Solvent extraction technique for removal and recovery of nickel from effluent by Tri methyl amine as a carrier

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ABSTRACT

Water pollution is one of the major worries of the day. Every community produces both liquid and solid wastes. As heavy metals are not biodegradable they tend to accumulate in living organisms causing various diseases and disorders. This paper deals with recovery of nickel ion from effluents resulting from the metal industry. Nickel is extracted with trimethyl amine in kerosene as organic solvent. The influencing parameters such as the effect of pH of the aqueous phase, effect of nickel concentration, effect of extractant concentration, effect of the diluents and the stripping reagent has been investigated. The efficiency of nickel extraction increased with increasing Nickel concentration. The extracted nickel in the organic phase can be back extracted in to 2M of HCl (75.3%) and 0.3M H_3PO_4 (57.8%)

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I. INTRODUCTION:

Nickel is long thought to be essential to plants and some domestic animals. Polluted waters are becoming a severe public health problem. Cobalt and Nickel are the most widely used metals in various industries due to the superior properties they posses [1]. Nickel is widely used in the industry and can be found in almost all environmental settings. The toxicological character of nickel to humans is that its ingestion is consistently associated among others, with lung and nasopharyngeal cancer [2]. The separation of Nickel in aqueous solutions has always been a problem in hydrometallurgy [3].

Liquid membrane technology and its inherent accompanying science had been demonstrate in a wide range of applications including; metal ion extraction, wastewater treatment, fermentation, pharmaceuticals [4] precipitation, adsorption, ion exchange [5,6] and solid phase extraction[7] have already been developed for the extraction. Various technologies were used to remove nickel from aqueous solutions. Among them solvent extraction seems to be the most efficient method for separation of Ni (II) ions from solutions, including leach liquoes [8] and ion exchange resins.[9-11] Di-2-ethyl hexyl phosphoric acid is widely used extractant for recovery of Co(II) and Ni (II) and for their separation [12]. Solvent extraction technique has been used by several researchers for extraction and separation of cobalt and nickel using several extractants such as PC 88A [13], cyanex 272 [14], Aliquat 336 [15], N-N'-carbonyl difatty amides [16].

In the presence study, the extraction of a cationic ion namely Ni (II) while it makes an ion –pair with Trimethyl amine as an extractant in kerosene was studied. The metal extraction and stripping extracted metal were investigated and operating conditions were optimized. Further recovery of metal and stripping reagents was also studied. The influencing parameters such as effect of pH, effect of Ni (II) concentration, effect of carrier concentration, and stripping reagent concentration etc., was also studied and reported here.

II. Experimental

A. Apparatus and measurements

A UV visible spectrophotometer (Elico SI 159, India) was used to measure the absorbance of the metal and to establish its (λ_{max}) and its concentration. The pH of an aqueous solution was measured by a pH meter (Elico Li 120, India).A mechanical stirrer (IKD-Ks-50, India) was used for agitation of solution.

B. Extraction experiments

The Ni (II) solution (feed phase) was prepared by dissolving a known of $NiSO_4$ in deionized water, which was used as the simulated wastewater. All experiments were carried out at ambient temperature. In the extraction equilibrium studies, equal volumes of organic and feed aqueous phases (10ml: 10ml) with known concentrations were shaken in a separating funnel. The phases were mixed gently for five minutes and allowed to separate. After phase separation, the Ni (II) concentration in the aqueous phase was determined with a UV-VIS Spectrophotometer, and the absorption wavelength was 470nm using DMG as the indicator. The Ni (II) concentration in the organic phase was calculated on the basis of a mass balance.

All the extraction equilibrium experiments were carried out in duplicate, and the analysis was carried out in triplicate for each run. The reproducibility was found to be ± 5%.

C. Stripping Experiments

The loaded organic phase was obtained from the extraction experiments, all the stripping experiments were carried out using the same procedures and condition of the extraction experiments. The results are expressed as distribution coefficient D, extraction efficiency %E, and recovery efficiency %R defined as,

$D = [Ni^{2+}]_{org.eq} / [Ni^{2+}]_{f.eq}$ ………………………..(1)

$\%E = (1 - [Ni^{2+}]_{f,eq} / [Ni^{2+}]_{f.ini}) \times 100$ ……………(2)

$\%R = \{[Ni^{2+}]_{s.eq} / [Ni^{2+}]_{f.ini}\} \times 100$ ……………(3)

Where the subscripts f, org, s, eq and ini represent the feed aqueous phase, organic phase, and stripping aqueous phase at equilibrium and initial respectively.

