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ORIGINAL ARTICLE

Green and simple approach for flotation, preconcentration and enhanced spectrophotometric assessment of Ni(II) in aqueous solution by complexation with 1-(3,5-dihydroxybenzylidene) thiosemicarbazone

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Abstract In the current work, 1-(3,5-dihydroxybenzylidene)thiosemicarbazone (H_3L) was produced under mechanochemical ball milling conditions using *para*-toluenesulfonic acid (p-TSA) as a catalyst in a solvent-free reaction. The generated material was characterized using a number of physical and spectroscopic methods. The synthetic material was also tested as an effective organic chelating agent in the flotation, preconcentration, and spectrophotometric measurement of Ni(II) in aqueous solutions, where H_3L reacted with Ni(II) to produce a coffee colored complex. Oleic acid (HOL) was used as a foaming agent to help the complex that was generated float to the scum layer. The concentration of Ni(II) was assessed using a spectrophotometer at 370 nm. The several factors that impact the flotation-separation process were evaluated and adjusted, including pH, the concentration of (Ni(II), H_3L, and HOL), surfactant type, sample volume, temperature, shaking duration, and ionic strength. Nearly 100% of Ni(II)-H_3L were successfully separated at 25 °C and pH 5 after 5 min of shaking. Utilizing the molar ratio approach, the stoichiometric ratio of the produced complex was determined to be (1:2) of M:L. The formation constant (K_f) was determined as 2.25×10^4. The analytical characteristics of the procedure (limit of detection, limit of quantification, and range of linearity) were evaluated and found to be (0.22 ng/mL, 0.74 ng/mL, and 5–400 ng/mL), respectively. The suggested method was employed to separate Ni(II) that had been spiked into some real

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water samples. Ni(II) was successfully preconcentrated from different aqueous volumes with a preconcentration factor of 200. Finally, the mechanism for the flotation-separation process was suggested.

1. Introduction

Metal-containing effluent is released into the environment either directly or indirectly as a consequence of heavy industries like mining, mineral processing, metal smelting, and casting processing. The majority of metals are not biodegradable, in contrast to organic pollutants, and can build up in the body due to their resilience and endurance. Numerous metal ions have been shown to be poisonous or even cancer-causing (Fu and Wang 2011; Genç-Fuhrman et al. 2016; Karnib et al. 2014). Copper, lead, zinc, nickel, mercury, cadmium, and chromium are toxic or hazardous elements that should be of particular worry when it comes to industrial wastewaters (Carolin et al. 2017; Imyim et al. 2016). Nickel, a dangerous and poisonous metal, is one of these metals and may be found in polluted natural water. Nickel is currently utilized in the production of nickel steel, non-ferrous metals, super-alloys, alnico magnets, coins, microphone capsules, rechargeable batteries, plating on pipe fixtures, etc. When ingested through vapors, nickel can cause lung cancer, bronchitis, asthma, and other respiratory system diseases. Nickel is a hazardous metal that may cause skin dermatitis when subjected to it (Cempel and Nikel 2006; Das et al. 2008; Trombetta et al. 2005). The highest concentration of nickel allowed in water by the World Health Organization (WHO) is 70 g/L (Matsumoto et al. 2005; Organization 2008). It has been demonstrated that even low amounts of nickel discharge cause irreversible damage to aquatic ecosystems; therefore, it is critical to reduce their negative effects prior to release into water sources. Furthermore, from an environmental standpoint, it is critical for the public health to identify the existence of nickel at trace amounts in water and other environmental supplies. Inductively coupled plasma optical emission spectrometry (ICP-OES) (Silva et al. 2009), graphite furnace atomic absorption spectrometry (GFAAS) (Bidabadi et al. 2009; Jiang et al. 2008; Matsumiya et al. 2004), flame atomic absorption spectrometry (FAAS) (Ghaedi et al. 2010; Karimi et al. 2008; Lemos et al. 2008; Manzoori and Bavili-Tabrizi 2003; Xie et al. 2008), electrothermal atomic absorption spectrometry (ETAAS) (Gil et al. 2008; Zendelovska et al. 2001), inductively coupled plasma mass spectrometry (ICP-MS) (Hu et al. 2006), and other atomic and molecular methods have been used for the determination of the trace level of metals (Ojeda and Rojas 2009). However, the majority of these processes are time-consuming and costly, and they all need specialized equipment, which limits their applicability. The spectrophotometric method is the most widely used among them due to its superior precision and sensitivity as well as its ease of use, affordability, and operation. Due to increased knowledge of ambient nickel pollution, the measurement of nickel(II) in water samples requires a distinct, more targeted, accurate, and efficient analytical method. Trace metals in water samples can be difficult to detect in a variety of circumstances. This is as a result of the low amounts of these metals and their extremely complex material matrices (Rezende et al. 2011). Therefore, separation and preconcentration methods are required to overcome the matrix effects and concomitants. For the separation and preconcentration of metals from real or simulated wastewater, numerous methods have been explored (Ahmad et al. 2009; Al-Qodah and Al-Shannag 2017; Fu and Wang 2011; Han et al. 2006; Hoseinian et al. 2015; Rubio et al. 2002). The literature clarified that one of the most popular methods for removing heavy metals from effluent is chemical deposition (El-Hendawy 2009; Esalah et al. 2000; Gutiérrez-Segura et al. 2012; Luo et al. 1992; Mansour et al. 2011). This method has a number of drawbacks, including slow solid–liquid separation, low particles density, poor settling, and issues with disposing of sediment, which frequently contains a lot of water (Kurniawan et al. 2006). Precipitate flotation, a technique that combines flotation and precipitation, is suggested due to difficulties in removing the metal precipitate from the suspension and to simplify the separation process. Due to its simplicity, speed, high separation yields ($R > 95\%$) for low concentrations (10^{-6}-10^{-2} mol/L), suitability for compounds with different physicochemical properties, flexibility of the equipment, and adaptability for recovery purposes, flotation technique is regarded as a good separation-preconcentration method (Ghazy et al. 2003; Shakir et al. 2007; Stoica et al. 1998). Precipitate flotation techniques come in two different kinds (Techniques and Lemlich 1972). Precipitate flotation of the first type (PFFT), which is the first kind, involves initially precipitating the desired ionic species by adding a non-surface active agent, followed by their elimination by adding a surface-active agent and gas bubbles. Precipitate flotation of the second type (PFST), which is the second kind, allows for the floatation of hydrophobic precipitates produced by the precipitation of ionic species without the use of a skimmer by merely introducing gas bubbles to the suspension (Grieves 1975). Based on all of the above, the current study aimed to the flotation, preconcentration and enhanced spectrophotometric assessment of Ni (II) in aqueous solution by complexation with a newly synthesized chelating agent. Due to their importance as sensitive chromogenic reagents and interesting complex-forming agents, many organic compounds have attracted a lot of attention lately. Thiosemicarbazone derivatives are regarded as significant thio-ligands with a high capacity to coordinate with a variety of metal ions and serve as an outstanding example of these organic compounds (Matesanz et al. 2018). The thiosemicarbazone motif converts into a potent electron-pair donor and may readily coordinate with a variety of metal ions when coupled to phenolic compounds, in addition to serving as tridentate chelators (S-N-N donor system) (Udhayakumari et al. 2013; Udhayakumari et al. 2014). Thiosemicarbazone may interact with metal ions with ease because of its elastic, planar, and aliphatic structure, which lowers steric hindrance (Meng et al. 2017). In addition to all of the above, the floatability of Ni(II) from aqueous solution by flotation-preconcentration technique using 1-(3,5-dihydroxybenzylidene)thiosemicarbazone as a complexing agent and oleic acid as a surfactant has not yet been reported in the literature, despite the fact that a vast array of reagents are available for the flotation-separation of Ni(II). As a result, the current study introduced the ball milling technique as a green mechanochemical methodology to synthesize 1-(3,5-dihydroxybenzylidene)thiosemicarbazone for the first time in a solid–solid manner. Ball milling technology was used to achieve a number of green chemistry principles, including a high yield, high purity, fast reaction time, cost-effectiveness, and solvent-free reaction (Fekri and Zaky 2014; Fekri and Zaky 2016; Khaligh et al. 2017; Sharghi et al. 2018). The prepared compound was used as a novel chelating reagent for the separation, preconcentration, and spectrophotometric evaluation of Ni(II) in aqueous solution using the PFFT procedure under the suggested conditions. It has a variety of donor atoms (rich in binding sites) that allow it to selectively bind to trace levels of Ni(II). The variables that influence the efficacy of flotation, such as solution pH, concentrations of (metal ion, chelating agent, and surfactant), flotation duration, sample volume, surfactant nature, and ionic strength, were examined. The developed technique for identifying Ni(II) ions in real water samples was also effectively used and demonstrated good precision, accuracy, and sensitivity. The chemical structure of 1-(3,5-dihydroxybenzylidene)thiosemicarbazone is shown in Fig. 1.

