Design of a new home-made ultrasonic extraction system

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Abstract

Innovative, sensitive, and accurate method for liquid-liquid extraction using an ultrasonic device is presented in this work. A working system was created, consisting of two basic components: the ultrasonic device and the pump device, to pump or withdraw the organic layer. a study of the key variables derived from the liquid-liquid system was carried out in the system containing Dithizone (1×10^{-3} M) in (**Chloroform**) $CHCl_3$ solvent. and aqueous copper (II) chloride($CuCl_2.2H_2O$) (1×10^{-6} M) solution to determine the degree to which they affect the extraction performance attained in this manner. The effect of initial sample copper concentration and ultrasonic time, temperature effect, and pump speed, were studied, establishing the best conditions for a sample of (10 mL) aqueous solution of Cu (II) chloride, the optimum copper (II) concentration in the analyzed sample is (1×10^{-6} M), the ultrasonic time for the device is (8 min), and the flow rate of the pump is (3mL/30sec) and a temperature (27ºC) and (pH=1). The extraction degree was optimum under these conditions (96±2%) and the relative standard deviation (RSD)% (0.29%), In this work, a simple method is proposed to extract and concentrate copper in aqueous copper chloride using an ultrasonic device in the presence of dithizone solvent. The main parameters affecting the extraction method such as copper ion concentration, pump speed, temperature, device time, and the effect of equal and different volumes were evaluated. The proposed method was applied for the determination of copper in aqueous copper chloride samples. Accuracy was assessed by comparing the results with a conventional extraction method (traditional methods).

Keyword--- ultrasonic device, Peristaltic pump, dithizone solution copper (II) chloride

1- Introduction

Copper is a low-concentration element that can be found in abundance in the earth's layers, particularly the crust, seas, and water bodies. Copper is an excellent conductor of electric current and, in general, of electricity. The most important natural sources of copper are volcanic activity, geological deposits, and soil and rock erosion, as well as human resources such as electricity manufacturing, agriculture, metal, sludge from publicly owned treatment plants, mining, and pesticide use, to name a few. Copper is an important element as a vital food, but only in small amounts, and if the concentration exceeds the normal limit, it is toxic to aquatic life [1]. A trace amount of copper (Cu) at the µg/kg level is essential for human health, whereas high levels become toxic [2]. Excess copper leads to DNA damage and disturbance in neuronal cells. In addition, free radical formation is usually accompanied by high concentrations of copper [3]. Copper can alter enzyme activity, metabolism, brain functions, and blood chemistry, in addition to hurting growth, reproduction, and survival. Copper is required for animal metabolism. Excessive copper consumption, on the other hand, can cause severe toxicological problems such as nausea, cramps, convulsions, and even death [4]. Copper enzymes involved in redox reactions can take advantage of copper's ability to switch between its oxidation state, Cu(II), and its reduced state, Cu(I). However, it is important to consider the possibility that copper is extremely dangerous because transitions between Cu (II) and Cu (I) may result in the synthesis of peroxide and hydroxyl molecules, which are known to affect biomolecules[5]. Excessive copper exposure, cellular damage, and Wilson's disease are all linked in humans[6]. Many other essential elements, such as copper, perform biological functions; however, high concentrations of these minerals frequently cause cell and tissue damage, resulting in a variety of undesirable effects and human diseases[7].

2-Classification of Extraction Methods:

The operation and types of phases of the extraction process are used to classify the extraction process (32).

a-Classification of extraction process, based on operation.

b- Classification of extraction process based on types of phases.

3-Advanced Extraction Methods:

1. Supercritical Fluid Extraction (SFE)
2. Ultra sonication-assisted Extraction (UAE)
3. Micro Bubbles Extraction (MBE)
4. Microwave-assisted Extraction (MAE)
5. Shake Flask Extraction and Matrix Solid Phase Dispersion (MSPD) Soxhlet method Extraction
6. Accelerated Solvent Extraction (ASE) or Pressurized Fluid Extraction (PFE) [35].

