# Utilizing a Cost-Effective Adsorbent Material Derived from Coconut Coir Fiber Modified with Hydrazone Compounds for Efficient Removal of Copper from Aqueous Environments

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**Abstract:** A hydrazone compounds derived from the condensation of 2,4-dinitrophenyl hydrazine with acetophenone, acetaldehyde, and benzophenone, were synthesized and their selectivity towards transition metal ions were investigated. The ligands were isolated in satisfactory yield of 75 %, 57 % and 85 % respectively. Sorbent material based on these hydrazone compounds was prepared by immobilizing the ligands into a cellulose extracted from coconut fibre. The capability of the sorbent material for the extraction of copper was studied by the batch method. The immobilized cellulose was used as a stationary phase in the solid phase extraction to extract $Cu^{2+}$ ions from aqueous solution. The optimum condition for an effective extraction such as pH, contact time, $Cu^{2+}$ and ligands concentrations were investigated. Results obtained showed that the studied sorbent exhibited preferential selectivity towards $Cu^{2+}$ over other transition metals studied. The method was tested for the extraction of $Cu^{2+}$ ions from real samples. Reasonable recovery (> 60 %) was found.

**Keywords**: Hydrazone compounds; Cellulose fibre; Soild phase extraction; Metal ions

## Introduction:

Hydrazone derivatives have been used in the synthesis of metal complexes that exhibit a variety of geometrical configurations and magnetic properties, expanding their applicability across multiple scientific fields. The careful structural elucidation of these compounds and their derivatives is crucial for fully understanding their biological activities and therapeutic potential [1]. A prominent compound often employed in this area is 2,4-dinitrophenylhydrazine (DNPH) [2]. Hydrazones have the ability to form a wide range of chromophoric complexes with transition metals [3, 4]. The regulation of heavy metals poses a significant challenge due to their persistence and resilience in environmental matrices [5]. The cations $Pb^{2+}$, $Cd^{2+}$, $Cu^{2+}$, and $Hg^{2+}$ are categorized as hazardous heavy metals, known for their harmful effects on both ecosystems and living organisms. Numerous research efforts have explored effective methods for the removal and remediation of heavy metals [6-9]. Adsorption of these metallic ions from aqueous solutions using various adsorbents, such as modified plant fiber and gelatin composite [10], kappa-carrageenan/cellulose hydrogel [11], acrylamide-grafted kola-nut pod husk cellulose [12], Alfa grass fibers [13], dendritic fibrous materials [14], has shown promising results in heavy metal extraction [15]. The extensive application of copper in industrial manufacturing processes may lead to increased copper concentrations in the environment. Nonetheless, heightened levels of $Cu^{2+}$ present considerable risks to both ecological stability and human health. Elevated concentrations can cause substantial harm to vital organs, including the liver, erythrocytes, heart, and brain [16]. The process of extracting copper from environmental samples utilizes various advanced techniques, each offering unique benefits. These methodologies are essential for assessing contamination levels and safeguarding environmental integrity. Prominent extraction techniques employed in this research include solid-phase extraction (SPE) [17]. The SPE methodology has garnered substantial acclaim within the domain of analytical chemistry as a proficient pre-concentration technique for the isolation of trace metals [18]. The preference for utilizing SPE to extract heavy metal ions from aqueous matrices is predominantly attributed to its operational ease, absence of contaminants, elevated enrichment potential, effective phase separation, temporal efficiency, and economic viability [19]. The effectiveness of this methodology depends on the properties of the adsorbent, particularly regarding selectivity, detectability, sample throughput, and reusability [20]. The batch methodology is employed as a solid-phase extraction (SPE) technique, wherein a solid phase is used as an extractant to isolate a specific analyte from a given solution. Thereafter, the solid material may either be subjected to immediate analytical procedures or undergo an elution process for the recovery of the analyte [21]. Generally, a specific selective component is attached to a solid support, such as silica, alumina, titanium dioxide, or a polymer, which functions as the solid phase in the batch methodology [22]. Fibrous materials have exhibited significant adsorption capabilities across a diverse array of applications. Research has explored the adsorption efficacy of botanical fibers on various ions, indicating enhanced performance following chemical modification [23]. Agricultural residues consist of lignocellulosic components, primarily cellulose, hemicellulose, and lignin [24]. The sorption capacity of lignocellulosic waste is comparable to that of other natural sorbents while also providing advantageous characteristics such as minimal to no cost, high accessibility, and a straightforward operational methodology. Coir fiber has been extensively studied for its potential as an adsorbent in the removal of various metal ions from water. The husk of the coconut is a byproduct that constitutes the mesocarp of the coconut and represents approximately 33-35% of the whole husk. The cellulose, hemicellulose, lignin, and ash content found within the coir fiber amounted to 38.01%, 2.30%, 45.43%, and 1.21%, respectively [25]. Hydrazone-modified coconut fiber is gaining recognition as an innovative adsorbent for metallic ion adsorption [23]. Its application has been documented in the recovery of $Au^{3+}$, $Cu^{2+}$, and $Ln^{3+}$ ions [26], as well as in the removal of heavy metals such as $Pb^{2+}$, $Cu^{2+}$, and $Zn^{2+}$ from wastewater [27]. The present work explores the effectiveness of three hydrazone compounds physically immobilized on supports derived from cellulose extracted from coconut fiber (coir). The goal is to utilize the selective complexation phenomenon for practical, low-cost applications. This includes reducing matrix interference, preconcentrating samples before analysis, and potentially removing trace toxic heavy metals from wastewater. These compounds include 2,4-dinitrophenyl hydrazine-acetophenone (DNPHACP, $\mathbf{L_1}$), 2,4-dinitrophenylhydrazine-acetaldehyde (DNPHACT,$\mathbf{L_2}$) and 2,4-dinitrophenyl hydrazine-benzophenone (DNPHB,$\mathbf{L_3}$). A batch extraction method was employed for the system. Key factors influencing the extraction, such as equilibrium time, pH, ligand and metal ion concentrations, foreign metal ions, and the reusability of the solid support, were investigated.

