole/L gold to the strip solution of 1M NaOH was investigated and shown in figure-6.8. The gold flux was increased with the increasing the carrier concentration into the PIM at the optimum parameters. The possible reason behind the increment of gold flux could be the formation of more gold and TBAN complex at feed and membrane phase by increasing the carrier concentrations in PIMs. Moreover, the rise in carrier concentration also increases the concentration gradient. Hence, gold flux; 0.00275 x 10^{-6} mole/L with 5% increases up to 1.0 x 10^{-6} mole/L with 50% TBAN concentration. It was seen that after 50% TBAN concentration the gold flux was almost constant and the further increase of carrier concentration (70%) leads to decrease the strength of PIMs and it could not be

possible to sandwich this PIMs in two compartment membrane transport cell. Therefore, the optimum membrane carrier concentration was chosen as 50% for further experiments.

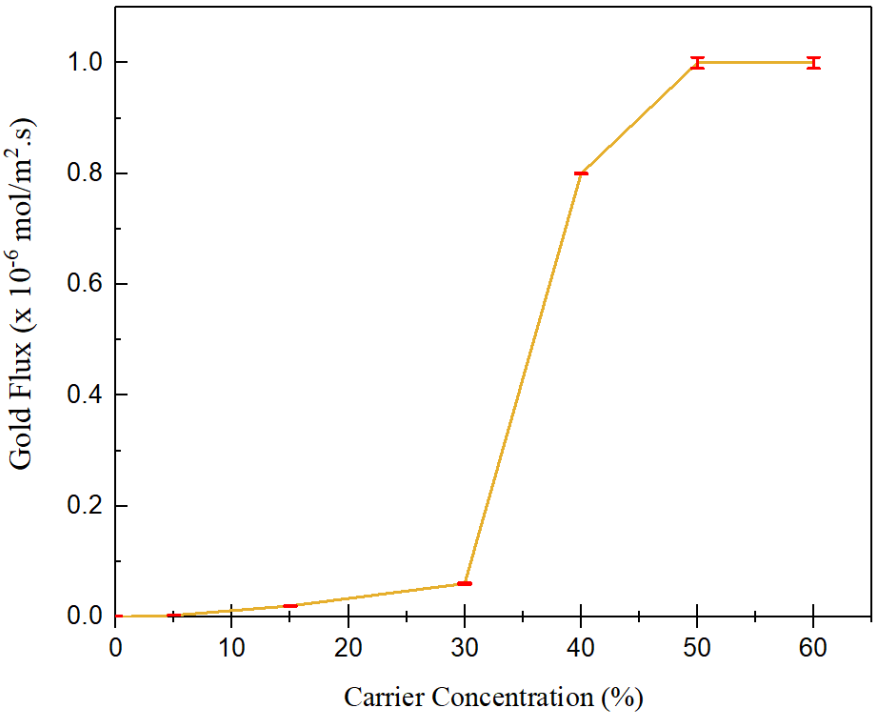

Figure 6.8-Effect of amount of carrier in membrane on gold recovery (Experimental conditions: pH of feed phase: 0.75; strip phase: 1M NaOH; stirring speed:550 rpm at room temperature)

6.3.2 Effect of stripping agent

In the PIMs system, the gold-TBAN complex formed at the feed and PIMs interface and the dissociation of this complex for gold ion extraction may be possible by choosing suitable back extractant. The regeneration of carrier takes place during the transportation and the metal is striped in the stripping step. Hence, water and sodium hydroxide (0.1-1.5 M) were evaluated for stripping of gold ions from the PIMs phase. Water was found insufficient in dissociating the gold-TBAN complex at and only 15% of gold was back extracted in this case. However, 0.5 M NaOH was able to back extract 78.56% of gold from the formed complex at feed and membrane phase as shown in figure-6.9. The flux of gold increases as the concentration of sodium hydroxide increases upto 1M and further increase of NaOH concentration doesn't show

any effect on gold transport. The need for a NaOH stripping solution may be a consequence of the use of bromide in this process instead of chloride, for which water stripping was seen to be effective (Doidge et al., 2016).

