CHAPTER 5

RECOVERY OF MANGANESE AND NICKEL FROM STAGE-1 LEACH LIQUOR

5. RECOVERY OF MANGANESE AND NICKEL FROM STAGE-1 LEACH LIQUOR

As seen in the previous chapter, the leach liquor obtained after stage-1 leaching contained a large amount of manganese and nickel. So in this chapter, the pregnant leach liquor from stage-1 leaching was processed for selective separation of manganese from other metals, particularly nickel via the solvent extraction (SX) route. The performance of two distinct organophosphorous extractants named D2EHPA and CYANEX272 was examined to understand their effectiveness towards manganese separation. As per literature, both the reagent has shown excellent selectivity for manganese in multi-metallic leach liquor containing nickel, cobalt etc. (Mantuano et al., 2006; Nadimi and Karazmoudeh, 2021; Yetunde et al., 2020; Zhu and Cheng, 2011). Though the performance of these extractants have not been compared specially in the context of tantalum capacitor leach solution, and reactivity of a particular extractant depends largely on the chemistry of solution to be treated. Therefore, in this study, we did a comparative study to choose a better extractant for selective separation of manganese from nickel.

A series of experiments were conducted using D2EHPA and CYANEX272 to study the effect of different parameters on the selective separation of manganese form the leach liquor. The theoretical reaction, during the extraction of metal ions from the leach solution using these carriers, is as follows (*Eq. 5.1*):

$$Mn^{2+}_{(aq)} + \frac{n}{2}[RH]_{2(org)} \rightleftharpoons MnR_2.(RH)_{n-2(org)} + 2H^{+}_{(aq)} \tag{5.1}$$

where, RH is the organic species.

The structure of both the extractant is shown in *Figure 5.1*.

(a) (b)

Figure 5.1 Structure of (a) D2EHPA and (b) CYANEX272

Since solvent extraction is a pH-dependent process, the solution's pH was adjusted to the desired level by drop-wise addition of 4 M ammonia solution and 2 M HCl. A light green precipitate of iron formed when the pH of the solution reached 2, which was filtered out. Following the removal of the precipitate, the addition of ammonia was maintained until the desired pH value (2 to 4.5) was reached.

The results of solvent extraction are presented by distribution co-efficient of the metal *(D_M)*, which is given by the ratio of concentration of metal in organic phase to that of metal in the aqueous phase at equilibrium, represented by *Eq. 5.2*:

$$D_{M=} \frac{Concentration\ of\ metal\ in\ loaded\ organic\ phase\ ([M]org)}{Concentration\ of\ metal\ in\ initial\ aqueous\ phase\ ([M]aq)} = \frac{[M]org}{[M]aq} \quad (5.2)$$

where,

[M] org = concentration of metal in the organic phase at equilibrium and

[M] aq= concentration of metal in the aqueous phase at equilibrium

From these, the separation factor for the separation of manganese from nickel ($\beta_{Mn/Ni}$), which is the ratio of distribution coefficient of these two metals, was calculated by *Eq. 5.3*:

$$\beta_{Mn/Ni} = \frac{D_{Mn}}{D_{Ni}} \quad (5.3)$$

where,

D_{Mn}= distribution coefficient for manganese

D_{Ni}= distribution coefficient for nickel

5.1 Separation of manganese using D2EHPA as extractant

Various parameters considered for optimization of manganese separation using D2EHPA as extractant include temperature, pH, carrier concentration, time, and organic to aqueous (O/A) ratio. The results of optimization studies will be discussed in the following sub-sections.

5.1.1 Effect of temperature

Temperature plays a critical role while separating manganese from nickel in solvent extraction using D2EHPA (Nadimi and Karazmoudeh, 2021; Zhu and Cheng, 2011). Therefore, the effect of temperature on extraction of both the metals was studied under three different temperatures from 35 to 45 °C while keeping other parameters such as pH 3.5, O/A 1:1, stirring speed 700 rpm, time 60 min, organic concentration 30% D2EHPA in kerosene, as constant. At 35 °C, about 58% of manganese was transferred into the organic phase along with 19% nickel. It can be seen from *Figure 5.2* that increasing temperature has a significant impact on reducing the amount of nickel extraction and increasing the separation between manganese and nickel. When the temperature was raised to 40 °C, nickel extraction was completely eliminated. However, in contrast to previous finding (Cheng, 2000), an increase in temperature also resulted in lowered manganese extraction. This decrease in extraction as a function of temperature could possibly be the result of lowered stability of the extracted complex at that temperature. The distribution coefficients of manganese and nickel and their separation factors with respect to equilibrium temperature are given in *Table 5.1*. As a result of these findings, it was decided to hold the temperature at 40 °C for future trials in order to entirely eliminate nickel transfer to the organic phase while sacrificing some manganese extraction.

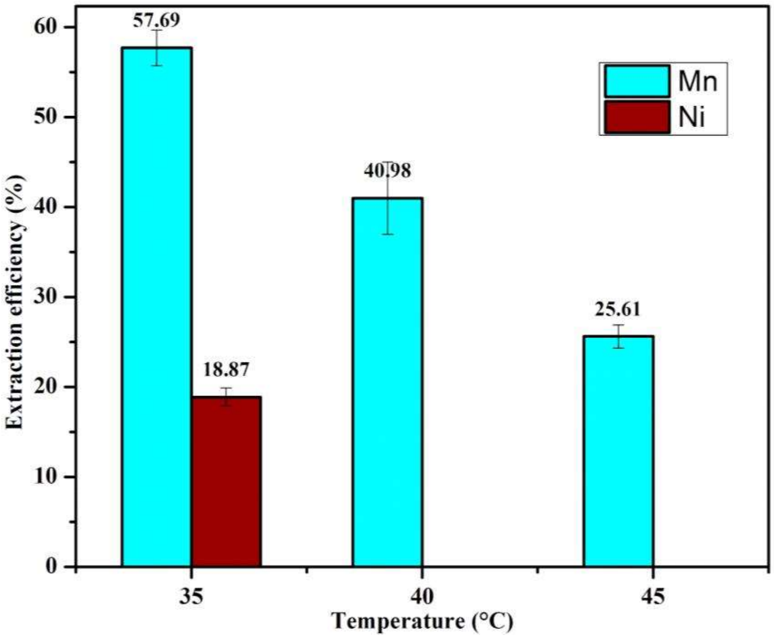

Figure 5.2 Effect of temperature on extraction of manganese and nickel (Conditions: concentration of D2EHPA- 30 vol% in kerosene, pH- 3.5, O/A- 1:1, contact time- 60 min, agitation speed- 700 rpm)