**Table 1:** AAS instrumental operating conditions and data acquisition parameters.

| Parameter | Operating Condition |
|---|---|
| Wavelength (nm) | 324.8 |
| Lamp current (mA) | 6 |
| Burner height (mm) | 7 |
| Flow rate (L $min^{-1}$) | 1.8 |
| Gas used | Acetylene flame, Air- $C_2H_2$ |
| Number of replicates | 3 |

### Chemicals and Reagents

Stock solutions (1000 ppm) of transition metal ions (sulfate of $Cu^{2+}$, nitrates of $Pb^{2+}$, $Ni^{2+}$and $Fe^{3+}$) were prepared by dissolving appropriate amount of metal salts in 2% $HNO_3$ solution. A 7.5% solution of sodium hydroxide (Merck), NaOH was prepared by dissolving 18.75 g of NaOH in a 250 mL de-ionized water. 2,4 dinitrophenylhydrazine (Riedel-de-Hean), acetophenone (BDH), acetaldehyde (Riedel-de Hean) and benzophenone (BDH), were used without further purification. Solvent including methanol (MeOH), ethanol (EtOH) (BDH), dichloromethane (DCM) (Acros), dimethyl sulphoxide (DMSO) (Carlo Erba), ethyl acetate (EtOAc) (T-Baker), acetone (Carlo Erba), and $CH_3COOH$ (TIMSTAR) were used as received. Real samples for analysis, namely, drink water (SHAIMA), and tap water (Collected from different locations at Sirte University campus and city centre). All samples were collected, filtered, and stored in plastic bottles. Vegetables (tomatoes and potatoes) were collected from the city market.

### Preparation Coconut Fibre

The coconut fibre was prepared in accordance with the general procedure described by Ashraf et. al., [28]. Coconut fruits were collected from the city market, cut, washed several times with tape water, dried and grounded (size 710 microns).

### Extraction cellulose from coconut fibre

Cellulose extraction is a three-step process [25]. Pretreatment 20 g of the sample with a 1:1 mixture of acetone and ethanol was conducted by reflux distillation, heated at 60°C for 2 h. Then 7.5% NaOH for 2 h at a temperature of 60 ℃. It is known that the alkaline delignification process converts solid biomass lignin into a soluble liquid phase. This was followed by bleaching with 3.6% sodium hypochlorite (NaClO) for 2 h at a temperature of 90 ℃. The bleached fibres were washed thoroughly with water to remove the traces of chlorine to became white. The cellulose extracted from coconut fibre where the percentage of cellulose obtained from (20 g) coconut fruit fibre powder reached 24.5% (4.9 g).