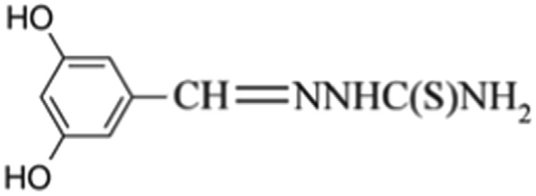


Fig. 1 Chemical structure of 1-(3,5-dihydroxybenzylidene)thiosemicarbazone (H_3L).

2. Experimental

2.1. Apparatus

The ball mill (MIXER MILL MM 200, Retsch GmbH, Haan, Germany) with a vibrational frequency of 25 Hz (1500 $\min^{-1}$), was used for the synthesis of the chelating agent. In the current investigation, two different types of flotation cells were used. Type 1 was a 2.9 cm long tube with an interior diameter of 1.2 cm. An investigation of the factors affecting the flotation-separation process used such a cell. Type 2 was a cylindrical tube with a quick-fit stopper at the top with an internal diameter of 6.0 cm and a length of 4.5 cm. Such a cell was used to float-separate Ni(II) from rather large quantities during the flotation-separation process. In order to determine the amount of Ni(II), absorbance measurements were carried out and recorded using a double beam UV–VIS spectrophotometer (UV–VIS DOUBLE BEAM PC UVD-3200, Labomed, Inc., Los Angeles, California, U.S.A) for the produced complex at λ_{max} = 370 nm. An elemental analyzer (Vario MACRO cube, Elementar, Langenselbold, Hesse, Germany) was used to do the elemental analysis. Using the KBr disc approach, FTIR spectra in the region of (400–4000 cm^{-1}) were captured using FTIR spectrophotometer (Mattson 5000, Mattson Instruments, Inc., Madison, Wisconsin, U.S.A). Thermal gravimetric analysis (TGA) was achieved by a Thermo-analyzer (TG 209 F1 Libra, NETZSCH, NEDGEX GmbH, SELB, Germany), with a heating temperature range of (20–800 °C), a flow rate of 15 mL/min of N_2 atmosphere, and rate of heating 10 °C/min. The conductivity measurements were made using a conductivity meter (Rex DDS-307A, INESA Scientific Instrument Co., Ltd., Shangai, China) at 25 °C. The melting points of the synthesized ligand and the produced complex have been determined using a digital melting point apparatus (Electrothermal IA 9100, Calibre Scientific, Reagecon Diagnostics Ltd., London, United Kingdom). The ^{1}H NMR spectra of the synthesized ligand was done in d_6-DMSO using a 400 MHz NMR-spectrometer (Avance DRX, Bruker, Billerica, Massachusetts, United States). Using a digital pH meter equipped with a glass electrode (Hanna 8519, Hanna Instruments, Inc., Leighton Buzzard, Bedfordshire, United Kingdom), the pH values of all working solutions were calculated. Using MST Magnetic Stirrer (VELP Scientifica Srl, Usmate Velate (MB), Italy), all working solutions were stirred. Shaking was done using a flask shaker (BALANCE LOAD, 5 speeds, Gallenkamp & Co. Ltd., London, England). The heating was done using a Thermolyne Type 1900 Hot Plate, Model HPA1915B (Thermolyne Corporation, Dubuque, Iowa, United States). Weighing was done with an analytical balance (Mettler AJ150, Mettler Toledo, Greifensee, Switzerland).

2.2. Materials and solutions

2.2.1. Materials

All the chemicals and reagents used in the current investigation were of analytical grade and supplied from Sigma-Aldrich (Darmstadt, Germany). They were not further purified before use. Deionized water of high purity (Milli-Q) was used for all experimental preparations. Chemicals used involved nickel acetate tetrahydrate $Ni(OCOCH_3)_2{\cdot}4H_2O$, 3,5-dihydroxybenzaldehyde, thiosemicarbazide, *para*-toluenesulfonic acid, oleic acid, Tween 60 (TW 60), cetyltrimethylammonium bromide (CTAB), sodium stearate (SS), sodium lauryl sulfate (SLS), HCl and NaOH.

2.2.2. Preparation of solutions

2.2.2.1. Stock solution of nickel(II). 0.2488 g of $Ni(OCOCH_3)_2{\cdot}4H_2O$ were dissolved in 1000 mL of deionized water to create a stock solution with a concentration of 1×10^{-3} mol/L.

2.2.2.2. Stock solution of oleic acid. By mixing 20 mL of HOL with 1 L of kerosene, a solution containing 6.36×10^{-2} mol/L of HOL was created.

2.2.2.3. Other ions stock solution. By dissolving the appropriate quantity of salt in deionized water, a stock solution containing 1000 mg/L of each interfering ion was created.

2.2.2.4. Synthesis of the chelating agent using ball milling technique. By combining equal amounts of 3,5-dihydroxybenzaldehyde (1382 mg, 10 mmol) with thiosemicarbazide (920 mg, 10 mmol), the chelating agent 1-(3,5-dihydrox ybenzylidene)thiosemicarbazone was created. The mixture was then subjected to a 10-min ball milling process utilizing five 10 mm balls with a 1500 min^{-1} rotational speed in the presence of 10% *para*-toluenesulfonic acid as a catalyst. When the mixture cooled, a light red precipitate developed, which was then removed, washed with absolute ethanol, recrystallized from absolute ethanol, and dried (see Scheme 1). The produced chelating agent is denoted by the notation (H_3L).

2.3. Analytical procedure

2.3.1. Flotation-separation protocol

A suitable known amount of Ni(II) solution (5 × 10^{-5} mol/L) was mixed with 2 mL of H_3L solution (1 × 10^{-4} mol/L) and all were added in an Erlenmeyer flask. The pH of the solution was adjusted by adding drops of 0.1 mol/L of (HCl or NaOH). The mixture was shaken well for few seconds to allow the complexation between H_3L and Ni(II) ions. A coffee color complex developed instantaneously. All contents were quantitatively transferred into flotation cell of type (1) and total volume was adjusted to 10 mL with deionized water. Then, 3 mL of HOL were added, with a concentration that is still below the critical micelle concentration (CMC). The cell was then shaken upside down by hand. Vigorous shaking of the flotation cell in the presence of the surfactant creates bubbles in the solution which enhance the floatability of Ni(II)-H_3L complex. At equilibrium, a foamy layer was obtained and the aqueous solution in the cell became completely cleared of the colored complex. The aqueous phase was run off through the bottom of the cell. The scum layer, in which Ni(II) was concentrated, was taken into a small vial to determine Ni(II) concentration spectrophotometrically.

2.3.2. Spectrophotometric determination protocol

After 5 min, to ascertain that flotation is completed, a suitable volume of the scum layer was transferred to a 1-cm quartz cell and the absorbance was measured at λ_{max} = 370 nm against a reagent blank to determine the concentration of Ni(II).

The floatability % (**F %**) of Ni(II) was calculated as follows:

$$F\% = \frac{C_e}{C_o} \times 100 \tag{1}$$

where, C_o (mg/L) is the initial concentration of Ni(II) in the mother liquor before flotation and C_e (mg/L) is the concentration of Ni(II) in the scum layer after flotation.

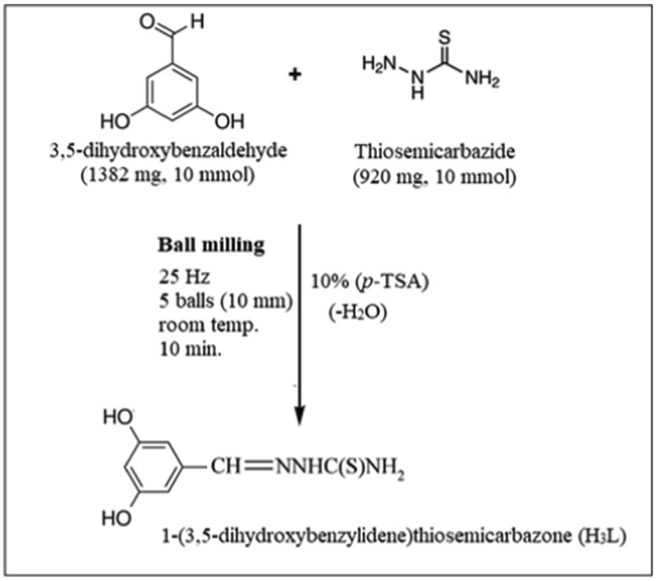
3. Results and discussion

3.1. Characterization of the prepared chelating agent and its Ni-complex

Table 1 provides the analytical data and physical properties of the prepared chelating agent and its Ni(II)-complex. The chelating agent, 1-(3,5-dihydroxybenzylidene)thiosemicarbazone, has been prepared under mechanochemical ball milling conditions in a solvent-free reaction of 3,5-dihydroxybenzaldehyde with thiosemicarbazide. Yield: 88.2%; color: light red; m.p.: > 285 °C. The suggested formula of H_3L was correlated by its elemental analysis results. Analytical calculations for $C_8H_9N_3O_2S$ (F.wt. = 211): C, 45.49; H, 4.26; N, 19.90; S, 15.16. Found: C, 44.98; H, 3.96; N, 19.70; S, 14.91. The suggested formula of Ni(II)-complex was $[Ni(H_2L)_2].2H_2O$: Yield: 86.5 %; color: coffee; m.p.: > 285 °C. The suggested formula was correlated by its elemental analysis results. Analytical calculations for $NiC_{16}H_{20}N_6O_6S_2$ (F. wt. = 514.69): C, 37.30; H, 3.88; N, 16.32; S, 12.43; Ni,11.40. Found: C, 36.99; H, 3.49; N, 16.01; S, 12.10; Ni, 11.03. The molar conductivity is acceptable for both the prepared chelating agent and its Ni(II)-complex as non-electrolytic activity and falling between 5 and 11 S.cm^2/mol (Geary 1971).