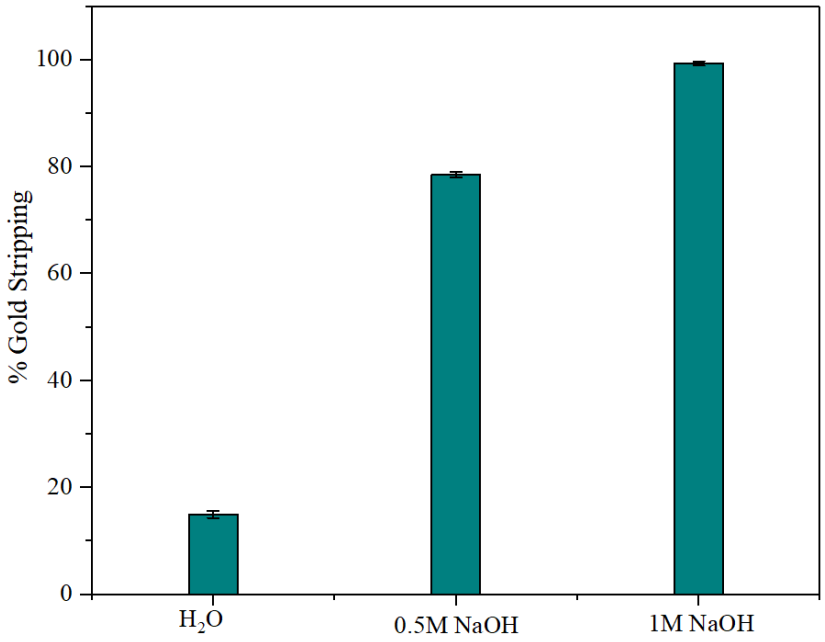

Figure 6.9-Effect of stripping reagent on gold stripping

Almost all gold (99.35%) was back extracted with 1M sodium hydroxide. Therefore, 1M sodium hydroxide was chosen for the back extraction of gold from stage-2 leach liquor.

The effect of sodium hydroxide concentration on gold stripping has been shown in figure-6.10. Chemical analysis of the strip solution revealed that it consists 9.91 mg/L gold along and no other trace metals were present. The PIMs treated gold solutions could be subjected to standard reduction processes for the isolation of metallic gold or could be used to synthesize nanoparticles or catalysts to possibly increase economic value.(Assunção et al., 2016; Mirgorod et al., 2014; Razi et al., 2010; Saito et al., 2009).

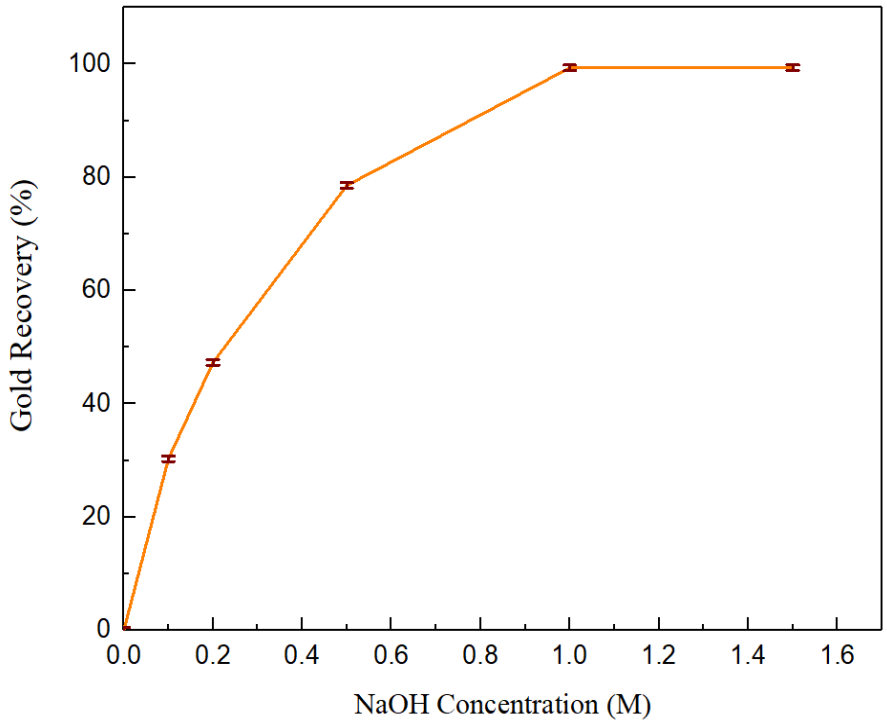

Figure 6.10- Effect of NaOH (stripping solution) on gold recovery from WPCBs solution (Experimental conditions: Carrier concentration: 50%; pH of feed phase: 0.75; stirring speed:550 rpm at room temperature)