### Synthesis Hydrazone Compounds

All compounds were synthesized following the general procedure reported by Salhin et.al. [29]. A 0.003 M (0.594g) of DNPH was dissolved in 4 mL of concentrated sulfuric acid in 50 mL beaker followed by 10 mL of EtOH. (0.007 M) of aldehyde or ketone dissolved in 10 mL EtOH was added to the beaker with stirring. Products were obtained in good yields: compound 1: orange precipitate (75%), compound 2: reddish orange precipitate (57%), and compound 3: orange precipitate (85%).

### Preparation of Adsorbent Material

Three ligands ($L_1$, $L_2$, and $L_3$) were dissolved (separately) in various organic solvents (MeOH, EtOH, DMSO, EtOAc, DCM, and acetone) [28]. The immobilized process on ground cellulose fibre was carried out as follows: in a 50 mL conical flask, ($4.0 \times 10^{-4}$ M) of $L_1$, ($8.0 \times 10^{-4}$ M) of $L_2$, and ($0.5 \times 10^{-5}$ M) of $L_3$ dissolved in 50 mL of DCM, then stirred for 30 min. Next, 1.0 g of cellulose fibre added to the ligand solution. This procedure was repeated with DMSO, MeOH, EtOH, EtOAc, and acetone. Each of the five mixtures was sealed with paraffin film and allowed to stabilize for 24 h. After stabilization, the cellulose fibre was filtered, washed with distilled water, and dried in an oven at 60 °C for 48 h to remove any residual solvent.

### Extraction of $Cu^{2+}$ (*Batch Method*)

A 10 mg of the adsorbent material (cellulose immobilized with $L_3$) was placed in a glass vial (20 mL). 10 mL of $Cu^{2+}$ solution (1 ppm, pH 5) was then added to the vial. The mixture was shaken mechanically (50 R/min) at room temperature for 10 min. After the equilibrium, the amount of unextracted $Cu^{2+}$ ions was determined by AAS. The amount of extracted $Cu^{2+}$ was then calculated by subtracting the remaining amount of $Cu^{2+}$ from the initial amount of $Cu^{2+}$ [30].

## Results and Discussion

### FT-IR analysis

The FT-IR spectra of three hydrazone ligands ($L_1$, $L_2$ and $L_3$) show characteristic absorption band in Table 2. Both the free cellulose fibre and cellulose-ligands immobilized produce similar spectra. Therefore, FT-IR fail to provide conclusive evidence on the presence of ligands in cellulose mixture. This can be attributed to the too small amount of the ligand in the network, as was also experienced by other researchers [31].

**Table 2:** Selected FTIR stretching ($cm^{-1}$) for the synthesized compounds ($L_1$, $L_2$, and L3).

| | N-H | C-H | C=N | C-C | C-N | $NO_2$ |
|---|---|---|---|---|---|---|
| $L_1$ | 3304 | 3118 | 1614 | 1594 | 1327 | 1513 |
| $L_2$ | 3290 | 3057 | 1612 | 1650 | 1264 | 1509 |
| $L_3$ | 3288 | 3057 | 1613 | 1651 | 1257 | 1508 |

## Differential Scanning Calorimetry.

The thermal stability of materials were investigated using Differential Scanning Calorimetry (DSC) and was performed under a nitrogen atmosphere with a heating rate of 10°C/min from -35°C up to 500°C. The free ligands (Fig. 1) are thermally stable compounds at 355, 453 and 326.5°C, respectively.

### 1 Cellulose Fibber

The thermogram (Fig.1D) reveals several significant thermal peaks that provide insights into the material's thermal behavior and phase transitions. The thermogram exhibits a prominent broad endothermic peak at approximately 87.7 °C due to the loss of adsorbed water. The data shows the glass transition ($T_g$) and melting transition ($T_m$) 260-270 °C, and thermally stable at 492.3°C.

### 2 Cellulose Fibre Immobilized Ligands.

The cellulose fibre and all the sorbent materials and C-$L_3$ after extraction $Cu^{2+}$ exhibited high thermally stable at 492,434, 497, 455 and 459°C, respectively.