3.1.1. FTIR spectra

There are a number of significant distinctive absorption frequencies shared by the produced chelating agent and its Ni



Scheme 1 Synthesis of 1-(3,5-dihydroxybenzylidene)thiosemicarbazone.

Table 1 Analytical data and physical properties of the prepared ligand and its Ni-complex.

Compound		**Λ (S.cm^2/mol)**	**Color**	**m.p* (°C)**	**Calculated (Found) %**					**Yield (%)**
Molecular formula	**F.wt***				**C**	**H**	**N**	**S**	**Ni**	
H_3L	211	10.08	light red	> 285	45.49	4.26	19.90	15.16	—	88.2
$C_8H_9N_3O_2S$					(44.98)	(3.96)	(19.70)	(14.91)		
$[Ni(H_2L)_2].2H_2O$	514.69	6.06	coffee	> 285	37.30	3.88	16.32	12.43	11.40	86.5
$NiC_{16}H_{20}N_6O_6S_2$					(36.99)	(3.49)	(16.01)	(12.10)	(11.03)	

F.wt: formula weight, **m.p**: melting point.

(II)-complex as shown in Fig. 2. Both compounds have a broad peak in the range of 3350–3490 cm^{-1}, revealing the possibility of a dimeric form of the uncoordinated chelating agent, i.e., two molecules of the thiosemicarbazide moiety's OH groups are connected by intermolecular hydrogen bonds. Three bands, weak ν(OH—O), medium ν(—OH) and ν (C—OH) were observed at 1700, 1350 and 1260 cm^{-1}, respectively; suggesting that the phenolic hydroxyls are not coordinated to Ni(II) (Parikh and Shah 1985; Verma et al. 1983). The peak shift form 1622 cm^{-1} to 1641 cm^{-1} for ν(CH═N) of the Ni(II)-complex indicating coordination of the imino nitrogen to Ni(II). A characteristic peak at 846 cm^{-1} was observed in the FTIR spectrum of chelating agent, which was absent in Ni(II)-complex. However, a new band at 621 cm^{-1} was noticed, which was predicted for the produced Ni(II)-complex, due to ν(C—S). Thus, it is suggested that C═S in the free chelating agent is converted into C-S in the formed Ni(II)-complex. Metal-nitrogen and metal-sulfur bonds were verified by the appearance of new bands in the region 350–450 cm^{-1}.

3.1.2. UV/VIS spectra

Fig. 3 shows the absorption spectrum curve for the chelating agent H_3L and its complex Ni(II)-H_3L. It was observed that Ni(II)-H_3L has a maximum absorption at $\lambda_{max} = 370$ nm which higher than that of H_3L which has a maximum absorption at $\lambda_{max} = 300$ nm. Accordingly, subsequent analysis of the Ni(II)-H_3L complex was carried out at 370 nm. Also, compared to the free chelating agent, the π-π* transition of imino group for the Ni(II)-H_3L complex was slightly altered, most likely as a result of imino-nitrogen coordination to Ni(II) by the chelating agent.

3.1.3. ^1H NMR spectra

The ^1H NMR spectrum of H_3L is given in Fig. 4. The signal at $\delta = 9.587$ ppm is due to (2H of 2OH), 8.213 ppm is due to (1H of azomethine CH = N), 7.795 ppm is due to (1H of NH), 7.258 ppm is due to (2H of terminal NH_2) and 6.713 ppm is due to (3H of ring). The peaks can be well assigned and further confirm the composition of the free ligand.

3.1.4. TG/DTG analysis

The produced Ni(II)-complex was subjected to the thermogravimetric (TG) and the differential thermogravimetry (DTG) analysis under continuous nitrogen flow in the temperature range of 30–800 °C to insight about its thermal stability and a general scheme for its thermal decomposition. Thermal data showed that the crystallized water molecules are volatilized within the temperature range 30–120 °C. This evidence supports the conclusions of elemental analysis and FTIR spectra indicating the produced Ni(II)-complex included crystallized water. The TG analysis for the Ni(II)-complex is represented in Fig. 5. It is clear that, the TG thermogram for the investigated complex displayed high residual part indicating high stability of the formed chelate.

3.2. Optimization of experimental variables

3.2.1. Effect of pH

In order to determine the effect of pH (1–8) on the floatability percentage of 5×10^{-5} mol/L of Ni(II) using 1×10^{-3} mol/L of HOL in the absence and presence of 1×10^{-4} mol/L of H_3L, a series of tests were conducted (see Fig. 6). As indicated by curve (a), the greatest floatability was ≈ 47%. While curve (b) demonstrated that the pH range (5–7) where the greatest percentage of Ni(II) (≈100%) could be removed. According to graphs (a and b), H_3L combines with Ni(II) to create a complex that makes them more hydrophobic. HOL then removes them from the bulk of solution. As can be observed, floatability rises progressively as pH rises reaching maximum (≈ 100%) at pH range of (5–7) then decreases. At pH range of (5–7), [Ni(II)-H_3L] being combined with un-dissociated oleic acid, which starts to dissociate around pH ≥ 5.2, to make it hydrophobic (Ghazy et al. 2006), through hydrogen bonding and/or chemically with oleate anions. With the help of air bubbles, these hydrophobic aggregates are floated to the solution surface. The floatability decreases above pH 7 due to the solubility of the Ni(II)-H_3L species or because the reaction is halted by the formation of an excessive amount of sodium oleate foams and a white emulsion. Consequently, pH 5 has been used in all subsequent tests.

3.2.2. Effect of H_3L and Ni(II) concentration

Using 1×10^{-3} mol/L of HOL, it was determined how the concentration of H_3L affected the floatability percentage of 5×10^{-5} mol/L of Ni(II) at pH 5. According to the findings in Fig. 7, the floatability percentage of Ni(II) rose when H_3L concentration increased up to 1×10^{-4} mol/L, which is twice the concentration of Ni (II). Additionally, any further excess of H_3L has little effect on the floatability percentage. Therefore, 1×10^{-4} mol/L of H_3L was used for the investigations that followed.

Another set of tests were conducted to examine the floatability percentage of various concentrations of Ni(II) using 1×10^{-4} mol/L of H_3L and 1×10^{-3} mol/L of HOL at pH 5. The floatability percentage of Ni(II) in the absence of H_3L is shown in Fig. 8 (curve a). The greatest floatability percentage was 43.8%, and as the concentration of Ni(II) increased, the

