

Original Research Article

Preconcentration and Separation of Ultra-Trace Cu (II) with Disks of Octadecyl Silica Membrane Modified Nano-Fe₃O₄-Encapsulated-Dioctyl Phthalate and Linked-Diethylenetriamine

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ARTICLE INFO

Article history

Submitted: 02 December 2020

Revised: 16 January 2021

Accepted: 01 February 2021

Available online: 01 February 2021

Manuscript ID: [AJCA-2012-1230](#)

DOI: [10.22034/AJCA.2021.260252.1230](https://doi.org/10.22034/AJCA.2021.260252.1230)

KEYWORDS

Cu²⁺

Separation

Octadecyl silica membrane

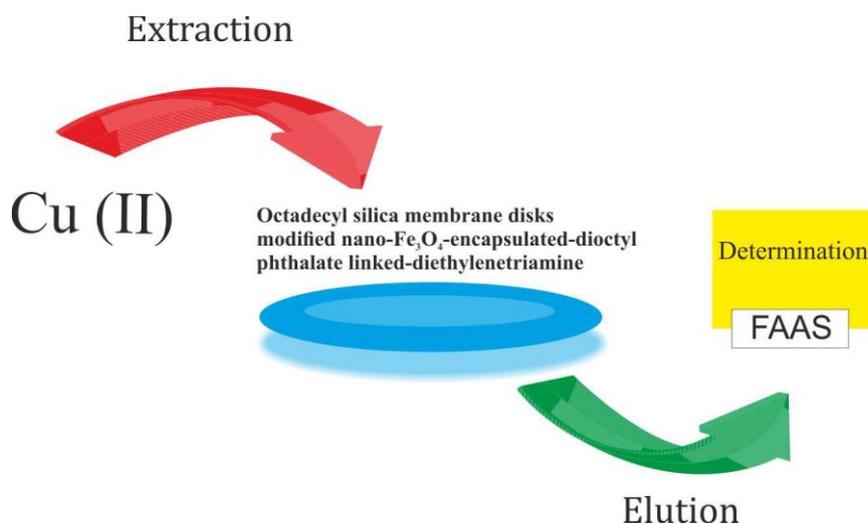
Fe₃O₄-encapsulated

Magnetic nano-Fe₃O₄-DOP-DTA

ABSTRACT

In this study, an efficient method was performed to extract and measure the Cu(II) metal ions using the modified disks of octadecyl silica membrane by nano-Fe₃O₄-encapsulated-dioctyl phthalate and linked-diethylenetriamine (magnetic nano-Fe₃O₄-DOP-DTA). This method involves forming a complex on the ENVI-18 DISK™ surfaces, followed by maintained species removed from the surface with the least amount of organic solvent. The act of elution in this technique is very impressive. The important factors are including the pH, stripping solvent, ligand values, rate of sample flow, and the effect of interfering ions were evaluated. The preconcentration factor was 500 in the optimum analysis situations of whole parameters. Analysis parameters contain the limit of detection and the most capacity of copper (II) ions sorption was achieved 6 µg/L and 385 ± 5 µg, respectively. Finally, the Cu²⁺ ions were extracted in various aqueous solutions by this technique.

GRAPHICAL ABSTRACT



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Introduction

Copper metal at little concentrations as a toxic substance causes environmental damage to pelagic and marine ecosystems [1-3]. Copper metal in high and low levels has different effects on herbs' life. At higher than allowed levels, copper ions stop the transfer process from the cell wall. Normal metabolism of many organisms requires 38 $\mu\text{g/L}$ of Cu^{2+} ions [4]. Moreover, in many industries copper has been recognized as a key element. Therefore, research on new methods for effective extraction, and measuring the concentration of this metal at very low levels in a diversity of manufacturing, pharmaceutical, and environmental samples is important. Assessment of Cu^{2+} ions is usually done by atomic absorption spectroscopy, and other spectrometric methods [5]. The preconcentration step of copper ions from different biological and aqueous samples causes separation from other metals and more accurate copper ions measurement. Significant procedures for the extraction of Cu^{2+} ions such as liquid-liquid microextraction have been developed in the attendance of various classical co-extraction ligands, and macrocyclics [3,6].

