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Separation of nickel (II) from acidic media using substituted 2-amino-pyrazoloquinazolinone

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ABSTRACT

This paper presents the extraction and separation of nickel (II) from sulfate solutions using the extractants 2-amino-3-(4- (X) phenyl azo)-8,9-dihydro-8,8-dimethyl-7H-pyrazolo [1,5-a] quinazolin-6- one (H_2NXPQ)/benzene (X = Br, Cl or CH_3) that have been previously prepared by the authors. Several experiments were performed to optimize the extraction controlling factors. The maximum extraction efficiency was achieved from a synthetic aqueous solution of pH 2.5 and assaying 20 mg/l Ni (II) ions by using 2.42×10^{-3} M concentration of (H_2NXPQ)/benzene at (1/1) A/O ratio for 10 min. contact time at room temperature. The maximum loading capacity remained constant after the four loading cycle from the synthetic acidic solution. The values of pH1/2 and K_{ex} as well as the values for the thermodynamic parameters ΔG, ΔH, and ΔS have been calculated. The extracted Ni (II) was effectively stripped from the organic phase using 0.5M HCl solution. The optimized extraction conditions have then been applied for Ni (II) extraction from the uranium - bearing leach liquor of El Sela mineralization.

KEYWORDS

Separation;
Solvent extraction;
Nickel;
Stripping;
Acidic media.

INTRODUCTION

The solvent extraction techniques have been applied since a long period of time. A survey of the concerned literature indicates that the solvent extraction of nickel ions is based on several works using a number of amine chelating agents. These involved triethylamine[1] and Alamine 336[2] as extractants from acidic solutions. The amine was also used for nickel and cobalt extraction by the aliphatic hydroxyoxime and carboxylic acid syste[3]. In the meantime, the properties of the nickel(II)/2-hydroxy-5-nonylacetophenone oxime (HNAPO) extraction system was studied in a micellar system[4]. On the other hand, the extraction kinetics of nickel from acidic chloride solutions containing chromium with aliphatic oximes from ammonium solutions were determined[5,6]. The separation, purification and recovery of nickel from ammoniacal/ammonium sulphate solutions using the commercially available LIX 54 β-diketone dissolved in a kerosene type diluent were also applied[7].

The solvent extraction of Ni and Co by a mixed system of pyridine-based chelating extractant, 2,6-bis-[5-n-nonylpyrazol-3-yl] pyridine (BNPP) and dinonyl naphthalene sulfonic acid (DNNSA) was also studied as a function of pH, diluents, temperature, and DNNSA concentration[8]. In addition, the extractive separation of Ni (II) from aqueous media by 3-phenyl-4-acetyl-5-isoxazolone[9] and pyrazolones derivatives[10] was also studied.

An imidazole reagent, benzo (15-crown-5)-1H-imidazole (4,5f) (1,10) phenanthroline was synthesized as well as the prepared complexes of Co (II), Ni (II), Cu (II) and where the structures of the formed complexes was found to be (2:1)[11]. The formation constant and the thermodynamic parameters of the nickel (II) complexes with 3-amino-5-methyl isoxazole Schiff bases and N, N; N, O and O, O donor ligands in solution were obtained[12], and furthermore the solvent extraction of cobalt, nickel, and copper ions by the ligand diphenylamino benzoic acid in chloroform was also carried out[13].

Together with nickel (II), the solvent extraction of uranium (VI) was studied with 3-methyl-4-(p-nitrobenzoyl)-5-oxo-phenylprazole dissolved in benzene[10]. The solvent extraction of uranium (VI) from sulfate solutions was obtained by Alamine® 336 in kerosene modified with 5% w/w 1-tridecanol and stripping with a 199 g/l Na_2CO_3 solution[14]. Also, the mixed solvent containing DEHPA (di-2-ethylhexylphosphoric acid) and Alamine 336 was used for uranium recovery from the acidic solution[15].

The present work is actually concerned with application of the previously prepared 2-amino-3-(4- (X) phenyl azo)-8,9-dihydro-8,8-dimethyl-7H-pyrazolo [1,5-a] quinazolin-6- one (H_2NXPQ) extractants for nickel extraction from its acidic solutions. This study has thus established the relevant experimental parameters; namely the pH, the extractant concentration, the aqueous/organic phase ratio (A/O), the temperature besides the loading capacity of the extractants as well as Ni (II) stripping from the latter. The thermodynamic parameters such as the free energy (ΔG), the enthalpy (ΔH) and the entropy (ΔS) changes associated with the extraction processes were evaluated. In the present application, El Sela acid leach liquor has several impurities such as Ni (II), etc., which affect the extraction of uranium from its acidic solutions. It was thus decided to remove nickel ions by the solvent extraction technique using the prepared extractants.

