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Vortex-Assisted Liquid-Liquid Extraction: An Innovative Approach for Copper Separation

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This study introduces an innovative, highly sensitive, and precise liquid-liquid extraction method based on the vortex phenomenon. A specialized extraction system was developed, incorporating two key components: a magnetic stirrer to generate the vortex and a pump to transfer the organic layer from the liquid-liquid system. The method's efficiency was evaluated using dithizone (0.01M) dissolved in CCl_4 and an aqueous Cu(II) chloride solution (1000 ppm), with key variables systematically investigated to optimize extraction performance. The optimal conditions for extracting Cu(II) from a 10 mL aqueous solution were determined as follows: a copper concentration of 0.0001M, a 10 mm magnetic stirrer, a shaking time of 15 minutes, and a pump flow rate of 3 mL/30 sec. Under these conditions, an impressive extraction efficiency of 92.5% was achieved. To assess the effectiveness of this novel vortex extraction technique, a comparative analysis was conducted against the traditional separation funnel method. The results confirmed that the vortex method is more efficient, faster, and significantly reduces solvent consumption, making it a promising alternative in analytical chemistry. Furthermore, a t-test analysis demonstrated a statistically significant improvement ($p < 0.05$) in extraction efficiency compared to conventional techniques.

Keywords: vortex extraction, dithizone, peristaltic pump, rotating magnetic stirrer, liquid-liquid extraction, t-test

Introduction

The concept of the vortex phenomenon is a concept as old as the topic of hydrodynamics, and it can be defined in fluid dynamics as a region in a fluid in which the flow rotates around the axis line and the rotational movement of fluids and maybe a straight or curved vortex formed in moving fluids [1]. It can be seen in many regular flow structures such as winds surrounding a tropical cyclone, eddies in the wake of a boat, and vortices in the tail of an aircraft [2-3]. This phenomenon has attracted the attention of many researchers and interested people during the past decades, and with the development of the phenomenon of vortices took an important space in many techniques, it had an important impact on medical applications such as four-dimensional heart blood flow and assessment of cerebral aneurysm risk [4-5]. This phenomenon has also been introduced as a new technology in many fields such as energy extraction from vortex motion [6], the transport processes in eddy flows applied to coal-fuel vortex furnaces [6], and renewable energy generation by eddy-induced motion [7] and in aircraft turbines [7], etc. The extraction separation method is considered one of the important methods in analytical chemistry and is widely used to determine the amount of a substance in a sample [8-9]. Extraction has many applications in almost all industries, such as pharmaceuticals, effluent treatment, petroleum, etc., depending on the properties of the material to be extracted [10]. More attention has been devoted to replacing traditional extraction techniques with modern, environmentally friendly ones in order to be more ergonomic, inexpensive, fast, and safe [10], to reduce the quantity and toxicity of the solvents and reagents used in the measurement step of the automated analyzers [10]. Thus, newly developed extraction techniques such as micro-solid-phase extraction (SPME) [11] and partial liquid-phase extraction (LPME) are proliferating [12]. Among the extraction methods that can be included in modern chemical separation methods, we cite ultrasound-assisted extraction (UAE) [13-14], microwave-assisted extraction (MAE) [15], supercritical fluid extraction (SFE) [16], and pressurized fluid aid extraction (PLE) [17]. The main objective of these methods is to reduce the extraction time and energy consumption, which is reflected in the final cost reduction, and this is one of the important aspects of these technologies, because they protect the environment and enhance the economic competitiveness and innovation of industries [10]. In this study, an innovative method was proposed to make the extraction easier and accurate and give high rates of extraction. The vortex extraction method offers significant environmental advantages over conventional techniques by reducing solvent consumption and minimizing waste, aligning with green chemistry principles. Its efficient design enhances phase separation and mass transfer, improving extraction yields while promoting sustainability. Additionally, the system's scalability makes it well-suited for industrial applications, particularly in the pharmaceutical and petroleum industries. Future research could focus on optimizing the method for a wider range of solvents and analytes, further expanding its applicability across various industrial and environmental settings [18].

