



Optimizing Liquid-Liquid Extraction of Nickel (II) Ions with Azo Derivatives: Analytical Applications and Insights

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Author's contribution

The sole author designed, analysed, interpreted and prepared the manuscript.

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ABSTRACT

A liquid-liquid extraction study was conducted to investigate the extraction of nickel (II) ions using the chelating agent 2-[(2,6-dimethylphenyl)azo]-4,5-diphenylimidazole (2,6-DMPADPI). The study explored various factors influencing the extraction percentage and extraction coefficient, including equilibrium time, metal concentration, acidic medium, types of solvents, batch extraction methods, leaching processes, and the effects of positive and negative ions. The optimal conditions for extraction were determined to be an acidity index of 9, an extraction time of 10 minutes, and a temperature of 298 K. Thermodynamic functions (ΔG , ΔH , ΔS) were calculated, demonstrating that the extraction reaction is exothermic, spontaneous, and accompanied by an increase in randomness. Additionally, UV-Visible and infrared spectroscopy (FT-IR) studies were performed on the chelating agent to characterize its properties. The study also examined some physical properties of the resulting complex and assessed its specific conductivity. These findings contribute valuable insights into the efficient extraction of nickel (II) ions using 2,6-DMPADPI.

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1. INTRODUCTION

Organic reagents, characterized by high molecular weights, typically exhibit limited solubility in water due to their possession of multiple coordinating bonds [1]. This characteristic has contributed to their widespread utilization across various domains, including medicine, technology, and sciences, as evidenced by their significant contributions. Noteworthy among their advantages is their heightened sensitivity and vibrant coloration of their complexes upon coordination with elements from the periodic table. The solubility of these complexes in organic solvents has been exploited in analytical chemistry for extraction processes [2-4]. Azo compounds, particularly prevalent among organic reagents, are widely recognized as azo dyes [5]. Comprising molecular structures containing functional groups or effective atoms, these compounds possess electron doublets that facilitate their binding with metal ions through coordinate bonds to form coordination complexes. Azo dye compounds constitute approximately 60-70% of all dye types, with their discovery credited to the scientist Peter Griess in 1858. Their nomenclature stems from the presence of the azo group (N=N) featuring sp^2 hybridization, associated with the aromatic system [6]. Azo compounds are distinguished as spectral reagents, characterized by their high stability, rapid reaction with metal ions, sensitivity, and exceptional selectivity [7]. Aromatic azo derivatives, especially in the form of Azo benzene, are more prevalent and widely employed than aliphatic azo derivatives due to their stability and high resonance. The reagent (2,6-DMPADPI) is considered a non-homogeneous azo compound, containing an imidazole ring with disparate nitrogen atoms [8]. Categorized as a single azo compound, it exhibits a characteristic walnut colour, a melting point of 168-170°C, a molecular weight of 352 g/mol, and is insoluble in water. However, it dissolves in various common solvents such as chloroform, carbon tetrachloride, and several alcohols. Solvent extraction, a method within non-direct separation techniques, involves the addition of an assisting phase by the chemical analyst without resulting in chemical reactions [9]. This economically significant method proves highly efficient in purifying metals, separating elements like iron, chromium, nickel, cobalt, and others, and purifying them from impurities, including radioactive substances.

Solvent extraction, broadly encompassing solid-liquid and liquid-liquid extraction processes, pertains to the extensive concept of selective dissolution [10,11]. In solid-liquid extraction, selective solvents dissolve specific components of solid models without affecting others, a phenomenon commonly termed selective dissolution [12]. In liquid-liquid extraction, the distribution and transfer of the solute between immiscible liquid phases dictate the process [13,14].

Nickel, denoted by the chemical symbol Ni and possessing atomic number 28 in the periodic table of elements, manifests as a silver-white metal with a subtle golden appearance, displaying magnetic properties at room temperature. Despite being utilized since 3500 BCE, nickel was initially isolated by the Swedish scientist Axel Fredrik Ronstadt, who erroneously identified it as copper ore.

2. EXPERIMENTAL

2.1 Chemicals

All chemicals were of high purity and used as received without any further purification. Hydrochloric acid (HCl) and nickel nitrate hexahydrate ($Ni(NO_3)_2 \cdot 6H_2O$) were supplied by B.D.H. Sodium hydroxide (NaOH), Chloroform (CCl_4) Ammonium thiocyanate (NH_4SCN), 2,6-dimethyl aniline ($C_8H_{11}N$), Diphenyl imidazole ($C_{15}H_{12}N_2$) was supplied by Sigma-Aldrich. All solutions were prepared by obtaining double distilled water (DDW).

