Liquid-Liquid Extraction of Copper (II) in a Synthetic Sample using a New Macrocyclic Compound

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ABSTRACT

The paper describes the synthesis and characterization of a novel macrocyclic ligand. Liquid-liquid extraction studies were conducted to assess the extraction performance of the new macrobicyclic ligand towards copper ions. Selective extraction of heavy metals is highly demanded due to their toxicity and market significance. The results of the experimental studies to determine the best extraction conditions demonstrates pH=9 in the presence of 8.0 ppm of copper (II) in 10 mL with shaking time equal to 30 minutes at 25°C with using 0.05% reagent and chloroform as an organic solvent. The article studies the influence of various parameters on the extraction percentage such as; effect of pH, shaking time, type of solvent, temperature, ionic strength, the effect of concentration of metal ion and reagent. IR and HNMR have been used for the characterization of the new macrocyclic compound. Thermodynamic parameters have been calculated based on the experimental results at different temperatures with ΔH (39.91 kJ/ mol), ΔS (0.155 KJ/ mol. K), and ΔG (-6.28 KJ/ mol), which, indicates that the reaction is endothermic, randomness and spontaneous. This process has been used for extracting copper ions using atomic absorption spectrometer (AAS).

Keywords: Solvent extraction, Copper ion, Synthetic sample, Macrocyclic compound.
INTRODUCTION

Heavy metals are well-known environmental contaminants, and their poisoning is becoming more of a consequence for ecological, evolutionary, dietary, and factors. (Nagajyoti et al., 2010). Copper is a required component not only for life in mammals but also for plants, and it plays a significant role in lipid and carbohydrate metabolism. As a necessary as well as a harmful element, it has numerous biological impacts. (Xiang et al., 2011). Copper is used in a variety of manufacturing and farming activities, and it may be discharged into the environment through a variety of sources, including mining, metal pipes, chemical and pesticide manufacturing process. Copper is also required for the production of hemoglobin and plays an important role in enzymatic activities. However, extremely excessive consumption will result in health issues. (Yunus et al., 2020).

Various methods such as ion exchange (Dabrowski et al., 2004), adsorption (Ali et al., 2016), membrane filtration (Camarillo et al., 2010), chemical precipitation (Matlock et al., 2002), and liquid-liquid extraction (LLE) have been used to extract Cu (II) ion and other heavy metal ions from aqueous phase (Halim et al., 2019). Among different techniques to extract Copper ions from the aqueous phase, (LLE) extraction is one of the effective methods to remove copper ions from the aqueous phase (Ghanadzadeh and Abbasnejad, 2011).

Liquid-liquid extraction is an attractive technique to extract copper ions from the aqueous phase due to its relatively simple process and low cost (Noah et al., 2018). LLE involves a mixture of immiscible solutions to promote mass transfer and subsequent layer separation. The phase separation process is a complex phenomenon involving several parameters, including physical properties, geometric considerations of the reactors and hydrodynamic conditions (Navarro et al., 2020). Since of the high compatibility among the ionic radii of metals and macrocyclic ring diameters, oxygen-containing compounds have been utilized extensively in separation among the variety of macrocycles known. LLE with macrocyclic compounds is a convenient technique for metal investigation due to their high selectivity and affinity towards specific metals. According to their distribution ratios, the benzene ring provides much stronger lipophilicity into a crown ether than the cyclohexyl ring. Besides, other pendent substituents on the crown ring also enhance lipophilicity (Karapinar et al., 2013). Also, removal of some metal ions can be carried out using ion exchanger (Khattab and Sedeeq, 2012). The present study aims to use a new synthesized macrocyclic compound as a ligand for the removal of copper ions in a synthetic sample.

EXPERIMENTAL

Apparatus

$^1$HNMR spectra was recorded with Bruker Avanceno (400 MHz) spectrometer and data were referenced relative to residual protonated solvent (7.26 ppm for CDCl). FT-IR analysis was carried out using Shimadzu Spectrophotometer with KBr pellets. Metal ions concentrations were determined using the Varian (220AA) FAAS (acetylene flame). The pH was adjusted using a Metrohm (model 780) digital pH-meter that had a combination glass-electrode. The separation of the phases was assisted by an automated shaker (YCW-0.12C).

Chemicals

All chemicals (Na$_2$SO$_4$, NaOH, HCl, CuSO$_4$.5H$_2$O, Ethanol, and Methanol) utilized in this study were analytical reagents grade by Fluka and Merck.