## UV/VIS Analysis.

The adsorption of different concentrations (0.5 to $22\times10^{-5}$ M) of the immobilized ligand ($L_3$) on cellulose fibre was measured at $\lambda_{max}$= 376 nm using a UV/Vis spectrophotometer. Results indicated that the adsorbed amount of ligand on the cellulose fibre increased proportionally with the $L_3$ concentration

## Solid-Phase Extraction of $Cu^{2+}$and $Pb^{2+}$

Batch Method: The adsorbent materials (C-$L_1$, C-$L_2$, and C-$L_3$) were used for the extraction of $Cu^{2+}$ and $Pb^{2+}$ from aqueous medium. Results showed that C-$L_3$ adsorbent material had a better extraction ability towards $Cu^{2+}$ (Fig. 2). Sorbent material C-L3, which was immobilized with benzophenone (L3), exhibited a higher extraction capacity for $Cu^{2+}$ (Fig. 3) compared to the other adsorbent materials under study. This selectivity may be attributed to the stronger coordination interactions resulting from the chemical structure of benzophenone. The additional benzene rings in L3 enhanced π–π interactions with the analyte, thereby improving its extraction capability [32].

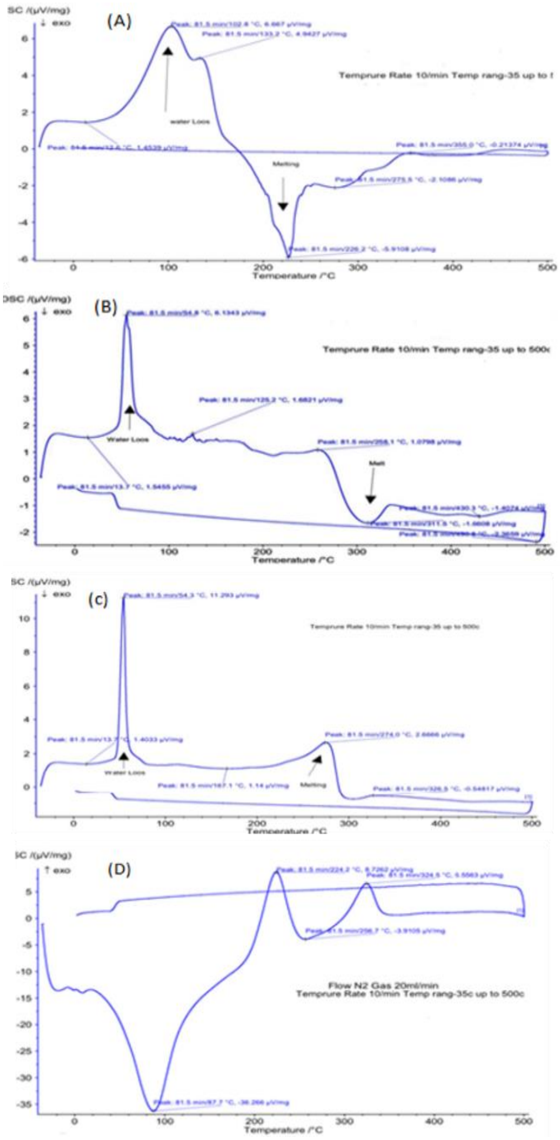

**Figure 1:** Differential scanning calorimetry (DSC) of free ligands: (A) $L_1$, (B) $L_2$, (C) $L_3$, and (D) cellulose fibre before ligand immobilized, was performed under a nitrogen atmosphere with a heating rate of 10°C/min from -35°C up to 500°C.

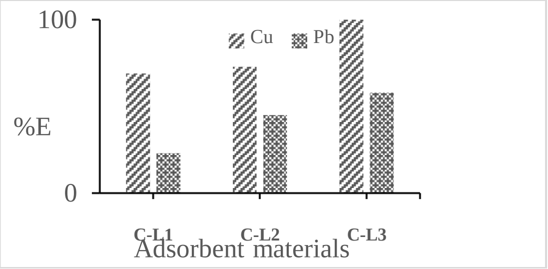

**Figure 2:** Effect of adsorbent material (C-$L_1$, C-$L_2$ and C-$L_3$) on the extraction of $Cu^{2+}$ and $Pb^{2+}$. pH 5 and contact time 60 min using batch method.