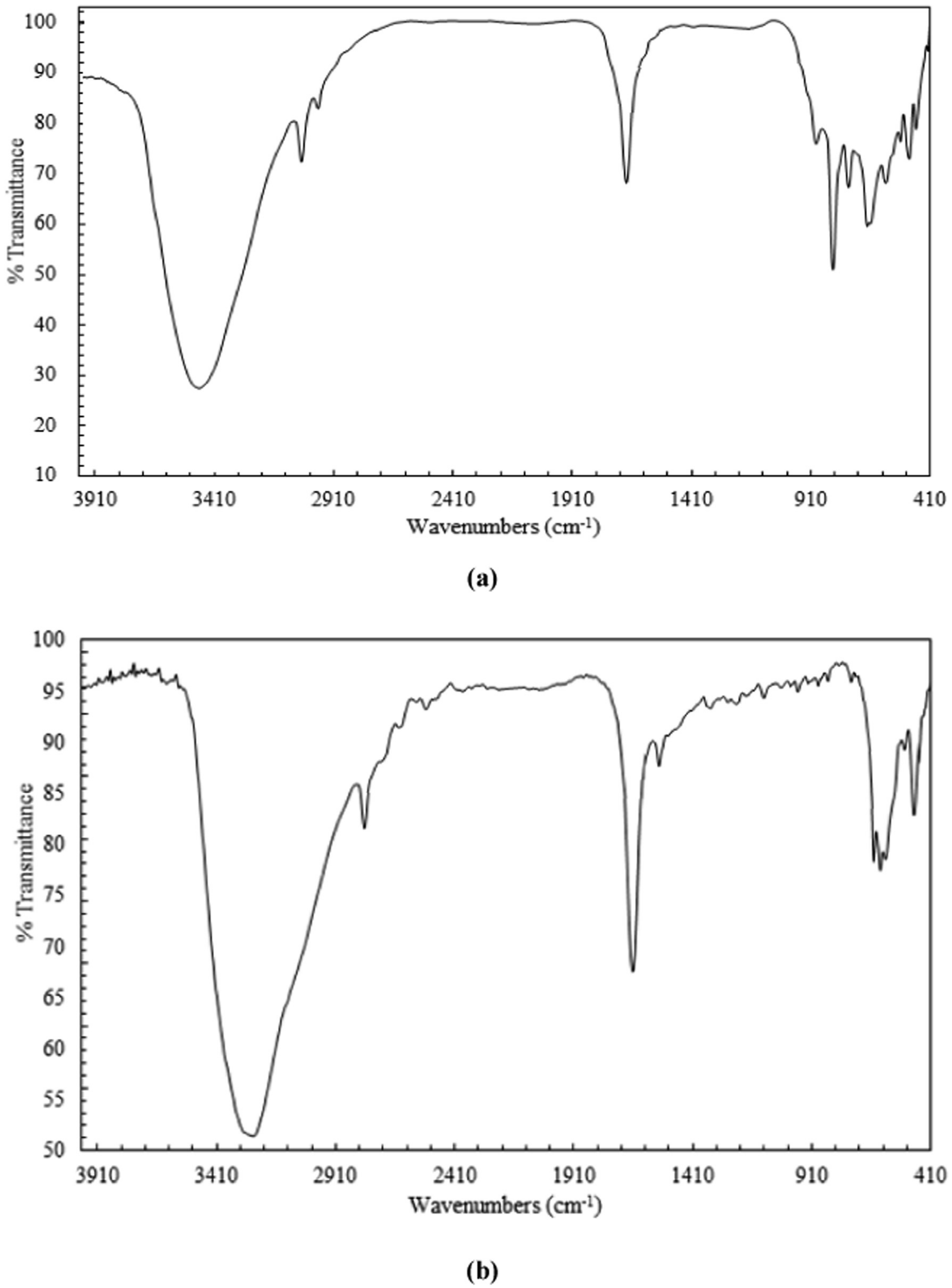


Fig. 2 FTIR spectra of: (a) H_3L and (b) Ni(II)-H_3L.

floatability percentage declined because there weren't enough oleate ions present to completely float all of the Ni(II). The floatability percentage of Ni(II) in the presence of 1×10^{-4} mol/L of H_3L is shown in Fig. 8 (curve b). The gathered information demonstrated that total flotation happens at a M:L ratio (1:2). The floatability percentage begins to decrease at a high metal ion concentration greater than the ratio of (1:2), which can be attributed to the absence of inadequate H_3L, which is required to bind all Ni(II). So, extra H_3L should be employed while analyzing Ni(II) in its unidentified samples.

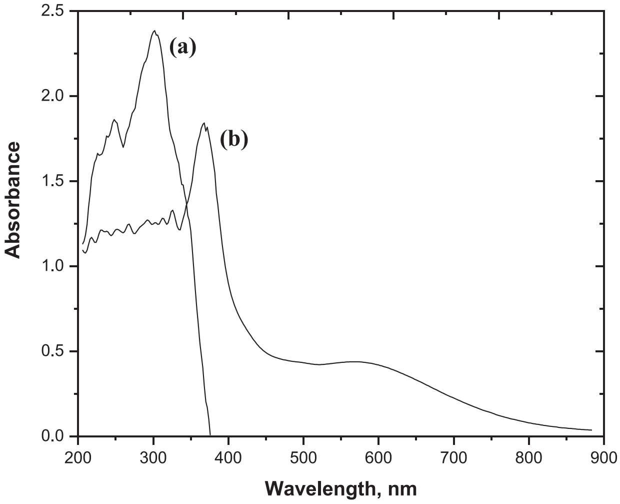


Fig. 3 Absorption spectra curve of: (a) H_3L and (b) Ni(II)-H_3L (5×10^{-5} mol/L of Ni(II) and 1×10^{-4} mol/L of H_3L).

Therefore, the optimal concentration of Ni(II) for all tests was determined to be 5×10^{-5} mol/L.

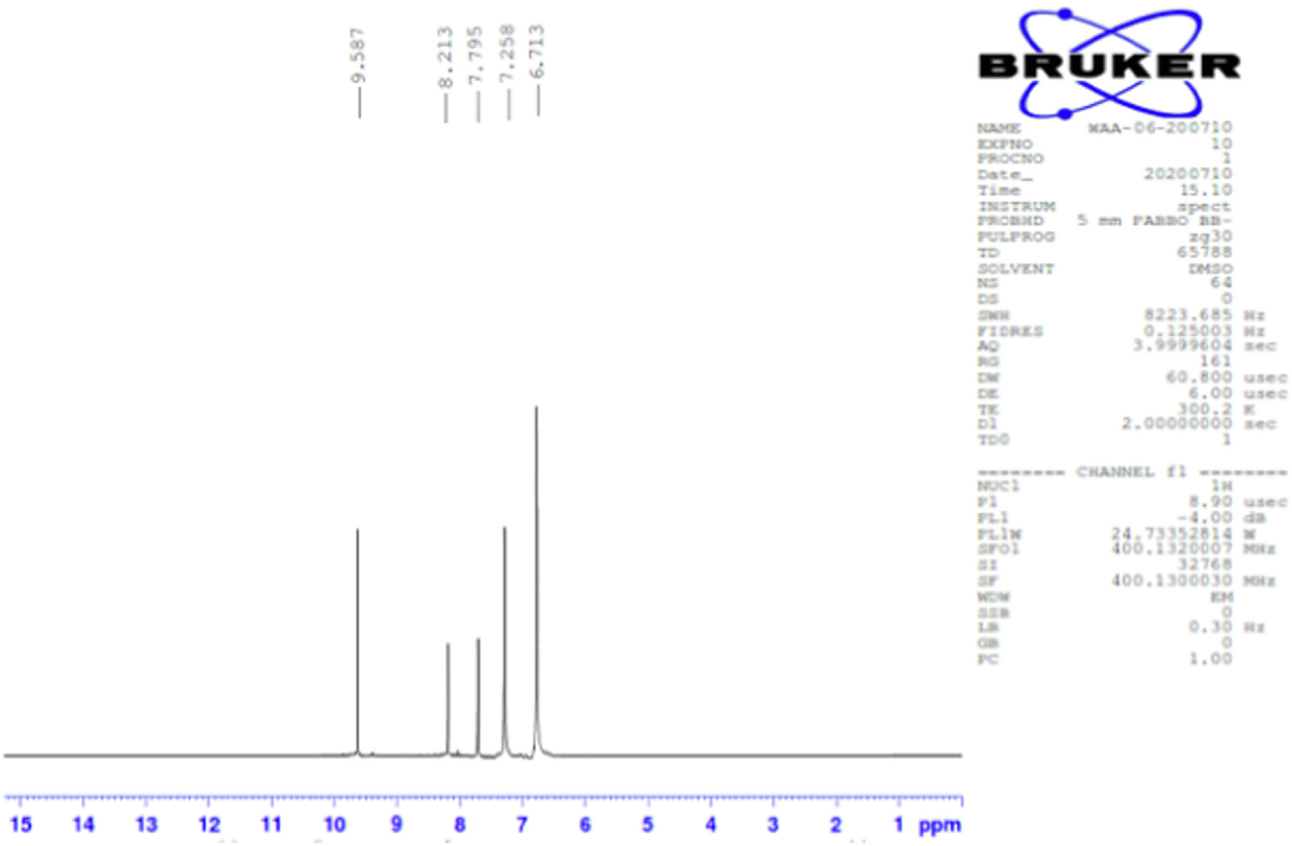
3.2.3. Effect of type and concentration of surfactant

Table 2 displayed how different surfactants affected the amount of 5×10^{-5} mol/L of Ni(II) that was removed while using 1×10^{-4} mol/L of H_3L at pH 5. The production of a foam layer and a thick layer of white scum at the top of the aqueous phase was discovered to make non-ionic surfactant (TW-60) and cationic surfactant (CTAB) ineffective for flotation of the generated complex, as a result, Ni(II) remained in the aqueous solution and could not be separated by flotation. However, the anionic surfactants (SS, SLS, and HOL) were very successful in causing the generated species, Ni(II)-H_3L, to float. HOL was chosen as an appropriate surfactant for all investigations as a result.

Another set of experiments was conducted to determine the floatability percentage of 5×10^{-5} mol/L of Ni(II) at various HOL concentrations (0.001–0.07 mol/L) in the absence and presence of 1×10^{-4} mol/L of H_3L at pH 5 (see Fig. 9). The floatability percentage was shown by curve (a) to be under 50%. The optimal floatability of Ni(II) is 100%, according to curve (b), when HOL concentrations are between 0.001 and 0.007 mol/L. The following explanation fits the results: Higher concentrations of HOL resulted in a decrease in floatability efficiency because the micelles generated by surfactant molecules competing with the created complex, Ni(II)-H_3L, caused the floatability efficiency to drop. Additionally, when the concentration of surfactant rises, the size of the bubbles decreases, which ultimately leads to the creation of a creamier foam. As a result, 1×10^{-3} mol/L of HOL was employed as a suitable concentration for the duration of the present study.