Preparation of Stock Solution

The stock solution (1000 ppm) of copper (II) was prepared by dissolving 0.3928 g of copper (II) sulfate (CuSO$_4$.5H$_2$O) in distilled water and diluted to the final volume100 mL. The solution was standardized and diluted as required to prepare working solutions.

Preparation of 0.05% Reagent

0.125g of the reagent (HBCO) was dissolved in chloroform in a 250ml volumetric flask and volume was made up to the mark.


Synthesis of 1,3-Bis-(2-formylnaphthoxy) propane-2ol.

According to the modified method (Ilhan et al., 2008) to a stirred solution of 2-hydroxybenzaldehyde (9.77g, 0.02 mol) and Na$_2$CO$_3$ (33.92 g, 0.32 mol) in 100 mL ethanol was added dropwise 2-hydroxy1, 3-dichloropropane (5.16 g, 0.04 mol) in ethanol (30 mL). The mixture was refluxed for 8h at 180–200 °C. After the addition was completed, 100 mL distilled water was added and it was put in an ice water. Using filtration, drying, and recrystallization from chloroform/methanol solution (1:1) to give white precipitate (yield 80 percent) IR (KBr pellets were used): 1668 (CO), 3448 (OH), 2931 (aromatic-CH), 2850, 2720 (C–H of aldehyde), 1668 (C–O).

Synthesis of 1,3-Bis-(2-acetonylphenoxy) propane-2ol.

According to the modified method (Mondal et al., 2012) to a stirred solution of 2-hydroxyacetophenone (10.89g, 0.08 mol) and Na$_2$CO$_3$ (33.92 g, 0.32 mol) in 100 mL ethanol was added dropwise 2-hydroxy1,3-dichloropropaneane (5.16 g, 0.04 mol) in ethanol (30 mL). The mixture was refluxed for 10h at 180–200 °C. Then the mixture was put in ice water. The resulting precipitate was collected by filtration, dried, and recrystallization from chloroform/methanol solution (1:1) to give white precipitate (yield 80%). IR (KBr pellets, cm$^{-1}$): 1658 (CO), 3485 (OH), 2995 (aromatic-CH), 2995, 2941 (CH$_3$), 1665 (CO).$^1$H NMR (δ, ppm): 7.2–7.5 (s, 8H, Ar-H), 4.3 (d, H, OH), 4.4 (q, 1H, CH), 4.1 (d, 4H, CH$_2$), 1.6 (s, 6H, CH$_3$).

Synthesis of (15e,30e)-7,23-Dihydroxy-7,8,23,24-Tetrahydro-6H,14H,22H,32H Tetrabenzo [F, K, R, W] [1,5,13,17] Tetraoxacyclotetracosine-14,32-Dione (DHTTD).

A mixture of 1,3-Bis-(2-formylnaphthoxy) propane-2ol (A) (72 mg; 0.25 mmol) and 1,3-bis-(2-acetonylphenoxy) propane-2ol (B) (82 mg; 0.25 mmol) was dissolved in a potassium hydroxide solution (10%, 140–160 ml) in methanol/water (3:1) and the mixture was refluxed for 8 h. After five days of stirring at room temperature, the solvent was reduced to almost half its original volume under decreased pressure. The resulting precipitate was collected by filtration, dried, and washing in 150 ml ethanol was reflex for two days to give yellow crystals, suitable for (yield 80%). IR (KBr pellets, cm$^{-1}$): 1651 (CO), 3581-3249 (O–H broad), 1251 (C–O–C).$^1$H NMR (300 MHz, CDCl3): δH 7.5 (s, 16H, Ar-H), 4-4.5 (d, 2H, 2OH), 2.5-3 (q, 1H, CH), 3.5-4.0 (d, 4H, CH$_2$).

Scheme 1: Synthesis of macrobicyclic compound.
Extraction of Copper (II) Ion Using DHTTD

The aqueous and organic layers were equilibrated in a 100 ml separator funnel with an aqueous/organic ratio of 1:1 (10 ml of an aqueous layer containing 20 ppm of Cu (II) ion and 10 ml of the organic layer containing 0.05% of DHTTD in chloroform) which was shaken vigorously for 30 minutes. The pH in the aqueous was adjusted to 7.5 with diluted HCl and NaOH solutions using pH-meter. The separator funnel was kept standing for at least 15 minutes after equilibration to allow tiny organic particles in the aqueous layer to enter the organic layer and complete phase separation. The amount of copper (II) present in the aqueous solution was investigated quantitatively by atomic absorption spectrometer. The extractability was estimated using the following formula:

\[
\% \, E = \left[ \frac{(A_0-A)}{A_0} \right] \times 100
\]

Where \( A_0 \) is the concentration of cation in the aqueous layer before extraction. \( A \) is the concentration of cation in the aqueous layer after extraction. The impact of ligand concentration on the partition coefficient \( D \) of metal ions among the aqueous and organic phases was investigated. (Asrafi et al., 2009).