Table 5.1 Distribution coefficient of Mn and Ni and their separation factor with variation in temperature (Conditions: concentration of D2EHPA- 30 vol% in kerosene, pH- 3.5, O/A- 1:1, contact time- 60 min, agitation speed- 700 rpm)

Temp (°C)	**30**	**35**	**40**
D_{Mn}	1.363681	0.694394	0.344333
D_{Ni}	0.232558	0	0
$\beta_{Mn/Ni}$	5.863827	-	-

5.1.2 Effect of pH

Extraction of any metal species from the aqueous to organic phase largely depends upon the pH of the initial aqueous solution. Therefore, the effect of pH was examined by increasing it from 2 to 4 at a temperature 40 °C, O/A 1:1, time 60 min, % v/v of D2EHPA is 30% in kerosene, stirring speed 700 rpm. pH isotherms (*Figure 5.3*) shows that increasing pH led to a progressive increase in manganese extraction from 19% to 41%, up to a pH of 3.5 where it peaked. A further increase in pH led to a decrease in manganese extraction to as low as 30%. A decline in extraction efficiency beyond a pH of 3.5 might arise from a decrease in the stability of metal ion complexes, deprotonation of acidic D2EHPA, and reduced H^+ ion concentration in the organic phase. At all pH ranges, nickel extraction remained nil. Hence a pH of 3.5 was taken as optimum from these experimentations. The distribution coefficients of manganese and nickel and their separation factors with respect to equilibrium pH are given in *Table 5.2*.

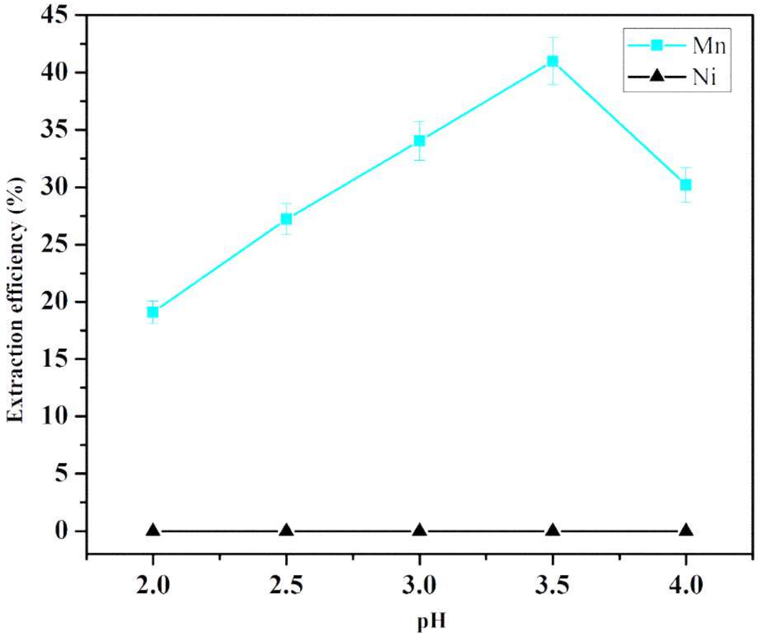

Figure 5.3 Effect of pH on extraction of manganese and nickel (Conditions: concentration of D2EHPA- 30 vol% in kerosene, temperature- 40°C, O/A- 1:1, contact time- 60 min, agitation speed- 700 rpm)

Table 5.2 Distribution coefficient of Mn and Ni and their separation factor with variation in temperature (Conditions: concentration of D2EHPA- 30 vol% in kerosene, temperature- 40°C, O/A- 1:1, contact time- 60 min, agitation speed- 700 rpm)

pH	**2**	**2.5**	**3**	**3.5**	**4**
D_{Mn}	0.236148	0.3739	0.516181	0.694394	0.432722
D_{Ni}	0	0	0	0	0
$\beta_{Mn/Ni}$	-	-	-	-	-

5.1.3 Effect of carrier concentration

Next, the manganese extraction efficiency was determined by changing the initial concentration of carrier into the kerosene from 10-40% while keeping other parameters constant. Increasing the concentration of carrier steadily increases the amount of manganese extracted into the organic phase (*Figure 5.4*). However, at a carrier concentration of 40% an unknown 3rd phase formation was observed at the interface between the aqueous and the organic phases. Therefore, to limit the amount of carrier consumption and avoid any 3rd phase formation, extractant concentration was limited to 30%. The distribution coefficients of manganese and nickel and their separation factors with respect to carrier concentration are given in *Table 5.3*.

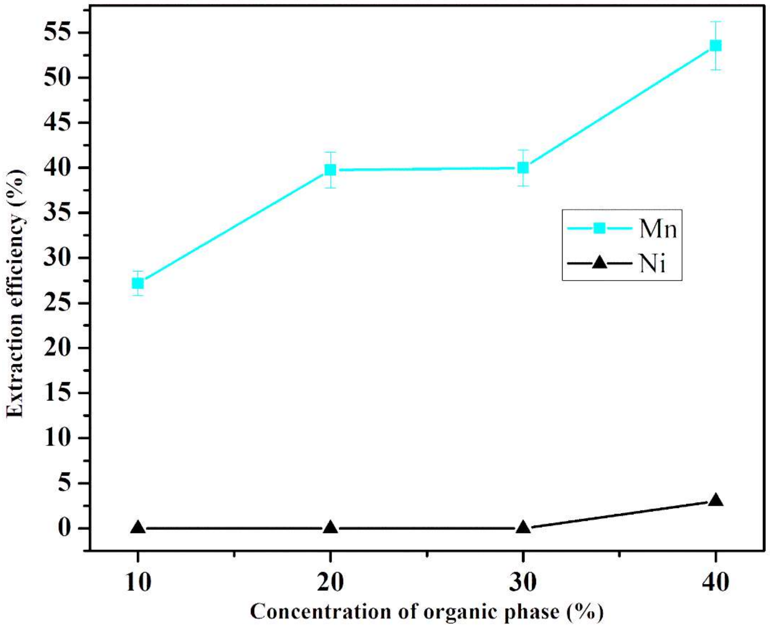

Figure 5.4 Effect of concentration of organic phase on extraction of manganese and nickel (Conditions: temperature- 40°C, pH- 3.5, O/A- 1:1, contact time- 60 min, agitation speed- 700 rpm)