EXPERIMENTAL

Materials

Preparation of the H_2NXPQ extractants

Three multidentate compounds namely, 2-amino-3-(4- (X) phenyl azo)-8, 9-dihydro-8, 8-dimethyl-7H-pyrazolo[1,5-a] quinazolin-6- one (H_2NXPQ), (X= Br, Cl or CH_3) were prepared. For this purpose, (10 mmole) enamindione namely; 2- ((dimethyl amino) methylene)-5,5-dimethyl cyclohexane-1,3-dione (one ß-diketone) was treated with (10 mmole) 4-aryl azo-3,5 diaminopyrazole derivatives in refluxing ethanol in the presence of a catalytic amount of piperidine. The formation of the compounds were assumed to take place via an initial Michael addition of the exocyclic amino group in the 4-aryl azo - 3, 5-diaminopyrazole derivatives to the α,β-unsaturated in the enamindione. The formed compounds have the empirical formula, $C_{18}H_{17}XN_6O$ where X = Br, Cl or CH_3. The corresponding molecular weights are 413.28, 368.83 and 348.41 for the Br, Cl and CH_3 derivative compound respectively.

More information about the synthesis and the interesting physical properties of the 2-amino-3-(4- (X) phenyl azo)-8,9-dihydro-8,8-dimethyl-7H-pyrazolo [1,5-a] quinazolin-6- one (H_2NXPQ) have previously been described by Khawassek et al[16].

Preparation of the synthetic Ni(II) and El sela solutions

A standard stock solution of 1000 mg/l (17×10^{-3} M) Ni (II) has been prepared by dissolving 4.478 g nickel sulphate hexahydrate ($NiSO_4.6H_2O$, Prolabo) in 1000 ml distilled water. This solution was actually used to determine the relevant factors of nickel extraction by the prepared solvents.

The applied leach liquor was prepared by mixing a powdered sample weighing 100 g from El Sela mineralization, south eastern Desert of Egypt with 300 ml sulfuric acid (100 g/l). The obtained slurry was agitated for 4 h at room temperature and the insoluble residue was separated by filtration[17]. The obtained leach liquor thus mainly contains uranium ions besides some metal impurities including the metal ions being studied; namely nickel. The former would indeed undergo several processes of purification to obtain the commercial pure concentrate known as the yellow cake. Extraction of nickel ions from this actual sulfate solution containing U (VI) was then undertaken by the prepared H_2NXPQ extractants using the determined optimum extraction conditions.

Preparation of the synthetic interfering ions solutions

Several standard stock solutions of 1000 mg/l of possible interfering ions during Ni (II) extraction by the prepared extractants have been prepared by dissolving suitable weights of their salts in 1000 ml distilled water e.g. Si^{4+}, Ca^{2+}, Fe^{3+}, Ti^{4+}, U^{6+}, REEs, Th^{4+}, etc. These interfering ions have individually been introduced into the synthetic aqueous Ni (II) solution in a suitable dilution to study the effect of their interferences on Ni (II) extraction.

Extraction procedure

A suitable aliquot of the synthetic Ni (II) ions solution assaying 20 mg/l was equilibrated with an equal volume of extractant/benzene for 10 min. in a separating funnel. Dilute H_2SO_4 or NaOH was used to adjust the pH of the aqueous solution to the desired value. After phase disengagement, the metal - loaded organic phase was separated and stripped with 0.5M HCl in an A/O ratio of 1/1 for a period of 5 min. contact time. The resulted aqueous phase was then spectrophotometerically analyzed for its nickel content. All experiments were carried out in duplicate. The standard deviation observed was less than 2%. The distribution ratio (D) was calculated as the concentration of the metal present in the organic phase to that in the aqueous phase at equilibrium. Several experiments have actually been carried out to obtain the optimum conditions for extraction of Ni (II) ions from the prepared synthetic solution; namely pH, extractant concentration, aqueous/organic phase ratio (A/O), temperature together with the proper stripping reagent and its concentration from the loaded organic solvent. The obtained optimum conditions have then been applied upon the prepared leach liquor of El Sela ore.

Analytical procedures

Analysis of El sela ore and its leach liquor

The major oxides SiO_2, Al_2O_3, TiO_2 and P_2O_5 have been analyzed using double beam UV-VIS recording Shimadzu UV160A spectrophotometer according to standard methods of analysis while the oxides of Na and K were determined by the flame photometric technique. The Fe_2O_3, MgO and CaO were however chemically determined by titration[18] whereas the concentration of the other elements have been determined through atomic absorption and X-ray fluorescence techniques using proper standards.