RESULTS AND DISCUSSION

Synthesis and Characterization

The target of the present study is to synthesize a new macrocyclic compound bearing hydroxyl group in several steps as shown in scheme (1). The hydroxyl group of salicylic has been converted into the ethoxy group by Williamson ether synthesis with 1,3-dichoropropane-2-ol to give bis aldehyde (A) and the bis ketone was synthesized in the same manner but 2-hydroxy acetophenone was used to give compound (B), furthermore, both compound A and B reacted with high dilution method to give the highlighted compound with very good yield.

The FT-IR spectrum Fig. (1) of both compounds bis aldehyde (A) and bis ketone (B) showed a strong band at 1668 and 1658 cm\(^{-1}\) for \((C=O)\) respectively but in compound \([(15E,30E)\,7,23\,dihydroxy\,7,8,23,24\,tetrahydro\,6H,14H,22H,32\,Htetrabenzo-[f, k, r, w]\,1,5,13,17\,tetraoxacyclotetraselaine-14,32-dione]\) (C) showed the presence of a strong peak at 1651 cm\(^{-1}\) for \((C=O)\) stretching vibration of macrocyclic chalcones, with lowered value.

![FTIR spectrum](image)

**Fig. 1:** FTIR for the aldehyde, ketone, and macrocycle Compounds.

In the \(^1\)H-NMR spectrum Fig. (2) of compound (C) disappearance of singlet signal at 10.4\(\delta\) of CHO and appearance new peak at 6.6 \(\delta\) for proton at \(\alpha\)-position of macrocyclic \(\alpha, \beta\)-unsaturated compound confirms the formation of target compound C.
Fig. 2: H-NMR for aldehyde, ketone, and macrocycle Compounds.

OPTIMIZATION CONDITIONS

To reach the best conditions of extraction, the effects of the following factors in the value of percent extraction was studied, represented by:

Effect of pH

The pH is one of the most significant effects in the metal-chelate formation and subsequent extraction. In this study, the effect of pH on the signal intensity of copper (II) in the surfactant-rich phase was estimated at different pH values ranging from 3.0 to 10.0 as shown in Fig. (3) The extraction percentage (%E) increased with an increase of pH. Acidic media was not suitable for extraction due to the effect on the protonated ligand molecules. Also the formation of metal hydroxides when the pH values were increased lead to select pH 7.5 as the optimum pH for this chelation (Hussein et al.).

Fig. 3: Effect of pH on the extraction of Cu (II) using (DHTTD).

Effect of Shaking Time

From 10mL aqueous solution containing 20 ppm of Cu (II) at pH=7.5, the metal ion was extracted by the macrocyclic compound as a reagent (0.05% dissolved in chloroform). The two phases have been shaken for different times ranged from 5 to 80 minutes with an electrical shaker. The results of this study in Fig. (4) demonstrate that the optimum shaking time of the two layers was (30min.).
Effect of Ion Strength on the Extraction

The high concentration of salt sometimes helps to remove metal ions from the aqueous layer to the organic solution. Salt increases the ionic strength of the aqueous layer and thereby increases the solubility of the metal complex into an organic solution. The addition of various types of salts as shown in Fig. (5) has a negative effect on the separation of copper ions and may be attributed to the competition effects of the cations and the copper ions to form ion-pair complexes with the macrocyclic compound. Therefore, the extraction process can be carried out without the addition of these salts.

Effect of Organic Solvents:

Extraction of 20ppm of Cu (II) was according to a general method using 0.05% organic reagent dissolved in different organic solvents with various dielectric constant values. According to the solvent extraction method which was dependent on the organic solvent used in the extraction method the results in (Table 1) demonstrate that there is no linear relation between the distribution ratio and dielectric constant of the organic solvents. These types of complexes were affected by many factors including the solubility of the extracted complex or geometry of the organic solvent. So, these results clarify the role of these organic solvents in the effect on extraction efficiency by the participation of organic solvents in the formation and stability of complex extracted to the
organic phase. The results of these studies are in agreement with the previous research (Pawar et al., 2018).

