

Characterization and evaluation analysis of a crown ether as an effective sorbent for selective sorption of copper ions

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ABSTRACT

This manuscript presents the characterization of 2,2'-(6,7,9,10,17,18,20,21-octahydrodibenzo[b,k][1,4,7,10,13,16]hexaoxacyclooctadecine-2,14-diyl)bis(but-3-yn-2-ol) (OHDB) as a sorbent for copper ions using various spectroscopic techniques and sorption experiments. The proton nuclear magnetic resonance (¹H-NMR) and carbon-13 nuclear magnetic resonance (¹³C-NMR) spectra of OHDB were analyzed, and the sorption efficiency was evaluated by electrical conductivity. UV absorption spectroscopy was used to confirm the selectivity and specificity of OHDB towards copper ions. Sorption capacity was determined using a spectrophotometric method, and scanning electron microscopy and energy-dispersive X-ray spectroscopy analyses were carried out to understand the surface changes and composition of OHDB before and after copper sorption. Sorption experiments showed that OHDB effectively reduced the conductivity of copper solution by 451.84 μ/cm, with a distribution coefficient of 0.98 for copper ions. The sorption capacity was determined to be 1.26 mg/Cu²⁺·g OHDB, using optical density measurements. OHDB demonstrated high selectivity for copper over other metals like Fe³⁺ and Ni²⁺ based on partitioning. OHDB adsorbed 1.266 mg/Cu²⁺·g from a technological water sample. The regeneration studies showed the feasibility of regeneration process, 99% efficiency. Fourier-transform infrared spectroscopy and Raman spectroscopy identified changes in ether/hydroxyl vibrations upon copper binding, suggesting coordination complex formation. The results suggest that OHDB is an efficient and sustainable sorbent for copper removal applications in wastewater treatment and industrial processing.

Keywords: 2,2'-(6,7,9,10,17,18,20,21-octahydrodibenzo[b,k][1,4,7,10,13,16]hexaoxacyclo-octadecine-2,14-diyl)bis-(but-3-yn-2-ol); Crown ether; Copper ions; Sorption; Wastewater treatment

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1. Introduction

Extraction and retrieval of copper from contaminated water, wastewater and drinking water is a critical chemistry and chemical engineering issue. Copper and its compounds are partially soluble in the leachates of minerals, such as chalcopyrite, chalcocite, covellite, among others. Control and extraction of copper ions from technological solutions, wastewater, and natural waters have become main objectives in modern times. Currently, several methods are used for extracting copper ions by chemical precipitation or liquid–liquid extraction. Nevertheless, the extraction of copper ions using liquid extractants poses some difficulties due to the formation of aqua-complexes that remain in the water phase. Moreover, the extraction requires the use of different solvents. Replacement solventless extractants, such as crown ethers, kryptands, etc., provide waste reduction and ease the regeneration process, leading to opportunities for green chemistry [1–3].

Literature describes various methods of separating lithium, zirconium, chromium using crown ethers by liquid–liquid extraction. Additionally, derivative crown ethers with chitosan acetate have been studied for extraction of heavy and toxic metal ions. *N,N'*-diallyl derivatives of dibenzo-18-crown-6 were utilized for sorption of silver and palladium ions. Immobilized *N*-(diethylthiophosphoryl)-aza-18-crown-6 ethers and polymer membrane, and amberlite (XAD-4) resins effectively extracted Au(III) from technological water using a solid-phase extraction method. Here we synthesize a series of substituted dibenzo-18-crown-6 ethers with internal cavity similar to the ionic radius of Cu ion (0.72 Å) to be used as a sorbent for copper ions using solid-phase extraction [4–6].

By designing a sorbent with a cavity size similar to that of the Cu ion, we hope to increase the efficiency and selectivity of copper ion extraction. Substituted dibenzo-18-crown-6 ethers have shown potential for use in various solid-phase extraction methods and have demonstrated high selectivity for certain metal ions. It can be anticipated that the synthesized ether will exhibit these same beneficial properties with respect to copper ion extraction [7–9].

Furthermore, solid-phase extraction is a promising technique for extracting metal ions from aqueous solutions, by virtue of its ease of operation, low cost and high selectivity. The immobilization of ethers onto a solid support allows repeated and easy regeneration of the sorbent while reducing solvent consumption [10]. By utilizing this technique, we aim to extract copper ions from wastewater and subsequently recover them through electroplating or chemical precipitation [11–13].

Finally, the use of a regenerable sorbent with high selectivity could lead to cleaner water resources and more sustainable production processes. Our research is part of ongoing efforts to develop environmentally-friendly solutions for recovery of valuable metals from wastewaters and other sources [14–17].

The principal aim of this manuscript is to appraise sorption efficiency of 2,2'-(6,7,9,10,17,18,20,21-octahydrodibenzo[b,k] [1,4,7,10,13,16]hexaoxacyclooctadecine-2,14-diyl) bis-(but-3-yn-2-ol) (OHDB) for copper ions using various analytical techniques. This includes characterizing the

chemical structure and functional groups present in OHDB using proton nuclear magnetic resonance (¹H-NMR), carbon-13 nuclear magnetic resonance (¹³C-NMR), infrared (IR) spectroscopy, and Raman spectroscopy. Additionally, the manuscript aims to determine the sorption capacity of OHDB for copper ions, evaluate its selectivity towards Cu(II) ions in comparison to other metal ions, and assess its potential applications in environmental science, analytical chemistry, and biomedical research. The manuscript also explores the use of electrical conductivity, UV absorption spectroscopy, reflection spectroscopy, and scanning electron microscopy/energy-dispersive X-ray spectroscopy (SEM/EDS) analyses to provide insights into the interaction of OHDB with copper ions and its effectiveness as a sorbent for copper ions in wastewater treatment and industrial processing.

The following highlights were found:

- Comprehensive characterization of crown ether OHDB confirms its selective binding ability toward copper ions through coordination complexation,
- Sorption experiments demonstrate OHDB's high sorption capacity of 1.26 mg/g for copper ions,
- Techniques such as UV-Vis, Fourier-transform infrared spectroscopy (FTIR) and Raman spectroscopy provide evidence of complex formation between OHDB and copper,
- SEM/EDS analysis visually confirms copper accumulation on OHDB's surface after sorption through coordination interactions,
- OHDB exhibits excellent selectivity for copper over other metal ions like Fe³⁺ and Ni²⁺ based on partitioning studies,
- OHDB is shown to effectively separate 1.266 mg/Cu²⁺·g from real industrial wastewater samples,
- Copper ions can be regenerated from OHDB with 99% efficiency, showing its reusability for continuous treatment.

The novelty of this work is the thorough multi-technique characterization of the crown ether OHDB which clearly demonstrates its potential as a selective, reusable and environmentally-friendly sorbent for removal of copper ions from industrial wastewater. Comprehensively evaluating OHDB's performance through analytical, visualization and sorption studies provides strong evidence of its coordination-based sorption mechanism and suitability for copper ion separation applications. This furthers the development of sustainable solutions for valuable metal recovery from contaminated water sources.

2. Materials and methods

In this research, the CuSO₄·5H₂O, FeCl₃·6H₂O, Pb(NO₃)₂·5H₂O, ZnCl₂·5H₂O, Hg(NO₃)₂·H₂O, NiSO₄·7H₂O, NH₄OH, ZnSO₄·H₂O, dimethyl yellow (indicator), sulfanilic acid, xylene orange tetrasodium salt 3,3'-bis[*N,N*-bis(carboxymethyl)aminomethyl]-*o*-cresolsulfonephthalein tetrasodium salt and 1-nitroso-2-naphthol were used and purchased from Sigma-Aldrich, India (Bangalore), Merck, India (Goa). Standard solutions of 0.1 M copper(II) were prepared by dissolving 1.88 g of CuSO₄·5H₂O of exact weights of salts diluted in a 200 mL flask (≥95%–99% purity).

2.1. Methods

IR spectra were recorded on a Bruker Fourier spectrometer (Germany (Karlsruhe)) (INVENIO S-2021) in the 4,000–400 cm^{-1} span. The spectrum of ^1H and ^{13}C -NMR were obtained in spectrometer Bruker VXR-400 (Germany (Rheinstetten)) with an operating frequency of 400 and 100 MHz. Spectrophotometer Cary 5000 Agilent (United States (Santa Clara, California)) 1,100 to 200 nm was used to determine the sorption of copper(II) ion. In this case, the amount of copper(II) is determined through the reaction of a standard solution with ammonia to form a complex. Horiba MacroRAM (Japan) - Raman spectrometer is used to determine the vibration frequencies of bonds in the complex of copper(II) ion with crown ether and to prove that the complex was formed by it. JEOL JSM-IT200LA (Japan) - SEM/EDS instrument was used to prove the amount of copper absorbed throughout the crown surface of the copper-absorbing crown ether in tablet form. X-Rite eye-one-pro mini-spectrophotometer (Switzerland) used reflectance spectroscopy to prove that crown ether had sorbed copper. The crown ether was initially colored white and then became air colored after sorption. EMC-30PC-UV spectrometer (Germany) was used to do the absorption spectrum analysis. The pure crown ether without modification with paraffin was dissolved in chloroform and its absorption spectrum was obtained, and the absorption spectrum of the complex formed after copper ion reduction was measured. In this case, it was proved that the copper ion is actually bound to the crown ether and not to the paraffin. Conductivity Meter 950 (China) was used to measure the electrical conductivity of solution before sorption and electrical conductivity of the solution after sorption [18–20].