However, classical techniques for extracting various metals may have some disadvantages such as long-term use of major amounts of excellent purity solvents. Commonly used device methods for removal of Cu^{2+} metal ions include liquid technique chromatography [7], flotation [8], liquid membrane [9], aggregate film formation [10], ion-pairing [11], supercritical fluid extraction [12], adsorption of the column from the composite of pyrocatechol violet-copper on activating carbon (heavy metals are extracted by a liquid membrane supported by hollow fibers containing a mobile carrier) [13], SPE extraction method using cartridge and C_{18} membrane disks [14].

One interesting and important method used for rapid preparation for extraction analysis is a

solid-phase extraction (SPE) method. This method has been introduced as an alternative to classical LLE (liquid-liquid extraction) methods, which reduces the application of expensive solvent, solvent disposal costs, long separation times for pre-concentration, and sample separation [15-17]. The use of SPE-bonded silica disks with octadecyl has been growing in recent years to determine and extract various organic species from biological matrices [18]. Furthermore, suitable ligands have been utilized for surface modification of SPE disks. These modified disks have demonstrated acceptable results in the extraction of heavy metal ions [19].

In this work, we have tried to develop a fast, selective, sensitive procedure for pre-concentration of an extremely low amount of copper (II) in aqueous media with disks of octadecyl silica modified nano- Fe_3O_4 -encapsulated-dioctyl phthalate and linked-diethylenetriamine. Finally, the copper (II) ions desorbed has been determined using the atomic absorption spectrometer.

Experimental

Chemicals

Acidic solutions (formic acid, hydrochloric acid, nitric acid), organic solvents (high purity), methanol, and chloroform (HPLC grade) were prepared from the Merck Co. The nitrate of lithium, magnesium, barium, potassium, lead, zinc, sodium, nickel, cadmium, calcium, zinc, strontium, and cobalt (II, III) were prepared in analytical grade. The double-distilled water with ultra purity was used in the experiment.

The solution of copper (II) as a stock solution was prepared following dissolved the powder of Cu metal (0.1000 g) in nitric acid solution (10 mL) and then diluted in a calibrated flask (1000 mL) with distilled water. The other solutions (working solutions) were prepared from stock copper(II) solution. All the dilutions were prepared with the highest pure deionized water.

Diethyl phthalate, sodium hydroxide (NaOH), DOP (purity > 99.55%) and diethylenetriamine (DTA) was purchased from BDH, UK.

Preparation of magnetic Nano-Fe₃O₄ adsorbent

The magnetic nano-Fe₃O₄ was first synthesized from the previously reported method [20]. A sample of FeCl₃·6H₂O powder (6.1 g) and FeSO₄·7H₂O powder (4.2 g) were added to the double-distilled water (100 mL). A solution of 6.5 M from NaOH (25.0 mL) was poured drop by drop into the before solution. This mixture was stirred for 240 min. After adding the NaOH solution, the nano-Fe₃O₄ was formed (black precipitate). This precipitate was washed with deionized water, and then was separated using the magnetic field, and collected precipitate dried at a temperature of 70 °C [21].

Preparation of Nano-Fe₃O₄-DOP adsorbent

The nano sorbent of Fe₃O₄-encapsulated-DOP was synthesized by adding the DOP (20.0 mL) to the nano-Fe₃O₄ sorbent (10.0 g). This mixture was stirred for 180 min at 90 °C and then the product was separated and washed with methanol, and then again was separated with the magnetic field and lastly dried at a temperature of 70 °C [21].

Preparation of magnetic Nano- Fe₃O₄ -DOP-DTA adsorbent

The nano-Fe₃O₄-DOP (10.0 g) addition to DTA (5 mL) and this mixture was blended with heavy grinding, then was mixed for 300 min with mortar. The nano-Fe₃O₄-DOP-TETA adsorbent is dried at 60 °C.

Apparatus

Determination of copper (II) ions of the samples was performed using the atomic absorption spectrometer with a model of Varian spectra A 200 and equipped with HI-HCl hollow cathode

lamp. The other information includes 0.7 nm of slit width, 324.8 nm of resonance fine, 15 mA of current, background correction with Deuterium lamp, air/acetylene (flame), and 1.7 mL/min for Acetylene flow. Measurement of pH was performed by a pH meter with GP 353 model.

