

Preliminary Cu (II) extraction analysis with biobased lipophilic 14, 16-hentriacontanedione

Abstract

This preliminary investigation emphasizes the use of renewable (sustainable) chelators otherwise known as greener chelators (which are currently more desired) for metals recovery. Importantly, the work showcases the application of lipophilic type of greener chelator (14, 16- hentriacontanedione - Htd). Lipophilic chelator can be readily recycled hence making it to be more economic than the corresponding hydrophilic ones. Hence, in this studies liquid-liquid biphasic Cu(II) extractions from a varying concentrations of synthetic Cu(OAc)₂ solutions with the chelator were demonstrated. It was observed that, the equilibrium equation for the Cu(II) extraction with the chelator is: $\text{Cu(OAc)}_{2(\text{aq})} + \text{HR}_{(\text{org})} \leftrightarrow \text{CuR(OAc)}_{(\text{org})} + \text{H}^+ + \text{OAc}^-$. The results also showed that, the % Cu(II) extracted with respect to the theoretical Cu(II) extraction by the renewable and greener lipophilic β -diketone is excellent at the conditions of the experiment. An extraction of 38% and 50% Cu(II) were found at Cu:L ratio of 14:1 and 30:1 respectively. Higher concentrations of chelator, higher Cu: L ratio and higher pH gave better amount of Cu (II) extracted. This biobased renewable chemical can find use as metals chelator and in other allied applications.

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Introduction

Metals are applied in modern low-carbon energy technologies such as; nuclear, solar, wind, bioenergy, carbon capture and storage (CCS), electricity grids,^{1,2} and manufacturing of consumer goods such as cell phones, television and computers.^{3,4} However, the natural deposits of metals are depleting with time, hence there is need to recover metals dispersed in the environment. Recently metals recovery using bio-derived materials has seen increased attention for the sake of long-term elemental sustainability.⁵⁻¹⁰ Chelating agents can be used to extract metals from the environment in order to enhance metal recovery, prevent toxic emissions and for removal of unwanted metals in chemical processes or products, such as in the case of removing metal catalysts from pharmaceuticals.

The extraction of metals with β -diketone chelators has been widely reported.¹¹⁻¹³ Other classes of chelators, such as carboxylic acids, ketones, alcohols, ethers and esters have also been used as metals extractants.¹⁴ Recently alternative more-benign chelating agents are preferred for metals recovery in order to avoid negative environmental impact from continuous use over variety of applications.^{15,16} More so, hydrophobic metal chelating extractants are crucial because they will not be so easily lost into the environment via aqueous waste streams.¹⁷ This has led to the search for new low-cost chelants where biomass is seen as preferred feedstock, thus further improving the sustainability of the concept of metal recovery.¹⁸ Thus, bio-derived lipophilic β -diketones will be useful in this regards. In addition, these lipophilic β -diketones will not be easily released into the environment like the commonly used chelants; hence they will have a less negative impact on the environment. However, there is currently limited evidence on the use of bio-derived lipophilic β -diketones and their modified analogues (3-substituted lipophilic β -diketones) in metal recovery, despite the obvious promise of their use.

Moreover, metal extraction via chelation is regarded as an

economical process,¹³ especially with lipophilic extractants, because the chelant can be recycled and reused. Furthermore, solvent extraction techniques are among the most studied methods for the production and recovery of various metal ions from different sources because of their simplicity, speed and wide scope.¹⁹ It has also been highlighted that solvent extraction technologies are particularly good for recovery of metals from secondary sources, such as low grade ores and mixed metals and can lead to excellent material and energy balances.²⁰ This initial study was carried out solely for the extraction of Cu(II) with the lipophilic β -diketone because Cu-diketonates are known to be stable over a broad pH range.¹⁶ More so the complexes of transition metals are found to be highly stable compared with those of non-transition elements.¹⁶ Attention is also given to copper recovery partly because of its technological and biological importance. Additionally copper species such as Cu(OH)⁺, Cu₂(OH)₂²⁺ and CuCO₃ are reported as toxic, and as such their reduced emission into the environment is highly desirable.²¹ Hence this paper reports the preliminary investigation of Cu(II) extraction analysis using a biobased (renewable) lipophilic 14, 16-Hentriacontanedione.

Experiment

Purification of hentriacontane-14,16-dione from wheat straw wax with petroleum ether

The isolation of the Htd was carried out as previously done by Horn et al.²² with some slight modifications as reported by Asemave et al.²³ The isolated 14, 16-hentriacontanedione (Htd) is given in Figure 1 below.

Procedure of the solvent extraction of the metal ions

The Cu(II) extraction procedures were performed as previously reported by Fanou et al.²⁴ with some slight modifications as reported by Asemave,²⁵ and Asemave et al.²³



Figure 1 A 3D view of the 14, 16-hentriacontanedione ($C_{31}H_{60}O_2$).