Experimental part

Chemicals. All chemicals used in this study were supplied by Fluka and BDH. A dithizone solution was prepared at a concentration of 0.01M by dissolving 0.0256 mg in 10 mL of carbon tetrachloride. To obtain a 0.001M dithizone solution, 5 mL of the 0.01M solution was diluted to 50 mL in a standard volumetric flask using carbon tetrachloride. The solution was stored in an opaque bottle to protect it from light.

An aqueous copper(II) chloride solution was prepared at a concentration of 0.01M by dissolving 0.42625 mg in a small volume of distilled water, followed by dilution to 250 mL in a standard volumetric flask. For further experimentation, a 0.0001M copper(II) chloride solution was prepared by taking 0.5 mL of the 0.01M solution and diluting it to 50 mL with distilled water in a standard volumetric flask, yielding a final copper(II) concentration of 0.635 ppm. The pH of the copper(II) chloride solution was adjusted to pH = 1 for the study.

Equipment. The equipment used in this study included a Nahita SH-3 magnetic stirrer for vortex generation and mixing, and an Ismatec peristaltic pump for controlled liquid transfer during the extraction process. A WTW Series pH meter (Germany) was employed for precise pH measurements, ensuring optimal experimental conditions. Additionally, the concentration of copper ions in the extracted solutions was determined using a SHIMADZU 6300 atomic absorption spectrophotometer.

Vortex extraction working procedure

In this method, a 0.001M dithizone solution is pumped through a rubber tube using a peristaltic pump, with the pump velocity stabilized at 30 sec/mL. The solution is then introduced into a specified volume of copper(II) chloride solution under optimized extraction conditions. These conditions include a temperature of 25–27°C, a pH of 1, and a magnetic stirrer rotation speed of 2000 rpm, which generates a vortex using a 10 mm rotating magnetic pole. The extraction process is carried out with a fixed vibration time of 15 minutes to ensure efficient phase interaction and maximum extraction efficiency.

Results and Discussion

Vortex extraction system design

A new vortex-based extraction system was designed using a magnetic stirrer, where the working mechanism is based on vortex formation. This system allows for multiple extractions in a short period while enabling easy monitoring of each stage of the extraction process. The system design, as illustrated in Figure 1, consists of the following key components:

1. *Magnetic stirrer* – The core component of the system, responsible for generating the vortex effect.
2. *Rotating magnetic stir bars* – Available in four different sizes (10 mm, 15 mm, 20 mm, and 25 mm), these stir bars influence the shape and size of the vortex, optimizing interaction within the metal solution during extraction.
3. *Peristaltic pump* – Facilitates the controlled transfer of the reagent solution to the sample, ensuring efficient back-and-forth movement for enhanced extraction.
4. *Thermometer* – Used to maintain a stable temperature range of 25–27°C during the extraction process.
5. *Transparent McCartney bottle* – A 40 mL container (diameter 29 mm, height 92 mm) that remains securely fixed throughout the study.

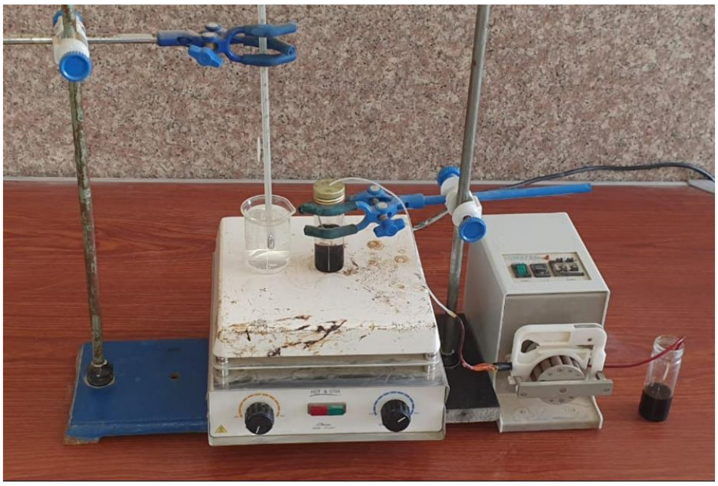

Figure 1. Experimental setup of the vortex-based extraction system.