Control analysis

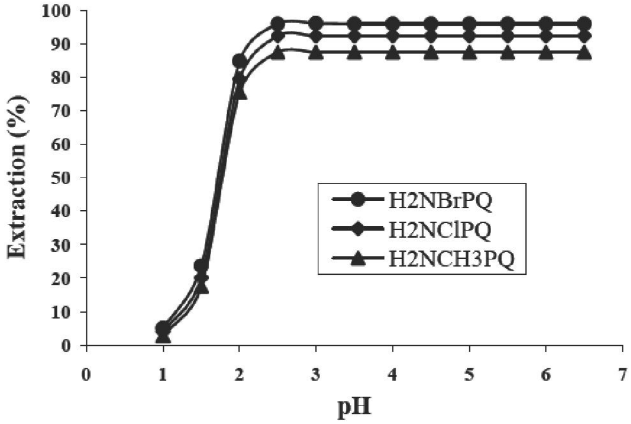
The analysis of nickel (II) in the several aqueous stream solutions has been performed with the double beam UV-VIS recording Shimadzu UV160A spectrophotometer using dimethyl glyoxime (Sigma-Aldrich). Also, the concentration of uranium and the studied interfering ions have spectrophotometrically been determined using proper standards[19].

RESULTS AND DISCUSSION

Optimization of the extraction conditions

Influence of pH

Extraction of 20 mg/l nickel (II) from the standard sulfate solution was studied using 2.42×10^{-3} M extractants concentration in benzene. The effect of pH was carried out by varying the pH values of the working synthetic aqueous solution from 1.0 to 7.0 using 10 min. shaking time, and (1/1) using A/O phase ratio at ambient room temperature. It was thus found that the extraction efficiencies of Ni (II) increased to their maximums values at pH 2.5 (Figure1). The reduced nickel (II) extraction at lower pH values could be attributed to formation of very stable sulfate complexes and other unextractable species of Ni (II) at these pH values.

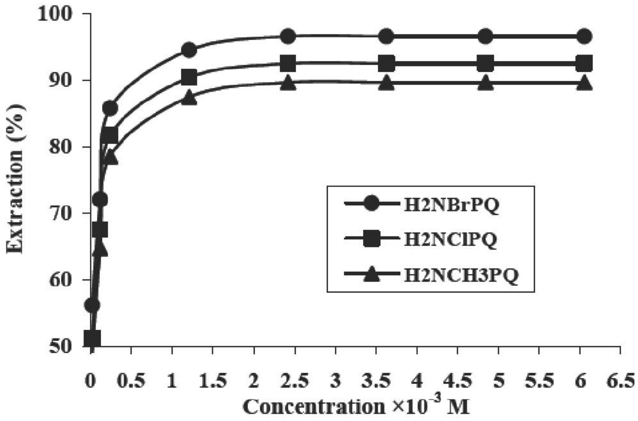


(A/O ratio 1/1, 10 min. of contact time, room temperature)

Figure 1: Effect of pH on nickel (II) extraction efficiency by the prepared exteractants

Influence of extractant concentration

The effect of the concentration of H_2NXPQ/benzene on the extraction efficiency of Ni (II) ions was studied in the range from 0.0241×10^{-3} to 6.05×10^{-3} M. In these experiments, the extraction conditions were fixed at pH 2.5 for 10 min. shaking time and using (1/1) A/O phase ratio at room temperature. The obtained results revealed that maximum extraction efficiencies of Ni (II) ions were achieved at the previously applied 2.42×10^{-3} M concentration of the three extractants (Figure 2). Further increase in the extractants concentration from 2.42×10^{-3} up to 6.05×10^{-3} M had not added any perceptible effect on the extraction efficiency of Ni (II).