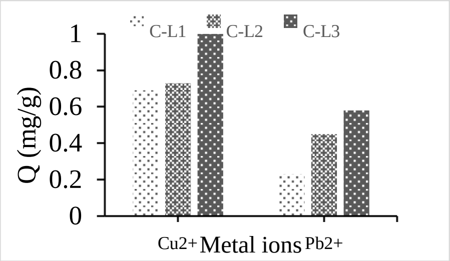

**Figure 3:** The capacity (Q) of the adsorbent material (C-L$_1$, C-L$_2$ and C-L$_3$) on the extraction of $Cu^{2+}$ and $Pb^{2+}$. pH 5 and contact time 60 min using batch method

### Effect of pH

A proper pH level reduces matrix interference while also improving the extraction process effectiveness. With the sorbent material (C-L$_3$), the $Cu^{2+}$ solution (1 ppm) was shaken for 60 minutes, over a pH range of 3 to 9 to study the effect of hydrogen concentration on the extraction behaviors of the sorbent material toward $Cu^{2+}$. A quantitative amount (99.9 %) with adsorbent capacity of (0.999mg/g) was reported at pH 5 (Fig. 4). Therefore, pH 5 was selected for additional research investigation.

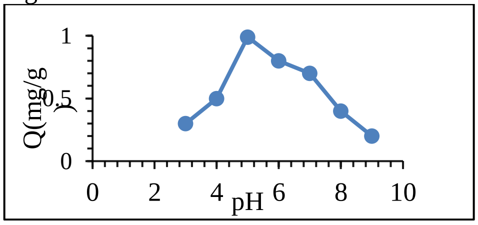

**Figure 4:** Study of the effect of pH on the extraction of $Cu^{2+}$ (1 ppm) with C-L$_3$ (10 mg). Contact time 60 min.

### Effect of Contact Time

The experiment was carried out by shaking $Cu^{2+}$ solution (1 ppm, pH 5) with 10 mg C-L$_3$ at different periods ranged from 1 to 90 min at room temperature. The amount (mg) of $Cu^{2+}$adsorbed per gram of sorbent is reached up to Q= 0.999 mg/g almost after 5 min of contact time. It is readily apparent from the figure that significant extraction (~90%) of $Cu^{2+}$ occurred within 5 min of contact (Fig. 5). The rate of extraction of $Cu^{2+}$ (in percentage) was initially high due to the availability of the ligand active sites on the cellulose fibre. However, after this range of time, approximated 99.9% of $Cu^{2+}$ was extracted. No appreciable changes were noticed upon the increasing of contact time. Therefore, 10 min of contact time was chosen for further in investigation.

### Effect of Shaking Speed

The experiment was carriedout by shaking $Cu^{2+}$ solution with 10 mg C-L$_3$ in the range of 50 R/min to 200 R/min for 10 min. (Fig. 6). Results showed no effect of shaking speed on the extraction. The amount (mg) of $Cu^{2+}$adsorbed per gram of sorbent is reach to 0.999 mg/g.

### Effect of Ligand Concentration

Firstly, the ability of the cellulose fiber before ligand immobilization toward $Cu^{2+}$ was investigated. Fig. 7 shows the ability of the cellulose fiber for the extraction of $Cu^{2+}$ ions, with a capacity equal to 0.5mg/g. However, this range of capacity was doubled upon the immobilization of L$_3$ on the cellulose fiber. Different ligand concentrations ranging from (0.5 - $22\times10^{-5}$ M) were immobilized on the cellulose fiber and the extraction efficiency of the adsorbent was investigated at the reported conditioned (pH 5, 10 min). Results (Fig 7) shows that all the applied ligand concentrations successfully extracted $Cu^{2+}$ (>95%) with $0.5\times10^{-5}$ M, ligand exhibiting the highest extraction. The amount (mg) of $Cu^{2+}$adsorbed per gram of sorbent is reach to 0.999 mg/g. Therefore, this concentration was used for further studies. the extraction efficiency of the adsorbent was investigated at the reported conditioned (pH 5, 10 min). Results (Fig 7) shows that all the applied ligand concentrations successfully extracted $Cu^{2+}$ (>95%) with $0.5\times10^{-5}$M, ligand exhibiting the highest extraction. The amount (mg) of $Cu^{2+}$adsorbed per gram of sorbent is reach to 0.999 mg/g. Therefore, this concentration was used for further studies.