Stages of the vortex extraction process

Vortex extraction involves pumping a specific volume of organic-phase dithizone solution into a specific volume of aqueous copper(II) chloride solution contained within a glass vessel. Inside this vessel, a rotating magnetic stir bar generates a vortex, initiating the extraction process. As the reaction progresses, the solution transitions from green to dark red, indicating the formation of the dithizone-copper complex and the completion of the extraction process. A key factor that enhances the extraction rate is the increase in the interfacial surface area between the organic and aqueous layers. This is achieved through two primary mechanisms in this novel vortex-based method: 1) Ellipsoidal Vortex Motion: The rotational motion of the magnetic stirrer generates thousands of bubble-like organic-phase droplets within the aqueous phase, significantly enhancing phase interaction. 2) “Devil’s Face” Phenomenon: Once the peristaltic pump and magnetic stirrer stop, the vortex-induced structures multiply, forming a distinctive pattern resembling a “devil’s face.” This phenomenon further increases the contact area between the two layers, facilitating a more efficient extraction process. This mechanism is visually represented in Figures 2 and 3, illustrating how the increased interfacial area accelerates extraction efficiency. After the extraction process, the organic layer is withdrawn in reverse using the peristaltic pump, and the remaining copper content in the aqueous phase is measured using flame atomic absorption spectroscopy [19, 20]. Figure 3 presents a sequential view of the extraction stages, highlighting the role of the vortex phenomenon in enhancing phase interaction and mass transfer.

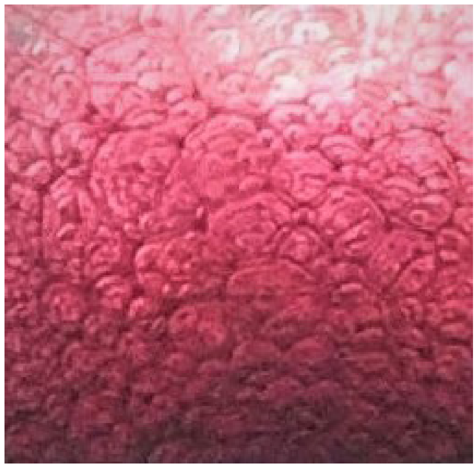

Figure 2. Formation of bubble-like structures in the organic layer.

The effect of main variables on the vortex extraction process

In this study, four key variables were investigated to determine their influence on the efficiency of vortex extraction. The primary objective was to evaluate their impact on the extraction percentage (%E) and the distribution constant (D).