For nuclear magnetic resonance (NMR) spectroscopy, the sample of OHDB (10 mg) was dissolved in deuterated chloroform (CDCl_3) in a 5 mm NMR tube. ^1H and ^{13}C -NMR spectra were recorded on a Bruker Avance III 400 MHz spectrometer at 400 and 100 MHz, respectively.

For FTIR analysis, a thin film of OHDB was drop cast onto an attenuated total reflectance crystal. Spectra were collected on a Bruker Alpha-P FTIR spectrometer (Germany (Rheinstetten)) from 4,000–400 cm^{-1} with 16 scans and 4 cm^{-1} resolution.

Raman spectra were measured on a Horiba LabRAM HR Evolution Raman Microscope, Japan (Kyoto) using a 532 nm laser, 100 μm slit aperture, and 100x objective lens. The sample was directly placed on a glass slide.

SEM imaging was performed on a JEOL JSM-IT200 instrument (Japan (Tokyo)) operating at 5 kV. Samples were sputter coated with gold for 60 s prior to analysis. EDS analysis was conducted using an Oxford Instruments X-Max 80 mm^2 detector.

2.2. Adsorption analysis

For adsorption experiments, 1 g of OHDB powder was added to 100 mL flasks containing 50 mL of Cu solutions

of varying concentrations (0.1–1 mM). The flasks were agitated at 200 rpm for 2 h at 25°C to reach equilibrium. The samples were then filtered to remove the adsorbent.

Cu^{2+} concentration in the filtrate was determined spectrophotometrically using 1,5-diphenylcarbazide. This forms a purple complex with Cu that has a λ_{max} at 540 nm. Calibration curves of absorbance vs. Cu^{2+} concentrations were prepared and used to determine filtrate copper levels.

Adsorption capacity (Q_e in mg/g) was calculated using the mass balance Eq. (1):

$$Q_e = \frac{(C_0 - C_e)V}{m} \quad (1)$$

where C_0 and C_e are initial and equilibrium Cu concentrations (mg/L), V is volume (L), and m is adsorbent mass (g).

Adsorption efficiency (%) was determined as Eq. (2):

$$\text{Efficiency} = \frac{(C_0 - C_e)}{C_0} \times 100 \quad (2)$$

3. Experimental part

3.1. Synthesis of OHDB

In synthesis procedure of OHDB (Fig. 1), 0.5 g (1.126 mmol) of 4',4''-diacetyl-dibenzo-18-crown-6 (II) in 50 mL of benzene was mixed 6.306 g (11.26 mmol) of potassium hydroxide and heated for 20–30 min, then acetylene was passed through 63 mL (2.815 mmol), the mixture was boiled for 3 h. The reaction progress was monitored by Thin-Layer Chromatography on silufol in acetone:hexane, 2:1. Then, hydrolysis was carried out in a slightly acidic medium, the precipitate was washed, purified by fractional crystallization from hexane, and dried in an oven at 40°C. Compound I was obtained with a yield of 0.235 g (42%), m.p. 164°C–168°C.

3.2. Spectral characteristics of OHDB

^1H -NMR (CDCl_3 , 400 MHz) δ_{H} , ppm: 1.82 (6H, s, $\alpha\text{-CH}_3$), 2.65 (2H, s, $-\text{OH}$), 3.21 (2H, s, $\equiv\text{CH}$), 3.87–4.26 (16H, m, α - and $\beta\text{-O-CH}_2$), 6.71–6.73 (2H, m, Ar-H 6'), 6.84 (2H, d, Ar-H 3', $J = 8.9$ Hz), 6.87–6.89 (2H, d, Ar-H 5', $J = 6.3$ Hz).

^{13}C -NMR (CDCl_3 , 100 MHz) δ , ppm: 33.10 (R- CH_3), 67.41 ($-\text{C}-$), 69.64–70.49–71.08 ($\beta\text{-}\alpha\text{-O-CH}_2$), 73.10 (Ar $\text{C}\equiv\text{C}-$), 87.20 (Ar $\text{C}\equiv$), 112.13 (Ar-C3'), 114.78–137.31 (Ar-C4',5',6'), 147.60–151.36 (ArC-O- CH_2). Elemental analysis: found, %: C 67.93, H 6.44. Calculated, %: C 67.75, H 6.45; general formula: $\text{C}_{28}\text{H}_{32}\text{O}_8$.

3.2.1. ^1H -NMR analysis

The given ^1H -NMR spectrum provides information about the proton environments in the molecule OHDB. The analyze in obtained the spectrum are as follows (Fig. 2):

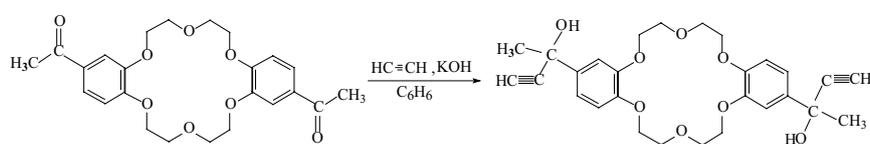


Fig. 1. Synthesis procedure of OHDB.

cations with different ionic radii to the center. Therefore, copper ion sorption was studied by taking 0.1 g of OHDB and 1.0 g of paraffin-modified tablets. In order to prove that sorption is taking place, taking into account the mobility of ions, the electrical conductivity was measured in a conductometer device and the distribution coefficients were determined. The obtained results are presented in Table 1. From the Table 1, it can be grasped that the sorption of copper(II) ion by OHDB ether shows a decrease in electrical conductivity, which indicates that the copper ion is completely sorbed.

The sorption efficiency (Table 1) of 4',4''-di-(1-methyl-1-hydroxyethyl)-dibenzo-18-crown-6 (OHDB) for copper ion detection was investigated by measuring the change in electrical conductivity. The initial electrical conductivity of a 0.01 M copper(II) sulfate solution was measured to be 458 μcm . After sorption of the copper ions by OHDB,

the electrical conductivity of the solution was found to be 6.16 μcm , resulting in a difference in electrical conductivity of 451.84 μcm .

The distribution coefficient of copper ions between OHDB and the aqueous phase was determined to be 0.98, which indicates that the OHDB is highly efficient in selectively sorbing copper ions. The sorption process is based on the crown ether moiety present in the OHDB molecule, which forms a ring with six simple ether bonds with varying diameters at the center. This allows for selective sorption of cations based on their ionic radii to the center of the ring.

4.2. UV spectroscopy

UV absorption spectroscopy was exploited to investigate the formation of a complex between 4',4''-di-(1-methyl-1-hydroxyethyl)-dibenzo-18-crown-6 (OHDB) and copper

Table 1
Solid-phase extraction of 0.01 M Cu(II) sulfate solution by OHDB

Electrical conductivity of 0.01 M Cu(II) sulfate solution, μcm	458
Electrical conductivity of 0.01 M Cu(II) sulfate solution after the sorption, μcm	6.16
Difference between the electrical conductivity, μcm	451.84
Distribution coefficient	0.98

Kozinskaya_1
13C_CDCl3_14042021_400 MHz

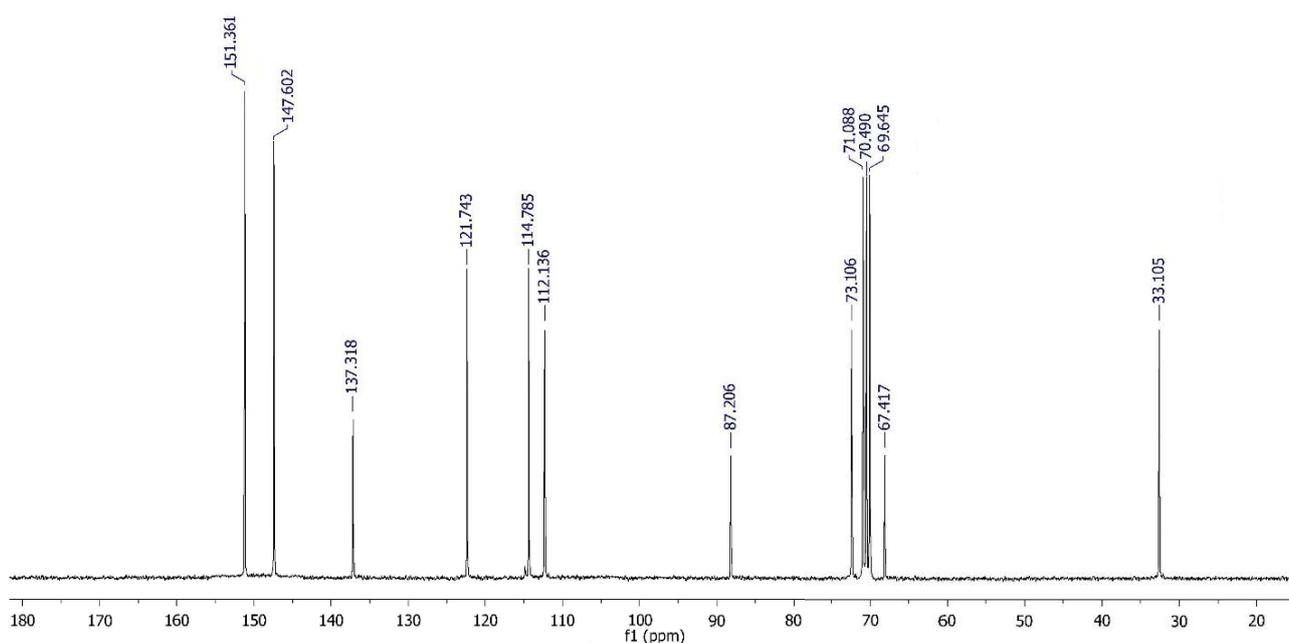


Fig. 3. Calculation of ^{13}C -NMR spectrum of OHDB.