Table 1: The effect of organic solvents.

| Solvent            | Dielectric constant, (€) | Ex % |
|--------------------|--------------------------|------|
| Chloroform         | 4.81                     | 92.1 |
| Dichloromethane    | 9.08                     | 78.5 |
| Dichloroethane     | 10.4                     | 72.8 |
| Carbon tetrachloride | 2.2                     | 69.5 |

Effect of reagent concentration on the extraction.

The effect of the concentration of the reagent was also estimated in the range from 0.01% to 0.05%. the results are demonstrated in Fig. (6). Copper (II) extraction increased by increasing reagent concentration up to optimum level whereas in which 20 ppm copper (II) wase extracted quantitatively by using 0.05% (v/v) reagent.

![Fig. 6: The effect of different concentrations of the reagent on the extraction of Cu (II) ion.](image)

Effect of temperature

The effect of temperature on the extraction of Cu (II) by 0.05% (DHTTD) was examined. 10 ml of the reagent was added to the aqueous solution (10mL contains 20 ppm Cu (II)) at pH=7.5. Shaking the solution for 30 min was carried out in the range 278 –318K. The results demonstrated in Fig. (7). As a relation among line D and 1/T indicate that with rising temperature from 278 to318K the extraction percent’s increasing from 88.6% to 98.9%, demonstrating that the extraction reaction is endothermic and the extraction was carried out at room temperature 298K to avoid the evaporation of chloroform. The thermodynamic parameters (ΔH, ΔS, and ΔG) of Cu (II) were calculated from the Van’t Hoff equation where the slope equals -ΔH/R.

\[
\text{lin } D = \frac{\Delta H}{RT} + \frac{\Delta S}{R} \tag{1}
\]

\[
\text{Slope } = \frac{\Delta H}{R} \tag{2}
\]

\[
\text{Intercept } = \frac{\Delta S}{R} \tag{3}
\]
where $D$ is the partition coefficient, $\Delta H$ is the enthalpy change for the extraction reaction, $\Delta S$ is the entropy for the extraction reaction, $T$ is the temperature and $R$ is the gas constant (8.314 J/mol K). Based on the Equation, the values of $\Delta H$ were calculated to be about 53.63 kJ/mol, representatively that the extraction processes are endothermic. So, the positive value of $\Delta S$ (0.211 kJ/mol.K) demonstrates the randomness of the extraction systems. Consequently, $\Delta G$ for this system at 298K has been calculated from the following expressions:

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

the negative values of $\Delta G$ (-9.25 KJ/mol) indicate that the extraction reactions are spontaneous (Soltani et al., 2015), (Nozari and Azizi, 2020), (Jawad and Husien, 2018).

![Fig. 7: Effect of temperature on the extraction efficiency.](image)

**Effect of Aqueous to Organic Volume Ratio**

Copper (II) was extracted from aqueous layer (5 to 50 mL) with 10 mL of 0.05% reagent in chloroform. Copper (II) was separated and determined as defined in the general procedure. It was found that extraction of copper (II) was quantitative when the aqueous to organic volume ratio was only 1:1 and it decreased with an increasing the volume of the aqueous phase. The results of (Table 2) shows the possibility to extract Cu (II) ion by the reagent understudy from large volumes of the aqueous phase with low distribution ratio and (% E). While using large volumes of the organic phase leads to high consumption of the hazardous organic reagent with nearly the same Ex.%. The results of this study are approved with other recent studies (Pawar et al., 2018).

**Table 2: Effect of aqueous to organic volume ratio.**

| Aqueous to organic phase ratio | Ex %  |
|-------------------------------|-------|
| 10:10                         | 97.2  |
| 20:10                         | 70.2  |
| 30:10                         | 55.1  |
| 40:10                         | 35.1  |
| 50:10                         | 21.5  |
| 60:10                         | 12.3  |
Effect of Metal Ion Concentration

To a series of 10 mL aqueous solutions of Cu (II) ion concentration ranging from 5ppm to 30 ppm at pH =7.5, 10 mL of 0.05% (DHTTD) solution was added to each one and shaking for 30 min. The separated aqueous solution was treated as in the general procedure. The results can be seen in Fig. (8), the extraction percent’s (%E) were decreased by increasing the copper (II) ion concentration.