III. Result and discussion

A. Effect of pH of feed phase

To investigate the effect of pH value on the extraction of Ni (II) ions into the TMA/ Kerosene system. The influence of pH on the extraction efficiency was studied for a wide range of pH from 1 to 12 ± 0.1and the results are shown in (Table 1). The distribution ratio D of Ni (II) ion calculated as fixed concentration of TMA. Table (1) shows the distribution coefficient (D) versus pH of the feed phase. Upon increasing the pH of aqueous phase from 1.0 to 6.0. The extraction efficiency of nickel also increases up to 90.38% and distribution co efficient were found at pH 7.0±0.1 At pH >7, the extraction efficiency and distribution coefficient decreased (8.2,3.6,2.6,1.0,0.7)respectively. This can be explained as when alkaline pH, the extraction was low, because the amine is strong base, In low pH the distribution coefficient was higher. For further studies, it was decided to maintain the extraction at ph 7.0 ± *0.1*.

Table.1 Effect of pH of feed phase

[TMA]/mol.L^{-1}	pH	[Ni^{2+}]$_{f,eq}$/mg/L^{-1}	%E	D
1.35	1	44.3	55.6	1.25
1.35	2	40.3	59.7	1.48
1.35	3	31.7	68.4	2.16
1.35	4	27.1	72.9	2.6
1.35	5	21.4	78.6	3.6
1.35	6	15.6	84.5	5.41
1.35	7	2.22	90.7	9.39
1.35	8	1.15	89.1	8.2
1.35	9	21.4	78.6	3.67
1.35	10	27.4	72.6	2.64
1.35	11	48.2	51.8	1.07
1.35	12	56.3	43.7	0.76

B. Effect of extractant (TMA) concentration:

The effect of extractant (TMA) concentration on the percentage extraction and distribution ratio (D) of the Ni (II) ion was investigated in the range of 0.33M to 1.35M of TMA in kerosene as diluent shown in Fig 1.The percentage of extraction increased with increase in concentration of TMA. Maximum sufficiently available extraction of 90.3 % was obtained in 1.35M of TMA because it was necessary for the amine to be sufficiently available for the formation and extraction of the complex [Ni (II)-TMA] into the organic phase. Further increase in the extractant concentration did not improve the extraction efficiency. This effect can be accounted for by analyzing the influence of the viscosity increase of TMA solution upon the diffusion of the metal complex in the extractant phase. This confirms that TMA is effective in extracting anionic ion. Hence, all of our subsequent experiments were performed using 1.35M of TMA as the extractant
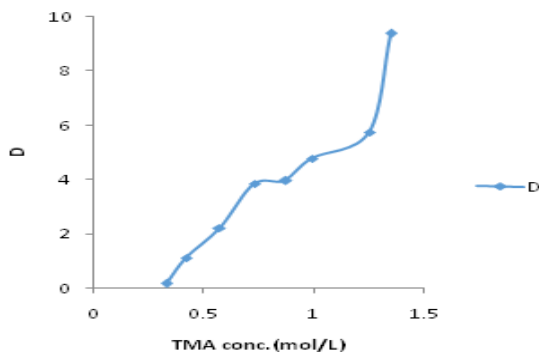
Fig: 1 Effect of TMA concentration:

C. Effect of equilibrium time:

The two immiscible of aqueous Ni (II) solution and solvent (Kerosene-TMA) were equilibrated for a period ranging from 30-600s. The results obtained are presented in Fig.2. Sharp increase of extraction was shown during the first min. This means that the extraction happened very fast with majority of metal extracted when only 1 min of equilibration was given. After 5 min, 90% of metal was extracted to the organic phase; the extraction rate of metal ion depends on the degree of hydration of the polar and ionic moieties of the extractant. No additional extraction was found beyond 5 min. Therefore, an equilibration time of 5 min was chosen for the subsequent extraction tests.
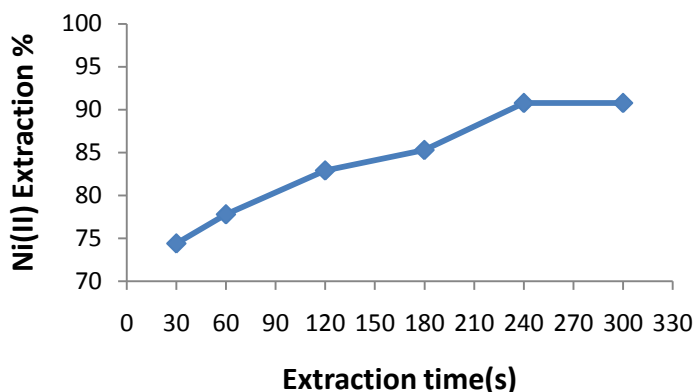