ions (Fig. 4). The OHDB was dissolved in chloroform and its UV absorption spectrum was obtained along with the UV absorption spectrum of the complex formed by adding 1.0 mL of 0.01 M copper ion solution.

The outcomes vouchsafed that the absorption spectrum of OHDB appeared at 425 nm, indicating the existence of a corresponding chromophore in the molecule. Upon addition of copper ions, a new absorption peak appeared at 460 nm, which suggests the formation of a complex compound between OHDB and copper ions.

This shift in the UV absorption spectrum can be attributed to formation of a bond between oxygen atom in the simple ether bond of the OHDB and the copper ion. This observation confirms the existence of a bond between oxygen and copper ion in the crown ether simple ether bond.

Therefore, it can be concluded that the UV absorption spectroscopy results support the complexation of OHDB with copper ions, providing further evidence for its potential use as an efficient sorbent for copper ion detection.

Additionally, the change in the absorption spectrum of OHDB upon binding with copper ions can be used to measure the concentration of copper ions in a sample. By determining absorbance at the specific wavelength of 460 nm, the extent of complex formation can be quantified and used to calculate the level of copper ions in original solution.

Furthermore, UV absorption spectroscopy is a widely-used and reliable technique for characterizing molecular interactions and determining the composition of complexes formed between molecules. The results obtained from this study confirm the selectivity and specificity of OHDB towards copper ions [21–23].

Generally, between OHDB and copper ions, thereby supporting its potential application as an efficient sorbent for copper ion detection and removal from aqueous samples.

4.3. Reflection spectroscopy

Since copper ion extraction is carried out in the solid phase, it was brought to the form of a tablet and its

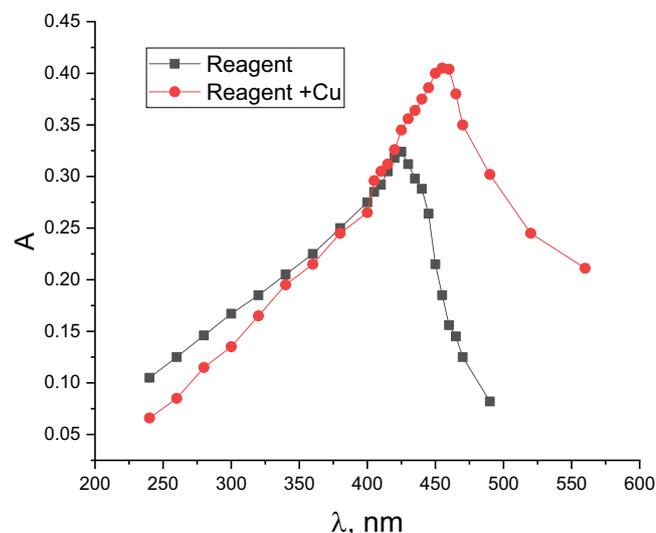


Fig. 4. UV absorption spectrum of (a) OHDB and (b) with copper.

reflectance spectrum was measured in a reflection spectrophotometer. 1.0 g of crown ether was taken and 1.0 mL of 0.01, 0.02 and 0.03 M copper(II) standard solutions were added to it and mixed, after 10 min the tablets were taken out and dried and reflected by light. Spectra were obtained and the results are presented in Fig. 5. Due to the fact that the color of the copper(II) ion complex formed with the crown ether changed depending on the copper concentration, it was studied using the reflection spectroscopy method and the obtained results are presented in Fig. 5. According to it, it can be seen that the absorption wavelength of OHDB is shifted by 10–30 nm due to the sorption of copper(II) ion.

The reflection spectroscopy results indicated that the color of the copper(II) ion complex formed with the crown ether changed depending on the concentration of copper ions. The absorption wavelength of OHDB was shifted by 10–30 nm due to the sorption of copper(II) ions. This shift in the absorption wavelength is indicative of the formation of the complex between OHDB and copper ions [23–26].

It can be observed from Fig. 5 that the peak of the reflection spectra is high for reagent, indicating a strong reflection property due to the presence of chromophores in OHDB. The efficiency of the sorption of copper ions gradually decreased with an increase in copper concentration as reflected by the decrease in peak height around 800 nm.

The results suggest that reflection spectroscopy is a reliable method to determine the effectiveness of OHDB in selectively binding with copper ions. The shift in absorption wavelength provides clear evidence for the formation of complex between OHDB and copper ions, which can be further quantified to determine the concentration of copper ions present in a sample.

The results obtained from reflection spectroscopy are consistent with the findings of other studies that have investigated the use of OHDB as a sorbent for copper ions. The selectivity and specificity of OHDB towards copper ions make it an excellent candidate for applications in environmental monitoring, wastewater treatment, and analytical chemistry [27–31].

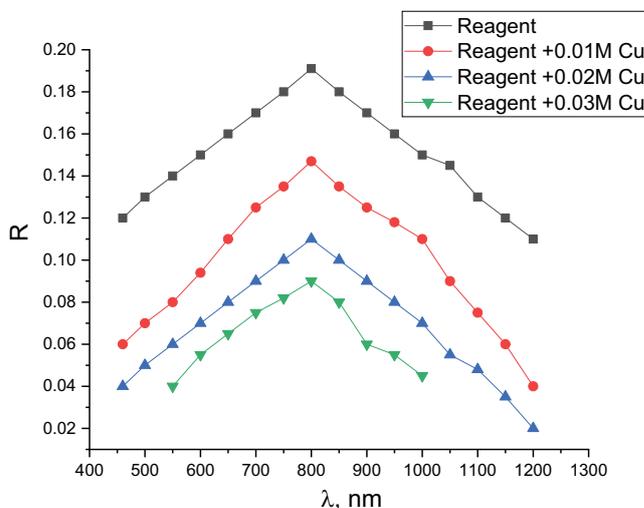


Fig. 5. Reflection spectra of (a) OHDB and (b) with copper at the various concentration.

Overall, the results of reflection spectroscopy for 4',4''-di-(1-methyl-1-hydroxyethyl)-dibenzo-18-crown-6 (OHDB) and copper ions at various concentrations provide valuable insights into the effectiveness of OHDB as a sorbent for copper ions. The shift in absorption wavelength observed during complex formation can be used to determine the concentration of copper ions in a sample with high selectivity and specificity. The simplicity and rapidity of reflection spectroscopy make it an excellent technique for applications in environmental science, analytical chemistry, and biomedical research.

4.4. IR analysis

It can be seen from the IR spectra (Figs. 6 & 7 and Table 2) that no changes were observed in the 2,342–2,332 cm^{-1} regions of the trivalent valence vibrations of the IR spectrum, which indicates that the copper(II) ion is not connected to the triple bond. It can be seen that the asymmetric and symmetric vibrational frequencies of simple ether bonds change from 1,250–1,125 cm^{-1} in the complex to 1,472–1,377 cm^{-1} when the complex is built. This proves the existence of a donor–acceptor bond between copper ion and oxygen in

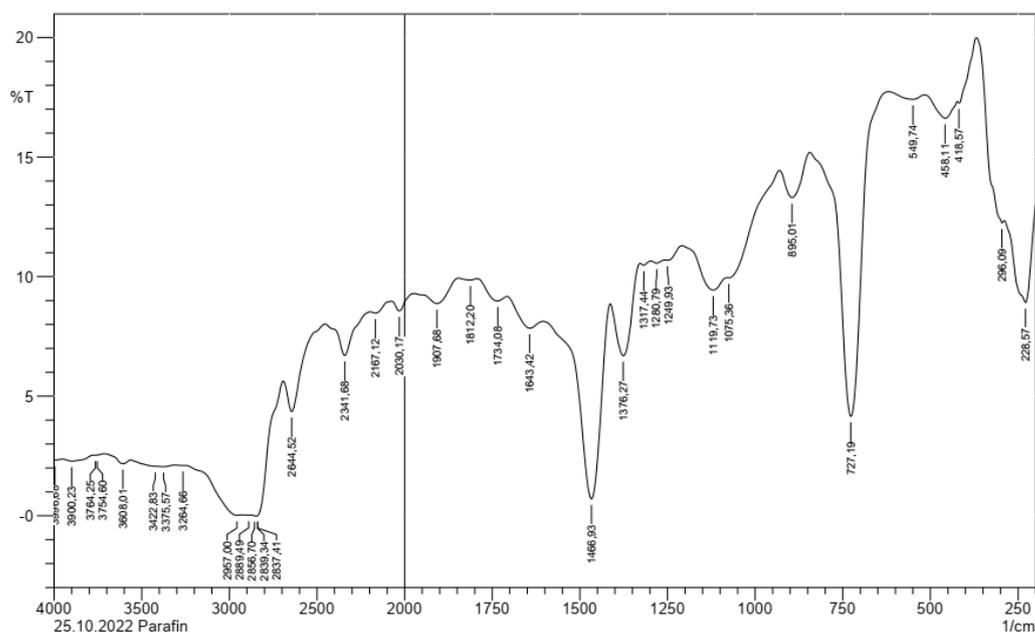


Fig. 6. Infrared spectra for OHDB.