![Graph showing the effect of copper (II) concentration on extraction percentage.](image)

**Fig. 8:** Effect of Cu (II) concentration on the extraction method.

Application of the Method

The most significant influence in the liquid-liquid extraction of metals is the selectivity of the extractant towards the quantified metal ions to be recovered. The impact of different cation ions (Zn (II) and Cd (II)) on the selectivity of the proposed method was investigated utilizing 0.05% (DHTTD) as a new extractant. From (Table 3) the results show that the extraction of Cu (II) ions in presence of number of cations can be carried out with increasing the pH. Weak acidic and basic media are suitable for the extraction because of the effect on the protonated ligand molecules considering complex formation with the metal ion. This step leads to extraction and determination of copper (II) in the presence of Zn (II) and Cd (II) in some natural samples.

**Table 3: Application of the extraction of Cu (II) with (DHTTD) reagent at different pH in an synthetic sample.**

| Metal ion | pH=6.5 %E | pH=7.5 %E | pH=8.5 %E | pH=9 %E |
|-----------|------------|------------|------------|---------|
| Cd (II)   | 0          | 1.3        | 62.5       | 85      |
| Zn (II)   | 0.6        | 1.3        | 71.4       | 97.5    |
| Cu (II)   | 70.2       | 96.2       | 98.1       | 99.0    |

**CONCLUSIONS**

The current study shows that the extraction of a copper ion with a new macrocyclic compound. Multivariable that affecting the extraction have been studied. pH, time of shaking, ionic strength, the concentration of the reagent, and organic solvents Thermodynamic parameters have been calculated based on the experimental results at different temperatures. The method has been applied for the solvent extraction of copper ions in a synthetic sample using atomic absorption spectrometer.
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REFERENCES
Ali, R.M.; Hamad, H.A.; Hussein, M.M.; Malash, G.F. (2016). Potential of using green adsorbent of heavy metal removal from aqueous solutions: adsorption kinetics, isotherm, thermodynamic, mechanism and economic analysis. *Ecolog. Engineer.,* 91, 317-332.

Asrafi, F.; Feyzbakhsh, A.; Heravi, N.E. (2009). Solvent extraction of cadmium (ii) from sulfate medium by Bis (2-ethylhexyl) Phosphoric Acid in Toluene. *International J. Chem. Tech. Research,* 1(3), 420-425.

Camarillo, R.; Llanos J.; Garcia-Fernandez, L.; Perez, Á.; Canizares, P. (2010). Treatment of copper (II)-loaded aqueous nitrate solutions by polymer enhanced ultrafiltration and electrodeposition. *Separarat. and Purificat. Technol.,* 70, 320-328.

Dabrowski, A.; Hubicki, Z.; Podkoscilny, P.; Robens, E. (2004). Selective removal of the heavy metal ions from waters and industrial wastewaters by ion-exchange method. *Chemosp.,* 56, 91-106.

Khatab, A.F.; Sedeeq, S.H. (2012). Removal of Cu (II), Zn (II) and Cd (II) from aqueous solution by using ion exchanger derived from sack polypropylene grafted with maleic acid and its derivatives. *Rafidain J. Sci.,* 23, 115-127.

Ghanadzadeh, H.; Abbasnejad, S. (2011). Separation of copper (II) with solvent extraction using lauric acid diluted in benzene. *J. Thermodyn. Catal.,* 2, 1-6.

Halim, S.; Chang, S.; Ahmad, S. (2019). Extraction of copper ions from aqueous solutions with oleic acid as green solvent. *J. Physics: Conference Series,* IOP Publishing, 012128.

Hussein, S.A.; Al-Kubaisy, R.; Al-Noor, T.H. (2015). Solvent extraction method for the separation of Zinc (II) By use 2-[4-bromo-2, 6-diethyl phenylazo]-4, 5-diphenylimidazole (BDPI). *J. Transact. on Engineer. and Sci.,* 3(6), 2347-1875.

Ilhan, S.; Temel, H.; Kilic, A. (2008). Synthesis and spectral studies of macrocyclic Cu (II) complexes by reaction of various diamines, copper (II) perchlorate and 1, 4-bis (2-carboxyaldehyde phenoxy) butane. *J. Coordinat. Chem.,* 61, 277-284.

Jawad, S. K.; Husien, N. S. M. (2018). Solvent extraction method for separation and determination of Zn(II) by Using of Imidazole Derivative. *International J. Engineeer. Technol.,* 7, 553-556.