Fig.2 Effect of equilibrium time:

D. Effect of Nickel concentration:

The extraction efficiency of various initial concentrations of Ni (II) in the aqueous phase with concentration ranging from 10mg/L to 50mg/L was determined at pH 7.0 ± 0.1 and contacted with organic layer (10ml) containing 1.35M of TMA as extractant. From Fig.3, the percentage of extraction efficiency of 90%, was achieved when the aqueous phase contained 10mg/L Ni (II) ions. When efficiency of extraction decreased the Ni (II) concentration increased. This difference in extraction efficiency is due to the availibility of decrease in the extractant in the organic phase. So, TMA is not able to completely remove the Ni (II) from the aqueous phase. However, the absolute amount of Ni (II) extracted, increased with increase of initial Ni (II) concentration.
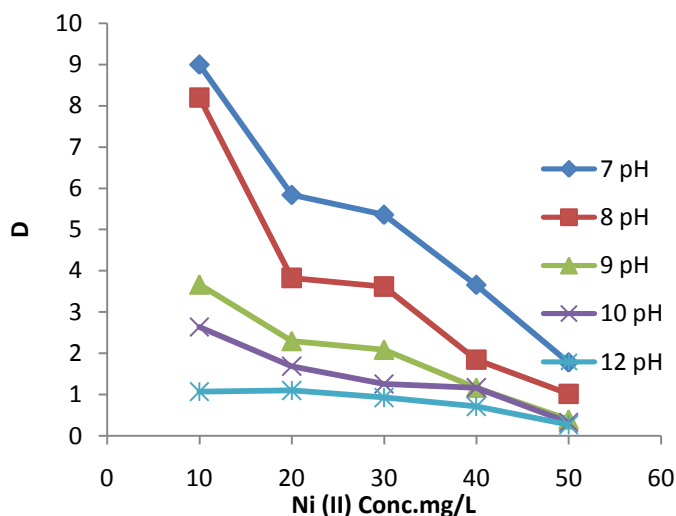
Fig.3 Effect of Ni (II) Concentration:

E. Effect of A/O ratio:

The volume phase ratio of aqueous to organic phase (A/O) was studied at pH 7.0 ± 0.1 with an initial Ni (II) concentration 10mg/L. About 90.7% extraction efficiency was achieved from 1:1 when the A/O volume ratio was increased to 2:1 to 12:1, the percentage of extraction decreased. Maximum extraction of 90.7% for 1:1 ratio, 89.1% for 3:1 ratio, 75.2% for 5:1 ratio, 66% for 7:1 ratio, 55.72% for 10:1 ratio, 42.9% for 12:1 ratio was achieved at 10mg/L initial nickel concentration. The A/O ratio effect is shown in (Table.2)   1:1 A/O ratio yielded a higher percentage of Ni (II) removal from aqueous solution. This could be due to the higher free concentration of organic phase when the aqueous to organic phase ratio (A/O) is lower [17] for further studies, it was decided to maintain 1:1 (A/O) ratio.

Table:2 Effect of A/O ratio:

Ratio (A/O)	Percentage of Ni (II) extraction		
	10mg/L	30mg/L	50mg/L
1:1	90.78	84.6	73.5
3:1	89.18	78.4	64.5
5:1	75.26	67.2	53.8
7:1	66.0	55.9	50.7
10:1	55.72	53.6	47.8
12:1	42.94	48.3	41.4

F. Stripping of loaded organic phase:

In any extraction process, it is imperative to back extract   the extracted species from the organic phase. HCl, H_3PO_4 were used as the stripping agent. The effect of concentration of stripping agent, stripping phase ratio, stripping contact time were also studied.

G. Effect of stripping reagent concentration:

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The concentration of stripping reagent plays an important role in stripping metal from the loaded organic phase, we tested several agent-namely sulfuric acid oxalic acid, sodium hydroxide, sodium carbonate, nitric acid, hydrochloric acid, sodium citrate, phosphoric acid for the stripping of Ni (II) ions from the organic phase. Among them HCl and H_3PO_4 were used as the stripping reagent in this work. The effect of its concentration on the recovery of Ni (II) is shown in (Table.3). For a feed concentration of 10mg/L the mineral acids 2.0M HCl and 0.3M H_3PO_4 had high stripping efficiencies of 75.3% and 57.8% respectively. Further increases in HCl and H_3PO_4 concentration had no significant improvement on the recovery efficiency. Hence, we selected HCl for further studies to determine its optimum molarity. So, 2M HCl was sufficient to strip the extracted Ni (II) ions from the organic phase (Jakovljevic et al. 2004) demonstrated, Co and Ni ions could be stripped with 2.0M HCl from organic phase containing cyanex 301/Aliquat 336 as compared to cyanex 301 alone.