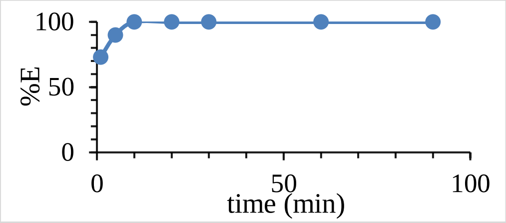

**Figure 5:** Effect of contact time on the extraction of $Cu^{2+}$ (1 ppm) with C-L$_3$ (10 mg), pH 5.

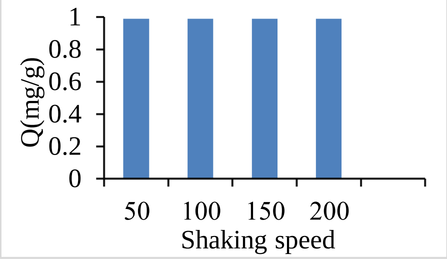

**Figure 6:** Effect of shaking speed on the extraction of $Cu^{2+}$ with C-L$_3$ (10 mg), pH 5 and contact time of 10 min.

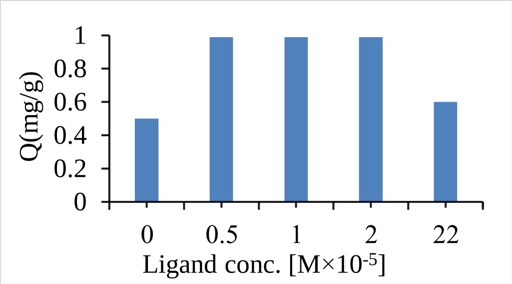

**Figure 7**: Effect of immobilized ligand (L$_3$) concentration on the $Cu^{2+}$ (1 ppm) extraction.

### Effect of Adsorbent Material Mass

The effect of the amount of adsorbent material on the extraction of $Cu^{2+}$ was also investigated using different amount of adsorbent material (5-500 mg). Results (Fig. 8) showed that no significant effect of the amount of adsorbent employed on the extraction of

$Cu^{2+}$ from aqueous solution. Therefore, 10 mg of adsorbent material was selected (99.9%) with the total amount of $Cu^{2+}$ adsorbed in milligrams per gram of sorbent was up to 1.8 mg/g.

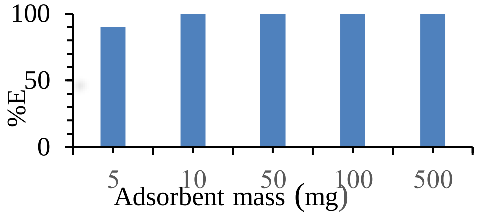

**Figure 8:** Effect of adsorbent material mass on the extraction with C-$L_3$ pH 5 and contact time 10 min.

### Effect of $Cu^{2+}$ Concentration

Studying copper concentration gives an idea about the extraction capacity of the adsorbent material (C-$L_3$). The current study was conducted by shaking different concentrations (0.05-100 ppm) of $Cu^{2+}$ ions with 10 mg of C-$L_3$ for 10 min. (Fig. 9) shows the effect the of copper concentration on the extraction using C-$L_3$ at the optimum conditions. Good extraction matrix for $Cu^{2+}$ in a concentration as low as 0.05 ppm (500 ppb) was recorded. The amount (mg) of $Cu^{2+}$adsorbed per gram of sorbent, (Q), is presented in Table 3. The sorbent capacity increased with the increase in initial $Cu^{2+}$ concentration. This shows that the sorbent material is a good extracting material for trace amounts of $Cu^{2+}$ in aqueous solutions comparing to other sorbents [33]. A liner range of a slope of 1.0788 was reported.

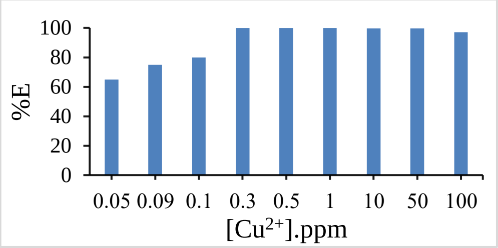

**Figure 9:** Effect of $Cu^{2+}$ concentration on the extraction using C-$L_3$ (10 mg), pH 5 and contact time 10 min.

**Table 3**: Effect of $Cu^{2+}$ concentration on the extraction using C-$L_3$ (10 mg). n=3.

| [$Cu^{2+}$] ppm | E% (±SD) | D | Capacity, Q (mg $g^{-1}$) |
|---|---|---|---|
| 0.05 | 65 (0.42) | 0.66 | 0.033 |
| 0.09 | 75 (0.42) | 0.76 | 0.068 |
| 0.1 | 80 (0.58) | 0.80 | 0.080 |
| 0.3 | 99.9 (0.07) | 0.996 | 0.299 |
| 0.5 | 99.9 (0.07) | 0.998 | 0.499 |
| 1 | 99.9 (0.07) | 0.999 | 0.999 |
| 10 | 99.8 (0.15) | 0.999 | 9.988 |
| 50 | 99.8 (0.15) | 0.999 | 49.95 |
| 100 | 97.1 (0.1) | 0.97 | 97.00 |