Sample extraction

SPE was carried out by disk of the glassy membrane, ENVI-18DISK™, phase of octadecyl silica bonded with 30 μm of particle and with a pore size of 70 Å (47×0.6 mm) prepared from Supelco in linkage with filtration apparatus in 47 mm of standard Millipore and equipped with a vacuum pump [22].

Sample treatment

The nylon filters (45 μm) was used to filter the aqueous samples. Polyethylene bottles were used for sampling. The containers were soaked in HNO₃ solution (1 M) overnight, then washed with distilled water. This experiment was performed in two days of sampling. Before analysis, a methanol solution (5 mL) was poured into a 90 mL part of the sample. The surface of the disks that are not modified with magnetic nano-Fe₃O₄-DOP-DTA and therefore can not retain copper (II) ions properly. In lieu, magnetic nano-Fe₃O₄-DOP-DTA (10 mg) was dissolved in 5 mL suitable of the water-miscible organic solvent. The most suitable solvent was acetone in process of analysis. The solution of magnetic nano-Fe₃O₄-DOP-DTA was poured copper (II) aqueous solution and then stirred until extraction of copper (II) metal ions.

Cleaning and conditioning of disk

Contamination from the environment and construction process of the disks are eliminated by placing in the device with a solution of methanol (10 mL). Then, as the air passes, the discs dry in a few minutes. The disk was washed again for effective extraction of the analytes with

methanol (10 mL) and water without disk surface drying. In the pre-extraction step, the surface of the disk must be wetted. Due to improper performance at this stage, it demonstrated flow rate and low analyte recovering. Before adding the sample, a noteworthy point for the surface of the disk is to avoid contact with air.

Sample addition

After the homogenization step, the sample solution with the exact volume (100 mL) transferring from the disk device to the top reservoir. Meanwhile, the sample solution was drained via disk using a moderate vacuum. The vacuum was used for 5 min until the disks dried.

Analyte elution

The analyte was selectively was eluted when only 5 mL of 0.1 M of acidic HCl solvent in methanol passed via a disk, and then solution collecting with a volumetric flask (5.0 mL) from the extraction funnel. The results revealed that the excellent eluting agents were alcoholic

Table 1. The effect of the presence of magnetic nano- Fe_3O_4 -DOP- DTA on extraction percent of Cu^{2+} ions^a

magnetic nano- Fe_3O_4 -DOP-DTA	pH	Cu^{2+} ions extraction (%)
Presence	2 to 6	96.4(2.4) to 63(2.2)
Absence	2 to 6	0.01(4.5) ^b

^a sample: Cu^{2+} ions (10 μg) in water (100 mL).

^b RSD_s (five individual analyzes)

Eluent selection

In this section, the proper eluent was chosen to recover the Cu^{2+} ions from the disk. 5 mL of various solvents of organic and different nonorganic (10% of methanol, V/V) were assessed. The result is presented in Table 2. Methanol or ethanol solvents (5 mL) revealed the best results for quantitative washing of Cu^{2+} ions of the disk. In this process, the hydrophobic surface of the disc will be further contacted with the eluent solvent by methanol.

organic solvents with the highest purity. By drawing the calibration curve by FAAS, the Cu^{2+} ions concentration was determined.

Results and Discussion

Study of ligand role

The efficacy of magnetic nano- Fe_3O_4 -DOP-DTA adsorbent presence on the amount of extraction of Cu^{2+} ions was performed using some experiments. The results demonstrated which the membrane disk alone does not keep the Cu^{2+} ions; however, the usage of an aqueous sample of Cu^{2+} ions (100 mL) with Cu^{2+} ions (10 μg) and magnetic nano- Fe_3O_4 -DOP- DTA (10 mg) led to proper retention (Table 1). Another cause could be a strong interaction between Cu^{2+} ions and magnetic nano- Fe_3O_4 -DOP-DTA. It is worth mentioning that the stable complexes formed between the Cu^{2+} and magnetic nano- Fe_3O_4 -DOP-DTA at acidic pH might be due to the procedures of ion-pair. Meanwhile, at higher pH (>2), the retention of Cu^{2+} ions recovery was found to be insignificant.

pH effect

All solutions pH was set to various pH value 2 to 9 by suitable buffer (sodium acetate, monosodium phosphate, hydrochloric acid, disodium phosphate, and acetic acid), and then these samples used for disks [23, 24].