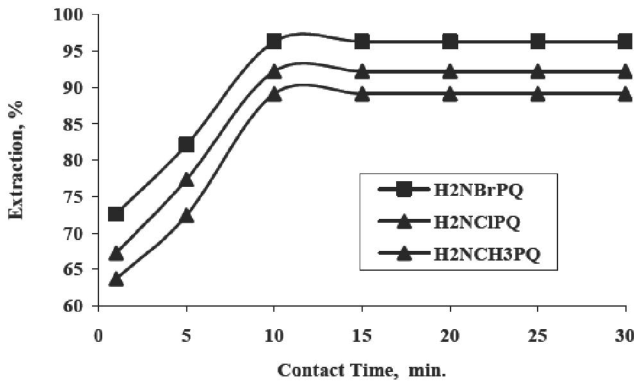


(pH 2.5, A/O ratio 1/1, 10 min. contact time, room temperature)

Figure 2 : Effect of extractant concentration on nickel (II) extraction efficincy

Influence of contact time

The results of the contact time is plotted in Figure 3 and which indicate that the extraction efficiencies of Ni (II) ions gradually increase by increasing the contact time till reaching their maximum efficiencies at 10 min. Therefore, the optimum contact time has been established to be 10 min. for attaining the maximum extraction efficiencies of Ni (II) at the applied experimental conditions.



(pH 2.5, 2.42×10^{-3} M extractants concentration, A/O ratio 1/1, room temperature)

Figure 3 : Influence of the contact time on Ni (II) extraction efficiency

Influence of temperature

The extraction efficiency of Ni (II) ions with 2.42×10^{-3} M concentration of H_2NXPQ/benzene at pH 2.5 and (1/1) A/O ratio for 10 min. contact time was studied in the temperature range of 303 to 333°K. The obtained experimental data showed that the extraction efficiencies were slightly decreased in the temperature range from 303 to 333°K (TABLE 1) and that the better extraction yield was achieved at room temperature. Consequently, all the experiments were carried out at room temperature (303 °K).

TABLE 1 : Influence of temperature on Ni (II) extraction efficiency

T (°K)	H_2NBrPQ	H_2NClPQ	H_2NCH_3PQ
303	96.5	92.63	89.71
313	95.7	92.02	89.11
323	95.1	91.43	88.43
333	94.7	90.8	88.1

Results are mean of triplicate value

Effect of the interfering ions

The possible interference of the associated major and trace elements could lead to adverse effects on the nickel (II) extraction efficiency if they form some com-

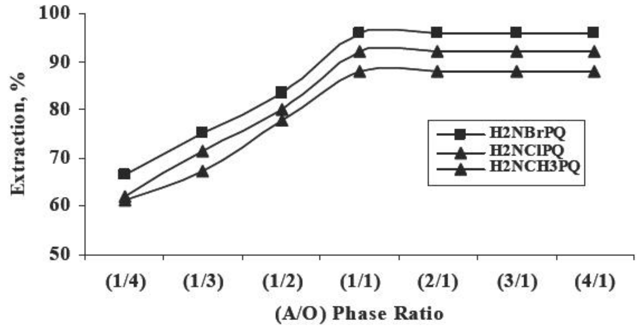
TABLE 2 : Effect of interfering ions on nickel (II) extraction efficiency using H_2NBrPQ/benzene

Interfering Ions	Tolerance limit, w/w*	Extraction efficiency, %	Interfering Ions	Tolerance limit, w/w*	Extraction efficiency, %
Si^{4+}	1000	99.0	Mn^{2+}	50	99.0
Ca^{2+}	500	99.0	REEs	40	98.0
Mg^{2+}	500	98.0	Ba^{2+}	100	99.0
Na^{+}	1000	98.0	Cr^{3+}	35	99.0
K^{+}	1000	98.0	Co^{2+}	5	99.0
Al^{3+}	500	98.0	V^{5+}	10	99.0
Fe^{3+}	200	98.0	Th^{4+}	10	98.0
Ti^{4+}	400	98.0	Mo^{6+}	10	98.0
U^{6+}	300	97.0	-	-	-

*** Weight ratio of the interfering ion to that of nickel (II)**

plexes that would compete with the working ligands. Thus, the effects of the studied interfering ions on the extraction efficiency of Ni (II) using H_2NBrPQ/benzene were studied at fixed pH 2.5, (1/1) A/O ratio and 10 min. contact time at room temperature.

From the obtained results shown TABLE 2 in reference to the tolerance limits, it was found that the ions such as Si^{4+}, Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, Al^{3+} and U^{6+} can actually be tolerated to a greater extent while ions such as Fe^{3+}, Mn^{2+}, REEs, Ba^{2+}, Cr^{3+}, V^{5+}, Th^{4+} and Mo^{6+} do actually interfere with Ni (II) extraction. However, some of the latter could be masked to avoid their interference. Thus after carrying out several experiments, the interferences due to vanadium (V) and thorium (IV) have been masked with fluoride ions, while manganese (II), REEs (III), Fe (III) and barium (II) were masked with oxalate ions.