### Effect of the Presence of Foreign Ions

In order to examine the selectivity of C-$L_3$ with respect to the extraction of $Cu^{2+}$, the interaction involving three foreign metal ions was systematically analyzed. A concentration of 1 ppm $Cu^{2+}$ was combined with (0.5-2 ppm) of each foreign metal ion ($Fe^{3+}$, $Ni^{2+}$and $Pb^{+2}$) and was separately agitated with 10 mg of C-$L_3$ for a duration of 10 minutes. The total concentration of $Cu^{2+}$ ions extracted was subsequently quantified. Table 4 illustrates that there were no significant interferences observed for the studied metal ions, with the exception of $Fe^{3+}$, for which the extraction percentage (%E) of $Cu^{2+}$ was diminished to 98%, when 2ppm $Fe^{3+}$ was used.

### Reusability of the Sorbent

The reusability of the C-$L_3$ sorbent was evaluated by conducting extraction-desorption experiments across three distinct extraction cycles in the acidic medium HCl (0.01-1 M). The extracted amount of $Cu^{2+}$ consistently exceeded 99.9% across these three cycles (Fig. 10).

**Table 4:** Effect of metal ion interferences on the extraction of $Cu^{2+}$ (1ppm) using C-$L_3$ (10 mg).

| Metal ion | [$M^{n+}$] added | %E $Cu^{2+}$ (±SD) | Q (mg/g) |
|---|---|---|---|
| $Cu^{+2}$ | 1 | 99.9 (±0.07) | 0.999 |
| $Ni^{+2}$ | 0.5 | 99.9 (±0.07) | 0.999 |
| | 0.8 | 99.9 (±0.07) | 0.999 |
| | 1 | 99.9 (±0.07) | 0.999 |
| | 2 | 99.9 (±0.07) | 0.999 |
| $Pb^{+2}$ | 0.5 | 99.9 (±0.07) | 0.999 |
| | 0.8 | 99.9 (±0.07) | 0.999 |
| | 1 | 99.9 (±0.07) | 0.999 |
| | 2 | 99.9 (±0.07) | 0.999 |
| $Fe^{+3}$ | 0.5 | 99.9 (±0.07) | 0.999 |
| | 0.8 | 99.5 (±0.44) | 0.796 |
| | 1 | 99.5 (±0.44) | 0.995 |
| | 2 | 98.1 (±0.1) | 1.961 |

A clear drop was observed after the third cycle. This loss of reactivity of the sorbent may have been caused by strong competition between protons and $Cu^{2+}$ ions to occupy the ligand active sites. That might cause irreversible metal ion adsorption [30].

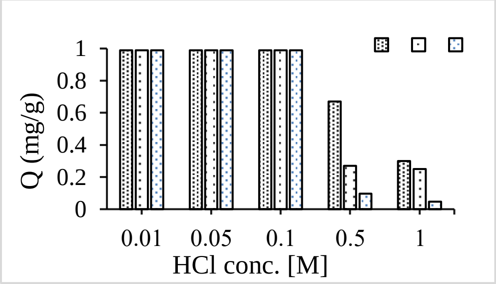

**Figure 10:** Reusability of C-$L_3$ on the extraction of $Cu^{2+}$,n=3.

### Adsorption Kinetic

The adsorption kinetics of $Cu^{2+}$ were studied on the surface of C-$L_3$, and was carried out by shaking $Cu^{2+}$ solution 50 R/min (1 ppm, pH 5) with 10 mg C-$L_3$ (Fig. 11). Results of the pseudo-second order adsorption kinetics was reported from a plot time vs $t/q_t$. An equation was used to derive the adsorption rate constant of the C-$L_3$. Pseudo- second order equation [34]. According to the following equation