Table 5.3 Distribution coefficient of Mn and Ni and their separation factor with variation in carrier concentration (Conditions: temperature- 40°C, pH- 3.5, O/A- 1:1, contact time- 60 min, agitation speed- 700 rpm)

Carrier concentration (vol%)	10	20	30	40
D_{Mn}	0.373409	0.659829	1.02714	1.152993
D_{Ni}	0	0	0	0.035551
$\beta_{Mn/Ni}$	-	-	-	32.43222

5.1.4 Effect of contact time

To determine the kinetics of extraction, SX experiments were conducted for different time intervals while keeping the rest of the parameters constant, as described above. It was found that kinetics of extraction of metal is relatively fast (*Figure 5.5*). Initial 15 minutes of contact was sufficient for organic to reach its maximum loading capacity of metallic species. No significant impact on extraction was seen beyond this period. The resulting distribution coefficients and separation factors are given in *Table 5.4*.

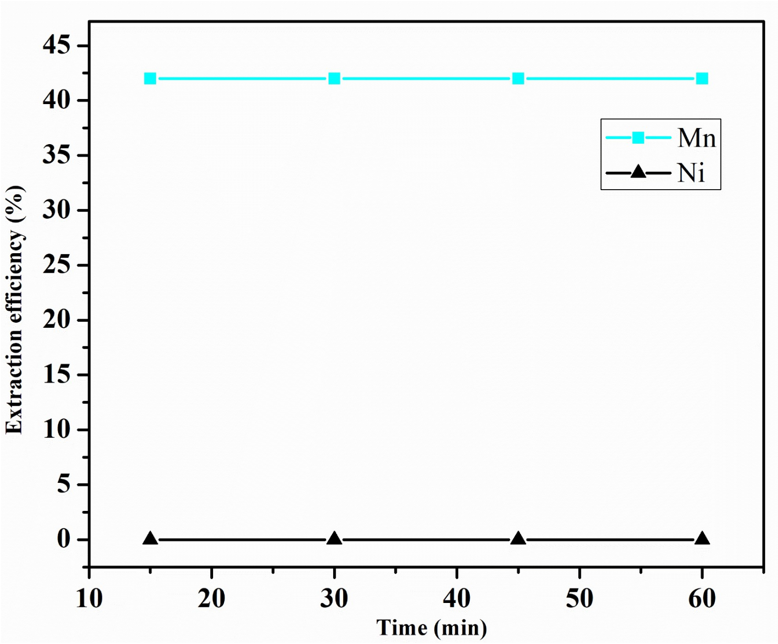

Figure 5.5 Effect of contact time on extraction of manganese and nickel (Conditions: concentration of D2EHPA- 30 vol% in kerosene, pH- 3.5, temperature- 40°C, O/A- 1:1, agitation speed- 700 rpm)

Table 5.4 Distribution coefficient of Mn and Ni and their separation factor with variation in equilibrium contact time (Conditions: concentration of D2EHPA- 30 vol% in kerosene, pH- 3.5, temperature- 40°C, O/A- 1:1, agitation speed- 700 rpm)

Time (min)	**15**	**30**	**45**	**60**
D_{Mn}	0.721631	0.700525	0.730838	0.694394
D_{Ni}	0	0	0	0
$\beta_{Mn/Ni}$	-	-	-	-

5.1.5 Effect of O/A ratio

Finally, the O/A ratio was varied from 1:5 to 5:1 while keeping the other parameters fixed. Extraction isotherm illustrated in *Figure 5.6* shows that an increase in phase ratio had a positive impact on extraction of manganese from 15% at O/A of 1:5 to 55% at 5:1, which is due to the higher availability of reaction sites with increased organic concentration. However, the highest quantity of manganese that could be extracted in a single-stage was only 55 percent even when the organic phase content was increased five times to the aqueous phase. The resulting distribution coefficient and separation factor can be seen from *Table 5.5*.

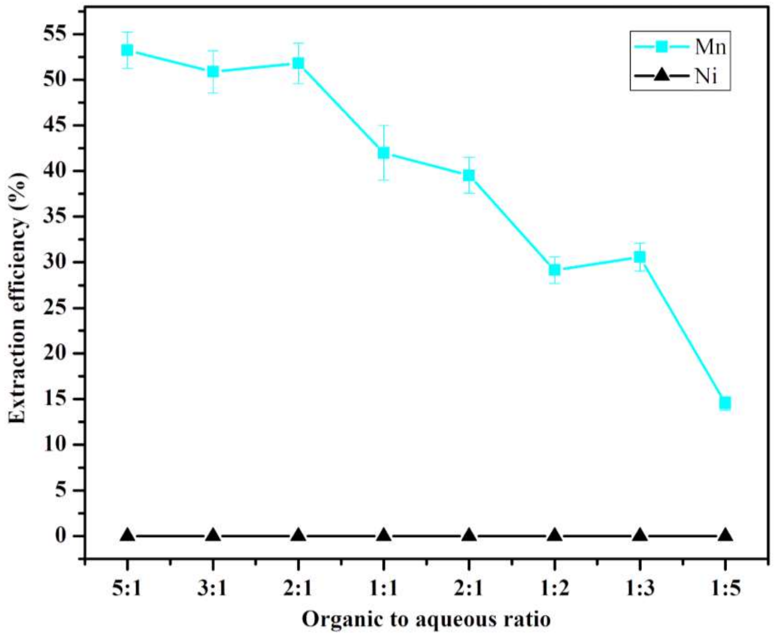

Figure 5.6 Effect of O/A ratio on extraction of manganese and nickel (Conditions: concentration of D2EHPA- 30 vol% in kerosene, pH-3.5, temperature- 40°C, contact time- 60 min, agitation speed- 700 rpm)

Table 5.5 Distribution coefficient of Mn and Ni and their separation factor with variation in O/A ratio (Conditions: concentration of D2EHPA- 30 vol% in kerosene, pH-3.5, temperature- 40°C, contact time- 60 min, agitation speed- 700 rpm)

O/A	**5:1**	**3:1**	**2:1**	**1:1**	**1:2**	**1:3**	**1:5**
$\mathbf{D_{Mn}}$	1.14	1.04	1.07	0.65	0.41	0.44	0.17
$\mathbf{D_{Ni}}$	0	0	0	0	0	0	0
$\boldsymbol{\beta_{Mn/Ni}}$	-	-	-	-	-	-	-

From the result of these experiments it was concluded that D2EHPA alone is not sufficient for complete manganese extraction from the solution in a single step. This led to the use of a modifier (try-butyl-phosphate) (Devi et al., 2000; Li et al., 2018), mixture of two extractants (Ahmadipour et al., 2011; Hosseini et al., 2011), or saponification (Chen et al., 2015a, 2015b), targeting a more efficient removal of manganese. However, the use of modifiers or saponification ultimately increases the total expense and complexity of the recovery process.