Table: 3 Effect of stripping agents on percentage of Ni (II) stripping from organic phase

Stripping agent	Percentage of Stripping
Sulphuric acid(1M)	45.9
Hydrochloric acid(2M)	75.3
Oxalic acid(1M)	25.4
Phosphoric acid(1M)	57.8
Acetic acid(1M)	14.3
Sodium hydroxide(1M)	Not Stripped
Pottassium hydroxide(1M)	Not Stripped
Sodium carbonate(1M)	Not Stripped
Sodium citrate(1M)	13.8

H. Effect of stripping phase ratio (O/A):

The stripping phase ratio (organic to aqueous phase,O/A) is an important parameter in stripping processes. From Fig.4 the percentage of stripping decreased with increased O/A ratio fig shows for O/A of 1/1 and 2/1, the stripping efficiency was 75.3% to 72.4% respectively. For O/A greater than 2/1 the percentage of stripping has decreased. This may be due to the amount of HCl in the aqueous stripping phase was less. The ability of the HCl to react with the nickel in the organic phase also decreased. Hence stripping efficiency decreased.
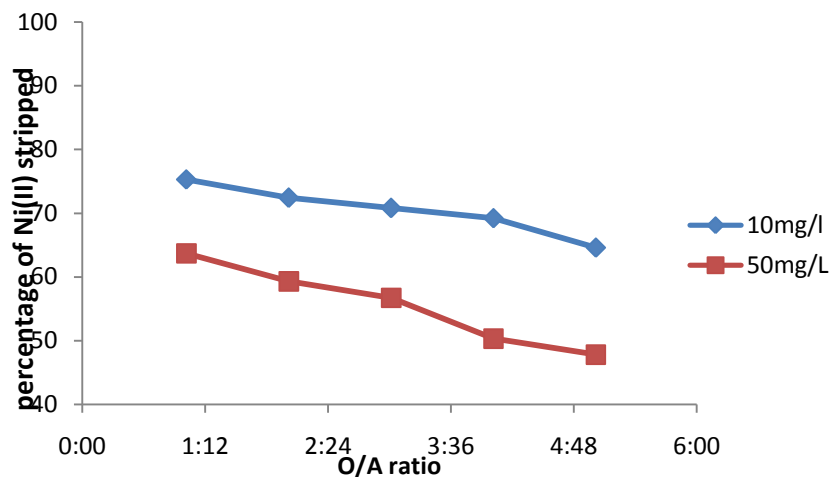

Fig.4 Effect of stripping phase ratio(O/A)

I. Effect of stripping contact time:

Different stripping contact times were studied and the percentage of stripping for each contact time is represented in (Table.4). The data obtained show that the percentage of stripping was independent of time. The underlying reason indicates fast stripping reaction rate. No further stripping was achieved when the contact time was increased beyond 5 min. From the data,the highest percentage of stripping ever achieved was 75.3% in 5 min.

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Time in minutes	Percentage of Ni(II) stripped			
	10mg/L	20mg/L	30mg/L	50mg/L
1.0	68.7	61.4	55.6	35.8
2.0	71.3	65.2	59.7	39.4
3.0	72.1	69.3	62.4	42.7
4.0	74.5	71.1	67.9	46.4
5.0	75.3	71.3	68.5	47.8

Table .4 Effect of stripping contact time:

J. Effect of stripping reagents:

In extraction processes it is very imperative to back extract the extracted Ni (II) from the organic phase and allow recycling of the organic solvent without loss of efficiency. Various inorganic acids such as HCl, H_3PO_4, H_2SO_4 were used as stripping agent in this study. HCl stripped the Ni (II) very well from the organic phase (Table.5) as compared to other inorganic acids. It means that the presence of HCl in the stripping phase helped the Ni (II) ion by converting the Ni (II) hydrophilic moiety (Muthuraman and Palanivelu 2006). Hence 2N HCl was found to be suitable for stripping of the extracted Ni (II).The maximum amount of Ni (II) (75.3%) was stripped with in 5min.Further increase in time did not improve stripping efficiency.