2.2 Characterization and Instrumentation

Various methodologies have been employed for the examination of the physical and chemical attributes of chelating agents. In the investigation of these properties, KBr pellet technology was utilized to acquire Fourier transform infrared spectra, which were subsequently recorded using a Nicolet 6700 FTIR spectrophotometer within the spectral range of 4000-500 cm^{-1} . Furthermore, the ultraviolet and visible absorption spectra of the dye solutions were documented employing a Shimadzu UV-Vis 160v spectrophotometer, spanning the wavelength range from 200 to 800 nm. The implementation of these characterization techniques has facilitated a comprehensive analysis of the chelating agent properties.

2.3 Preparation of the the reagent (2,6-DMPADPI)

In Fig. 1 show Preparing the reagent the organic reagent 2-[(2,6-dimethylphenyl)azo]-4,5-diphenylimidazole (2,6-DMPADPI) was synthesized through a two-phase process, by dissolving (1.21 g), (0.01 mol) of 2,6-Dimethylaniline in a solution containing (3 ml) of concentrated hydrochloric acid and 15 ml of distilled water. This melting occurred inside an ice bath containing (50 g) of crushed ice. After that, a solution consisting of (0.7 g) of sodium nitrate dissolved in (10 ml) of distilled water was gradually added to the mixture while ensuring continuous stirring, with careful attention to maintaining the temperature below (5°C) Celsius. The resulting solution underwent a (30 min) quenching period to terminate the nitrification process.

In the subsequent step, the diazonium salt, formed in the initial stage, was added dropwise with constant stirring to a solution containing (2.2 g) (0.01 mol) of the imidazole derivative dissolved in a solvent mixture consisting of (150 ml) ethanol and (50 ml). 10% sodium hydroxide. The solution showed a clear brown colour and was left undisturbed overnight. Next, for the purpose of obtaining the reagent in its crystalline state, hydrochloric acid (0.1 M) was added precisely dropwise to adjust the acid function, with the aim of obtaining a pH of 6. The resulting

precipitate was allowed to settle, subjected to filtration, and washed with distilled water to remove the by-product. For sodium chloride resulting from the neutralization process. The resulting brown precipitate underwent a drying process, followed by two successive recrystallizations from a mixture of ethanol and water (1:1), and subsequent air drying. Determination of the melting point resulted in a range of 168-170°C. The payout ratio was calculated, resulting in a total return of 78%.

2.4 Nickel (II) Ion Extraction

The extraction procedure was conducted by liquating (5 mL) of a nickel solution with a concentration of (300 µg/5 mL) equivalent to (10.223×10^{-4} M) from ions into a container. The acidity of the solution was adjusted to a pH of 8 and transferred to a separating funnel with a capacity of (60 mL). Subsequently, (5 mL) of the organic layer, comprising a (0.2%) solution of the reagent (2,6-DMPADPI) dissolved in chloroform, was introduced as the organic phase. The resulting mixture was vigorously shaken for a duration of (15 min), followed by allowing a specific period for the separation of the organic phase (containing the formed complex) from the aqueous phase. The aqueous phase, which retains residual nickel, was isolated for subsequent determination of the nickel (II) ion content.

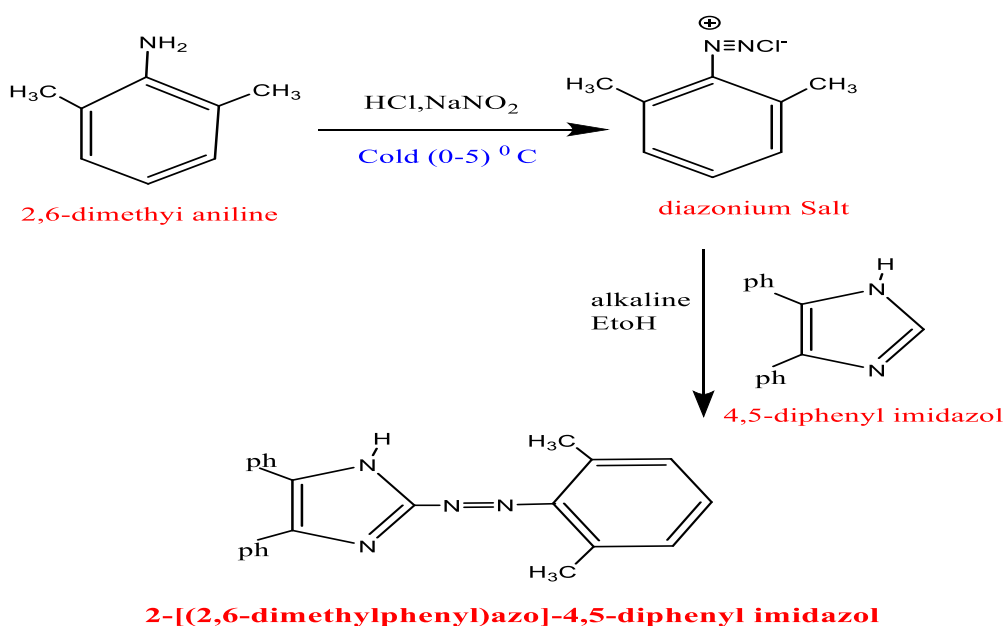


Fig. 1. Preparing the reagent (2,6-DMPADPI)