3.2.4. Effect of shaking and flotation time

Using 1×10^{-4} mol/L of H_3L and 1×10^{-3} mol/L of HOL at pH 5, the effect of shaking duration on the floatability percent-



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PROCNO                   1
Date_             20200710
Time                 15.10
INSTRUM              spect
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PULPROG               zg30
TD                   65788
SOLVENT               DMSO
NS                      64
DS                       0
SWH               8223.685 Hz
FIDRES            0.125003 Hz
AQ               3.9999604 sec
RG                     161
DW                  60.800 usec
DE                    6.00 usec
TE                   300.2 K
D1              2.00000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                    1H
P1                    8.90 usec
PL1                  -4.00 dB
PL1W           24.73352814 W
SFO1           400.1320007 MHz
SI                   32768
SF             400.1300030 MHz
WDW                     EM
SSB                      0
LB                    0.30 Hz
GB                       0
PC                    1.00
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Fig. 4 ^{1}H NMR spectra of H_3L.

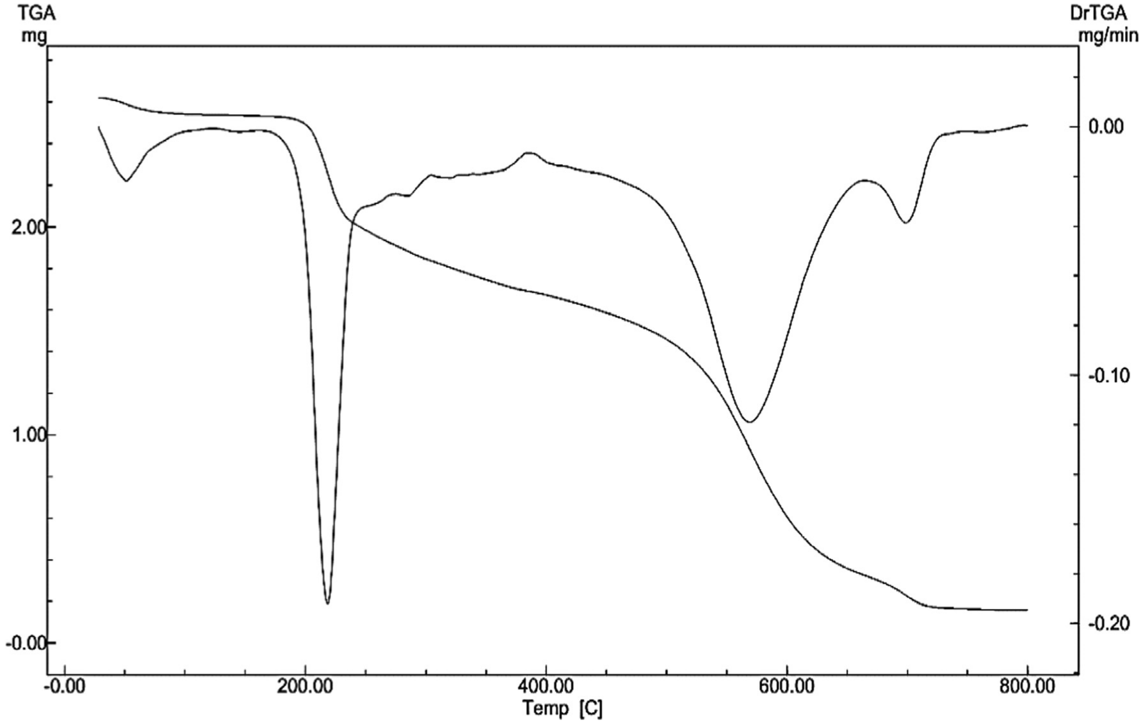

Fig. 5 TG/DTG curve of Ni(II)-H_3L.

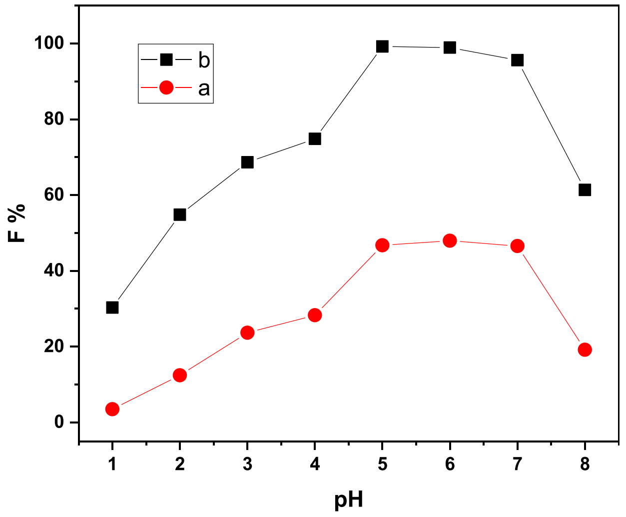

Fig. 6 Effect of pH on the floatability % of 5 × 10^{-5} mol/L of Ni (II) using 1 × 10^{-3} mol/L of HOL (a) in absence, and (b) in presence of 1 × 10^{-4} mol/L of H_3L.

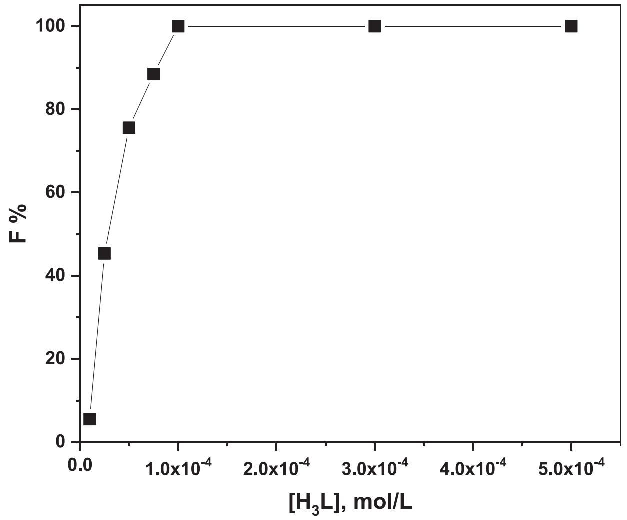

Fig. 7 Effect of H_3L concentration on the floatability % of 5 × 10^{-5} mol/L of Ni(II) at pH 5 using 1 × 10^{-3} mol/L of HOL.

age of 5 × 10^{-5} mol/L of Ni(II) was examined throughout a range of (1–30 min). It was discovered that the maximum floatability percentage could be attained in 5 min, as illustrated in Fig. 10. The outcome demonstrates that the flotation-separation process is a quick method. For the next trials, a shaking time of 5 min was used.

Investigations were done into how flotation time affected the stability of the produced complex inside the scum layer. The period between the addition of all reagents (Ni(II), H_3L, and HOL) to the flotation cell and the beginning of flotation is known as flotation time. Additional experiments from 5 min to 48 h have been run to verify the stability of the Ni (II)-H_3L complex. It had been shown that the floatability percentage and the absorbance of the floating [Ni(II)-H_3L] complex in the scum layer remained stable for around 36 h.

3.2.5. Effect of sample volume

A series of tests were conducted using the recommended large flotation cells to successfully float a 5 × 10^{-5} mol/L of Ni(II) from different volumes (10–2500 mL). According to the data obtained and displayed in Fig. 11, 5 × 10^{-5} mol/L of Ni(II)

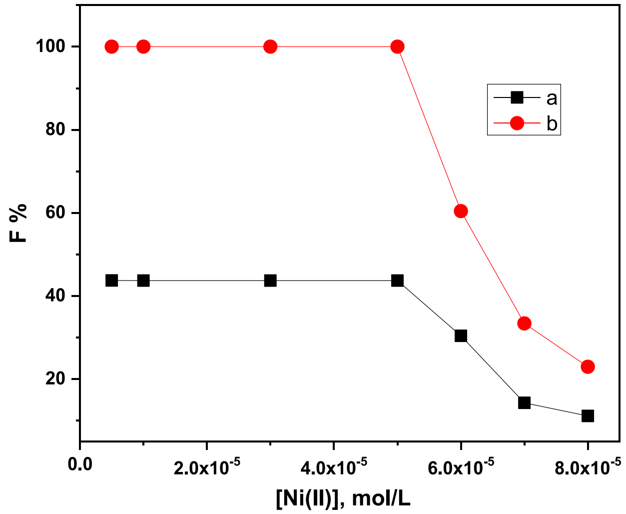

Fig. 8 Floatability % of different Ni(II) concentrations at pH 5 (a) in absence, and (b) in presence of 1 × 10^{-4} mol/L of H_3L using 1 × 10^{-3} mol/L of HOL.