4-Experimental

Chemicals:

Every chemical used in this study was provided by businesses (Fluka & BDH). At a concentration of (1*10^¯ 3M), dithizone solution ($C_{13}HI_2N_4S$) (Fluka) was created by dissolving (0.0256g) in (10 mL) of $CHCl_3$ (BDH). To meet the needs of the study, a different group of Dithizone solutions with a concentration of (0.001M) was created by mixing (5mL) of the previous Dithizone solution of (0.01M) with (50mL) of $CHCl_3$ in a standard volume vial, then store the mixture in an opaque bottle away from light [8] [9]. An aqueous solution of copper (II) chloride ($CuCl_2.2H_2O$) (Fluka) at a concentration of (0.01M) was prepared by dissolving (0.42625mg) in a small volume of distilled water, then completing the volume to (250 mL) in a standard volumetric vial and saving the solution for use. Another group of $CuCl_2.2H_2O$ solutions with a concentration (of 1*10^¯ 6 M) was prepared for the study's requirements by taking (0.5 mL) of the previous copper (II) chloride solution of (0.01M) and diluting it in (50mL) of distilled water in a standard volumetric vial when the concentration is Copper (II) standard (0.06356 ppm). The acidity of the $CuCl_2.2H_2O$ solution is adjusted to pH=1, and the pH is measured using a pH meter after a small amount of HCl is added (BDH).

5-Equipment:

Glassware, volumetric flasks, and beakers were washed and rinsed with acetone and heated (150 °C), Ultrasonic device(AUSTRIA), thermometer, and Peristaltic pump to pump the reagent and withdraw the organic layer; pH - meter WTW –SERLES Germany, to determine the required pH and Atomic Absorption Spectroscopy device SHIMADZU - 6300, used to measure the proportion of copper (II) remaining in the aqueous layer.

6-Ultrasonic device extraction working procedure:

(10 mL) of an aqueous copper chloride solution ($CuCl_2.2H_2O$) at a concentration of (1×10^{-6} M) was pumped into a volumetric vial containing (10 mL) Dithazone solution at a concentration of (0.001 M). By a peristaltic pump, through a rubber tube, after fixing the pump speed at (3 mL/30 sec) and after determining the optimal conditions for completing the extraction process which is: temperature (27 °C), pH = 1, and an ultrasonic device that generates vortices and waves help in the extraction process and with a constant vibration time of (8 minutes), The ultrasonic waves create cavitation bubbles in the solution, which generate localized high pressures and temperatures upon collapse. This promotes the breakdown of copper-containing minerals and facilitates the release of copper ions into the solution.

7-Result and Discussion:

8-Ultrasonic extraction system design:

A new working system was designed using ultrasound technology, which is a device for generating eddy currents and waves that aid in the extraction process. This system allows the extraction process to be repeated several times in a short time, and it is easy to follow the stages of the:

- A device that generates vortices and waves that help in extraction, an ultrasonic device, which is the main part of the design, which has different timings (90 seconds - 8 minutes)
- The peristaltic pump device, which allows the reagent material to be transferred back and forth from the analyzed sample.
- A thermometer for measuring the temperature that has been stabilized at (27 °C).
- A round flask with a single-hole lid, for pumping organic matter.

Figure (1).

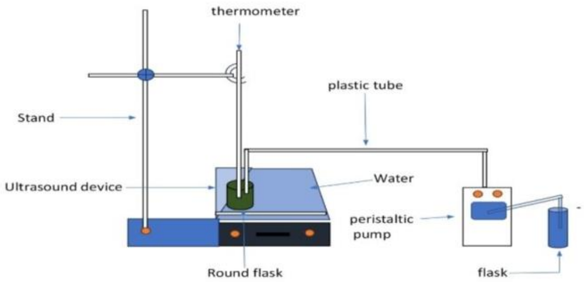

Figure (1) Ultrasound extraction

9-The effect of the main variables study:

In this work, four main variables were studied to find out their impact on the percentage of extraction that occurs using the ultrasound device compared to other traditional methods, as follows:

9-1-The effect of the concentration of $CuCl_2.2H_2O$ on the extraction process:

The concentration of the metal ion has a direct influence on the formation process of the extracted compound [10], which is important in obtaining the best values for the distribution constant D and the degree of extraction %E. Therefore, the extraction of copper (II) was carried out by taking two volumes of $CuCl_2.2H_2O$ (10 mL) per of them, the concentration of the first (1 x 10^⁻4 M) and the concentration of the second (1 x 10^⁻6 M), and after pumping (10 mL) of a dithizone solution at a concentration of (1 x 10^⁻3 M), with a with time (6 min) for the device, the organic layer was withdrawn from the aqueous layer by the pump. The percentage of copper remaining in the aqueous layer is measured in both samples. After calculating the values of D and %E, it was found that the second concentration (1 x 10^⁻6 M) is better for the ultrasonic extraction process, because it gives higher values than the first concentration (1 x 10^⁻4M), as shown in the table 1.