(pH 2.5, 10 min. contact time, room temperature)

Figure 4 : Effect of the phase ratio (A/O) on nickel (II) extraction efficiency

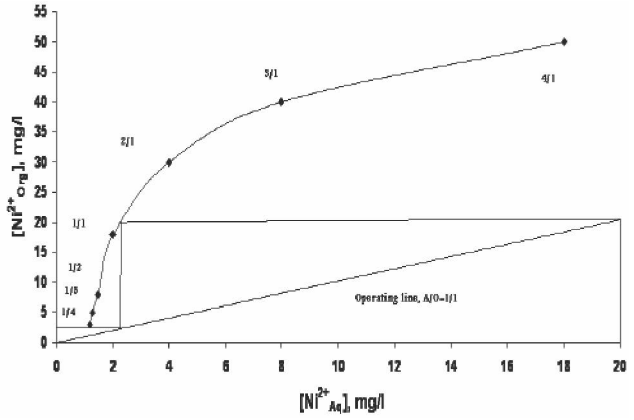
Calculation of the theoretical stages of extraction

The effect of the aqueous to organic phase ratio (A/O) was investigated in the range from 4/1 to 1/4 keeping constant the other factors (pH 2.5, 10 min. contact time, room temperature). The obtained results shown in Figure 4 indicated that the maximum extraction efficiency was achieved at an A/O ratio of 1:1 and remained constant thereafter.

For extraction of nickel (II) from sulfate solution, it is required to determine the number of stages at an equal A/O ratio for which the McCabe–Thiele plot was constructed with the feed solution at pH of 2.5, 2.42×10^{-3} M H_2NBrPQ/benzene and 10 min. contact time at room temperature within the A/O ratios 1/4 to 4/1 while keeping the total volume of phases constant. Figure 5 illustrates quantitative nickel (II) extraction in two counter-current stages extraction at A/O ratio of 1/1 for which a two stages counter-current simulation study at A/O of 1/1 was carried out for extraction of nickel (II) and the raffinate analysis (0.8 mg/l nickel) shown 96 % nickel extraction.

Practical loading capacity of the extractants

The loading capacities of the three studied extractants were determined by repeatedly contacting 10 ml of the organic phase for six times with the same volume of the synthetic nickel (II) aqueous phase assaying 100 mg/l at room temperature for 10 min. contact time and at a pH value of 2.5. After equilibrium and phase separation of each contact, the aqueous phase was analyzed for nickel (II) and its cumulative concentration in the organic phase was calculated by difference (TABLE 3).



(pH 2.5, 10 min. contact time, room temperature)

Figure 5 : McCabe–Thiele plot for extraction of Ni (II) ions using H_2NBrPQ extractant

The obtained results demonstrate that transfer of Ni (II) ions from the aqueous phase to the organic phase has continued during each contact and complete load-

TABLE 3 : Cumulative Ni (II) amount in 10ml organic phase (extractants) vs. its amount left 10 ml of its successive aqueous phases

Contact No.	H_2NBrPQ		H_2NClPQ		H_2NCH_3PQ	
	Organic	Aqueous	Organic	Aqueous	Organic	Aqueous
1	0.92	0.08	0.83	0.17	0.75	0.25
2	1.81	0.11	1.62	0.21	1.47	0.28
3	2.61	0.2	2.32	0.30	2.11	0.36
4	3.10	0.51	2.90	0.42	2.57	0.54
5	3.10	1.00	2.90	1.00	2.57	1.00
6	3.10	1.00	2.90	1.00	2.57	1.00

(pH 2.5, 10 min. contact time, A/O ratio 1/1, room temperature) ing of the solvent was attained after the 4th contact. Accordingly, a maximum concentration (saturation capacity) of 3.10, 2.90 and 2.57 mg/10 ml of Ni (II) ions has been obtained after 4th contacts in the working extractants; namely 2.42×10^{-3} M concentration of H_2NBrPQ, H_2NClPQ and H_2NCH_3PQ in benzene respectively.

According to the prepared concentration of the extractions, the amount of the H_2NBrPQ extractant in 10 ml of its solution in benzene attains 10 mg. Referring to the results shown in TABLE 3, it is clear that this extractant would be practically saturated with 3.10 mg Ni (II). Since the input quantity of Ni (II) in the working 10 ml solution is 0.2 mg, it would theoretically (Figure 6) need 1.4 mg H_2NBrPQ extractant. Therefore, each Ni (II) would replace $2H^+$ ions from 1 mole of extractant. On the other hand, accordingly to the above mentioned practically determined loading capacity (TABLE 3), it is found that the working H_2NBrPQ extractant has been saturated with 3.10 mg Ni (II) by successive mixing with 10 ml of 100 mg/l Ni (II). Therefore, it might be possible that the 1 mole Ni (II) might require 2 mole extractant where 1 H^+ ion would be provided from each molecule.