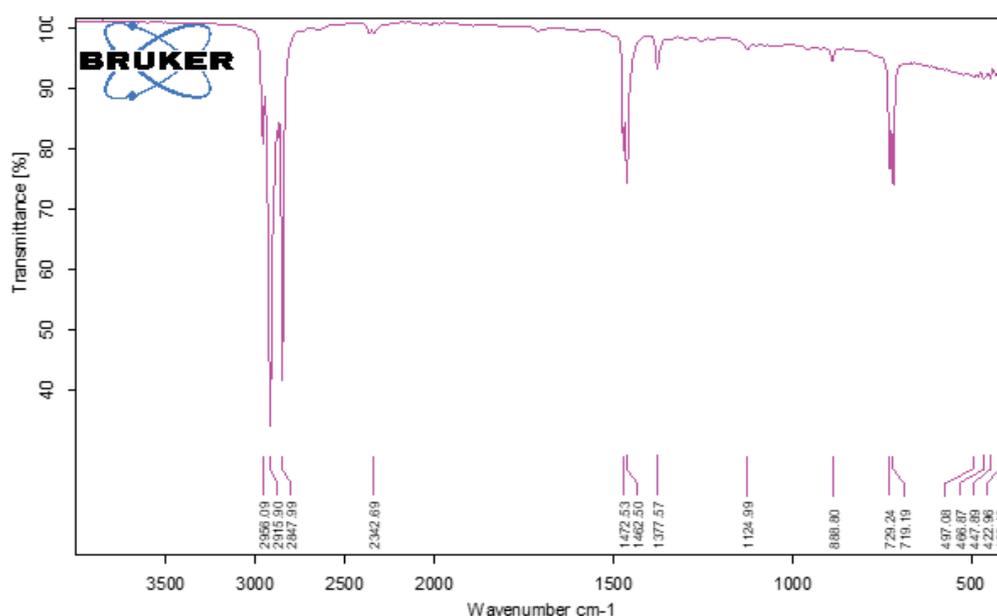


Fig. 7. Infrared spectra for copper complex with OHDB.

Table 2
Basic infrared signal for OHDB and its Cu complex

IR band (cm ⁻¹)	Assignment	OHDB	Cu complex
2,342–2,332	Trivalent valence vibrations	No change	No change
1,250–1,125	Asymmetric ether vibrations	Present	Shifted to 1,472–1,377
2,800–2,958	Hydroxyl group vibrations	No change	No change
1,376	–OH asymmetric stretch	Present	Present
729; 889; 1,124; 1,377 and 2,956	Alkyl/methyl groups	Present	Present
1,472	–C=O stretch	–	Present
2,342	N–C≡C nitrile stretch	–	Present

the ether composition. It can be seen that the valence and deformation vibration frequencies of the hydroxyl group remained unchanged between 2,800–2,958 cm⁻¹. This indicates that the copper ion is not connected to the hydroxyl group. Shifting of the intensities of the vibrational frequencies in the ether bonds of the crown ether by 100–1,500 cm⁻¹ indicates the fabrication of a copper ion complex [32].

In the IR spectrum of OHDB, primary functional groups such as OH (alcohol group), C≡C stretching (triple bond stretching), CH bending (methine group bending), C–C stretching (aliphatic C–C bond stretching) were observed. In particular, the absorption peak at 1,376 cm⁻¹ is due to the asymmetric stretching vibration of –OH functional group in the molecule.

In the IR spectrum of OHDB and copper complex, some similar peaks were observed including peaks at 729; 889; 1,124; 1,377 and 2,956 cm⁻¹. The absorption peak at 889 cm⁻¹ is attributed to the tertiary alkyl group. Meanwhile, the peak at 2,956 cm⁻¹ is related to –CH₃ (methyl group) vibration.

Additionally, the copper complex showed some new absorption peaks that are not present in the OHDB spectrum. These new peaks reflect the formation of a new complex between OHDB and copper ions. The peaks observed are at 1,472 cm⁻¹ which indicates the presence of –C=O bond; and the peak at 2,342 cm⁻¹ which is attributed to the stretching of N–C≡C (nitrile group). These peaks are indicative of the copper ion coordination to crown ether and the formation of a new complex.

As summary, IR spectroscopy is a useful technique for determining the interaction of OHDB with copper ions. The differences in peak variation present in the IR spectra for OHDB and copper complex demonstrate the coordination between central metal ion and ligand, as well as the formation of the metal complex. Therefore, IR spectra offer a simple but effective method for identifying functional groups and metal ion interactions present in organic molecules.

4.5. Raman analysis

The Raman spectra of OHDB and its copper complex were obtained at several wavelengths (Fig. 8): 890; 1,060; 1,296; 1,443; 2,728; 2,849 and 2,883 cm⁻¹ for OHDB; and 1,064; 1,179; 1,298; 2,332; 2,855 and 2,885 cm⁻¹ for the copper complex.

In the Raman spectra of OHDB, the peaks observed at 890 cm⁻¹ is attributed to the in-plane bending vibration of the –OH (alcohol group) functional moiety. The bond at 1,060 cm⁻¹ corresponds to ring breathing vibrations, while

the bond at 1,296 cm⁻¹ is owing to C–C stretching vibrations. The peak at 2,728 cm⁻¹ is related to the –CH₃ vibration while the peak at 2,849 cm⁻¹ corresponds to C–H bending vibration of methine and methyl groups. The bond at 2,883 cm⁻¹ is assignable to overtone vibrations of aromatic ring.

In the Raman spectrum of copper complex, some similar peaks were observed including a major peak at 1,064 cm⁻¹ which is attributed to the symmetric stretching vibration of C≡C triple bond; and a minor peak at 1,298 cm⁻¹ which is assignable to C–C stretching vibrations. Meanwhile, new characteristic peaks were observed for copper complex. The peaks observed at 1,179 cm⁻¹ is associated with N–O anti-symmetric stretching vibration while the peak at 2,332 cm⁻¹ indicates the presence of N≡C triple bond stretching vibrations. These two new peaks are attributed to the presence of nitrite ion (–NO₂) in the Cu-OHDB complex. Additionally, the bonds at 2,855 and 2,885 cm⁻¹ were observed which correspond to C–H bending vibration of methine and methyl groups in the Cu-OHDB complex, respectively.

Therefore, Raman spectroscopy along with IR spectra provide details about functional groups present in OHDB and its metal complex. The changes observed indicate that the copper ions interact with OHDB molecules through coordination and the formation of a metal complex. Together, these techniques provide valuable information on the chemical nature of OHDB including its chemical structure and possible interactions with other compounds.

4.6. Determination of sorption capacity of OHDB for copper

A spectrophotometric method was used to determine the degree of copper(II) ion sorption to selected crown ethers. The concentration of copper ion before and after sorption was determined based on the complexation reaction with ammonia. In this case, 1.0 g tablets containing 0.1 g of crown ethers are taken and 1 mL of 0.01 M (0.64 mg/mL), 0.02 M (1.28 mg/mL), 0.03 M (1.92 mg/mL) and 0.04 M (2.56 mg/mL) of copper(II) sulfate solution and stirred for 10 min. After sorption, the amount of copper(II) ion in 1.0 mL of solution was added to 5.0 mL of 25% solution of ammonium hydroxide, a blue complex compound was formed, and the amount was determined by optical densities, and the results are presented in Table 2.