Table 1

Optimal copper (II) concentration for the ultrasonic extraction process

sample NO.	Copper(II) concentration	D	E%
1	1×10^-4 M	3.7	89 %
2	1×10^-6 M	14	92 %

9-2-Study the effect of change in the Ultrasound time:

In this study, three times equal volumes (10 mL) of $CuCl_2.2H_2O$ solution and dithizone solution were steadily pumped with varying Ultrasound times for each (3 min), (8 min), and (13 min) for the extraction process. pump speed (4mL /30Sec), at a temperature of 25C. (Fig. 1) shows that the values of %E increase with increasing vibration time, allowing more time for waves to pass through and complete the extraction. We believe that (8 minutes) is the best extraction time, Where the extraction rate in the time of (8 minutes) was approximately %E (94.5%) because the extraction degree is satisfactory and longer time means more energy consumption. Table 2,
Figure 1

sample NO.	Ultrasound time	E%
1	3 min	92
2	8 min	94.5
3	13 min	91

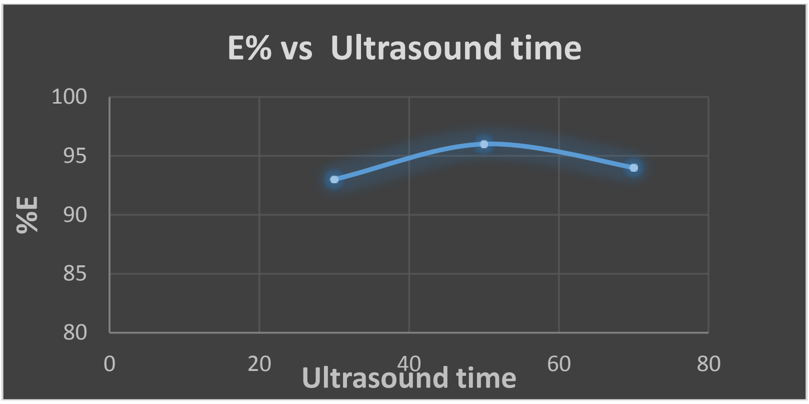

Figure 1. The effect of change in the Ultrasound time

9-3-Effect of changing in the rate of pump speed:

The change in pump velocity to three speeds (3mL/30sec), (5mL/30sec), and (7mL/30sec) was studied and ultrasonic time(8min). (Fig. 2) shows that the value of the degree of extraction %E rises slightly as the pump speed increases between (3mL/30sec and 5mL/30sec), after that the values of %E decreases as the rate of pump speed increases The reason is due to the low flow rate of the pump the mechanical energy generated by ultrasound is applied further to the samples to speed up the extraction. This technique relies on the application of high-frequency sounds and a limited amount of solvent to produce an efficient extraction of the compounds On the contrary, the high speed of the pump does not allow the ultrasonic extraction process to be completed to sequentially increase the organic layer of peristalsis, Where the results show that the best speed of the pump is (3mL/30sec), the values of %E (95.3%).

(Table3, Figure 2)

sample NO.	pump speed	E%
1	3mL/30sec	95.3%
2	5mL/30sec	93%
3	7mL/30sec	90%

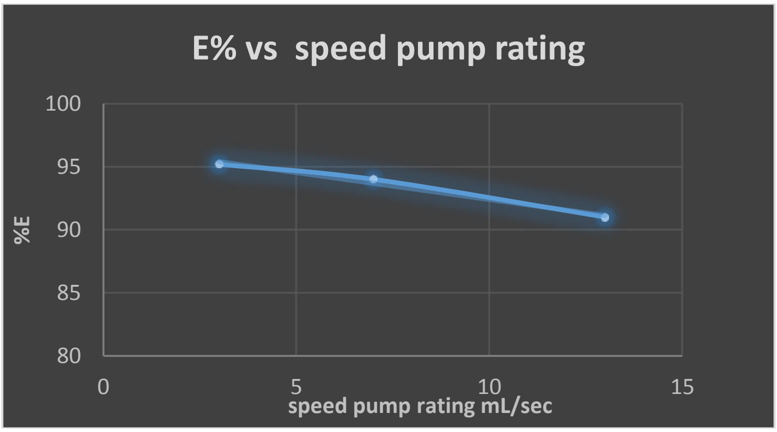

Figure 2. Effect of change in the rate of pump speed

9-4-Studying the effect of temperature:

An equal volume of copper(II) chloride solution (10 mL) and dithizone solution (10 mL) were studied at different temperatures (25 °C, 27 °C, 30 °C) under optimal conditions of vibration time of the ultrasonic device (8 minutes), and speed of the peristaltic pump (3 mL/30 seconds). The results showed that The percentage of extraction decreases with increasing temperature at (30°C) as it negatively affects the extraction process as a result of evaporation of the solvent, so the best temperature for extraction is at 27°C (17). Table 4, Figure 3 Shows the results of the study.

Temperature °C	E%
25 °C	90%
27°C	95.8%
30°C	88%

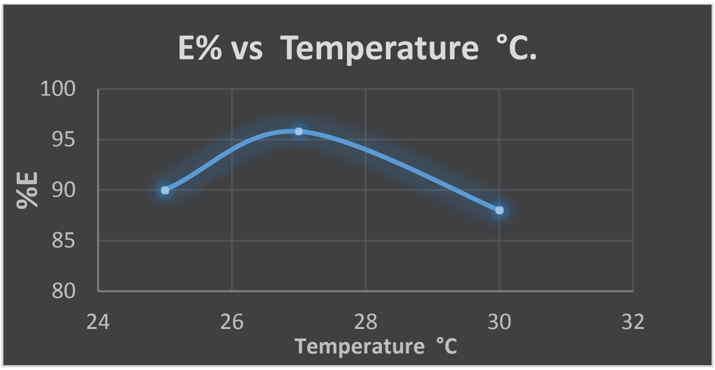

Figure 3. Studying the effect of temperature

9-5-Study the effect of equal volumes:

During the extraction process, volumes of copper(II) chloride solution was injected (10, 15, 20, 25 mL) in dithizone solution respectively in the same volume for each stage of the study. When the pump speed is(3mL/30sec), the Ultrasound time is (8 minutes), and the temperature is (27 °C). The results of the study were as follows: The results of the study showed that the constant volume (10 mL) between the two solutions gives a higher result for the values of E% and the distribution coefficient D than the total volume (20 mL) between the two solutions. Help generate stable waves within the remaining space of the bottle, giving better scope for the extraction process, the values of E% (95.4%). As shown in the figure 4. Table 5

sample NO.	Volume	E%
1	5 ml	89%
2	10ml	95.4%
3	15ml	94%
4	20ml	92%
5	25ml	91.4%

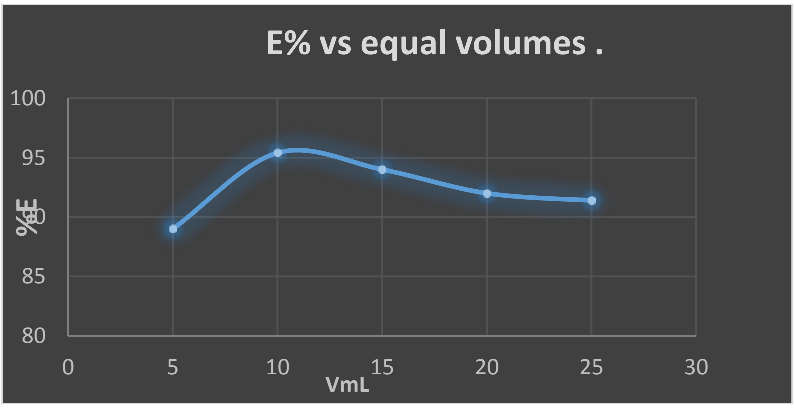

Figure 4. Study the effect of equal volumes

10-Accuracy of the ultrasound extraction method:

An analyzing sample was made from a substance called copper solution with a concentration of (0.06356ppm), and it was analyzed by both methods. This ultrasonic extraction technique was compared to the traditional approach described in [13], which uses funnel division in the dithizone extraction procedure. Using the ideal conditions investigated for the ultrasonic extraction—pump speed (3mL/30sec), vibration time (8min), and temperature (25–30°C)—the extraction degree was higher (90 ± 0.2). The table shows the outcomes.