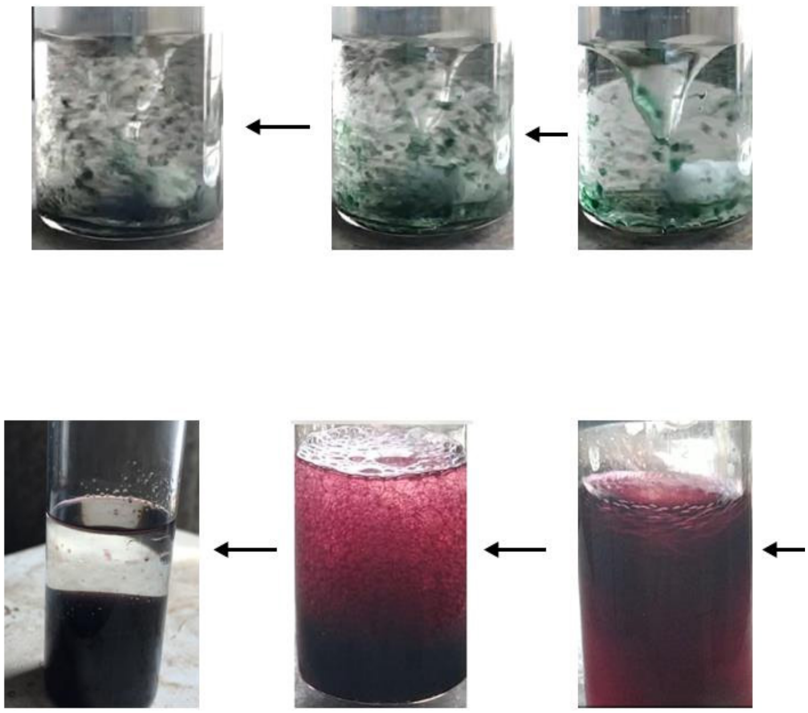

Figure 3. Sequential stages of the vortex extraction process.

Effect of copper(II) chloride concentration

Thermodynamic and kinetic equilibrium principles [21, 22] indicate that the concentration of metal ions directly affects the formation of the extracted complex, which is crucial for achieving optimal values of the distribution constant (D) and extraction efficiency (%E). To examine this effect, two copper(II) chloride solutions (10 mL each) were prepared with different concentrations: 0.001M and 0.0001M, both adjusted to pH = 1. The extraction process was carried out by pumping 10 mL of a 0.001M dithizone solution into each copper(II) chloride solution using a peristaltic pump at a flow rate of 3 mL/30 sec. The extraction was facilitated by vortex mixing with a 10 mm rotating magnetic stir bar, and the solutions were shaken for 5 minutes. After extraction, the organic phase was separated from the aqueous phase using the pump, and the remaining copper concentration in the aqueous layer was measured. Following the calculation of D and %E, it was observed that the 0.0001M Cu(II) solution yielded a significantly higher extraction efficiency compared to the 0.001M solution. This result suggests that lower Cu(II) concentrations favor the formation of the extracted complex under vortex conditions, enhancing the efficiency of the process.

Effect of shaking time

To investigate the effect of shaking time on the extraction efficiency, four equal volumes (10 mL each) of copper(II) chloride solution and dithizone solution were processed using the vortex extraction method, while varying the shaking time at 5 min, 10 min, 15 min, and 20 min. The extraction was performed under constant conditions, including a peristaltic pump speed of 3 mL/30 sec and a rotating magnetic stir bar size of 10 mm. Figure 4a illustrates that the extraction efficiency (%E) increases as the shaking time increases. This trend suggests that longer vortex agitation enhances phase interaction, allowing more time for the formation of the extracted complex. However, 15 minutes was identified as the optimal shaking time, as it provided a high extraction efficiency while minimizing excessive energy consumption. Beyond this duration, the increase in extraction efficiency was marginal, making longer shaking times unnecessary.

Effect of rotating magnetic pole size

In this study, the same experimental conditions as previously described were maintained while varying the size of the rotating magnetic pole. (10 mm, 15 mm, 20 mm, and 25 mm) to assess its impact on the extraction efficiency (%E).

As shown in Figure 4b, %E initially increases with an increase in magnet size but begins to decline at larger sizes. The results indicate that the 10 mm and 15 mm magnetic stir bars generate a stable and well-formed vortex, effectively enhancing phase interaction and facilitating efficient extraction. However, with 20 mm and 25 mm magnetic poles, the vortex motion becomes turbulent and unstable, disrupting the extraction process and leading to a decrease in efficiency. Thus, the 10 mm and 15 mm sizes were identified as the most suitable for generating an optimal vortex, ensuring consistent mixing and efficient extraction within the given solution volume.

Effect of pump speed

In this study, the same experimental conditions were maintained while varying the peristaltic pump speed at four different rates: 3 mL/30 sec, 5 mL/30 sec, 7 mL/30 sec, and 9 mL/30 sec. The objective was to assess how the pump flow rate influences the extraction efficiency (%E). As illustrated in Figure 4c, extraction efficiency initially increases with an increase in pump speed but declines at higher speeds. This trend occurs because moderate flow rates allow sufficient time for vortex formation and optimal phase interaction, maximizing the contact surface area between the organic and aqueous layers. However, at higher pump speeds, the vortex extraction process is disrupted, preventing the organic layer from fully interacting with the aqueous phase, leading to a decrease in %E. Based on these results, a pump speed of 3 mL/30 sec was identified as the optimal flow rate, providing a balance between controlled reagent introduction and efficient vortex formation for maximum extraction efficiency.