To improve extraction efficiency, we used a multistage extraction method, with the raffinate obtained after each successive extraction stage. The release of hydrogen ions (H^+) into the aqueous phase during complex formation (*Eq. 5.1*) lowers its pH, blocking further interaction between the two phases. For example, after the first and second stages of extraction, the pH was reduced to 1.6 and 1.7, respectively. Therefore, the pH of the raffinate after each subsequent extraction step was adjusted to the optimal value (pH 3.5) by adding ammonia drop-by-drop. The quantity of manganese transported to the organic phase increases with the number of extraction stages, reaching 82% and 97% in the second and third extraction stages, respectively. The overall extraction summary using D2EHPA as extractant is tabulated in *Table 5.6.*

Table 5.6 Variation of concentration of metal ions in the solution during SX with D2EHPA (all the concentration are in mg/l unless otherwise stated)

	Aqueous phase before extraction	SX with D2EHPA (3-stage)		
		Organic	Raffinate	% Extraction
Mn	1043	698.81	28.58	97
Ni	270	-	~270	nil
Fe	2.4	2.06	0.34	85.8
Ag	3.51	-	3.51	nil

5.2 Separation of manganese using CYANEX272 as extractant

Various parameters considered for optimization of manganese separation using CYANEX272 as extractant include temperature, pH, carrier concentration, and organic to aqueous (O/A) ratio. The results of optimization studies will be discussed in the following sub-sections.

5.2.1 Effect of carrier concentration

In these experiments, the carrier concentration in the organic phase was varied from 0.2 M to 0.02 M at 35°C, with O/A ratio unity, stirring speed 700 rpm, pH 3, for 30 min of contact time. Almost 99% of manganese got transferred into the organic phase at 0.2 M concentration (*Figure 5.7*), more than previously reported extraction under similar operating conditions (Yetunde et al., 2020). Unfortunately, the amount of nickel co-extracted under these conditions was quite high (44%). It is of interest to note that decreasing the carrier mole fraction by half significantly decreased the co-extraction of nickel from 44% at 0.2 M to 7% at 0.1 M, with a little compromise in total manganese extraction to 93%. However, a further decrease in carrier concentration to 0.05 M and 0.02 M led to inefficient manganese extraction at mere 34.7% and 21%, respectively. The reason for the decrease in extraction fficiency wih the carrier concentration is that as the concentration of carrier decreases, there is a proportional reduction in the quantity of reaction sites available for interactions between metals and organics. Consequently, this decline in available reaction sites leads to a noticeable decrease in extraction efficiency. Therefore from these experiments, 0.1 M CYANEX272 in kerosene was taken as optimum carrier concentration. The distribution coefficients of manganese and nickel and their separation factors with respect to carrier concentration are given in *Table 5.7*.

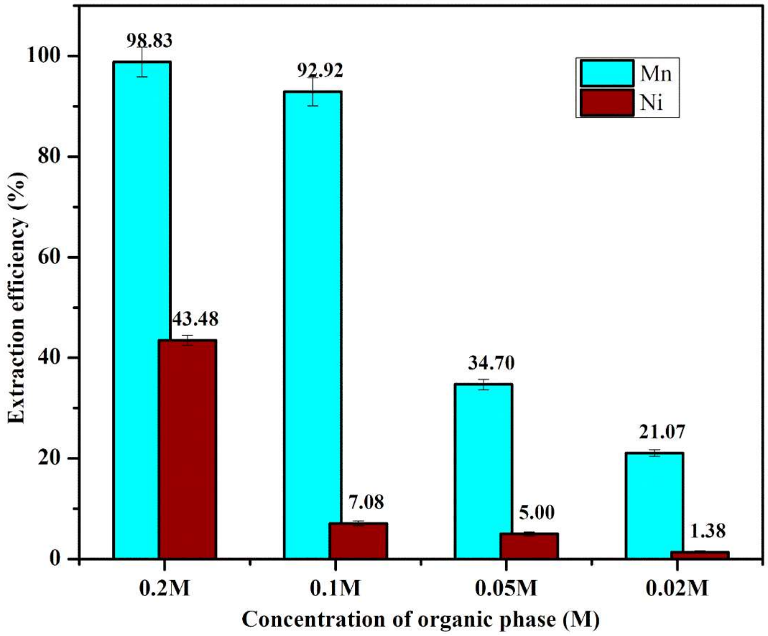

Figure 5.7 Effect of concentration of organic phase on extraction of manganese and nickel (Conditions: pH-3, temperature- 35°C, O/A- 1:1, contact time- 30 min, agitation speed- 700 rpm)

Table 5.7 Distribution coefficient of Mn and Ni and their separation factor with variation in carrier concentration (Conditions: pH-3, temperature- 35°C, O/A- 1:1, contact time- 30 min, agitation speed- 700 rpm)

Carrier concentration (M)	**0.2**	**0.1**	**0.02**
D_{Mn}	84.39	13.13	0.27
D_{Ni}	0.77	0.08	0.01
$\beta_{Mn/Ni}$	109.69	172.27	19.06

5.2.2 Effect of temperature

The positive effect of temperature seen on manganese/nickel ion separation with D2EHPA, prompted us to study the effect of temperature employing CYANEX272. Here the temperature was varied from 35-45°C while keeping other parameters constant. Unlike in the former case, the temperature caused the extraction of both of the metals to increase (*Figure 5.8*). At 40 °C, in excess of 98% manganese was extracted along with as high as 20% nickel. The resulting distribution coefficients and separation factors are given in *Table*

5.11. An increase in temperature wasn't favourable for better separation of these two metals; hence temperature was set to 35 °C in further experiments.