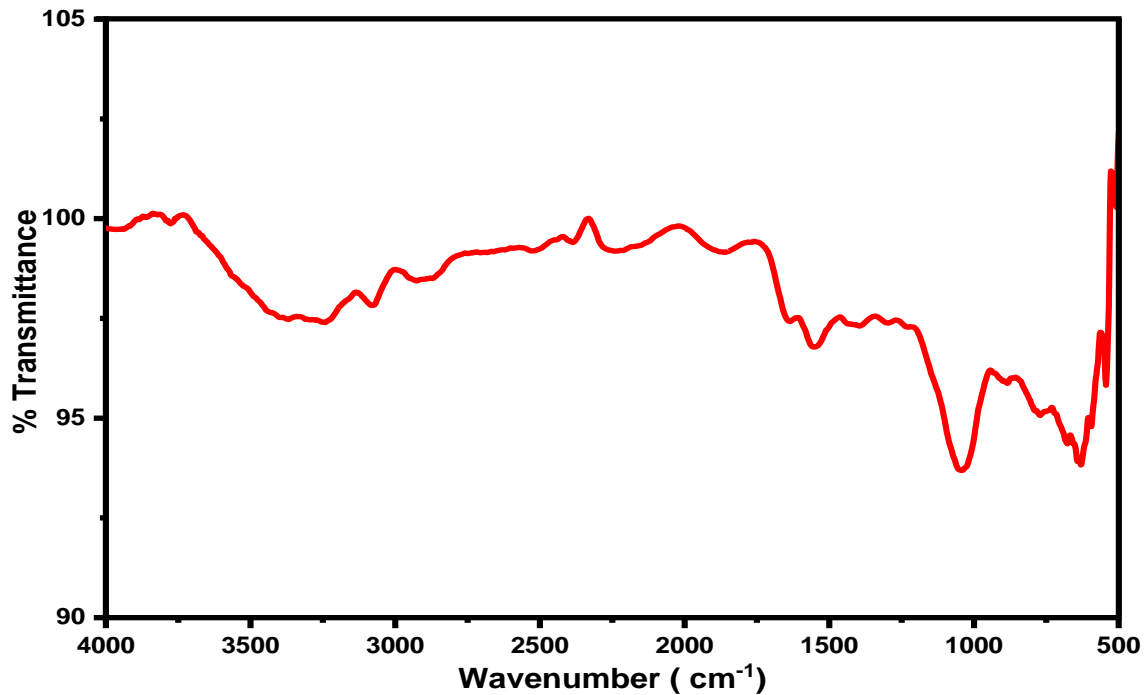


Fig. 2. Infrared spectrum of the reagent

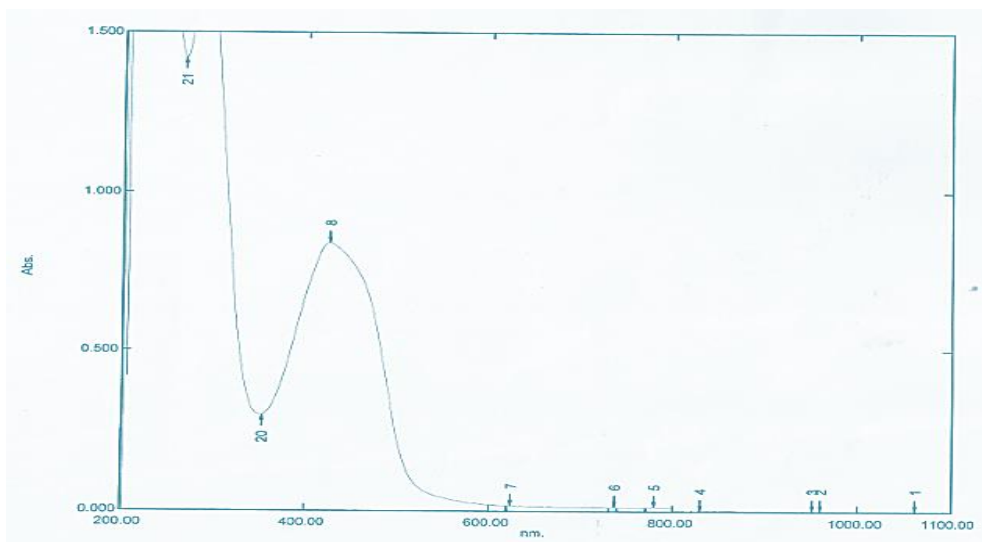


Fig. 3. UV-Vis spectrum of (0.2%) of the reagent solution (2,6-DMPADPI) dissolved in chloroform