From previous results, the theoretical capacity of the three extractants can be calculated from Figures 6 and 7 where one mole of Ni (II) would require 2 H^+ ions. The latter would thus be provided from 2 mole of the extractant.

Physical and thermodynamic parameters

Several experiments were applied to determine the corresponding physical and thermodynamic parameters of the studied system. These parameters are important when the laboratory procedures are turned to pilot scales. Thus during the studies of the pH influence, the obtained relation of logD versus pH for the extraction of Ni (II) ions (Figure 6) indicated that the plot has a slope of about 1.75, proving that two moles of H^+ ions were released during complex formation between H_2NXPQ and Ni^{2+}.

On the other hand, the logD versus log [extractant] plot showed that the distribution ratio increased with increasing the extractant concentration in the organic phase (Figure 7) and that the obtained slope value approximately equal 1. It was thus suggested that one mole of the ligand is sharing in the formation of the extracted Ni (II) complex.

Taking all of the experimental data into consideration, the extraction of Ni (II) by H_2NXPQ appears to proceed as follows:

$$Ni^{2+}_{(A)} + (H_2NXPQ)_{(O)} \xrightleftharpoons{K_{ex}} (NiNXPQ)_{(O)} + 2H^{+}_{(A)} \quad (1)$$

$$K_{ex} = \frac{\left[(NiNXPQ)_{(O)}\right]\left[H^{+}_{(A)}\right]^2}{\left[Ni^{2+}{}_{(A)}\right]\left[(H_2NXPQ)_{(O)}\right]} \quad (2)$$

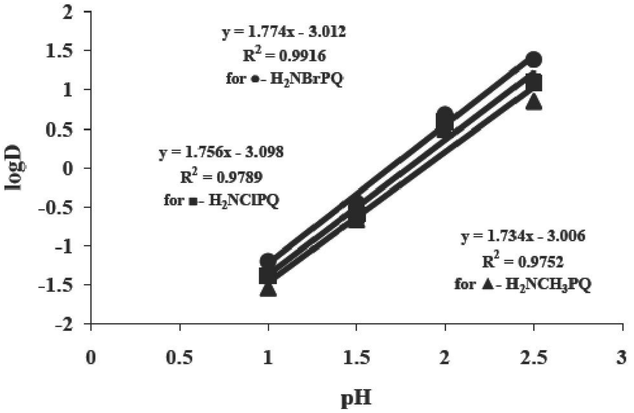


Figure 6 : Plot of log D of nickel (II) extraction with the working extractants vs. equilibrium pH

$$K_{ex} = D + \frac{\left[H^{+}_{(A)}\right]^2}{\left[(H_2NXPQ)_{(O)}\right]} \quad (3)$$

$$\log D = \log K_{ex} + \log\left[(H_2NXPQ)_{(O)}\right] + 2pH \quad (4)$$

where K_{ex} is the extraction constant, D is the distribution ratio of the metal ion, (H_2NXPQ) is the extractant, and all the charged species are assumed to be in the aqueous phase.

From the plot of log D Vs pH (Figure 6), the value of $pH_{1/2}$ (the pH at which 50 % of the metal ion is extracted) was found to be 1.70, 1.76 and 1.73 for H_2NBrPQ, H_2NClPQ and H_2NCH_3PQ respectively, from the following equation:

$$\log D = 1.774pH - 3.012 \text{ for } (H_2NBrPQ) \quad (5)$$

$$\log D = 1.756pH - 3.098 \text{ for } (H_2NClPQ) \quad (6)$$

$$\log D = 1.734pH - 3.006 \text{ for } (H_2NCH_3PQ) \qquad (7)$$

The K_{ex} values for the nickel (II) ions could be measured from equation (4) where the obtained results have shown that the highest value of the extraction constants are attained at 303 °K; a matter which indicates that the best extraction is obtained at room temperature (TABLE 4).