Table 2 Applicability of different foaming reagents for the flotation process (Experimental conditions: Ni(II) concentration: 5 × 10^{-5} mol/L; H_3L concentration: 1 × 10^{-4} mol/L; pH 5).

Surfactant		**Floatability %**
Anionic	HOL	98.8
	SS	93.7
	SLS	86.3
Cationic	CTAB	Foam, no flotation
Non-ionic	TW-60	Foam, no flotation

HOL: oleic acid, **SS**: sodium stearate, **SLS**: sodium lauryl sulfate, **CTAB**: cetyltrimethylammonium bromide, **TW-60**: Tween 60.

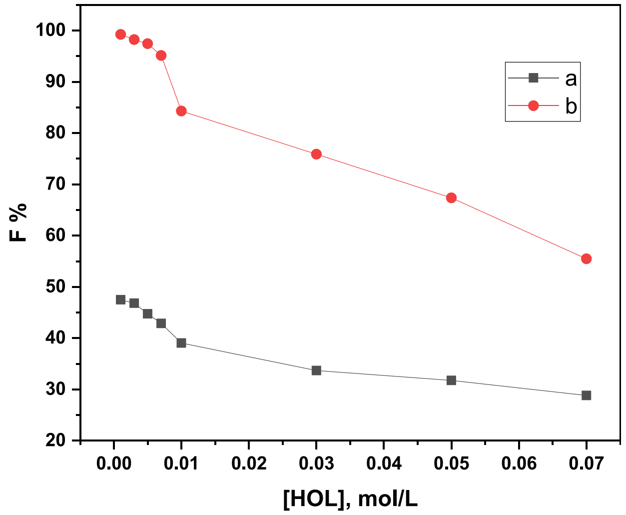

Fig. 9 Effect of HOL concentration on the floatability % of 5 × 10^{-5} mol/L of Ni(II) (a) in absence, and (b) in presence of 1 × 10^{-4} mol/L of H_3L at pH 5.

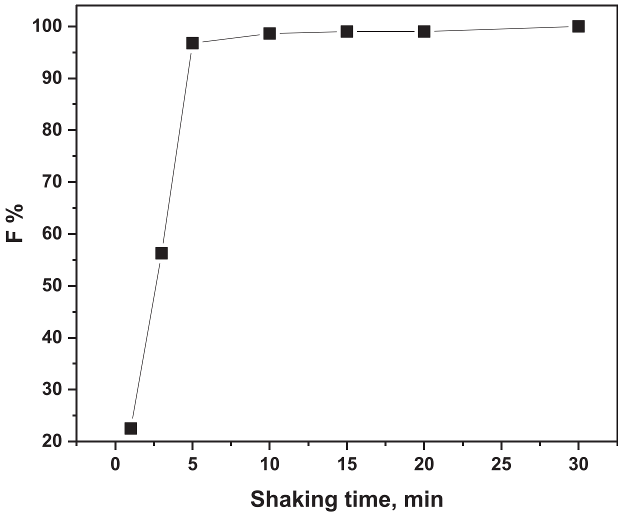

Fig. 10 Effect of shaking time on the floatability % of 5 × 10^{-5} mol/L of Ni(II) at pH 5 in presence of 1 × 10^{-4} mol/L of H_3L and 1 × 10^{-3} mol/L of HOL.

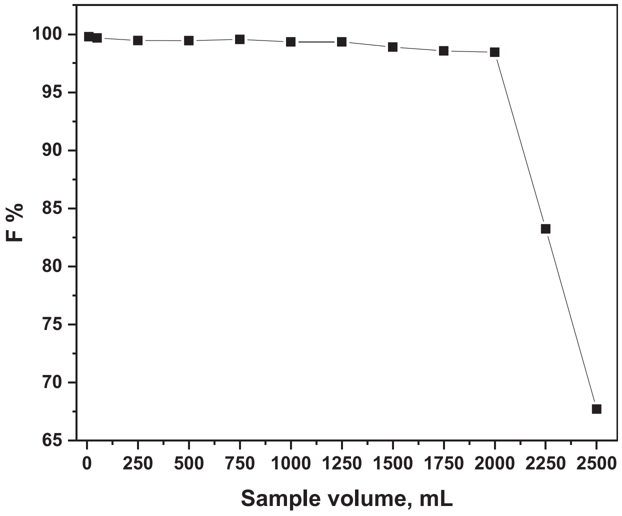

Fig. 11 Effect of sample volume on the floatability % of 5 × 10^{-5} mol/L of Ni(II) in presence of 1 × 10^{-4} mol/L of H_3L and 1 × 10^{-3} mol/L of HOL at pH 5.

may be entirely removed from different quantities up to two liters, at which point the floatability percentage reduced to 65.89%. So, using 15 mL of 1 × 10^{-3} mol/L of HOL and a pre-concentration factor of 200, 5 × 10^{-5} mol/L of Ni(II) could be pre-concentrated, separated, and measured from various aqueous volumes ranging from 10 mL to 2 L.

3.2.6. Effect of temperature

For testing the optimum temperature needed for complete floatability of 5 × 10^{-5} mol/L of Ni(II), a run of trials was done at a range of (5–80 °C) using 1 × 10^{-4} mol/L of H_3L and 1 × 10^{-3} mol/L of HOL at pH 5. This was accomplished by heating or cooling two solutions (one containing HOL and another containing Ni(II)) to the same temperature in a water bath. The HOL solution was quickly added to the Ni(II) solution. The flotation technique was then carried out after the mixture was added to the flotation cell. The results showed that the flotation-separation process is unaffected by temperatures up to 80 °C (see Table 3). Accordingly, consequent trials have proceeded at room temperature (25 ± 2 °C).

3.3. Stoichiometric ratio and the probable structure

Utilizing the molar ratio approach, the stoichiometry of the produced compound was demonstrated under the ideal conditions (Beltran-Porter et al. 1983; Momoki et al. 1969). Plot in Fig. 12 of absorbance against $[H_3L]/[Ni(II)]$ molar ratio revealed an inflection at a molar ratio of 2.0, indicating the existence of two H_3L molecules in the complex. As a consequence, the findings indicated that the stoichiometric ratio was (1:2) for $Ni(II):H_3L$. Also, the complex-formation constant (K_f) was evaluated (De Beer et al. 1994) and was found to be 2.25×10^4. As a result, the complex's structure may possibly be described as follows:

$$Ni(II) + 2H_3L \rightleftharpoons [Ni(H_2L)_2] + 2H^+ \quad (2)$$

3.4. Effect of ionic strength

Table 4 summarizes the effect of varying the ionic strength of different salts on the floatability % of 5×10^{-5} mol/L of Ni(II) using 1×10^{-4} mol/L of H_3L and 1×10^{-3} mol/L of HOL at pH 5. The salts used are generally similar to those present in natural water samples. As seen, it is clear that all added salts to the medium have not markedly affected the flotation-separation process. Only the chloride salts of calcium and magnesium have a little drop in floatability percentage as a result of the production of calcium and magnesium oleate, which lowers the concentration of HOL required for flotation. By adding much more HOL, the antagonistic effects of $CaCl_2$ and $MgCl_2$ can be mitigated.

3.5. Interference study

1×10^{-4} mol/L of H_3L, 5×10^{-5} mol/L of Ni(II) and various quantities of each interfering ion (individually or in combination) were introduced to a flotation cell of type 1. Prior proto-

Table 3 Effect of temperature on the flotation process (Experimental conditions: Ni(II) concentration: 5×10^{-5} mol/L; H_3L concentration: 1×10^{-4} mol/L; HOL concentration: 1×10^{-3} mol/L; pH 5).

Temperature, °C	Floatability %
5	96.7
10	97.8
15	98.2
25	100
35	100
45	98.7
60	98.3
70	98.2
80	97.8

Table 4 Effect of ionic strength on the flotation process (Experimental conditions: Ni(II) concentration: 5×10^{-5} mol/L; H_3L concentration: 1×10^{-4} mol/L; HOL concentration: 1×10^{-3} mol/L; pH 5).