Finally, pure ethanol or methanol used for stripping the Cu^{2+} ions, and then the eluted ions were determined by FAAS. Figure 1 displays the result of recovery from Cu^{2+} ions in different pH. As the results show, the recovery of Cu^{2+} ions at

pH values between 4 and 4.5 is the maximum. Also by increasing the pH, the recovery was reduced. This is since in an acidic solution with protonation of magnetic nano-Fe₃O₄ -DOP- DTA happens, as a result, little interaction will occur between the copper (II) and magnetic nano-Fe₃O₄-DOP-DTA, whereas, at higher pH of 5, the Cu(OH)₂ is produced. Therefore, the buffer with a pH of 4.5 (sodium acetate-acetic) was applied for

copper (II) preconcentration. In addition, because octadecyl silica within the disk is hydrolyzed and at a pH above 7 and also precipitates Cu(II) ions, other solvents with pH above 7 were not examined. Furthermore, at lower pH of 4, the atoms of nitrogen of the magnetic nano-Fe₃O₄-DOP-DTA can be protonation and reduced the complex stability.

Table 2. Effect of various solvents on elution of Cu²⁺ ions from the disk ^a

Elution solvent	Recovery (%)		
	2 (mL)	5 (mL)	10 (mL)
Acetonitril	32.7(4.2) ^b	42.7(5.2)	53.3(3.5)
Acidified methanol ^c	55(2.1)	87.0(2.0)	83.7(1.5)
Ammoniacal methanol ^d	55(2.3)	87.3(2.1)	83.7(2.0)
Methanol	81(2.1)	94.3(2.4)	93.8(2.5)
10% methanol (V/V), Formic acid (1 M)	54.7(1.0)	63.6(1.8)	71.2(2.1)
10% methanol (V/V), Hydrochloric acid (1 M)	58.7(1.7)	91.8(2.2)	91.4(2.7)
10% methanol (V/V), Hydrochloric acid (1 M)	52.7(2.3)	84.7 (2.1)	92.8(1.5)
10% methanol (V/V), Nitric acid (2 M)	52.5(1.7)	82.6(2.0)	87.6(1.4)
10% methanol (V/V), Nitric acid(1 M)	33.7(2.3)	84.9(2.1)	89.4(1.5)
Ethanol	82.5(2.2)	95.3(1.7)	97.5(2.7)

^a sample: 10 µg of Cu²⁺ ions in 100 mL of water.

^b RSDs (five individual analyzes)

^c solvents with HCl (0.1M)

^d solvents with NH₃ (0.1M)

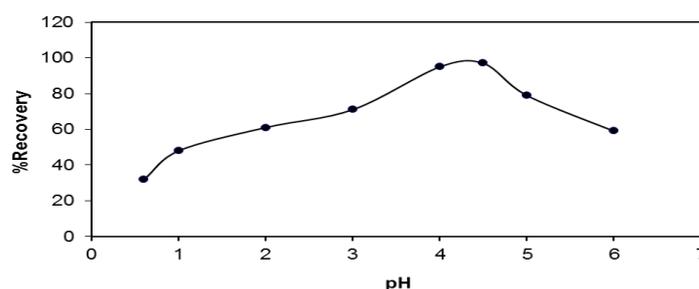


Figure 1. Effect of sample pH and solvent of magnetic nano- Fe₃O₄ -DOP- DTA on the recovery of copper (II)

Counter anions effect

The various counter anions have been investigated to evaluate their effect on the

copper (II) ions recovery. As can be seen, the counter anion nature directly affects the Cu²⁺ ions retention with the modified disk.

The retention result ascertained that the magnetic nano-Fe₃O₄-DOP-DTA acts like a neutral ionophore within a pH of 4.0 to 4.5, in consequence, the Cu²⁺ ion has been retained like a complex with membrane disk. Based on the results, acetate ions have the greatest effect as a counter ion for the extraction of copper(II) metal ions. Table 3 reveals the results of the concentration effect of CH₃COONa ions on Cu²⁺

ions recovery. As shown, by increasing the acetate concentration to 0.1 M, the recovery percentage of Cu²⁺ also increases. Furthermore, acetate ions act as an appropriate buffer in ion-pair formation. Therefore, no need to add a buffer solution in SPE extraction experiments.

Evaluation of the effect of various counter anions with a concentration of 0.01 M to recover copper (II) metal ions from the modified disk.