Statistical analysis: t-test for extraction efficiency

To evaluate the effectiveness of the vortex extraction method, a t-test was conducted to compare its extraction efficiency with that of the traditional separation funnel method. The statistical analysis aimed to determine whether the observed improvement in efficiency is statistically significant.

Hypothesis Formulation: Null hypothesis (H_0): There is no significant difference in extraction efficiency between the vortex method and the traditional method Alternative hypothesis (H_1): The vortex method provides a significantly higher extraction efficiency than the traditional method.

The extraction efficiencies for both methods are summarized in Table 1.

Table 1. Comparison of Vortex Extraction and Traditional Method.

Method	Mean Extraction Efficiency (%)	Standard Deviation (SD)	Sample Size (n)
Vortex Extraction	92.5	1.8	5
Traditional Method	78.5	2.3	5

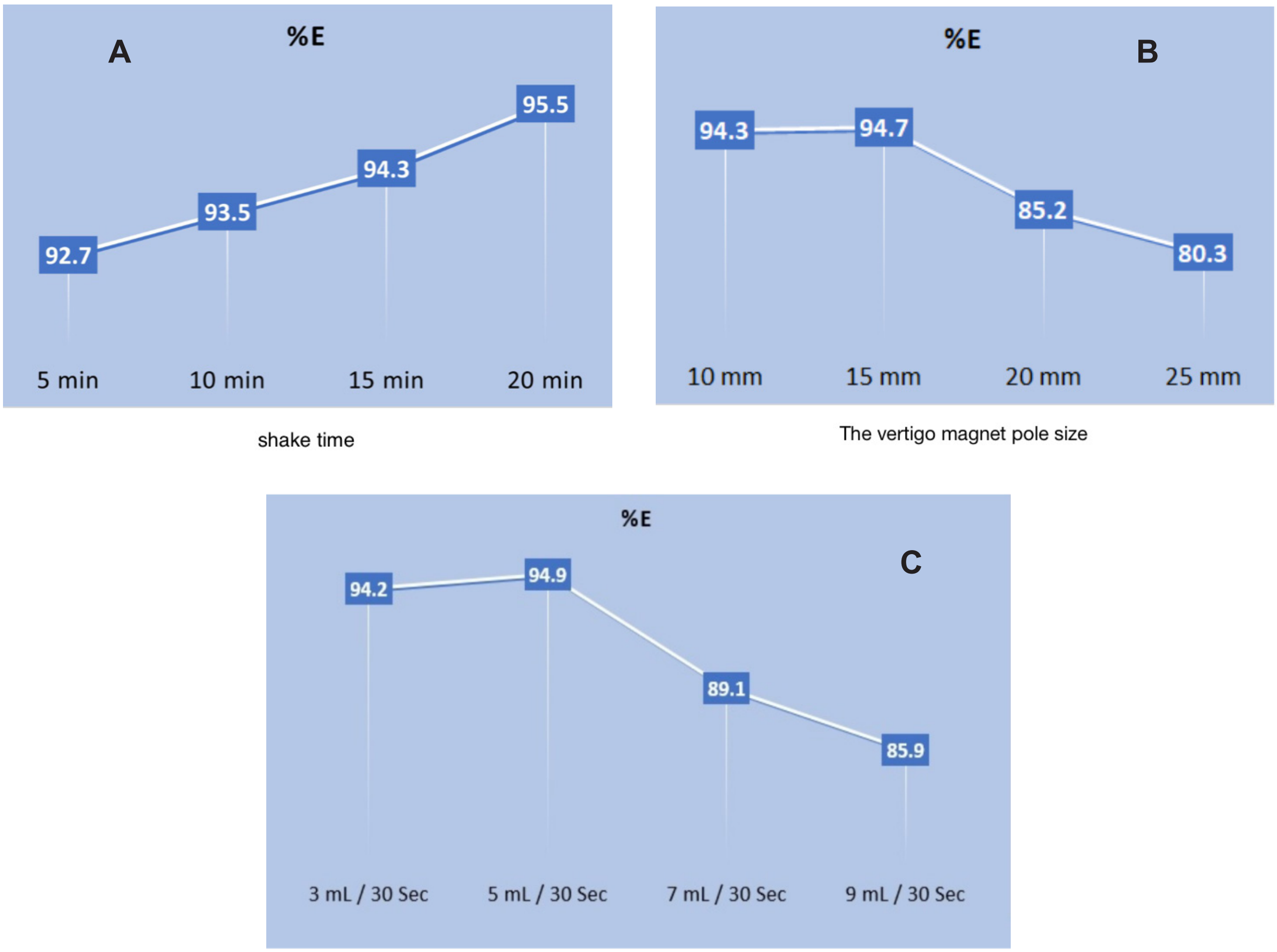

Figure 4. Effect of a) shaking time, b) rotating magnetic pole size, c) pump speed on extraction efficiency in the vortex extraction process.

The calculated t-value is 10.72, which is significantly high. The critical t-value at a 95% confidence level (α = 0.05) for degrees of freedom (df = n1 + n2 - 2 = 8) is 2.31. Since the calculated t-value (10.72) is much greater than the critical t-value (2.31), we reject the null hypothesis (H_0) and conclude that the vortex extraction method provides a significantly higher extraction efficiency than the traditional method ($p < 0.05$). This statistical validation confirms that the vortex method is a superior extraction technique, offering greater efficiency, reduced processing time, and lower solvent consumption [23].

Accuracy of the vortex extraction method

To evaluate the accuracy and effectiveness of the vortex extraction method, its performance was compared to the traditional separation funnel method, as described in [24]. An analytical sample of copper(II) solution with a concentration of 1000 ppm was prepared and analyzed using both methods. The vortex extraction process was conducted under optimized conditions, including: Pump speed: 3 mL/30 