2.5 Determination of Nickel in the Aqueous Phase

The nickel (II) ion remaining in the aqueous phase after the extraction procedure was determined based on the colorimetric method [15]. The absorption was measured, and from the absorption reading, the concentration of the remaining nickel element can be known after

referring to the calibration curve. It is found through test experiments based on the principle of extraction. (Abstraction) The concentration of nickel transferred to the organic phase is equal to the calculated difference between the total (initial) concentration and the estimated nickel concentration in the aqueous phase after the extraction process. The difference between the two concentrations method was adopted in most

experiments in calculating the distribution value for ease of dealing with the aqueous phase.

3. RESULTS AND DISCUSSION

3.1 Characterization of (2,6-DMPADPI)

3.1.1 Functional groups identification

Fig. 2 depicts the Fourier Transform Infrared (FT-IR) spectrum of the ligand, wherein the spectral analysis reveals distinctive bands. The peak at 3267.52 cm^{-1} is attributed to the stretching vibration of hydroxyl groups (OH), while the band at 1649.19 cm^{-1} corresponds to the imine functional group (C=N). Furthermore, the bands located at 1599.04 cm^{-1} , 1568.18 cm^{-1} , and 1467.88 cm^{-1} are indicative of the stretching vibrations associated with aromatic carbon-carbon bonds (C=C). Additionally, the band observed at 1506.46 cm^{-1} is associated with the azo functional group (N=N), and the band at 3063.06 cm^{-1} signifies the stretching vibration of aromatic carbon-hydrogen bonds (C-H).

3.1.2 Ultraviolet visible spectroscopy

The UV-vis spectrum recorded for (0.2%) of the reagent solution (2,6-DMPADPI) dissolved in chloroform is shown in Fig. 3. It is clear from the absorption spectrum of the reagent that the highest absorption value is at the wavelength ($\lambda_{\text{max}}=424\text{nm}$).

3.2 The Effect of (PH) on Extraction

It is known that the PH has an important role in the process of extracting metal ions [16], and to know the effect of this factor on the study of nickel (II) ion extraction and thus on the D values by using different solutions of the pH (1-9).

Table 1. Shows the results reached by the study

pH	D	E%
1	0.143	12.51
2	0.242	19.48
3	0.643	39.14
4	0.795	44.29
5	0.978	49.44
6	1.334	57.15
7	2.434	70.88
8	4.455	81.67
9	3.311	69.79

($10.223 \times 10^{-4}\text{M}$) of nickel(II) ion has been extracted, which that equivalent (300 μg) in (5

ml) from solutions that have difference in their pH (1-9 PH) as an aqueous phase with an equivalent volume of (0.2%) reagent solution (2, 6-DMPADPI) dissolved in chloroform as an organic phase Equilibration time: ten minutes Temperature: $^{\circ}\text{C}$ (3 ± 25).

It is clear from Table (1) that the values of (D) and the values of %E increase with the increase of the PH until (pH = 8). When the PH increases more than (8), the nickel (II) ion precipitates. The reason may be because of the formation of a precipitate of nickel hydroxide when the pH is more than (8).

3.3 Effect of Equilibrium time on Extraction

Calculating of the change in the (D) values and the %E values for the extraction of nickel (II) has been followed as a function of the equilibrium time. The results of this study shown in Table (2).

Table 2. Effect of equilibrium time on extraction

Time (min)	D	E%
5	2.872	74.17
10	4.455	81.67
15	4.122	80.48
20	2.633	72.47
25	2.225	69.92
30	2.103	67.77

Aqueous phase: (5ml) of nickel ion solution ($10.223 \times 10^{-4}\text{ M}$) in (300 μg /5ml) Organic phase: (5ml) of a (0.2%) solution of the reagent dissolved in chloroform Temperature: $^{\circ}\text{C}$ (25 ± 3). From the Table 2 the best shaking time to extract the nickel (II) ion with the reagent (2,6-DMPADPI) is (10) minutes, after that we observe a decrease in the values of (D) with the passage of time. Increasing the equilibrium time leads to an increase in contact between the two immiscible phases (Organic and aqueous), which increases the surface area between them. The decrease is due to several reasons, including the breakdown of the extracted complex or the formation of a third phase. This study is consistent with other studies [17].