Table 3. Evaluation of the effect of various counter anions with a concentration of 0.01 M to recover Cu²⁺ ions from the modified membrane disk ^a

Anions	Recovery (%)
SCN ⁻	41.6
ClO ₄ ⁻	32.7
Br ⁻	22.9
Cl ⁻	21.7
Acetate	90.7
Picrate	70.3

^a sample: 10 µg of Cu²⁺ ions in 100 mL of water

Flow rate effect

Process rate is one of the significant factors affecting SPE extraction. Hereupon, the result of flow-rate on performances of extraction was

studied. The results of Figure 2 display that the retention of Cu²⁺ with a range of about 10-100 mL/min is not extremely affected flow rate and result in an acceptable and good result. So, the total flow-rate of the experiment was 89 mL/min.

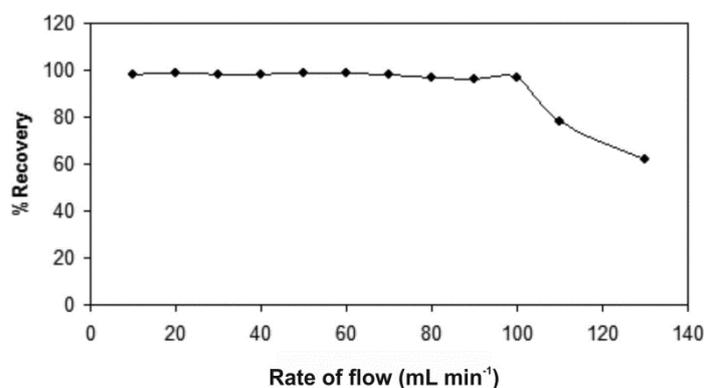


Figure 2. Extraction of copper (II) against in rate of flow

Amount of the magnetic nano-Fe₃O₄-DOP-DTA

The optimized amount of magnetic nano-Fe₃O₄-DOP-DTA for extraction of copper (II) ions evaluated by adding different amounts of magnetic nano-Fe₃O₄-DOP-DTA (2-20 mg).

Results of the test demonstrate that the copper (II) ions extraction was maximized with 10 mg of magnetic nano-Fe₃O₄-DOP-DTA in the solution (Table 4). Therefore, subsequent extractions were carried out with a 15 mg value of magnetic nano-Fe₃O₄-DOP-DTA.

Table 4. Influence of the magnetic nano- Fe₃O₄ -DOP- DTA value on the recovery of Cu²⁺ions ^a

Magnetic nano- Fe ₃ O ₄ -DOP- DTA amount (mg)	Recovery(%) of Cu ²⁺
2	28(1.9) ^b
5	40(2.8)
8	83(2.2)
10	94.7(2.7)
15	94.8(2.5)
20	94.7(2.2)

^a sample: 10 µg of Cu²⁺ ions in 100 mL of water.^b RSD_s (five individual analyzes)*Analytical performance*

When the solutions of 10 µg Cu²⁺ in the range 10-3000 mL in optimum situations were passed via the disk, copper (II) ions were retained in samples. Afterward, too have a concentration factor greater than 500 in this method, the breakthrough volume needs to be greater than 2500 mL. This procedure has a well linear range of 0.3-22 mg/L. The detection limit (LOD) and limit of quantitation (LOQ) for this procedure of determination of copper (II) ions were 6 and 24.50 ng per 1000 mL, respectively.

The modified disk's capacity (5 mg magnetic nano-Fe₃O₄-DOP-DTA) was characterized with a solution of 50 mL volume, 8 mg of Cu²⁺, and buffer of CH₃COONa/CH₃COOH (0.1 M) with a pH

value of 4.0-4.5, following by Cu²⁺ ions determination with AAS. Maximum disk capacity achieved from measurements (three replicate) is 387±2 µg of Cu²⁺ on the disk.

In binary mixtures of heavy metals, to survey in selective separation and extraction of Cu²⁺ ions, this method was used. The 50 mL of an aqueous solution comprising 10 µg copper (II) ions and mg value of different cations were derived. As seen in Table 5, the Cu²⁺ in the mixture was retained nearly entirely with the disks. However, the disks retain very few other ion metals and can be effectively extracted from copper (II) ions. In other tests, we found that concentrations greater than 0.5 M of NH₂OH.HCl was proper as a reducing agent.