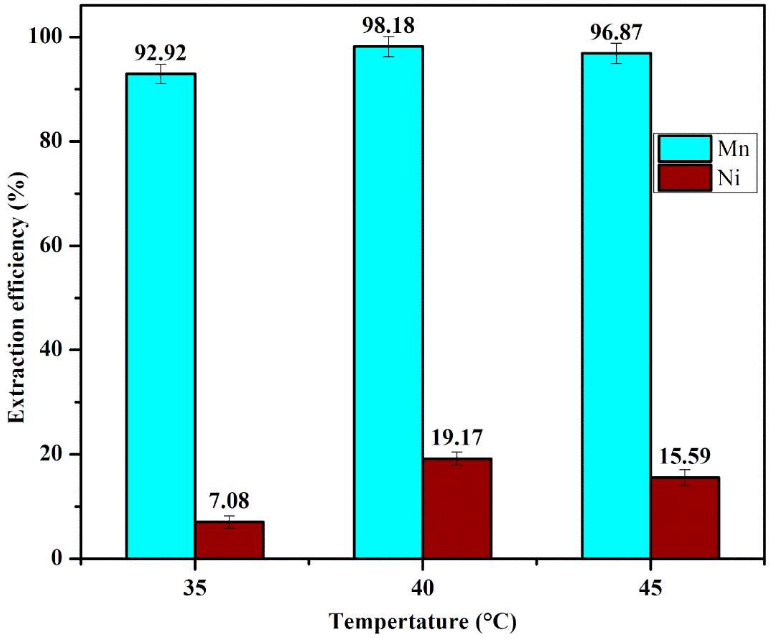

Figure 5.8 Effect of temperature on extraction of manganese and nickel using CYANEX272 as extractant (Conditions: concentration of CYANEX272- 0.2 M in kerosene, O/A- 1:1, pH-3, contact time- 30 min, agitation speed- 700 rpm)

Table 5.8 Distribution coefficient of Mn and Ni and their separation factor with variation in temperature (Conditions: concentration of CYANEX272- 0.2 M in kerosene, O/A- 1:1, pH-3, contact time- 30 min, agitation speed- 700 rpm)

Temp (°C)	**35**	**40**	**45**
D_{Mn}	13.13	53.99	30.97
D_{Ni}	0.08	0.24	0.18
$\beta_{Mn/Ni}$	172.27	227.62	167.73

5.2.3 Effect of pH

Under the set experimental condition of 0.1 M CYANEX272, temperature of 35 °C, O/A of 1:1, 700 rpm stirring speed, 30 min contact time, the effect of pH was investigated from pH 2 to 4.5. Extraction isotherm for pH (*Figure 5.9*) shows a positive slope, indicating an increase in the total amount of manganese transferred into the organic phase by increasing the pH from 2 to 4, reaching the maximum extraction of 95.3% at pH 4. A further increase in pH caused a decrease in manganese extraction. Besides that, the co-extraction of nickel remained quite low below pH 3, due to preferential loading of manganese, and increases afterwards. Therefore, a pH of 3 with a reasonable separation between the two metals was taken as optimum. The variation in distribution coefficients and separation factors are given in *Table 5.9*.

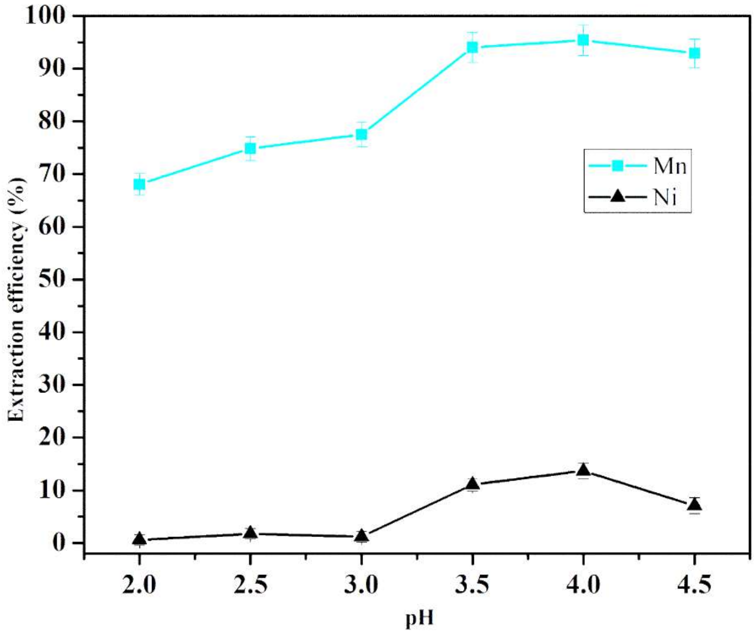

Figure 5.9 Effect of pH on extraction of manganese and nickel using CYANEX272 as extractant (Conditions: concentration of CYANEX272- 0.2 M in kerosene, temperature- 35°C, O/A- 1:1, contact time- 30 min, agitation speed- 700 rpm)

Table 5.9 Distribution coefficient of Mn and Ni and their separation factor with variation in pH (Conditions: concentration of CYANEX272- 0.2 M in kerosene, temperature- 35°C, O/A- 1:1, contact time- 30 min, agitation speed- 700 rpm)

pH	**2**	**2.5**	**3**	**3.5**	**4**	**4.5**
D_{Mn}	2.13	2.98	3.44	15.77	20.62	13.13
D_{Ni}	0.01	0.02	0.01	0.12	0.16	0.08
$\beta_{Mn/Ni}$	345.76	165.67	285.96	126.35	130.02	172.27

5.2.4 Effect of O/A ratio

Finally, the leach liquor with pH 3 at 35 °C was contacted with different organic to aqueous ratios to derive its effect on the extraction efficiency of metals. From *Figure 5.10* it is clear that unlike the pH of the aqueous solution; O/A ratio shows a monotonic effect on the extraction of manganese. The amount of manganese ion remaining in the aqueous phase increases with aqueous phase concentration, which is associated to the maximal loading capacity of the organic phase. O/A ratios greater than 2:1 are favourable for near-complete manganese extraction, but also result in excessive organic consumption. As a result, a 1:1 O/A ratio was chosen as the best compromise between excessive organic consumption and declining manganese extraction. The variation of distribution coefficients of and separation factors with respect to carrier concentration are given in *Table 5.10*.