On the other hand, the interesting thermodynamic parameters (enthalpy (ΔH), Gibbs free energy (ΔG) and entropy (ΔS)) associated with the extraction of the nickel (II) ions by H_2NXPQ/benzene system could be calculated from the Vant hoff's equation[20] (R is the universal gas constant (8.314 $J.mol^{-1}. K^{-1}$) and T is the absolute temperature (°K)):

$$\Delta H = -2.303\left(\frac{\Delta \log K_{ex}}{\Delta(1/T)}\right) \qquad (8)$$

$$\Delta G = -2.303RT \log K_{ex} \qquad (9)$$

$$\Delta G = \Delta H - T\Delta S \qquad (10)$$

$$-2.303RT \log K_{ex} = \Delta H - T\Delta S \qquad (11)$$

$$\log K_{ex} = \frac{\Delta S}{2.303R} - \frac{\Delta H}{2.303RT} \qquad (12)$$

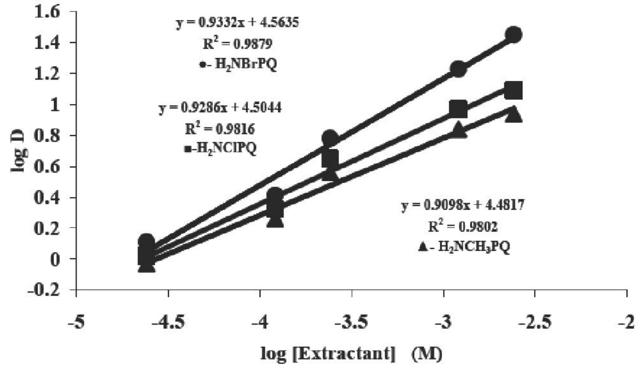


Figure 7 : Plot of log D of Ni (II) extraction vs. log [Extractant]

The values of K_{ex} for a given reaction are first determined at various temperatures followed by plotting of $\log K_{ex}$ versus 1/T (Figure 8) where the corresponding relations are manifested in straight lines having a slope = - ΔH/ (2.303 R) and an intercept = ΔS/(2.303 R).

TABLE 4 : Influence of temperature on the extraction parameters

T (°K)	1/T	H_2NBrPQ			H_2NClPQ			H_2NCH_3PQ		
		Extraction %	K_{ex}	log K_{ex}	Extraction %	K_{ex}	log K_{ex}	Extraction %	K_{ex}	log K_{ex}
303	3.300×10^{-3}	96.5	11.37×10^{-2}	-0.944	92.63	5.188×10^{-2}	-1.285	89.71	3.597×10^{-2}	-1.444
313	3.190×10^{-3}	95.7	$8.433 \text{ X } 10^{-2}$	-1.035	92.02	4.764×10^{-2}	-1.322	89.11	3.380×10^{-2}	-1.471
323	3.096×10^{-3}	95.1	$7.830 \text{ X } 10^{-2}$	-1.106	91.43	4.405×10^{-2}	-1.356	88.43	3.155×10^{-2}	-1.501
333	3.003×10^{-3}	94.7	$6.850 \text{ X } 10^{-2}$	-1.164	90.8	4.073×10^{-2}	-1.390	88.1	3.062×10^{-2}	-1.514

Results are mean of triplicate value

TABLE 5 : The thermodynamic parameters of the studied extraction system

Parameter at $T=303^0$ K	H_2NBrPQ	H_2NClPQ	H_2NCH_3PQ
ΔH (KJ / mol)	-14.23	-6.77	-4.67
ΔG (KJ / mol)	19.717	14.213	13.051
ΔS (J / mol. K)	-65.12	-46.93	-43.09

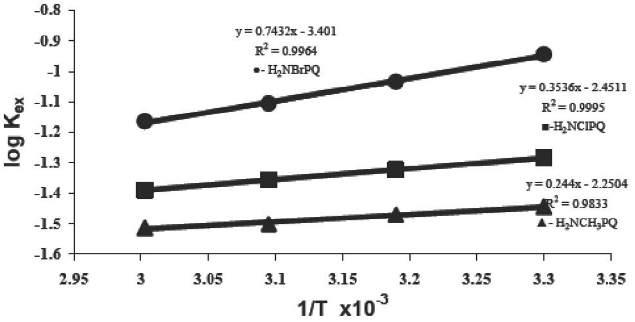


Figure 8 : Plot of $\log K_{ex}$ versus 1/T of the studied extraction systems

From the obtained data, the thermodynamic parameters ΔH, ΔG and ΔS have been calculated (TABLE 5). The negative values of ΔH and ΔS have shown that the chelation process is exothermic, indicating that the complexation reaction favored at ambient room temperatures, ΔG is positive, the process proceeds spontaneously in reverse[21,22].

Results of Ni (II) stripping

Several reagents; namely NaOH, KOH, Na_2CO_3, NaCl, HCl and H_2SO_4 were applied for the stripping of Ni (II) ions from the three working organic phase at an (A/O) ratio of 1/1 for 5 min. contact time. The organic phase was first loaded with Ni (II) ions by contacting it for 10 min with an aqueous phase of Ni (II) ions at pH 2.5.