Table 6

Comparison of the results of ultrasonic extraction and the conventional method

Extraction method	Cu(II) concentration (ppm)	Dithizone concentration (M)	shake time (min)	D	E%
ultrasound extraction	1000	0.001	8	10	90%
Traditional[14]	1000	0.001	30	1.73	78.5 %

11-Conclusions:

The phenomenon of ultrasound has been used as a new method in the extraction process.

It showed good results and is close to the method of classical extraction.

Finding a new method for the process of withdrawing the organic layer from the aqueous layer or vice versa using a pump.

The use of the pump in the process of pumping the reagent solution to the metal solution at a constant rate of speed for ease and speed of work.

Control the device's vibration time (increase or decrease) and adjust the temperature using bubbles.

The conclusion from (Table 6) shows that the novel extraction technique using the ultrasound device is suitable for ease of use, speed of work, reduction of material and solvent use, as well as the minimal environmental impact that enters it in the use of green chemistry. In contrast to multiple extractions, which require additional time and physical effort when employing a separation funnel, ultrasound extraction is completed in a single step.

References

[1] M. A. Khalikova, E. Lesellier, E. Chapuzet, D. Šatínský, and C. West, “Development and validation of ultra-high performance supercritical fluid chromatography method for quantitative determination of nine sunscreens in cosmetic samples,” *Anal. Chim. Acta*, vol. 1034, pp. 184–194, 2018.

[2] Agency for Toxic Substances and Disease Registry (ATSDR) Toxicological Profile for Copper. Atlanta, GA: Centers for Disease Control; 2002. [Google Scholar].”)([“Tchounwou P, Newsome C, Williams J, Glass K. Copper-induced cytotoxicity and transcriptional activation of stress genes in human liver carcinoma cells. Metal Ions Biol Med. 2008;10:285–290. [PMC free article] [PubMed] [Google Scholar].”

[3] C. Leong and L. Lebel, “Can conformity overcome the yuck factor? Explaining the choice for recycled drinking water,” *J. Clean. Prod.*, vol. 242, p. 118196, 2020.

[4] D. Bakircioglu, N. Topraksever, and Y.B. Kurtulus, J AOAC Int. 100, 1531 (2017)

[5] E. Vanli, M.N. Mısır, H. Alp, T. Ak, N. Özbek, Ü. Ocak, and M. Ocak, J. Fluoresc. 27, 1759 (2017).

[6] M. Ghorbani, M. Aghamohammadhassan, H. Ghorbani, and A. Zabihi, “Trends in sorbent development for dispersive micro-solid phase extraction,” *Microchem. J.*, vol. 158, p. 105250, 2020.

[7] P. Medeiros and M. Sivapalan, "From hard-path to soft-path solutions: slow–fast dynamics of human adaptation to droughts in a water-scarce environment," *Hydrol. Sci. J.*, vol. 65, no. 11, pp. 1803–1814, 2020.

[8] Paula, H.M., Oliveira Ilha, M.S. and Andrade, L.S. (2014). Concrete Plant Wastewater Treatment Process by Coagulation Combining Aluminum Sulfate and Moringa oleifera Powder. Journal of Cleaner Production, 76, 125-130."

[9] S. F. Hammad, I. A. Abdallah, A. Bedair, and F. R. Mansour, Homogeneous liquid–liquid extraction as an alternative sample preparation technique for biomedical analysis," *J. Sep. Sci.*, vol. 45, no. 1, pp. 185–209, 2022.)(I. S. Kurtz, S. Sui, X. Hao, M. Huang, S. L. Perry, and J. D. Schiffman, "Bacteria-resistant, transparent, free-standing films prepared from complex coacervates," *ACS Appl. bio Mater.*, vol. 2, no. 9, pp. 3926–3933, 2019.

[10] toxicity and oxidative stress," *J. Vasyl Stefanyk Precarpathian Natl. Univ. Ser. Soc. Hum. Sci.*, no. 2, 1, pp. 39–51, 2015.

[11] R. Dahal, K. Moriam, and P. Seppala, "Downstream process: liquid-liquid extraction," *Chem. Technol. AALTO Univ.*, 2016