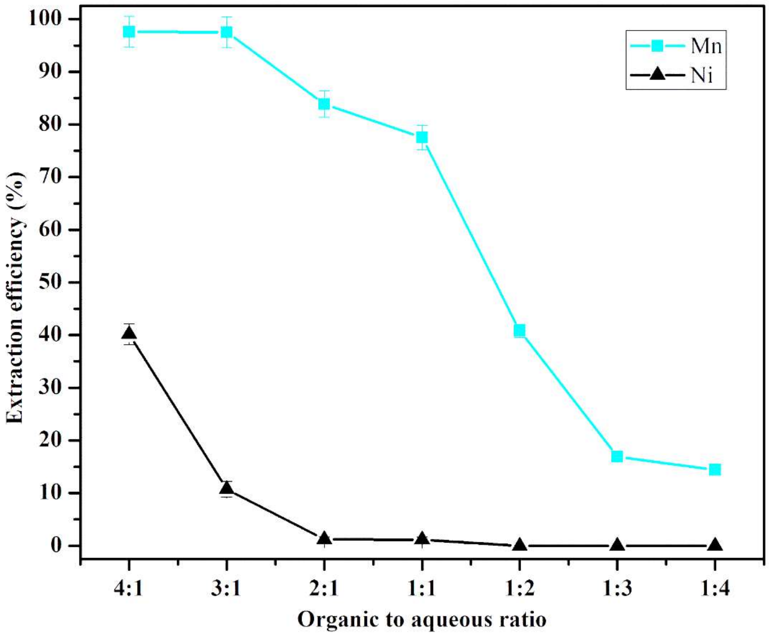

Figure 5.10 Effect of O/A ratio on extraction of manganese and nickel using CYANEX272 as extractant (Conditions: concentration of CYANEX272- 0.2 M in kerosene, pH-3, temperature- 35°C, contact time- 30 min, agitation speed- 700 rpm)

Table 5.10 Distribution coefficient of Mn and Ni and their separation factor with variation in O/A ratio (Conditions: concentration of CYANEX272- 0.2 M in kerosene, pH-3, temperature- 35°C, contact time- 30 min, agitation speed- 700 rpm)

O/A	4:1	3:1	2:1	1:1	1:2	1:3	1:4
D_{Mn}	40.51	39.29	5.20	3.44	0.69	0.20	0.17
D_{Ni}	0.67	0.12	0	0.01	0	0	0
$\beta_{Mn/Ni}$	60.29	326.48	-	285.96	-	-	-

From the above experiment, it was seen that under the optimized condition of 0.1 M CYANEX272, temperature of 35 °C, O/A of 1:1, 700 rpm stirring speed, pH 3, and 30 min of contact time the extraction efficiency of manganese was limited to 77.5%. A large amount of manganese was still left into the raffinate. Therefore, multistage extraction was needed to separate remaining manganese from raffinate with minimal loss.

5.2.5 Multi-stage extraction- McCabe-Thiele plot

Based on the concentration of manganese in the organic and aqueous layer with varying O/A ratio, McCabe-Thiele extraction isotherm (*Figure 5.11*) was constructed. The plot theoretically determines the number of extraction stages required for near quantitative extraction of manganese from the initial concentration of 1043 mg/l under the optimized condition of 0.1 M CYANEX272, temperature of 35 °C, O/A of 1:1, 700 rpm stirring speed, pH 3, and 30 min of contact time. The 1st step in plotting McCabe-Thiele plot is to construct the equilibrium isotherm (blue line). To do this, the metal (manganese) content in both organic and aqueous phase under different O/A ratio were determined experimentally and was plotted in a graph, where X-axis and Y-axis represents metal content in aqueous and organic phase, respectively. After plotting equilibrium curve, the operating/working line (black line) was constructed. The operating line is the straight line where the slope of line equals the desired phase ratio (A/O). Number of extraction stages required (green line) was obtained by drawing a horizontal line from the point of intersection of operating line with initial concentration of aqueous feed phase (red line) to the equilibrium curve. According to this plot, two extraction stage is required for near complete extraction of manganese to the organic phase.

Experimental results are in well agreement to the prediction of McCabe-Thiele plot. Experimentally, after the 1st and 2nd stages of extraction, the concentration of manganese in the raffinate were 277.4 mg/l and 8.73 mg/l respectively, corresponding to 99.16% of the total extraction of manganese. The calculated organic phase concentration of manganese after these two-stage extractions was 1034.27 mg/l. The raffinate obtained after this two-stage extraction is rich in nickel (256.1 mg/l) with less than 10 mg/l impurity elements, which can be further subjected to precipitation to obtain nickel hydroxide precipitate.

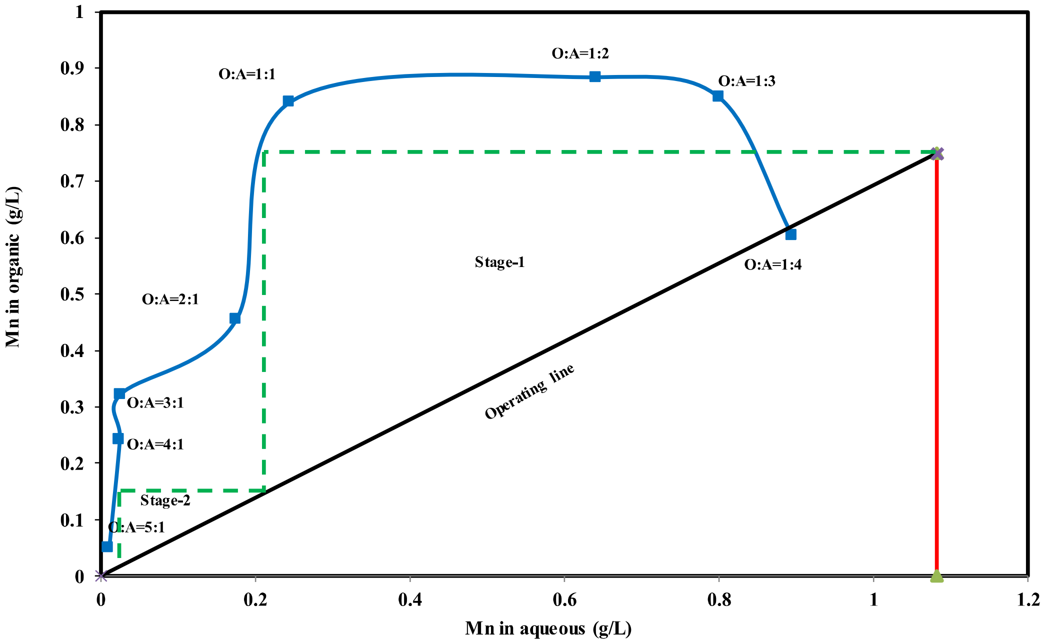

Figure 5.11 Manganese distribution isotherm and McCabe-Thiele plot to determine number of extraction stages

In contrast to what was determined in previous study (Pérez-Garibay et al., 2012), the results of this investigation showed that CYANEX272 was a more efficient extractant, even with lesser consumption of organic carrier, for selective recovery of manganese from mixed-metal solutions, particularly those including nickel. Indeed, it can be ascertained from the results that parameters like pH, O/A ratio, and extractant concentration are critical in metal separation and must be closely monitored.