Salt	Concentration, mol/L	Floatability %
NaCl	0.1	100.0
	0.5	98.7
KCl	0.1	100.0
	0.5	97.9
Na_2SO_4	0.1	99.6
	0.5	97.8
$MgCl_2$	0.1	97.3
	0.5	92.1
$CaCl_2$	0.1	96.9
	0.5	91.8

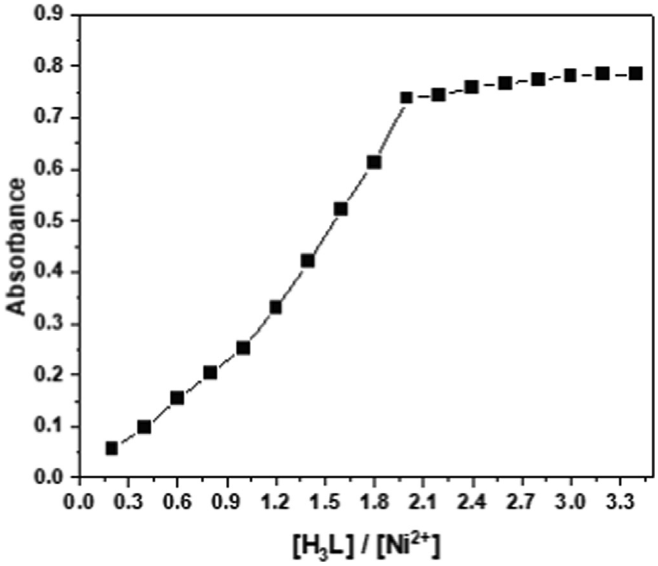

Fig. 12 Molar ratio method for the complexation of H_3L with Ni(III) at pH 5.

cols were followed for the flotation-separation and spectrophotometric determination of Ni(II). The findings, which are shown in Table 5, revealed that none of the tested foreign ions, even those with large concentrations (in contrast to Ni(II)), significantly influenced the floatability percentage of Ni(II). Excessive H_3L was added to the mixture to counteract the effect of interfering ions, which reduce the floatability percentage of Ni(II). Consequently, the suggested technique might be used for removing Ni(II) from water samples with complicated nature.

Table 5 Effect of different foreign ions on the flotation process (Experimental conditions: Ni(II) concentration: 5×10^{-5} mol/L; H_3L concentration: 1×10^{-4} mol/L; HOL concentration: 1×10^{-3} mol/L; pH 5).

Foreign ion(s)		Concentration, mg/L	Floatability %
Cations			
Individually	Ag(I)	350	97.9
	Li(I)	300	98.3
	Cu(II)	900	97.4
	Pb(II)	850	98.7
	Hg(II)	900	98.8
	Ca(II)	4000	96.9
	Cd(II)	500	97.2
	Mg(II)	2400	97.3
	Te(II)	300	98.2
	Mn(II)	350	98.1
	Sr(II)	100	96.8
	Co(II)	200	97.9
	Zn(II)	50	98.6
	Cr(III)	100	96.9
	Mo(III)	100	98.1
	La(III)	450	97.7
	W(III)	100	98.6
	As(III)	100	98.2
	In(III)	50	97.9
	Sn(IV)	100	97.9
	Zr(IV)	100	98.8
	V(IV)	50	98.2
	Th(IV)	150	97.8
Binary	Cu(II) + Mg(II)	450	97.2
	Cu(II) + Ca(II)	500	96.8
	La(III) + Ti(IV)	400	97.7
	Cu(II) + Sr(II)	200	96.8
	Co(II) + Sr(II)	100	97.4
	Cu(II) + W(III)	50	98.8
Tertiary	Cu(II) + Ca (II) + Mg(II)	350	98.2
	Cu(II) + Ca (II) + Hg(II)	450	98.1
	Cd(II) + Ca (II) + La(III)	500	98.6
	Te(II) + Mg (II) + La(III)	400	97.8
	Cu(II) + Cr (III) + Zn(II)	50	97.9
Anions			
Individually	Nitrate	1000	98.2
	Bicarbonate	900	98.8
	Citrate	1000	99.2
	Sulphate	190	97.1
	Phosphate	800	95.4
	Chloride	150	96.4
	Oxalate	190	95.6

3.6. Analytical application

Many water samples from different sites in Egypt (Mansoura, Talkha, Damietta, Gamasah, Ras El-Bar, Alexandria, and Sharm El-Sheikh) were collected at a depth of 50 cm below the top level. All of the samples were then filtered using G4 sintered glass. After that, 500 mL of each filtered sample was placed into a beaker, to which 15 mL of concentrated nitric acid and 10 mL of 30 percent (v/v) H_2O_2 were added to remove and decompose organic compounds. All filtered samples were then heated for 30 min at less than 90 °C, allowed to cool, and then pre-treated for the measurement of Ni(II) content as follows. After that, each sample of the cleaned water was carefully kept for future use in a dark plastic container. A 100 mL aliquot of treated water sample was introduced to a flotation cell of type 2, and then Ni(II) was added with an excess of H_3L. The earlier processes for flotation separation and spectrophotometric determination of Ni(II) have been carried out. A series of experiments were conducted to recover spiked quantities of Ni(II) applied to certain real water samples in order to assess the applicability of the suggested approach. The findings obtained, which are shown in Table 6, demonstrated that the recovery was thorough and satisfactory.

3.7. Analytical characteristics

Under optimum parameters for the proposed flotation-separation procedure of Ni(II), the following characteristics were obtained and presented in Table 7. Beer's law was obeyed over 5–400 ng/mL concentration range, the correlation coefficient (R^2) was calculated and found to be 0.9998. According to IUPAC recommendations, the limit of detection (LOD) and limit of quantification (LOQ) were calculated to be 0.22 and 0.74 µg/L, respectively. The molar absorptivity (ε) was 6.08×10^4 L/mol.cm with RSD of 1.7 % for n = 5.

3.8. The suggested flotation-separation mechanism and chemistry behind complexation

To investigate the flotation-separation mechanism and chemistry behind complexation, several experimental studies were conducted, and based on experimental data and observations, the suggested flotation-separation mechanism and chemistry behind complexation may be summed up as follows:

- The floated species, Ni(II)-H_3L-HOL, have the same coffee color as that isolated in the aqueous solution, Ni(II)-H_3L.
- The period when the color of the sublate begins to fade after 36 h following the flotation process; such a time is longer than that necessary for our investigation; did not have an impact on the intensity of color for the scum layer.
- Temperature increases up to 80 °C had little effect on the flotation process, showing that the floated complex is not readily dissociated by heat.
- The results of the current work has shown that complexation of 1-(3,5-dihydroxybenzylidene)thiosemicarbazone with $Ni(OCOCH_3)_2$ produced a coffee color tetradentate (bis-bidentate) nickel complex. The results suggested that

Table 6 Recovery of different concentrations of Ni(II) added to some real water samples (Experimental conditions: Ni(II) concentrations: 1.0 × 10^{-5} and 2.0 × 10^{-5} mol/L; H_3L concentration: 1 × 10^{-4} mol/L; HOL concentration: 1 × 10^{-3} mol/L; pH 5).

Sample	Location	Found Ni^{2+} concentration before addition, ppb	Added concentration of $[Ni^{2+}] \times 10^{-5}$ mol/L	Recovery %
Distilled water	Our lab.	ND*	1.0	100
			2.0	100
Domestic water	Talkha	0.38	1.0	99.5
			2.0	98.6
	Mansoura	0.26	1.0	100
			2.0	99.7
Seawater	Sharm El-Shiekh	0.55	1.0	98.9
			2.0	97.5
	Gamasa	0.75	1.0	99.2
			2.0	98.8
	Ras El-Barr	0.80	1.0	99.2
			2.0	98.5
	Alexandria	0.85	1.0	99.1
			2.0	98.2
Nile water	Talkha	0.30	1.0	98.2
			2.0	97.3
	Damietta	0.35	1.0	98.3
			2.0	97.5
	Mansoura	0.33	1.0	97.2
			2.0	96.8
Wastewater	Talkha	0.44	1.0	98.8
			2.0	97.2
	Mansoura	0.65	1.0	98.3
			2.0	97.5

ND*: not detected.

the thiosemicarbazone ligand behaved as bidentate ligand coordinated to the Ni(II) ion via its N and S atoms (see Fig. 13).

- The isolated complex's elemental analysis revealed [C: 37.30 (Found 36.99), H: 3.88 (Found 3.49), N: 16.32 (Found 16.01), and Ni: 11.40 (Found 11.03), showing the complex possesses the molar ratio of M:L (1:2).
- As a result, Ni^{2+} ions might combine with H_3L in a M:L ratio of (1:2) to produce a coffee color complex according to the following equation:

$$Ni^{2+} + 2H_3L \rightleftharpoons [Ni(H_2L)_2] + 2H^+ \tag{3}$$

- The pH of the solution affects the chemical species of HOL (Ramachandra 1982), where dissociation starts at pH > 5.2 (Ghazy et al. 2006) and IR analysis was used to calculate the proportion of its forms, and the findings were published in the literature (Pol'kin et al. 1968). The (–COOH) and (–COO^-Na^+) groups' distinctive bands at 1300–1800 cm^{-1} are connected to the IR spectra of HOL (Pol'kin et al. 1968). Moreover, as stated (Klassen and Mokrousov 1963), when HOL is ionized, the C═O stretching band at 1705 cm^{-1} shifts to bands in the 1520–1540 cm^{-1} region, which are typical of sodium oleate. Therefore, the suggested mechanism could occur either through a coordinate bond between HOL and the formed complex in solution, which results in the formation of a self-floatable species, Ni(II)-H_3L-HOL, or through physical interaction (for example, Van Der Waals forces or hydrogen bond formation) between the hydrophilic part of oleic acid and the active sites of H_3L in the formed complex.