3.4 Effect of Element Concentration

The Ni^{2+} ion extracted from its aqueous solutions that containing increasing amounts of the ion, ranging from (50 μg -350 μg), equivalent to ($1.703 \times 10^{-4}\text{ M}$ – $11.927 \times 10^{-4}\text{ M}$) with the reagent (2,6-DMPADPI) Under the best conditions that

had been achieved, the results of this study are shown in Table (3).

3.5 The Effect of Organic Solvent Polarity on Extraction

The extraction process for the nickel ion has carried out using different polar solvents to determine the effect of this on the (D) value of the element. It is clear from Table (4) that there is no linear relationship between the values of the distribution ratios and the dielectric constant of the solvents, and this is contrary to what is indicated by the Born relationship represented by equation (1).

Table 3. Shows the effect of Ni²⁺ ion concentration by using the reagent (2,6-DMPADPI)

Conc.	D	%E
0.00017	1.55	60.78
0.00034	2.85	74.02
0.00051	3.22	76.30
0.00068	3.57	78.11
0.00085	4.28	81.06
0.00102	4.45	81.65
0.00119	4.38	81.41

$$\Delta G = \frac{Ze^2}{r} \left[\frac{1}{\epsilon_w} - \frac{1}{\epsilon_o} \right] \quad (1)$$

Where Z is the charge of the ion, r is the radius of the ion, ϵ_w and ϵ_o are the dielectric constants of water and organic solvent, respectively, and ΔG is the free energy of ionic transfer. From this,

Table 4. Effect of organic solvent polarity on extraction concentration (10.233×10⁻⁴ M) which equivalent (300µg/5ml) of nickel (II) ion

Organic solvent	Dielectric constant for the solvent	1/ξ	D	E%
Nitrobenzene	35.70	0.028	1.610	61.68
Amyl alcohol	15.80	0.063	2.121	67.95
Dichloromethane	9.08	0.110	1.395	58.24
Chloroform	5.70	0.175	4.455	81.67
Diethyl ether	4.10	0.243	1.162	53.74
Benzene	2.80	0.375	1.112	52.65
Toluene	2.40	0.413	1.255	55.65
CCl ₄	2.28	0.438	2.896	74.33

Table 5. Effect of temperature on extraction

T(K)	1/T×10 ⁻³	D	Ln D
298	3.355	4.455	1.494
303	3.300	3.146	1.146
308	3.246	2.217	0.796
313	3.194	1.541	0.495
318	3.144	1.302	0.263

we conclude that the extraction system in this study cannot be controlled by the dielectric constant of the solvent. The reason for this is due to the fact, that the extracted complex is a neutral and chelating complex, and this type of complex is affected by several factors, including the solubility of the extracted complex or the Vacuum Composition of the organic solvent, and this is what supports. In turn, the role of the composition of the organic solvent in achieving the best extraction away from the polarity of the organic solvent used, which has a role, but not the main role, in preparing the optimal extraction, as the possibility of the participation of the organic solvent in the extraction process is not excluded. The results of this study are consistent with other studies approved by previous studies on this topic [18].

It is clear from the results shown in Table (4) that the best value for the distribution ratio (D) and the extraction percentage (%E) for extracting the nickel (II) ion with the reagent (2,6-DMPADPI) is when using chloroform as an organic solvent for the reagent.

3.6 Effect of Temperature on Extraction

The value of (D) is calculated when the extraction of the nickel (II) ion by using the reagent (2,6-DMPADPI) at different temperatures (25-45 °C). From the results shown in Table (5), it found that the value of (D) decreases when the temperature increases.