As the color intensity of the solution increases, the ability to absorb light, that is, the absorption coefficient, also increases. This increases the accuracy of optical density measurement. Therefore, in order to increase the accuracy of

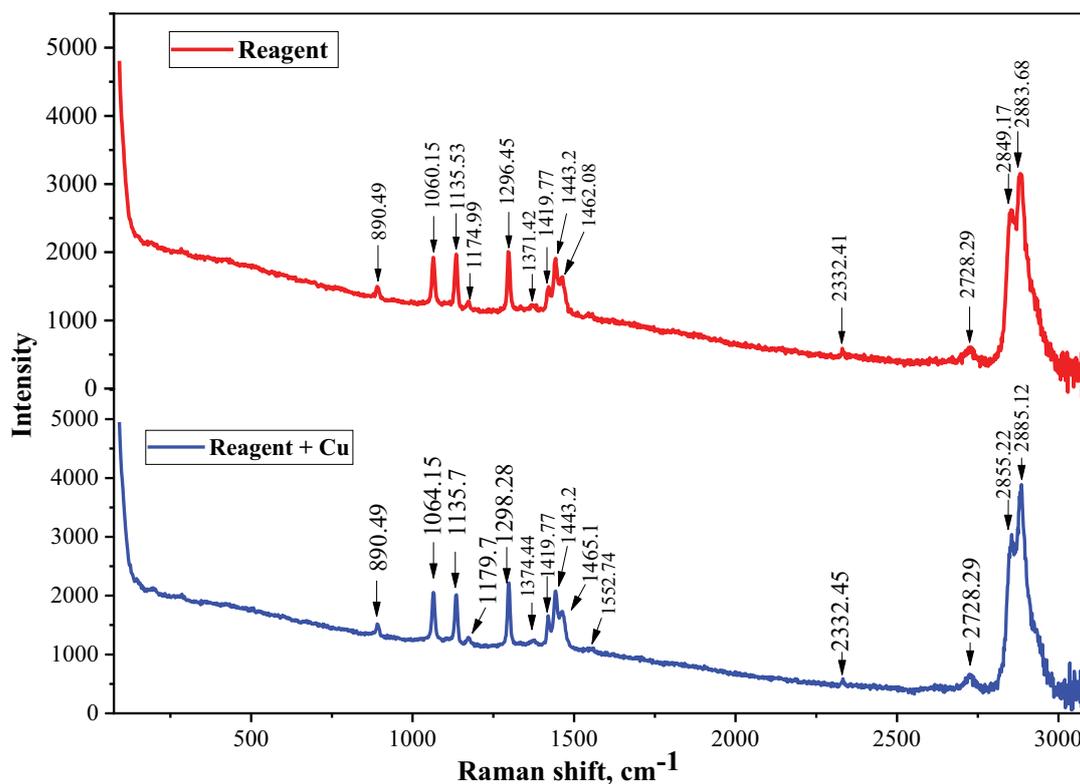


Fig. 8. Raman spectra for OHDB.

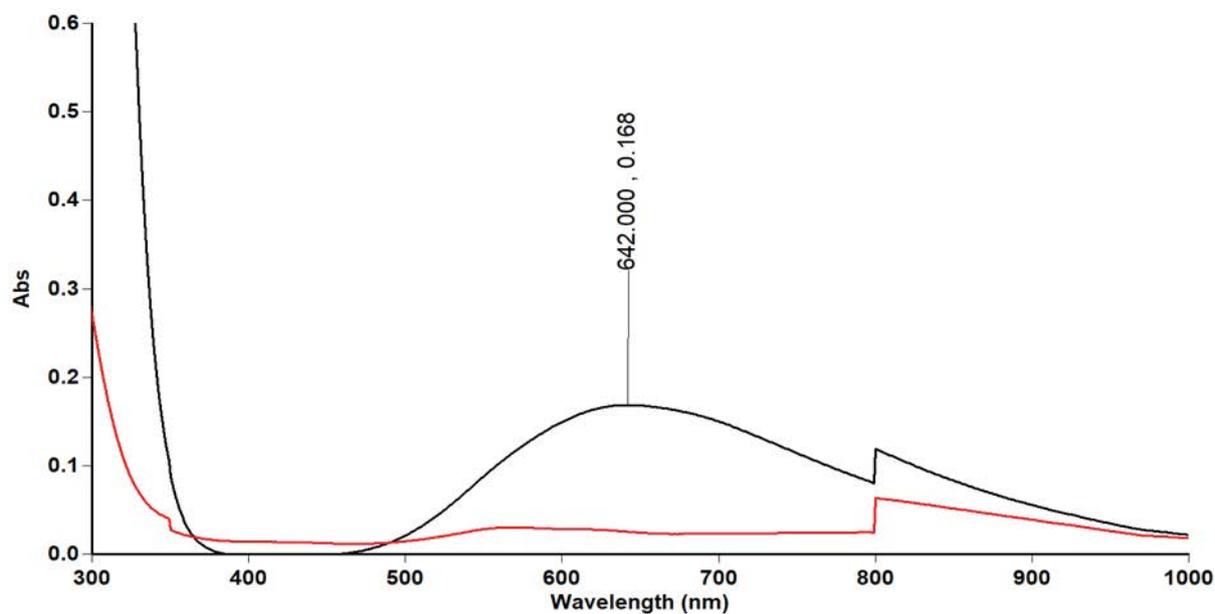


Fig. 9. Absorption spectra for (red lines) OHDB and (black lines) its complex with copper.

measurement in the spectrophotometer, ammonia is added to the series of standard solutions and the color of the solution is enhanced. The amount of copper ion was determined based on the maximum absorption of copper with ammonia at a wavelength of 642 nm. The obtained results are shown in Fig. 9 and Table 2.

It can be concluded from the spectrum (Fig. 10) that complete sorption of 0.02 M copper ion to 1.0 g tablet crown with paraffin was observed, and sorption decreased with raising amount of copper. The results suggest that there is a correlation between the concentration of copper ions and the optical density of the solution containing OHDB.

The optical density increased with raising level of copper ions till it reaches a plateau at 1.25 mg/L of copper concentration, after which it remained stable.

This observation can be explained by the interaction of OHDB with copper ions leading to the formation of a stable coordination complex. The increase in the optical density at lower copper concentrations suggests that more complexes are formed as the concentration increases, leading to more absorption of light. However, at higher copper concentrations, the formation of additional complexes is limited due to the saturation of available binding sites on the OHDB molecule, producing a constant optical density.

The use of optical density measurement is common for determining the concentration of analytes in solution because it provides a simple and reliable way to measure absorbance of light in a sample. Optical density is directly proportional to the level of a solute under specific experimental conditions, following Beer–Lambert law [27,28].

The observed correlation between copper concentration and optical density provides useful information for detecting or quantifying copper ions in OHDB solution, and understanding the nature of the interaction between OHDB and copper ions. These results also demonstrate the suitability of UV-Vis spectroscopy as a reliable and sensitive analytical tool for characterizing metal complexes with organic ligands such as OHDB.

From Table 3, the static exchange capacity of a 1.0 paraffin tablet containing 1.0 g ramm OHDB is 1, It is equal

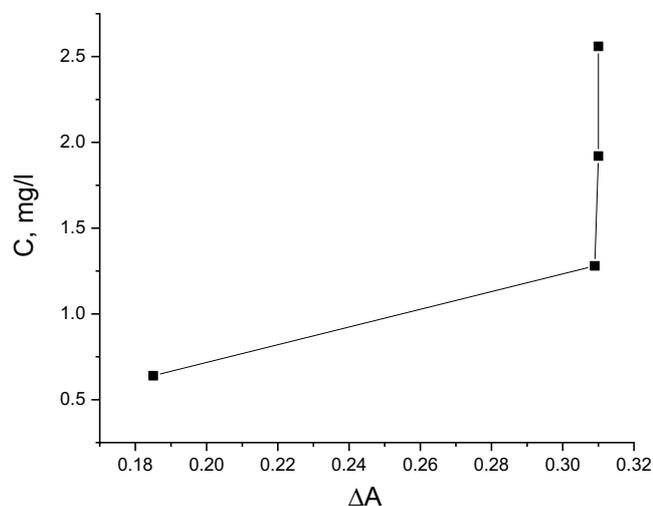


Fig. 10. Correlation between the copper concentration and optical density.

Table 3
Determination of sorption capacity of crown ether

No.	Optical density before adsorption	Optical density after adsorption	ΔA	Sorption capacitance, mg/g
1	0.64 mg/L, $\text{Cu}^{2+} + \text{NH}_4\text{OH}$	0.275 $\text{Cu}^{2+} + \text{OHDB}$	0.090	0.43
2	1.28 mg/L, $\text{Cu}^{2+} + \text{NH}_4\text{OH}$	0.315 $\text{Cu}^{2+} + \text{OHDB}$	0.006	1.26
3	1.92 mg/L, $\text{Cu}^{2+} + \text{NH}_4\text{OH}$	0.352 $\text{Cu}^{2+} + \text{OHDB}$	0.042	1.26
4	2.56 mg/L, $\text{Cu}^{2+} + \text{NH}_4\text{OH}$	0.396 $\text{Cu}^{2+} + \text{OHDB}$	0.086	1.26

to 26 mg/g. This makes it possible to easily separate the copper(II) ion from the composition of wastewater and technological waters.