Karapinar, N.; Karapinar, E.; Ozcan, E. (2013). Liquid-liquid extraction of transition metal cations by glyoximes and their macrocyclic glyoxime ether derivatives. *J. Chem.,* 7(10), 10-13.

Matlock, M.M.; Howerton, B.S.; Atwood, D.A. (2002). Chemical precipitation of lead from lead battery recycling plant wastewater. *Industr. and Engineer. Chem. Research,* 41, 1579-1582.

Mohamed, S.K.; Akkurt, M.; Hawaiz, F.E.; Ayoob, M.M.; Hosten, E. (2017). Crystal structure of (6E, 20E)-3, 24-difluoro-13, 14, 28, 29-tetrahydro-5H, 22H-tetraabenzo [e, j, p, u][1, 4, 12, 15] tetraoxacyclodocosine-5, 22-dione. *Acta Crystallographica Section E: Crystallographic Communications,* 73, 13-16.

Mondal, R.; Mandal, T.K.; Mallik, A.K. (2012). Simple synthesis of a new family of 22-to 28-membered macrocycles containing two chalcone moieties. *Arkivoc,* 95,110.

Nagajyoti, P.C.; Lee, K.D.; Sreekanth, T. (2010). Heavy metals, occurrence and toxicity for plants: a review. *Environmental Chem. Lett.,* 8, 199-216.

Navarro, P.; Vargas, C.; Castilo, J.; Sepulveda, R. (2020). Experimental study of phase entrainment in copper solvent extraction. *Dyna,* 87, 85-90.

Noah, N.F.M.; Jusoh, N.; Othman, N.; Sulaiman, R.N.R.; Parker, N.A.M.K. (2018). Development of stable green emulsion liquid membrane process via liquid–liquid extraction to treat real
chromium from rinse electroplating wastewater. *J. Industrial and Engineer. Chem.*, 66, 231-241.

Nozari, I.; Azizi, A. (2020). An Investigation into the extraction behavior of copper from sulfate leach liquor using acorga M5640 extractant: *Mechanism, Equilibrium, and Thermodynamics. Mining, Metall. and Explorat.*, 37, 1673-1680.

Parwar, R.; Suryavanshi, V.; Patil, M., Mulik, G.; Patil, S. (2018). Liquid-liquid extraction of Zinc (II) from acid media with nn-heptylaniline as an extractant: Analysis of pharmaceutical and commercial sample. *Biomedic. J. Scientif. And Technic. Research*, 10, 7860-7866.

Soltani, H.; Yaftian, M.R.; Zamani, A.; Ghorbanloo, M. (2015). Selective liquid-liquid extraction of lead ions using newly synthesized extractant 2-(Dibutylcarbamoyl) benzoic acid. *Analytic. and Bioanalytic. Chem. Research*, 2, 91-98.

Xiang, G.; Wen, S.; Jiang, X., Liu, X.; He, L. (2011). determination of trace copper (II) in food samples by flame atomic absorption spectrometry after cloud point extraction. *Iranian J. Chem. and Chemic. Engineering*, 3(59), 101-107.

Yunus, K.; Zurai dah, M.; John, A. (2020). review on the accumulation of heavy metals in coastal sediment of peninsular Malaysia. *Ecofeminism and Climate Change*, 1(1), 21-35.

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Parwar, R.; Suryavanshi, V.; Patil, M., Mulik, G.; Patil, S. (2018). Liquid-liquid extraction of Zinc (II) from acid media with nn-heptylaniline as an extractant: Analysis of pharmaceutical and commercial sample. *Biomedic. J. Scientif. And Technic. Research*, 10, 7860-7866.

Soltani, H.; Yaftian, M.R.; Zamani, A.; Ghorbanloo, M. (2015). Selective liquid-liquid extraction of lead ions using newly synthesized extractant 2-(Dibutylcarbamoyl) benzoic acid. *Analytic. and Bioanalytic. Chem. Research*, 2, 91-98.

Xiang, G.; Wen, S.; Jiang, X., Liu, X.; He, L. (2011). determination of trace copper (II) in food samples by flame atomic absorption spectrometry after cloud point extraction. *Iranian J. Chem. and Chemic. Engineering*, 3(59), 101-107.

Yunus, K.; Zurai dah, M.; John, A. (2020). review on the accumulation of heavy metals in coastal sediment of peninsular Malaysia. *Ecofeminism and Climate Change*, 1(1), 21-35.