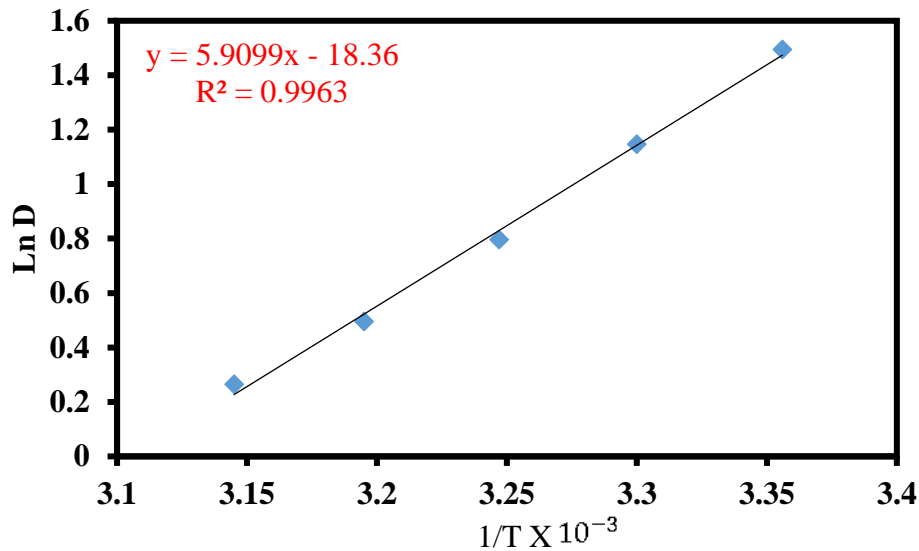


Fig. 4. Effect of temperature on extraction

Table 6. Shows the calculation of the thermodynamic functions for extraction

T(K)	-ΔH (KJ.mol ⁻¹)	-ΔG (KJ. mol ⁻¹)	ΔS (KJ .mol ⁻¹ .K ⁻¹)
298	0.04913	3.70156	0.012256
303		2.88727	0.009367
308		2.03872	0.00646
313		1.28893	0.003961
318		0.69772	0.00204

Aqueous phase: (5 ml) of nickel ion solution (10.223×10⁻⁴)

Organic phase: (5 ml) of a (0.2%) solution of the reagent dissolved in chloroform Balancing time: 10 minutes [19].

$$\ln K (D) = -\frac{\Delta H}{RT} + \text{con} \quad (2)$$

The values of other thermodynamic functions (ΔS, ΔG) had also calculated from the following (Gibbs) equation [20, 21].

$$\Delta G = -RT \ln K (D) \quad (3)$$

$$\Delta G = \Delta H - T \Delta S \quad (4)$$

We note from the Table 6 that the negative sign of the enthalpy values shows that the reaction between the nickel element and the detector is heat-emitting, while the negative sign of the free energy of extraction shows that the reaction is spontaneous [22,23]. A positive sign of entropy means an increase in randomness [24].

3.7 The Effect of Interactions

3.7.1 The effect of positive ions in extraction

The effect of the presence of some positive ions in the extraction process studied by choosing several transitional positive ions within the same cycle and other transition elements that were randomly chosen such as (Cu⁺², Ag⁺¹, Cr⁺³, Pb⁺², Fe⁺³, Cd⁺²). The results of this study are shown in Table (7), as we note that these ions negatively affect the extraction, and this may be due to competition between the positive ions and nickel (II) for coordination with the detector.

Table 7. The effect of positive ions in extraction

Positive ions	D	E%
-----	4.455	81.67
Fe ³⁺	1.680	62.68
Pb ²⁺	2.01	66.81
Cr ⁺³	2.23	69.07
Ag ⁺¹	1.51	60.17
Cu ²⁺	1.43	58.91
Cd ²⁺	2.41	70.71

Aqueous phase: - (5 ml) of a nickel ion solution (10.223×10^{-4} M) (300 μ g) of some positive ions at the pH (8.00)

Organic phase: - (5 ml) of a solution (0.2%) of the dissolved reagent with chloroform.

Equilibration time: (10) minutes Temperature: (25 \pm 3)

3.7.2 The effect of negative ions in extraction

The effect of negative ions also studied, as shown in Table (8) below.

Table 8. The effect of negative ions in extraction

Negative ions	D	%E
----	4.45	81.67
SCN ⁻	2.85	74.02
CN ⁻	7.68	88.48
SO ₄ ⁼	2.12	67.97
Br ⁻	1.32	56.98
IO ₃ ⁻	1.45	59.18
C ₄ H ₄ O ₆ ⁼	3.36	77.10
Cr ₂ O ₇ ⁼	2.25	69.55

3.8 The Effect of Small Batch Technology on Extraction

The extraction process of nickel ion carried out using small batch technology instead of using a single batch of the organic phase and the extraction done in three stages after dividing the volume of the organic phase (5 ml) into three equal volumes, each volume (1.7 ml), and thus calculating the value of the distribution ratios. After completing the last stage, the results, as shown in Table (9), indicate a slight increase in the value of the distribution ratio and the percentage of extraction, which means the possibility of using extraction in one batch to shorten the effort and time.

Table 9. The extraction results of Nickel ion by using the batch method

Extraction type	D	%E
One payment	4.455	81.67
Small batches	4.892	83.02

3.9 The Effect of the Salting Process on Extraction

It is clear from the results shown in Table (10) that the value of D decreased in the presence of

ammonium chloride salt. In general, the salting process aims to reduce the hydration energy of the extracted ion, which leads to the ease of replacing water molecules with reagent molecules.

Table 10. Effect of the salting process on extraction

Extraction type	D	%E
Extraction without salting agent	4.455	81.67
Extraction with salting agent	3.645	78.471

3.10 Determine Several Physical Properties of the Extracted Complex

3.10.1 Determination of the melting point of the complex

The melting point of the reagent and the complex determined, and the results as shown in Table (11).