The obtained results shown in TABLE 6 indicate that, the NaOH and KOH did not show stripping effect from the organic phase while 1 M Na_2CO_3 and NaCl solutions have shown low stripping efficiencies of

18.0 and 23.0% respectively. In contrast, 0.5 M HCl and 1 M H_2SO_4 solutions have shown high stripping efficiencies attaining 99.2 and 90.3%, respectively.

TABLE 6 : Effect of various reagents at different concentrations on the stripping efficiency of Ni (II) ions from the loaded H_2NXPQ organic phase

Reagent	Reagent concentration, M							
	0.1	0. 3	0.5	0.7	0.9	1.0	2.0	3.0
	Stripping efficiencies, %							
NaOH	0	0	0	0	0	0	0	0
KOH	0	0	0	0	0	0	0	0
Na_2CO_3	1.7	3.9	8.1	11.8	14.9	18.0	18.1	18.0
NaCl	2.4	7.8	13.9	17.6	20.1	23.0	23.0	23.3
HCl	65.7	85.3	99.2	99.2	99.2	99.3	99.2	99.2
H_2SO_4	40.8	55.8	70.2	79.2	84.3	90.3	91.2	92.1

Application of the optimum extraction condition

The working El Sela sample has first been subjected to a complete chemical analysis to determine its major oxides and the interesting trace elements (TABLE 7). Also, the prepared leach liquor has similarly been subjected to complete chemical analysis for both the major and trace elements (TABLE 8). The latter has then been treated for nickel (II) extraction using the H_2BrPQ extractant and applying the previously determined optimum leaching conditions. The loaded organic was then directed for nickel (II) stripping using 0.5 M HCl and shaking the two phases for 5 min to back extract Ni (II) ions. The determination of nickel concentration whether in the prepared leach liquor or in the aqueous raffinate solutions (after extraction) or else in the stripping solutions was spectrophotometrically determined by dimethyl glyoxime.

TABLE 7 : The chemical analytical data of the major oxides and trace elements of El Sela uraniferous granite

Major Oxides	SiO_2	TiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	P_2O_5	1000°C	Total
Wt %	70.23	0.26	13.25	4.21	1.1	0.6	4.17	3.21	0.22	1.99	99.24

Trace elements (ppm)

Element	Rb	Sr	REEs	Ba	Cu	Zn	Co	V	Cd	Ni	Th	U
Conc. (ppm)	190	123	900	133	40	36	70	20	10	62	18	205

TABLE 8 : Chemical composition of the prepared pregnant solution

Constituent	Si^{4+}	Fe^{3+}	Ti^{4+}	V^{5+}	Th^{4+}	REEs	Al^{3+}	SO_4^{2+}	Na^+	P_2O_5	U^{6+}	Ni^{2+}
Conc. (g/l)	0.78	4.26	0.840	0.006	0.006	0.298	2.9	40.8	0.98	0.345	0.063	0.02

However in order to insure a high degree of selective Ni (II) extraction, it was found beneficial to add 5 mg ammonium fluoride as well as 10 mg of ammonium oxalate as masking agents for the interfering ions during the extraction process from leach liquor.

CONCLUSION

This study presents the data obtained of nickel (II) extraction from acidic solution using 2-amino-3-(4- (X) phenyl azo)-8,9-dihydro-8,8-dimethyl-7H-pyrazolo [1,5-a] quinazolin-6- one (H_2NXPQ) extractants (X = Br, Cl or CH_3). The optimum conditions for extraction of Ni (II) ions from its synthetic solution involved 2.42×10^{-3} M concentration of (H_2NXPQ)/ benzene, a pH of 2.5 and using an A/O ratio of 1/1 in 10 min. contact time at room temperature. The maximum loading capacities showed that, nickel (II) concentration in the organic phase was constant after 4th loading of the acidic solution.

The thermodynamic parameters ΔG, ΔH, ΔS and the extraction constants were calculated. It was found that the extraction reaction could spontaneously be reversed since ΔG has a positive sign while ΔH and ΔS have been shown to have a negative sign indicating that the chelating process is exothermic, i.e. the complex reaction favors an ambient room temperature.

In an application procedure, the determined optimum conditions were used to recover Ni (II) from El Sela leach liquor and it was found necessary to add ammonium fluoride and ammonium oxalate as masking agents to avoid co-extraction of the present interfering ions during the extraction process. The loaded solvent (H_2NXPQ) was then stripped using 0.5 M HCl as a suitable stripping agent for Ni (II) ions.

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