sec; Magnetic stir bar size: 10 mm; Shaking time: 15 minutes; Temperature: 25–27°C; Dithizone concentration: 0.001 M. Under these conditions, the extraction efficiency (%E) for the vortex method was determined to be 92.5 ± 0.2%, which was significantly higher than the efficiency obtained using the traditional method. The comparative results are summarized in Table 2.

Table 2. Comparison of extraction efficiency between the vortex extraction method and the traditional separation funnel method [22].

Extraction method	Copper(II) concentration, ppm	Dithiazone concentration	E%	Shake time
Vortex	1000	0.001 M	92.5	15 min
Traditional	1000	0.2 M	78.5	30 min

Conclusions

The results confirm that the innovative vortex extraction method offers significant advantages over the traditional separation funnel method. This technique stands out due to its ease of operation, speed, reduced material and solvent consumption, and minimal environmental impact, making it highly compatible with green chemistry principles. Unlike conventional multi-step extraction, which requires extended processing time and manual effort using a separation funnel, the vortex extraction method completes the process in a single step, significantly improving efficiency, reproducibility, and sustainability. The method's ability to enhance phase interaction through vortex-induced motion results in a higher extraction efficiency (%E), making it a superior alternative for analytical applications. Furthermore, the scalability of this technique makes it suitable for various industrial applications, including pharmaceutical, environmental, and petroleum industries, where efficient and environmentally friendly extraction methods are in high demand. Future research could focus on optimizing the vortex system for different solvents, analytes, and real-world sample matrices to further expand its applicability. Thus, the vortex extraction method is a promising advancement in analytical chemistry, combining high efficiency, operational simplicity, and environmental sustainability, making it an excellent alternative to traditional extraction techniques.

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