Tabel.5 Effect of HCl and H_3PO_4 Concentration on stripping of Ni(II)from loaded organic phase

(a) (b)

| $[HCl]/mol.L^{-1}$	$[Ni^{2+}]_{f,ini}/mg/L^{-1}$	$[Ni^{2+}]_{s.eq}/mg/L^{-1}$	% R	$[H_3PO_4]/mol.L^{-1}$	$[Ni^{2+}]_{f, ini}/mg/L^{-1}$	$[Ni^{2+}]_{s.eq}/mg/L^{-1}$	% R
0.5	10	6.25	62.5	0.1	10	1.63	16.5
1.0	10	0.59	5.90	0.2	10	2.06	20.6
1.5	10	3.50	35.1	0.3	10	5.78	57.8
2.0	10	7.53	75.3	0.4	10	4.2	42.1
				0.5	10	2.5	25.0
				0.1	50	7.63	15.2
				0.2	50	6.27	12.5
				0.3	50	17.18	34.3
				0.4	50	22.0	44.09
				0.5	50	17.17	34.4

$[TMA]=1.35 \ mol.L^{-1}$

K. Reusability of solvent:

Stripped organic solvent was reused to re extract Ni (II) from aqueous solution. The feed aqueous phase was equilibrated with the organic phase at 1:1 phase ratio. The extraction efficiency (90%) of Ni (II) efficiency slightly dropped. This might be due to loss of TMA during stripping.

L. Application of the developed solvent extraction (or) LLE for industrial wastewater:

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The developed solvent extraction (or) LLE system was tested for applicability to real industrial wastewater (under optimized condition, feed phase =10mg/L at pH 7±0.1 extractant concentration=1.35 x10^{-2} mol/L, equiibrium time=5min, strip phase=2M HCl,A/O ratio=1:1) the textile effluent was extracted and the extracted Ni(II) was stripped into the HCl solution. Based on the above data, a proposed flow sheet for extraction and recovery of Ni (II) ion from industrial wastewater is given in Fig.5
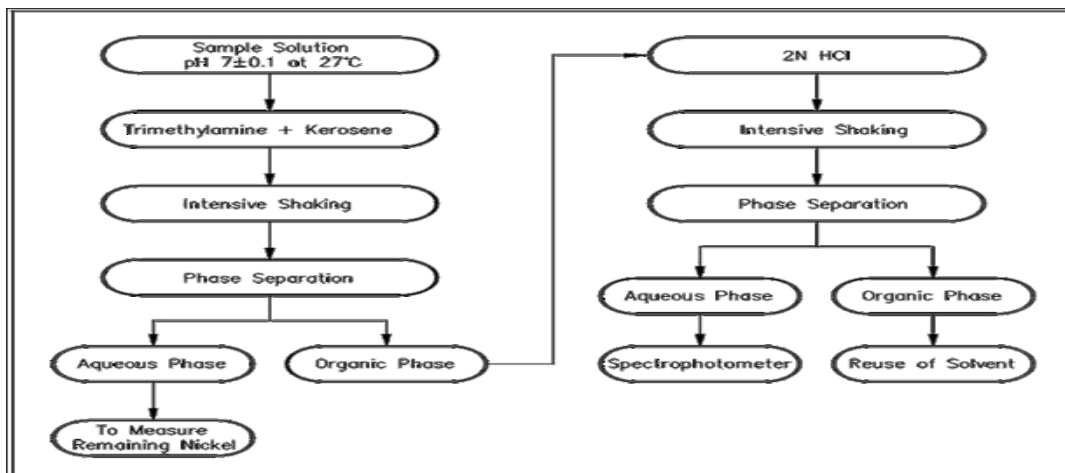
IV. Conclusion:

Solvent extraction of Ni (II) from aqueous solutions was carried out using TMA as extractant. The extraction efficiency of Ni(II) more than 90% was extracted with the help of 1.35M TMA in kerosene solution in a short time of 5 min. more than 75.3% of Ni (II) could be recovered with 2 mol/L^{-1} of HCl and 57.8% of Ni(II) recovered with 0.3mol/L^{-1} of H_3PO_4 solution. In 2M HCl, the recovered solution contained high concentration of Ni (II) ions. The maximum extraction efficiency was obtained at pH 7.0 ± 0.1.The A/O ratio 1:1 is maintained in this study. Stripping reaction was completed within 5 min and 75.3% of the Ni (II) was stripped from loaded organic phase. Solvent (Kerosene+TMA) can be reused as many as 10 times it was slightly varied its loss of efficiency. Under optimized condition real textile wastewater was tested and the result was found to be satisfactory.

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