Table 11. Shows the fusion refinement values for clarification and complex

Matter	Melting point
C ₂₃ H ₂₀ N ₄	168 - 170
Ni(C ₂₃ H ₂₀ N ₄) ₂	200 - 202

3.10.2 Molar-electrical conductivity

The molar conductivity of the solid complex prepared and dissolved in ethanol measured at room temperature and at a concentration of (1×10^{-3} M), where the molar conductivity value of the complex was (6.2 Ohm⁻¹.cm².mol⁻¹). It is clear from this value of conductivity that the solid complex is an uncharged complex due to the low value of molar conductivity [25].

3.11 The Proposed Vacuum form of the Extracted Complex

After determining the possible formula of the extracted complex in the organic phase, its possible vacuum form studied, since the valence ratio of the complex to the ion (Ni²⁺) with the reagent (2-6-MPADPI) was in the ratio (2:1), that is, one mole of the ion with two moles of the reagent. Therefore, the vacuum form of the complex can be visualized as shown in the Fig. 5.

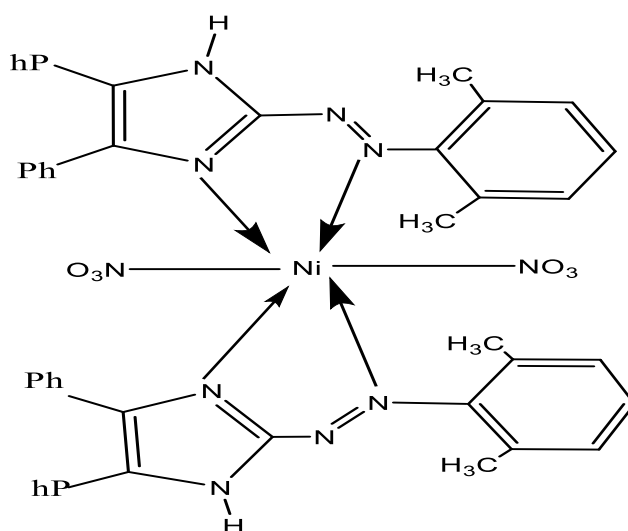


Fig. 5. Shows the vacuum form of the complex

4. CONCLUSION

- 1- The azo reagent (2,6-MPADPI) is characterized by its high efficiency in extracting nickel (II) ions.
- 2- The basic medium is considered the most suitable for extracting the nickel (II) ion using the reagent (2-6-MPADPI).
- 3- The distribution ratio (D) and thus (%E) increases with increasing ion concentration (Ni^{2+}) in the aqueous phase with the reagent (2-6-MPADPI).
- 4- The value of the distribution ratio (D) does not depend on the polarity of the organic solvent, as the relationship is non-linear between $\ln(D)$ and $(1/\xi)$.
- 5- The values of the distribution ratio (D) for ion extraction (Ni^{2+}) decrease in the presence of some negative ions, while they increase in the presence of other negative ions.
- 6- The values of the distribution ratio (D) decrease with increasing temperature, and from the negative values of extraction enthalpy (ΔH_{ext}) for the extraction reaction of the nickel (II) ion with the reagent, the reaction is heat-emitting.
- 7- Through the methods adopted to determine the valence of the extracted complex in the organic phase, the results showed that the valency of the extracted complex (metal: reagent) is (2:1), and from the stability constant of the extracted complex, the complex has high stability.

DISCLAIMER (ARTIFICIAL INTELLIGENCE)

Declaration of generative AI and AI-assisted technologies in the writing process During the preparation of this work the authors used Chat GPT in order to correct the grammar of some sentences. After using this tool, the authors reviewed and edited the content as needed and takes full responsibility for the content of the publication.

COMPETING INTERESTS

Author has declared that no competing interests exist.

REFERENCES

1. Saunders KJ. Organic polymer chemistry: an introduction to the organic chemistry of adhesives, fibres, paints, plastics and rubbers. Springer Science & Business Media; 2012.
2. Dey S, Maity A, Shyamal M, Das D, Maity S, Giri PK, Misra A. An antipyrine based fluorescence "turn-on" dual sensor for Zn $2+$ and Al $3+$ and its selective fluorescence "turn-off" sensing towards 2, 4, 6-trinitrophenol (TNP) in the aggregated state. Photochemical & Photobiological Sciences. 2019;18:2717-2729.
3. Płotka-Wasyłka J, Rutkowska M, Owczarek K, Tobiszewski M, Namieśnik J. Extraction with environmentally friendly solvents. TrAC Trends in Analytical Chemistry. 2017;91:12-25.