Table 5. Extraction of Cu²⁺ in a mixture contains a cation ^a

Cation	Amount (mg)	Found (%)	Cu ²⁺ ions recovery(%)
Co ²⁺	2.23	1.7(2.6) ^b	99.6(2.2)
Zn ²⁺	2.56	1.90(2.2)	94.4(2.2)
Mg ²⁺	14.6	0.8(1.9)	94.2(1.4)
Hg ²⁺	0.42	2.44(2.2)	97.4(2.5)
Sr ²⁺	2.49	2.25(2.3)	94.1(2.4)
UO ²⁺	2.40	2.3(1.4)	94.1(2.8)
Mn ²⁺	2.54	1.65(2.7)	93.2(2.7)
K ⁺	92.7	1.22(2.4) ^b	94.2(2.6)
Ni ²⁺	1.39	2.2(2.4)	94.7(2.5)
Na ⁺	92.6	1.13(2.6)	94.3(1.5)
Cd ²⁺	2.54	1.95(2.4)	94.2(2.3)
Pb ²⁺	0.43	2.74(1.3)	97.6(2.2)
Ca ²⁺	23.8	2.45(3.3)	94.4(1.5)
Ag ⁺	2.35	3.25(2.5)	93.2(2.5)
Cr ³⁺	1.78	2.76(2.1)	97.6(2.8)
Ba ²⁺	2.44	3.23(2.6)	94.5(2.6)

^a sample: 10 µg of Cu²⁺ ions in 100 mL of water and acetate ions (0.1 M)^b RSD_s (five individual analyzes)

Water sample analysis

Various aqueous samples were used in a real sample to assess the usability of the technique for the extraction and specification of Cu²⁺ ions. Seawater from the Caspian sea, The rainwater (Tehran, 25 January 2020), tap water (Tehran), and snow water (Tehran, 15 February 2020) samples were analyzed (Table 6).

Table 6. Extraction of Cu²⁺ ions added in 1000 mL from various aqueous samples (CH₃COONa (0.1M) at pH= 4.0-4.5)

Aqueous samples	Cu ²⁺ ions (µg/L)	Cu ²⁺ ions recovery (µg/L)	Analysis of ICP-AES
Rain water	0.0	2.29(2.7) ^a	ND ^b
	10.0	12.45(2.2)	12.7
Tap water	0.0	1.54(1.6)	ND
	10.0	11.74(2.6)	11.5
Sea Water	0.0	12.07(2.7)	12.4
	10.0	22.25(2.5)	22.6
Snow water	0.0	4.03(2.3)	ND
	10.0	14.54(2.6)	14.1

^a RSDs (five individual analyzes)

^b Not detected

Conclusion

This study demonstrated that small amounts of copper (II) ions were successfully extracted by Octadecyl Silica membrane disks modified with magnetic nano-Fe₃O₄-DOP-DTA in aqueous samples. The proposed solid-phase extraction method was easy, reliable, accurate, with a high capability to determine the copper (II) ions in water samples. Moreover, this procedure was without interference comparing to other methods to assess the Cu²⁺ ions. The total flow-rate of the experiment was 89 mL/min. LOQ for this procedure of determination of copper (II) ions was 24.50 ng per 1000 mL. The most capacity of copper (II) ions sorption was achieved 385±5 µg. This technique can be applied as an alternative procedure for the determination and extraction of Cu²⁺ ions in binary mixtures.

Acknowledgment

The Cu²⁺ ions added to real samples can be successfully recovered (Table 6). According to the obtained results, the results of Cu²⁺ ion recovering are entirely dependable and are satisfied with the result obtained by the ICP-AES method.

Authors would like to acknowledge the Islamic Azad University of Varamin-Pishva for supporting this research study.

Disclosure statement

No potential conflict of interest was reported by the authors.

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HOW TO CITE THIS ARTICLE

Ali Moghimi*, Milad Abniki. Preconcentration and Separation of Ultra-Trace Cu (II) with Disks of Octadecyl Silica Membrane Modified Nano-Fe₃O₄-Encapsulated-Dioctyl Phthalate and Linked-Diethylenetriamine. *Adv. J. Chem. A*, 2021, 4(2), 78-86.

DOI: [10.22034/AJCA.2021.260252.1230](https://doi.org/10.22034/AJCA.2021.260252.1230)

URL: http://www.ajchem-a.com/article_125410.html