5.2.6 FT-IR analysis

FT-IR spectrum for 0.2 M CYANEX272 mixed with kerosene and metal loaded organic phase after extraction under optimized condition with CYANEX272 is shown in *Figure 5.12*. The interaction of manganese ions with phosphinic acid extractant is evident in the figure. Extractant before and after loading shows similar characteristic vibration bands at 2752-2854 cm^{-1} and 1376-1453 cm^{-1} corresponding to C–H stretching and bending vibrations, respectively of $–CH_3$ moiety. The characteristic peaks at 1603 cm^{-1} and 1168 cm^{-1} correspond to –OH and P=O bond. Evidently, the interaction of the metal with organic solvent affects the total transmittance at these vibrational bands. The shift of –OH band after loading at 1603 $cm^{-1,}$ along with an increase in transmittance, indicate the formation of a complex of manganese with hydroxyl group. Furthermore, a marginal shift in P=O band at 1168 cm^{-1}, with higher intensity, when extractant is loaded with manganese is an evidence in favor of complex formation through co-ordination with metal.

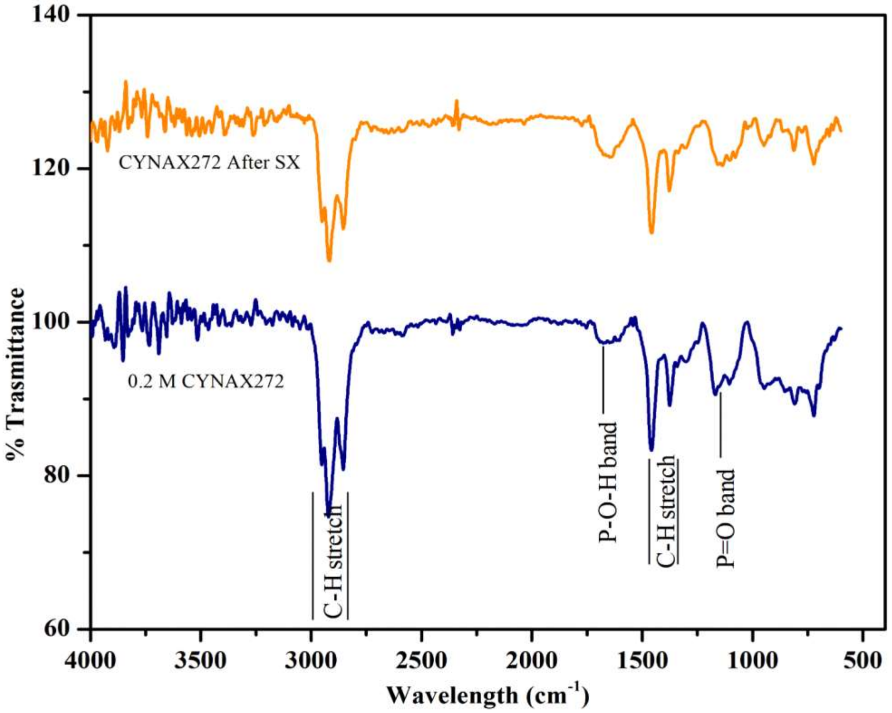

Figure 5.12 FT-IR plot of organic phase (CYANEX272 in kerosene) before and after extraction of manganese (SX- solvent extraction, ST- stripping)

5.2.7 Stripping of manganese from loaded organic phase

The manganese loaded organic phase obtained using CYANEX272 under the optimized condition was finally treated with different stripping reagents (2 M HCl, 2 M HNO_3, 2 M H_2SO_4) to back-extract manganese into the aqueous phase. The results are presented in *Figure 5.13*.

HNO_3 was proved to be a better stripping reagent for manganese than other two aqueous solutions. Nearly, 76%, 79%, and 65% manganese was stripped using HCl, HNO_3, and H_2SO_4, respectively at 2 M concentration. Stripping efficiency was further assessed by varying the concentration of nitric acid from 2 M to 4 M. Increasing the concentration of stripping reagent increases the amount of manganese stripped into the aqueous phase from 79% at 2 M to 90% at 4 M (*Figure 5.14*). As a result of these experiments, 4 M nitric acid was chosen for successful manganese back-extraction into aqueous solution.

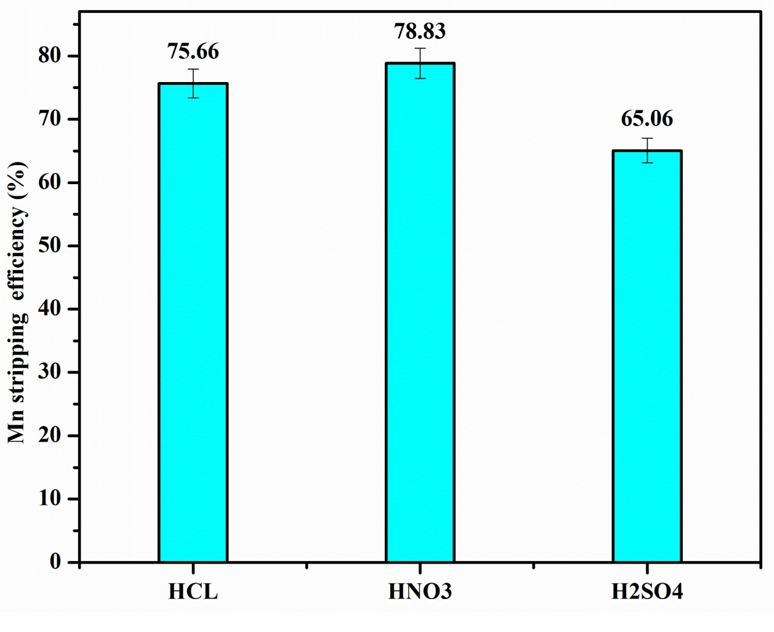

Figure 5.13 Effect of type of stripping reagent on back extraction of manganese from CYANEX272 loaded organic phase (Conditions: concentration of stripping reagent- 2 M, temperature- 30°C, O/A- 1:1, contact time- 30 min, agitation speed- 700 rpm)