$$\frac{t}{qt} = \frac{1}{K2\ qe2} + \frac{t}{qe}$$

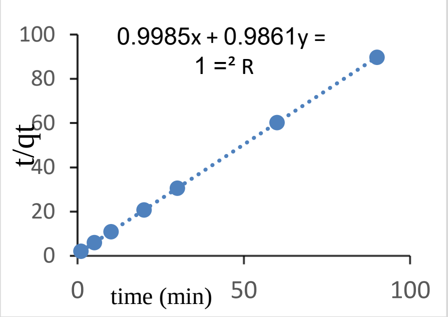

**Figure11**: pseudo-second order adsorption kinetics.

### Preconcentration and recovery of $Cu^{2+}$ from real sample

At the optimum condition of the method, the efficiency of the adsorbent material was examined for the extraction of $Cu^{2+}$ from real samples. Three different water samples and two vegetables were tested. The samples were first directly analysed for their $Cu^{2+}$ contents. Samples were then spiked with standard $Cu^{2+}$ concentration (1 ppm). The content of $Cu^{2+}$ present in the samples was tested by AAS. Results showed the absence of $Cu^{2+}$ ion in all the water samples, while the vegetables were found to contain a little amount of $Cu^{2+}$. (0.36 ppm in tomatoes and 0.87 ppm in potatoes). Therefore, 1 ppm $Cu^{2+}$ was spiked into the water sample before the extraction took place following the adopted procedures. C-$L_3$ shows good recovery results. Recovery of 99.9% of the spiked $Cu^{2+}$ into the water sample was reported (Table 5). The efficiency of copper extraction from vegetables tends to be lower compared to water due to their complex composition. Vegetables contain proteins, fibres, and carbohydrates, which can interact with copper to form complexes. These complexes are less likely to interact with the adsorbent material, leading to a decrease in adsorption efficiency compared to water. This phenomenon has been discussed in studies on metal adsorption and complexation in biological matrices [35].

**Table 5:** Extraction $Cu^{2+}$ from real sample pH 5, using batch method, n=3.

| Sample | Average (E %) (±SD) | | Q (mg/g) |
|---|---|---|---|
| S.1 | 99.9 | 0.07 | 0.999 |
| S.2 | 99.8 | 0.18 | 0.998 |
| S.3 | 99.9 | 0.07 | 0.999 |
| S.4 | 69.4 | 0.5 | 0.25 |
| S.5 | 66.6 | 0.41 | 0.58 |

Where; S.1: lab, S.2: drinking water (SHIMA), S.3: downtown park, S.4 & S.5: tomato and potato.

### Comparison with Previous Studied.

The present method was compared with previously reported approaches for the extraction of $Cu^{2+}$ from an aqueous medium. The sorption characteristics of the studied sorbent material are comparable to those of the solid-phase extraction system for $Cu^{2+}$ ions [36]. Table 6 summarizes earlier reports on the solid-phase extraction of $Cu^{2+}$. This work demonstrates high selectivity and good capacity for $Cu^{2+}$.

**Table 6:** Summary of some of the early reports on the solid phase extraction (SPE) of $Cu^{2+}$.

| Ionophore (Support) | Q (mg/g) | Time (min) | Reference |
|---|---|---|---|
| Silica immobilized hydrazone compound. | 0.054 | 90 | [30] |
| Coconut fibre (coir) immobilized hydrazone compound. | - | 25 | [32] |
| Tannin-immobilized cellulose fibre extracted from coconut husk. | 0.729 | 30 | [36] |
| C-$L_3$. | 0.999 | 10 | Present work |

### Conclusion

The applications of hydrazone compounds had drawn out lots of attention towards the extraction of metal ions. Using 3 different novel hydrazone compounds namely 2,4-dintrophenyl hydrazone acetophenone (DNPHACP), 2,4-dintrophenyl hydrazone acetaldehyde (DNPHACT) and 2,4-dintrophenyl hydrazone benzophenone (DNPHB) had successfully synthesized and characterized. An adsorbent material was fabricated by immobilization the hydrazone ligands on cellulose extracted from coconut fibre. The prepared material shows higher thermal stability of C-$L_3$ (>300 °C) compared to free ligand (<300 °C). C-$L_3$ adsorbent exhibits selective extraction towards $Cu^{2+}$ in neutral medium, where 99.9% extraction of $Cu^{2+}$ was achieved using batch method of extraction. 10 mg of C-$L_3$ ($0.5\times10^{-5}$ M) was found the best quantities for SPE extraction of $Cu^{2+}$ from acidic medium (pH 5). The distribution coefficient (D) was found equal to 0.999 mg $L^{-1}$. The adsorption kinetics of $Cu^{2+}$ were studied on the surface of C-$L_3$ and found of the pseudo-second order. This method is recommended for selective removal of $Cu^{2+}$ ion from water sample.

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