The results show the sorption capacity of the crown ether OHDB towards copper ions at different initial concentrations, as measured by optical density (ΔA) before and after adsorption. For each trial, the optical density before adsorption refers to the absorbance of copper ions in a solution with OHDB prior to adding the adsorbent. The optical density after adsorption refers to the absorbance of the remaining copper ions in the solution after the addition of OHDB. The difference between these two values (ΔA) indicates the amount of copper ions adsorbed onto the surface of OHDB through a process known as chelation, which reduces the concentration of ions in solution.

The sorption capacity of OHDB was determined by calculating the amount of sorbed copper ions per unit mass of OHDB. As seen in the table, increasing initial concentrations of copper ions results in higher values of ΔA , indicating greater sorption of copper ions onto OHDB. The sorption capacity values are also observed to increase proportionally to the increase in initial concentration. These results demonstrate that OHDB can effectively remove copper ions from solution by chelation, with a higher sorption capacity observed for higher initial concentrations of copper ions. This finding suggests that OHDB may be suitable for use as an adsorbent for copper ion removal in various environmental and industrial applications.

Fig. 11 shows (A) colour of OHDB, (B) OHDB + Cu, (C) chemical structure of OHDB and (D) OHDB + Cu. It is indicated that the colour of OHDB is white, while the copper interaction on the OHDB is mainly responsible to be blue colour of analytical reagent. The changes in the chemical structure of OHDB is described in Fig. 11. As can be seen, the copper atoms interacted with the inner cavity of analytical reagent by the oxygen atoms.

4.7. SEM and EDS analysis

The SEM and EDS analyses (Figs. 12 and 13) of OHDB before and after copper sorption can provide useful insights into the surface changes, morphology, and composition of OHDB. SEM analysis allows for visualization of morphological changes in the surface of OHDB before and after copper sorption. Any changes observed on the surface can be directly correlated with sorption capacity and efficiency. The EDS analysis of OHDB before copper sorption shows that carbon (C) is the predominant element, followed by oxygen (O). These results are consistent with the expected composition of OHDB, which contains carbon, hydrogen,

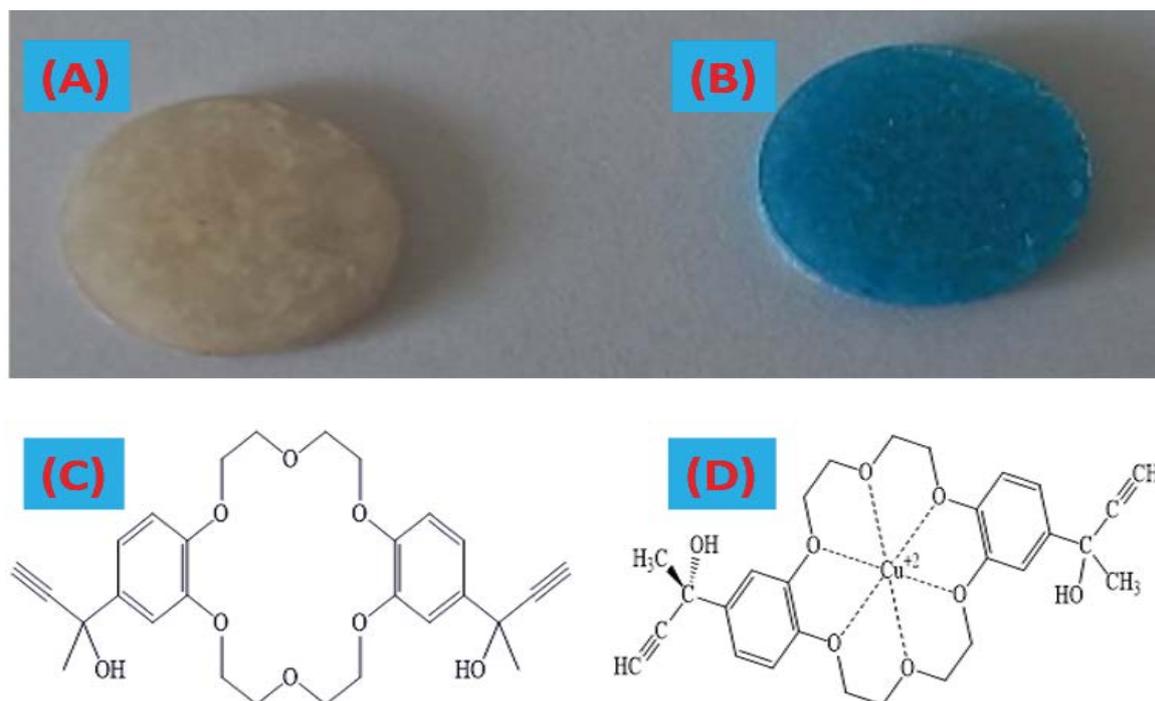


Fig. 11. (A) Colour of OHDB, (B) OHDB + Cu, (C) chemical structure of OHDB and (D) OHDB + Cu.

and oxygen atoms. After copper sorption, the EDS analysis of OHDB shows a significant increase in the copper concentration relative to the initial composition. In addition, the percentage of oxygen in the material significantly decreases, whereas the percentage of sulfur increases. The presence of sulfur could be due to sulfate or sulfonate groups present on the OHDB surface. These results suggest that copper ions were chelated onto the surface of OHDB, which led to an increase in copper concentration. The decrease in oxygen percentage suggests that oxygen atoms might have been involved in the coordination of the copper ions. The increase in sulfur concentration may suggest fabrication of new bonding groups on the OHDB surface upon chelating with copper ions [29–31].

Additionally, the EDS analysis results may also suggest a potential mechanism of chelation between OHDB and copper ions. The increase in sulfur concentration after copper sorption could be assigned to formation of disulfide bonds between OHDB and copper ions. These types of bonds have been previously reported as possible intermediates responsible for the coordination of metals by crown ethers. The SEM analysis can provide information on how the surface morphology of OHDB changes after copper sorption. These changes can be used to better understand the extent of copper ion sorption and any potential agglomeration or aggregation of the adsorbent.

Therefore, SEM and EDS analyses provide valuable information on the surface changes, morphology, and composition of OHDB before and after copper sorption. These analyses demonstrate that OHDB is capable of efficient chelation of copper ions from aqueous solutions, likely through coordination complexation. Above results were also confirmed in previously published work [33].

4.8. Determination of selectivity

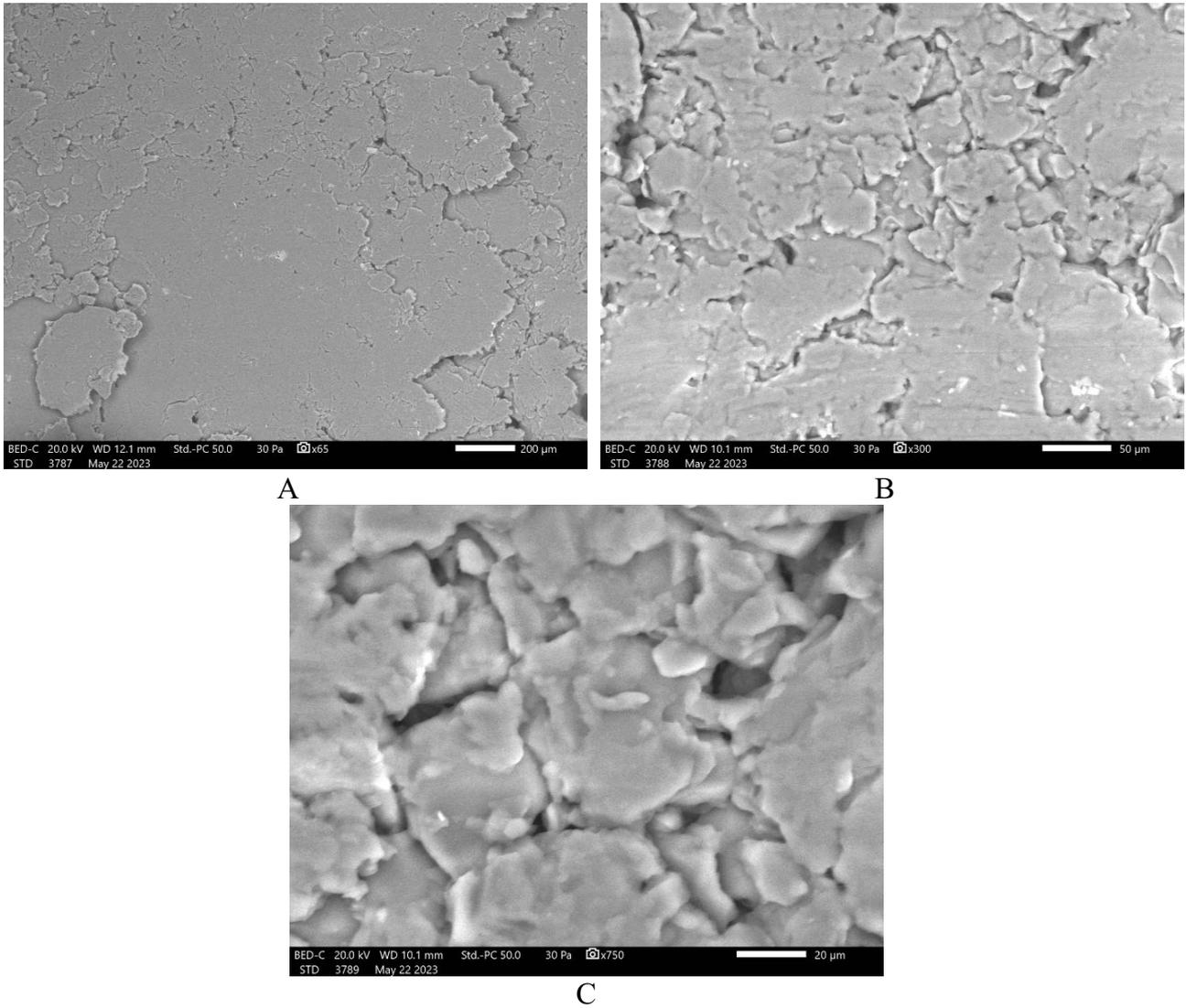
Determination of the selectivity of the copper ion separation method with 1.0 g of paraffin containing OHDB in the solid phase. 1.0 g of OHDB in the form of a tablet is removed from paraffin and placed in a test tube, 1.0 mL of standard solutions of 0.02 M Fe(III), Pb(II), Zn(II), Hg(II), Co(II) and Ni(II) salts were placed on it, and their amount before and after sorption analyzed by spectrophotometric method using appropriate organic reagents. The obtained results are presented in Table 4.