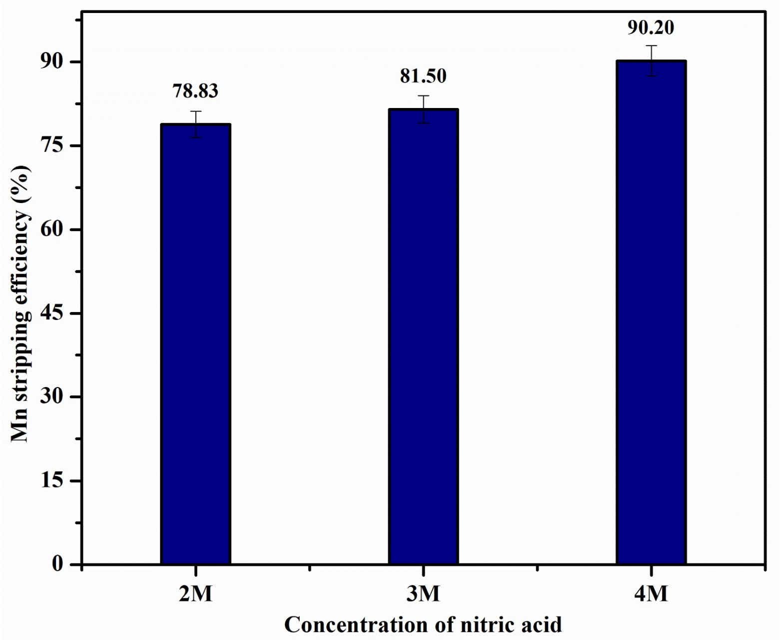

Figure 5.14 Effect of concentration of nitric acid on back extraction of manganese from CYANEX272 loaded organic phase (Conditions: temperature- 30°C, O/A- 1:1, contact time- 30 min, agitation speed- 700 rpm)

The overall extraction summary using CYANEX272 as extractant is tabulated in *Table 5.11*. The concentration of organic and aqueous phase during various stages of treatment can be seen from this Table.

Table 5.11 Variation of concentration of metal ions in the solution during various stages of treatment (all the concentration are in mg/l unless otherwise stated)

	Aqueous phase before extraction	SX with CYANEX272 (2-stage)			Stripped solution	% stripping
		Organic	Raffinate	% Extraction		
Mn	1043	1034.27	8.73	99.16	932.7	90.17
Ni	270	13.9	256.1	0.05	2.09	15.04
Fe	2.4	0.59	1.81	24.6	0.4	67.80
Ag	3.51	2.06	1.46	58.4	1.02	49.51

The stripped solution produced with the above optimized conditions contained high purity manganese solution at a concentration of 932.7 mg/l and less than 5 mg/l impurity elements. The flowsheet for proposed recovery route is presented in *Figure 5.15*. The proposed method is an efficient method for separation of manganese and nickel from capacitor leach liquor.

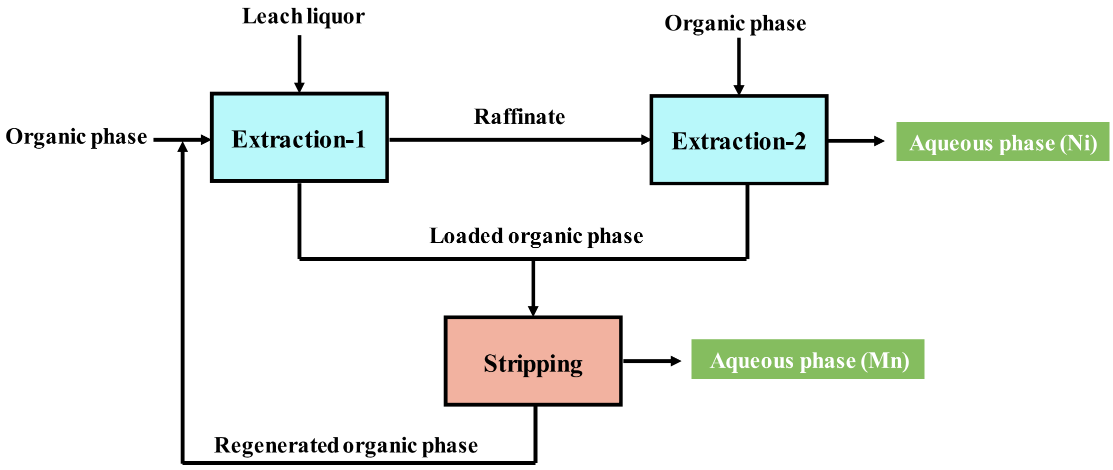

Figure 5.15 Flowsheet of overall extraction-stripping cycle for separation of manganese from stage-1 leach liquor using CYANEX272 as extractant

5.3 Conclusions

In this chapter a purification method was developed for selective separation of manganese and nickel from stage-1 leach liquor using solvent extraction with two distinct organophosphorous extractant i.e., D2EHPA and CYANEX272. The major outcomes of this study is given below:

- D2EHPA and CYANEX272 both showed excellent selectivity for manganese. However, CYANEX272 proves to be a better extractant than D2EHPA in terms of extraction efficiency and reagent consumption.
- 0.1 M CYANEX272, temp 35°C, O/A 1:1, pH 3, and 30 min contact time are the optimized parameters for maximum transfer of manganese into the organic phase, in a single-stage extraction, without loss of nickel.
- McCabe-Thiele plot was constructed to theoretically determine the number of extraction stages required for near complete extraction of manganese. Experimental results confirmed the prediction of McCabe-Thiele plot. More than 99% of manganese transferred to organic phase in two-stage extraction leaving most of the nickel into the raffinate.

- 4 M HNO_3 is a suitable stripping reagent for back-extraction of manganese into aqueous phase. The final strip solution contained manganese with nearly 99.6% purity with less than 3 mg/l nickel.