4. Mialane P, Mellot-Draznieks C, Gairola P, Duguet M, Benseghir Y, Oms O, Dolbecq AJCSR. Heterogenisation of polyoxometalates and other metal-based complexes in metal-organic frameworks: from synthesis to characterisation and applications in catalysis. *Chemical Society Reviews*. 2021;50(10):6152-6220.
5. Selvaraj V, Karthika TS, Mansiya C, Alagar M. An over review on recently developed techniques, mechanisms and intermediate involved in the advanced azo dye degradation for industrial applications. *Journal of Molecular Structure*. 2021;1224:129195.
6. Mikaberidze A. Historical dictionary of Georgia. Rowman & Littlefield; 2015.
7. Wang X. Azo polymers. Springer Berlin Heidelberg; 2016.
8. Jerca FA, Jerca VV, Hoogenboom R. Advances and opportunities in the exciting world of azobenzenes. *Nature Reviews Chemistry*. 2022;6(1):51-69.
9. Dean JA. Chemical separation methods; 1969.
10. Gamse T. Liquid-liquid extraction and solid-liquid extraction. Institute of Thermal Process and Environmental Engineering, Graz University of Technology. 2002;2-24.
11. Cortina JL, Warshawsky A. Developments in solid-liquid extraction by solvent-impregnated resins. *Ion Exchange and Solvent Extraction*. 2021;195-293.
12. Mary P, Studer V, Tabeling P. Microfluidic droplet-based liquid-liquid extraction. *Analytical Chemistry*. 2008;80(8):2680-2687.
13. Puthran D, Patil D. Usage of heavy metal-free compounds in surface coatings. *Journal of Coatings Technology and Research*. 2023;20(1):87-112.
14. Shahat A, Hassan HM, El-Shahat MF, El Shahawy O, Awual MR. Visual nickel (II) ions treatment in petroleum samples using a mesoporous composite adsorbent. *Chemical Engineering Journal*. 2018;334:957-967.
15. Skoog DA, West DM, Holler FJ, Crouch SR. Fundamentals of analytical chemistry. Cen; 2013.
16. Khazaeli S, Nezamabadi N, Rabani M, Panahi HA. A new functionalized resin and its application in flame atomic absorption spectrophotometric determination of trace amounts of heavy metal ions after solid phase extraction in water samples. *Microchemical Journal*. 2013;106: 147-153.
17. Mishra BB, Devi N. Solvent extraction and separation of europium (III) using a phosphonium ionic liquid and an organophosphorus extractant-A comparative study. *Journal of Molecular Liquids*. 2018;271:389-396.
18. Albo Hay Allah MA, Alshamsi HA. Green synthesis of ZnO NPs using *Pontederia crassipes* leaf extract: Characterization, their adsorption behavior and anti-cancer property. *Biomass Conversion and Biorefinery*. 2022;1-14.
19. Ibrahim HK, Allah MAAH, Muneer A. Adsorption of titan yellow using walnut husks: Thermodynamics, kinetics and isotherm studies. *Annals of the Romanian Society for Cell Biology*. 2021;25(6):12576-12587.
20. Rashwan WE, Shouman MA. Sorption isotherm studies for the removal of brilliant blue dye from aqueous solution by modified egyptian kaolin. *Asian Journal of Applied Sciences*. 2015;3(6).
21. Ibrahim HK, Allah MAAH, Al-Da'amy MA, Kareem ET, Abdulridha AA. Adsorption of basic dye using environmental friendly adsorbent. In *IOP Conference Series: Materials Science and Engineering*. 2020, June;871(1):012027. IOP Publishing.
22. Ibrahim HK, Allah MA, AL-Da'amy MA. Adsorption of anionic dye using Walnut husks: Thermodynamics and kinetics. In *AIP Conference Proceedings*. 2023, July;2830(1). AIP Publishing.
23. Hashem HF, Arif IE, Hussein AF. Spectrophotometric determination of Chromium (III) with (Chromazurol S). *Research Journal of Pharmacy and Technology*. 2019;12(10):4607-4612.
24. Ibrahim HK, Abdulridha AA, Allah MAAH. Glutaraldehyde and terephthaldehyde-crosslinked chitosan for cationic and anionic dyes removal from aqueous solutions: Experimental, DFT, kinetic and thermodynamic studies. *International Journal of Biological Macromolecules*. 2024;262:129730.
25. Youhong H, Yulan Z, Shaozu W. Synthesis and characterization of Cu (II), Ni (E), Cd

(II) and Zn (II) with salicylaldehyde-1H-benzotriazol-1-acylhydrazone and 2-hydroxy-naphthylaldehyde-1H-

benzotriazol-1-acylhydrazone. Synthesis and Reactivity in Inorganic and Metal-Organic Chemistry. 1995;25(3):451-461.

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