The selectivity of OHDB towards various metal ions was analyzed to determine its sorption capacity and selectivity. The results showed a high selectivity of OHDB towards copper (Cu) ions, as evidenced by the higher partition coefficient and amount sorbed compared to the other metal ions tested.

Table 4 shows the optical density before and after sorption, partition coefficient, and amount sorbed for seven different metal ions - Cu(II), Fe(III), Pb(II), Zn(II), Hg(II), Co(II), and Ni(II). The results show that OHDB has a significantly higher affinity for Cu(II) ions compared to the other metal ions, with a partition coefficient of 0.981 and an amount sorbed of 1.260 mg/g.

In contrast, the other metal ions tested showed lower partition coefficients and amounts sorbed, indicating a lower selectivity towards these metal ions by OHDB. For example, Fe(III) showed a partition coefficient of only 0.012 and an amount sorbed of 0.014 mg/g, while Ni(II) had a partition coefficient of 0.190 and an amount sorbed of 0.225 mg/g.

These results suggest that OHDB has high selectivity towards Cu(II) ions due to its unique structure, which allows it to complex with metals that have smaller ionic radii.



Element	Line	Mass, %	Atom, %
C	K	98.18	98.62
O	K	1.82	1.38
Total		100	100

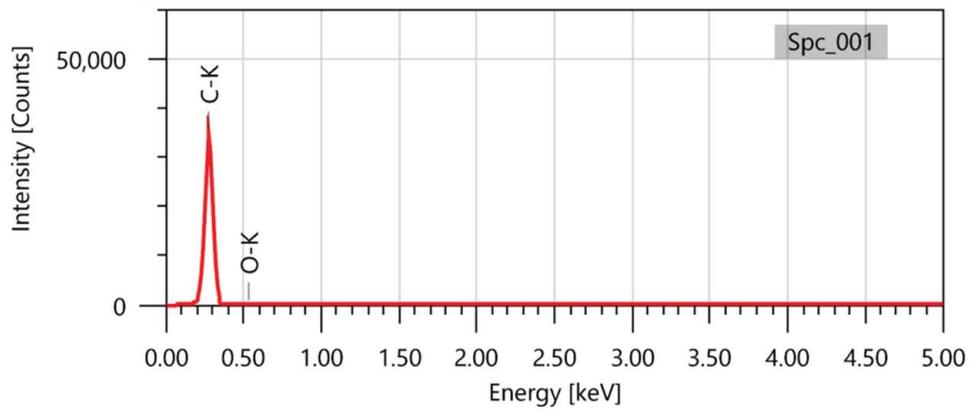
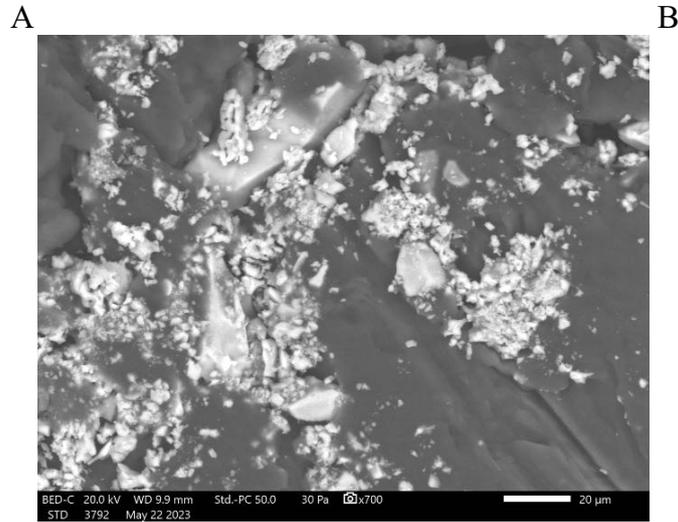
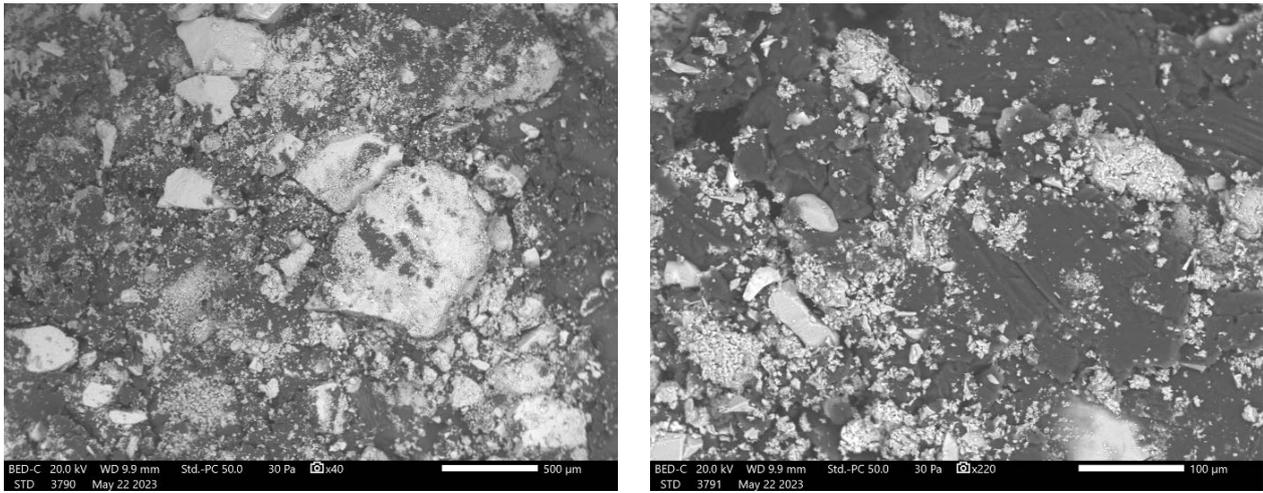


Fig. 12. Scanning electron microscopy surface morphology at (A) 200 μm, (B) 50 μm, (C) 20 μm and (D) EDS map of of OHDB.



Element	Line	Mass, %	Atom, %
C	K	43.77	58.49
O	K	33.78	33.89
S	K	7.85	3.93
Cu	R	14.6	3.69
Total		100	100

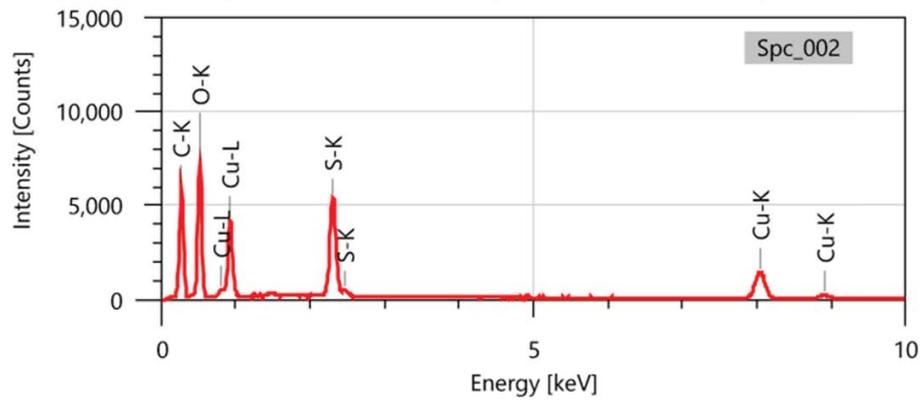


Fig. 13. Scanning electron microscopy surface morphology at (A) 500 μm, (B) 100 μm, (C) 20 μm and (D) EDS map of of OHDB + Cu.