Table 7 Analytical characteristics for the spectrophotometric determination of Ni(II).

Parameter	Value
λ_{max}, nm	370
Linear range, ng/mL	5–400
Linearity correlation coefficient (R^2)	0.9998
Molar absorptivity coefficient (Ɛ), L/mol.cm	6.08 × 10^4
Sandell's sensitivity, µg/cm^2	0.0085
Limit of detection (LOD), ng/mL	0.22
Limit of quantification (LOQ), ng/mL	0.74
Relative standard deviation (RSD), %	1.7

- As a result, depending on the pH of the solution, oleic acid might interact with the generated complex either in its undissociated (RCOOH) or dissociated ($RCOO^-$) form as follows:

$$R-COOH + [Ni(H_2L)_2] \rightleftharpoons R-COOH \cdots [Ni(H_2L)_2] \tag{4}$$

$$R-COO^- + [Ni(H_2L)_2] \rightleftharpoons R-COO^- \cdots [Ni(H_2L)_2] \tag{5}$$

- This hypothesis was validated by subsequent IR analyses, where the absence of bands for HOL in the IR spectrum of the complex that had been removed from the float layers (after thorough washing) indicates that HOL can combine with Ni(II)-H_3L chelates through weak bonds, depending on the solution pH (Ghazy et al. 2004). Combining HOL with the generated chelates results in hydrophobic aggregates that float on the solution surface with the aid of air bubbles produced within the flotation cell by shaking (Ghazy et al. 2004).

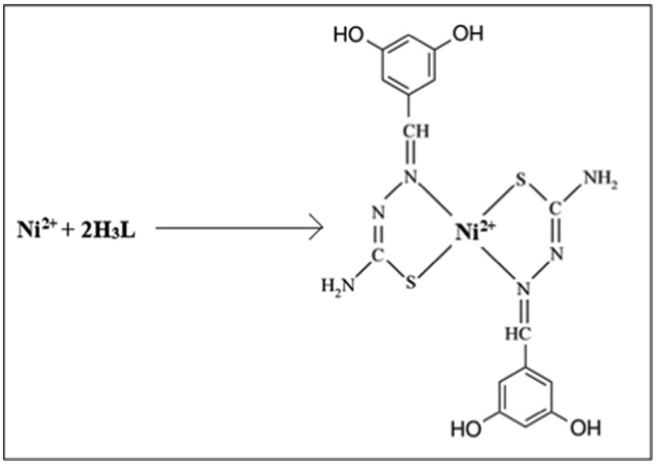

Fig. 13 The suggested chemical reaction of Ni(II) with H_3L at pH 5.

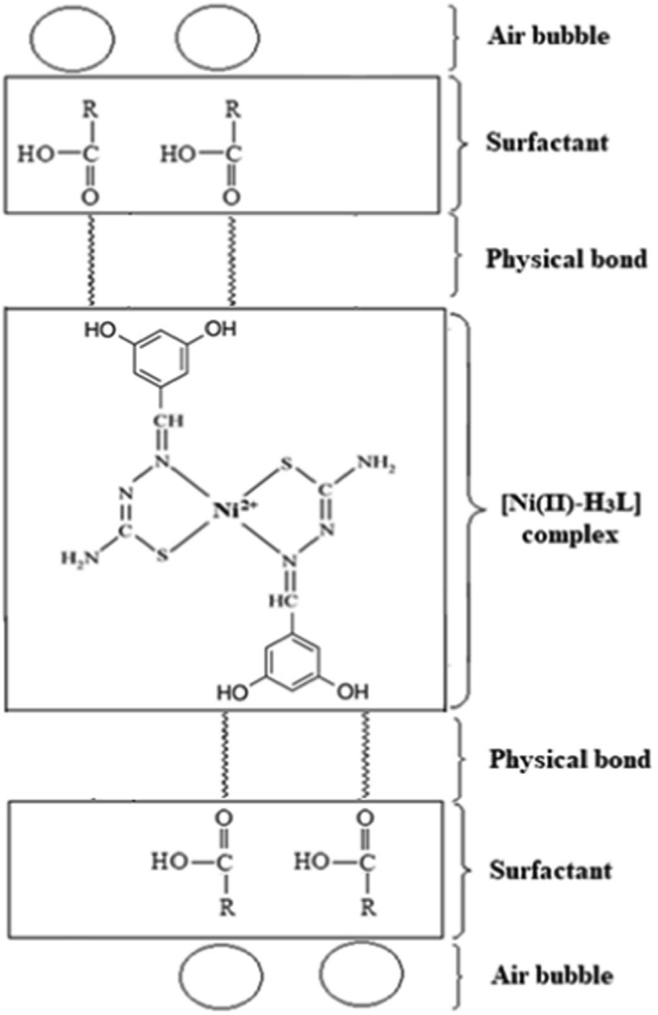

Fig. 14 The suggested flotation-separation mechanism of Ni(II) using H_3L at pH 5.

Table 8 Comparison between the current work and some reported studies on the separation/preconcentration of Ni(II).

Separation/preconcentration technique	Determination method	D_L (μg/L)	PF	%RSD	References
CPE	FAAS	1.22	29	2.89	(Manzoori and Bavili-Tabrizi 2003)
CPE	ICP-OES	6.3	9.79	2.6	(Silva et al. 2009)
CPE	ETAAS	–	15	–	(Gil et al. 2008)
SPE	FAAS	0.80	43	–	(Lemos et al. 2008)
SPE	FAAS	0.92	200	–	(Xie et al. 2008)
SPE	FAAS	0.75	330	0.9	(Ghaedi et al. 2010)
CME	ICP-MS	0.0015	10	4.1	(Hu et al. 2006)
DLPME	GFAAS	0.033	200	8.2	(Jiang et al. 2008)
SFODME	GFAAS	0.0004	497	3.6	(Bidabadi et al. 2009)
Flotation	GFAAS	9.0	–	–	(Karimi et al. 2008)
Flotation	ETAAS	0.7	93	< 1	(Lemos et al. 2008)
Flotation	FAAS	0.0025	100	< 1.2	(Akl and Ahmad 2019)
Flotation	Spectrophotometry	1.1	200	1.7	This work

CPE: cloud point extraction; **SPE:** solid phase extraction; **CME:** capillary micro-extraction; **DLPME:** dispersive liquid phase micro-extraction; **SFODME:** solidified floating organic drop micro-extraction; **FAAS:** flame atomic absorption spectrometry; **GFAAS:** graphite furnace atomic absorption spectrometry; **ETAAS:** electro-thermal atomic absorption spectrometry; **ICP-MS:** inductively coupled plasma mass spectrometry; **ICP-OES:** inductively coupled plasma optical emission spectrometry**;** **PF:** pre-concentration factor; **D_L:** detection limit; **%RSD:** percentage relative standard deviation.

Finally, it can be concluded based on the facts presented above that the flotation-separation process took place via physisorption with the aid of air bubbles. Fig. 14 shows the potential separation method.

3.9. Comparison with other reported methods

The suggested combined process of flotation-separation with spectrophotometric determination employing H_3L as a chelating agent and HOL as a surfactant was compared to other published methods for determining Ni(II) in different water samples (see Table 8). As can be observed, the suggested approach and the methods that have been previously published seem to be comparable.

4. Conclusions

Herein, 1-(3,5-dihydroxybenzylidene)thiosemicarbazone (H_3L) was prepared via facile solid state ball milling technique as a green and solvent-free mechanochemical approach and introduced as an effective organic chelate for the separation and preconcentration of Ni(II) from aqueous solutions utilizing a straightforward, quick, and affordable flotation method with oleic acid (HOL) as a surfactant. The characterization of the prepared chelating agent was investigated by various methods. The obtained results displayed that H_3L acted as a neutral bidentate (N, and S) ligand. The effective elements were selected taking into account several trials in order to fulfill the goal of the current study. The obtained findings demonstrated that 5 min of shaking at 1×10^{-3} mol/L of HOL in the presence of 1×10^{-4} mol/L of H_3L produced the maximum floatability percentage of 5×10^{-5} mol/L of Ni(II). Also, it was shown that the floatability % of Ni(II) was ≈ 100% at the Ni (II)-H_3L ratio of (1:2) and pH 5. Large flotation cells have made it possible to identify Ni(II) in water samples with large volumes and significant preconcentration factors. The recommended method could be applied to treat wastewater without cooling, was interference-free, and was unaffected by temperature increases up to 80 °C. This made the method cost-effective. Additionally, the proposed method was effectively used to recover Ni(II) ions supplied to several real water samples. The creation of weak physical interactions between the HOL surfactant and the generated complex, Ni(II)-H_3L, was discovered to be the basis of the flotation-separation process. In addition, the suggested ion-flotation methodology provides a non-polluting method for the preconcentration and separation of trace metals. It has been demonstrated to be a green technology for the treatment of water and wastewater.

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Declaration of Competing Interest

The author declares that he has no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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