6.3.3 PIMs stability studies

The CTA-TBAN based PIMs have been reuse for checking its suitability for reusing and its stability for multiple cycles. Like the previous study, in each set of experiments, the feed phase and strip phase were replaced with the fresh solutions and the optimum parameters were used for all the seven experiments. The PIMs stability for gold transportation from the stage-2 leach liquor using TBAN as carrier has been shown in figure-6.11. The flux of gold was constant till sixth cycle and decreased slightly in seventh cycle signifying the constancy of PIM for seven duplicate experiments. Each experiments (each one lasting for 350 min) were conducted with 0.506 x 10^{-4} mole/L gold containing in feed phase and 1M sodium hydroxide as strip phase.

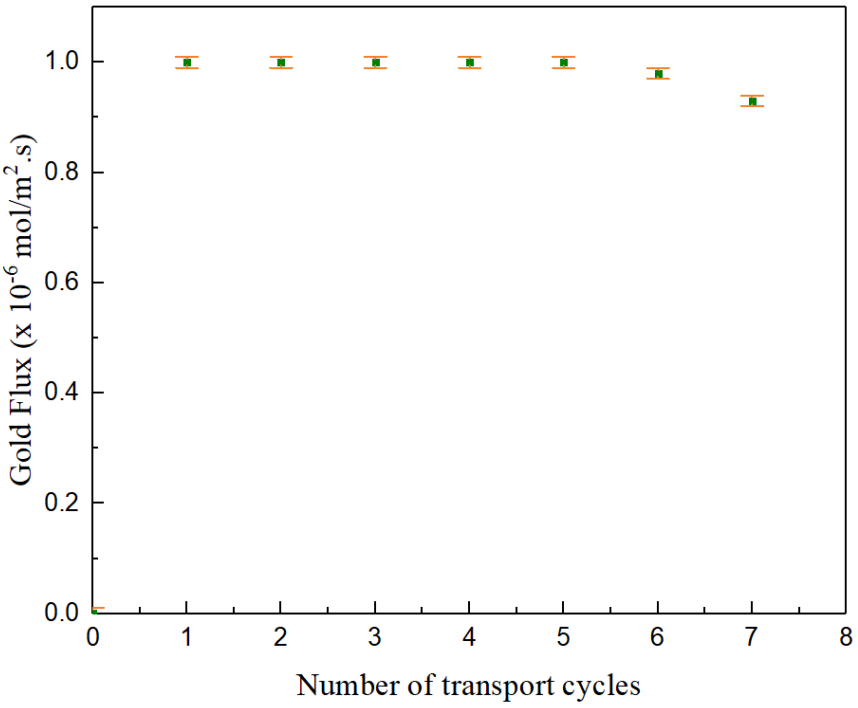

Figure 6.11- Stability of non-plasticized TBAN carrier based PIMs for gold transport (Experimental conditions: Carrier concentration: 50%; pH of feed phase: 0.75; strip phase: 1M NaOH; stirring speed:550 rpm at room temperature)

Conclusions

- The investigation of effect of carrier concentration reveals that the transport of nickel and gold ions increases with increasing the amount of carrier in PIMs.
- 99.7 % nickel was selectively recovered from SX raffinate using PIMs containing 50% of ACORGA M5640 at the optimized parameters; pH of feed phase; 7.5, strip phase;1M HNO3.
- 99.3 % gold was selectively recovered from stage-2 leach liquor using PIMs containing 50% of TBAN at the optimized parameters; pH of feed phase; 0.75, strip phase;1M NaOH.
- The stability and extraction efficiency of ACORGA M5640 and TBAN based PIMs were found constant upto seventh cycle, and sixth cycle respectively.
- Absence of plasticizers in membrane components reduces the overall cost of this route.