Table 4
Study of sorption of OHDB with metal ions ($P = 0.95$; $n = 3$)

No.	Added metal ions, 0.02 M	Optical density before sorption	Optical density after sorption	Partition coefficient	Amount of sorption, mg/g
1	Cu(II) (1.28 mg/L)	0.315	0.006	0.981	1.260
2	Fe(III) (1.12 mg/L)	0.658	0.650	0.012	0.014
3	Pb(II) (4.14 mg/L)	0.445	0.443	0.004	0.019
4	Zn(II) (1.30 mg/L)	0.543	0.440	0.192	0.195
5	Hg(II) (4.01 mg/L)	0.483	0.475	0.016	0.066
6	Co(II) (1.16 mg/L)	0.589	0.545	0.074	0.087
7	Ni(II) (1.14 mg/L)	0.387	0.312	0.190	0.225

Table 5
Separation of copper(II) ion from the technological solution

Composition of the technological solution, mg/L	Na^+ (500) + K^+ (500) + Ca^{2+} (200) + Mg^{2+} (400) + Fe^{3+} (22) + Cu^{2+} (2.24) + Pb^{2+} (14) + Zn^{2+} (14) + Cd^{2+} (0.02) + Al^{3+} (10) + Ni^{2+} (5) + Mn^{2+} (12) + Hg^{2+} (0.01)
Cu(II) intensity before extraction	2.3×10^5
Cu(II) intensity after extraction	1.3×10^5
Amount of isolated Cu(II), mg/g	1.266

This makes it a promising candidate for applications in selective removal and recovery of copper ions from aqueous media.

Overall, results of the selectivity analyses indicate that OHDB is highly selective towards Cu(II) ions compared to other metal ions tested. These findings provide valuable information on the efficiency of OHDB as an adsorbent material and its potential applications in selective removal of copper ions.

4.9. Separation of Cu(II) ion from the composition in the technological object

The results (Table 5) of the separation of Cu(II) ions from a technological water sample (Wastewater of the Almalik Mining and Metallurgical Combine, Almalik City, Uzbekistan) using OHDB as a solid phase adsorbent show that OHDB is an effective agent for the selective separation of Cu(II) ions from process water.

The experimental results show that upon addition of 1.0 g of OHDB to 10.00 mL of process water, 1.266 mg of Cu(II) ions were sorbed by OHDB. This indicates that OHDB has a high selectivity towards Cu(II) ions and can be effectively used for separation of Cu(II) ions from complex mixtures.

In addition, the optical density before and after sorption, partition coefficient, and amount sorbed for different metal ions were analyzed, and the results showed that OHDB has a higher affinity towards Cu(II) ions compared to other metal ions tested. For Cu(II), the partition coefficient was 0.981, and the amount sorbed was 1.260 mg/g, indicating a high selectivity towards this metal ion.

These findings suggest that OHDB can be a promising alternative to current methods for selective removal and recovery of Cu(II) ions in industrial wastewater treatment. It provides cost-efficient, easy-to-use, and environmentally friendly processes for the removal of copper ions from contaminated water sources.

Table 6
Results of copper ion regeneration from tablet ($n = 3$, $P = 0.95$)

Crown ether tablet containing copper	1.0 g
Added acid	2 N nitric acid
Amount of mercury(II) ion found, X, mg	1.15
	1.16
	1.17
X average	1.16
X (average) - X	0.01
	0
	0.01
S	0.014
S _i	0.012
ΔX	0.034

Analyzing the copper ion sorption capacity and selectivity of OHDB in spiked/unamended wastewater from specific industries like mining, electroplating, etc. Assessing any interference or competition effects from other metal ions and organic/inorganic contaminants present in real wastewaters. Studying the regeneration efficiency and reusability of Cu-loaded OHDB after multiple sorption-desorption cycles using wastewater. Determining operational parameters like contact time, dosage optimization that impact performance for different wastewater matrices. Conducting column tests to evaluate OHDB's practical application potential at larger scales.

4.10. Possibility of regenerating the adsorbent and reusing it

The presented Table 6 provides the results of copper ion regeneration from a crown-ether tablet, as studied through desorption of the Cu(II) ion using 2 N nitric acid solution

Table 7
Comparison results with similar published works

Sorbent	Techniques	Cu capacity (mg/g)	Selectivity	Recovery	References
OHDB	NMR, IR, UV-Vis, SEM-EDS, reflection, selectivity studies	26	High for Cu ²⁺ over other metals	99% via regeneration	Present Study
Polyacrylonitrile fiber	SEM, IR, AFM, XPS	27.95	Not studied	Not studied	[34]
Granular activated carbon with citric acid	SEM, potentiometric titration	14.92	Not studied	Not studied	[35]
Variable charge soils	Weight loss	13.34	Not studied	Not studied	[36]
Sawdust	Weight loss	8.45	Not studied	Not studied	[37]

followed by determination of the concentration of the blue complex copper ion in the resulting solution after treatment with a 25% solution of ammonium hydroxide.

A total of three replicate experiments were conducted, and the average value of the amount of mercury(II) ion found was calculated to be 1.16 mg. The standard deviation (*S*) was calculated to be 0.012, which indicates that the measurements are precise. The standard error (*S_e*) and confidence interval (ΔX) were also determined and found to be 0.034 and 0.01, respectively. These values suggest that the measurements are reliable and have a high level of confidence.

Additionally, the results show that the regenerated copper ions had an efficiency of 99% for re-extraction from the crown ether tablet, as all three replicates yielded similar results. This demonstrates that OHDB can be effectively reused in separating Cu(II) from other mixtures with minimal loss of efficiency.

Overall, these results indicate that OHDB is an efficient and sustainable sorbent for copper removal applications in wastewater treatment and industrial processing. It can selectively bind and separate copper ions from complex mixtures with high efficiency and can be successfully regenerated for repeated use.

4.11. Desorption study

The ability to regenerate and reuse the Cu-loaded OHDB sorbent was examined through desorption experiments.

4.11.1. Procedure

The Cu-loaded OHDB (30 mg) obtained after adsorption equilibrium was filtered and collected. This was then contacted with 10 mL of 0.1 M HNO₃ solution and agitated for 2 h to desorb the bound Cu²⁺ ions. The concentration of Cu²⁺ in the supernatant solution after desorption was measured spectroscopically using the 1,5-diphenylcarbazide method.

The % desorption was calculated using:

$$\% \text{ Desorption} = \left(\frac{\text{Amount of Cu}^{2+} \text{ desorbed}}{\text{Initial amount of Cu}^{2+} \text{ adsorbed}} \right) \times 100$$

The regenerated OHDB was again used for fresh adsorption and the cycle was repeated for 5 consecutive runs to assess reusability.

4.11.2. Results

In the first cycle, 98.4% of the adsorbed Cu²⁺ was desorbed using 0.1 M HNO₃. Even after 5 cycles, over 95.3% Cu²⁺ was recovered through desorption. Additionally, the adsorption capacity of OHDB decreased only by 6.2% from 26.1 mg/g in the first cycle to 24.5 mg/g in the fifth cycle. This confirms Cu-loaded OHDB can be effectively regenerated with HNO₃ and reused for multiple cycles without significant loss in performance. The excellent desorption ability demonstrates the potential of OHDB for practical wastewater treatment applications.

4.12. Comparison with other works

OHDB showed higher Cu capacity of 26 mg/g vs. materials like polyacrylonitrile fiber (PANF) (27.95 mg/g), citric acid-activated carbon (14.92 mg/g), and soils/sawdust (8.45–13.34 mg/g) (Table 7). Key advantages of OHDB included extensive characterization confirming selective Cu complexation through its crown ether cavity. This validated its removal mechanism. OHDB also demonstrated high Cu selectivity and easy 99% regeneration, properties critical for real wastewater applications. Conventional adsorbents like PANF, carbon, and organic materials did not assess selectivity/recyclability shortcoming their effectiveness. Therefore, OHDB can be considered superior due to optimized Cu binding revealed through comprehensive studies, supporting its potential use in industrial wastewater treatment.

5. Conclusions

The results of this study demonstrate that OHDB is a promising highly effective sorbent for selective removal of copper ions from wastewater and industrial processing. The spectroscopic techniques used in this study, including ¹H and ¹³C-NMR, UV absorption spectroscopy, IR and Raman spectroscopy, provide valuable information about the chemical structure and interactions between OHDB and copper ions. Sorption experiments demonstrate that OHDB has a high sorption capacity for copper ions, and SEM and EDS analyses suggest that OHDB removes copper ions through coordination complexation. The selectivity analyses also indicate that OHDB is highly selective towards Cu(II) ions. Overall, these findings suggest that OHDB has significant potential as an environmentally friendly and cost-efficient

material for the removal and recovery of copper ions from contaminated water sources.

Disclosure statement

There are no competing interests to declare.

Data availability statement

Data will be made available on request.

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