Results and discussion

Slope analysis for Cu(II) extraction from $Cu(OAc)_2$ solution with Htd

Slope analysis is a common method for stoichiometric assessment in the solvent extraction of metals. In order to achieve this, the distribution constants for the removal of Cu(II) from $Cu(OAc)_2$ solutions with different concentrations of the Htd and the corresponding ΔpH were taken. Then equilibrium slope analysis for the extraction were obtained as plots of $\log D$ vs $[Htd]$ and $\log D$ vs ΔpH as given in Figure 2 & Figure 3. These plots show the dependence of distribution constant on the amount of chelator and pH as previously found.²⁶ Generally the slope of such plots are taken as the mole of the ligand (in this case the β -diketone) required for 1 mole of the metal ion, or as the mole of H^+ release for extraction of 1 mole of metal respectively.^{27,28} Sepulveda et al.²⁹ also reported plots of $\log D$ as function of equilibrium pH and $\log [chelator]$ from which the slope was used to obtain the stoichiometry of the equilibrium of extraction equation. Table 1 is the determined distribution of Cu(II) extracted based on the concentration of the β -diketone.

Table 1 Dependence of distribution of Cu(II) extracted on concentration of the Htd

[Htd], M	Log [Htd]	D	Log D	ΔpH	Log D
0.00156	-2.8069	0.16662	-0.7783	0.48	-0.7783
0.00094	-3.0269	0.08258	-1.0831	0.26	-1.0831
0.00062	-3.2076	0.05006	-1.3005	0.1	-1.3005
0.00031	-3.5086	0.02945	-1.5309	0.02	-1.301

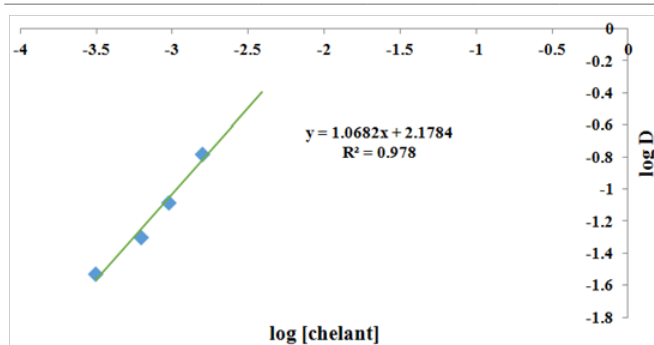


Figure 2 Plot of the $\log D$ vs $\log [Htd]$ for the extraction of Cu(II) from $Cu(OAc)_2$ solution.

The plots of $\log D$ vs $\log [Htd]$ and plot of $\log D$ vs ΔpH have slopes of approximately 1 implying that there is involvement of one mole of β -diketone and release of one proton for each mole of Cu(II) extracted. Therefore, the stoichiometry for the removal Cu(II) from $Cu(OAc)_2$ solution with the Htd under this condition is 1:1, Cu: L. Begum et al.³⁰ performed Cu(II), Zn(II) and Ni(II) extraction with cyanex 272 (dissolved in hexane) and found that at lower OAc^- ion concentration (0.01 to 0.05M), the distribution ratio of Cu(II) increased with increase in OAc^- ion, after that the distribution ratio was independent in the OAc^- concentration in the medium range

of 0.05 to 0.25M. Subsequently, at higher OAc^- ion concentration of 0.25-0.5M, the extraction efficiency decreased. This happened because OAc^- ion concentration increased in the aqueous phase, the species Cu(II), $[Cu(OAc)]^+$ and $[Cu(OAc)_2]$ were formed gradually as described below (Figure 4).³⁰

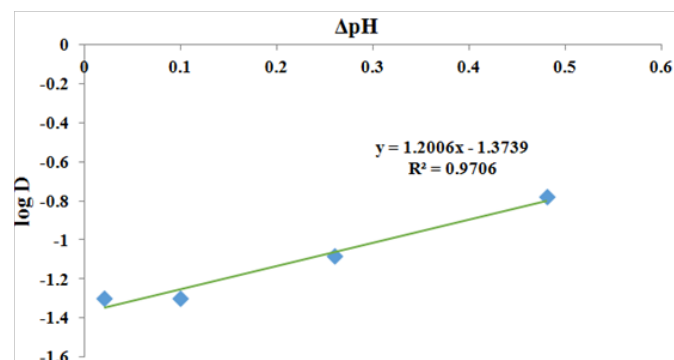


Figure 3 Plot of $\log D$ vs ΔpH for the extraction of Cu(II) from $Cu(OAc)_2$ solution with the Htd.

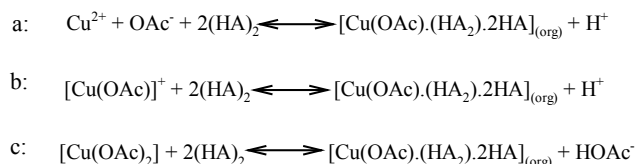


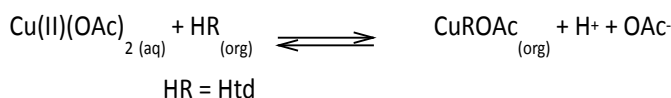
Figure 4 Equilibria for Cu(II) extraction with Cyanex 272 at low.

(a) Medium

(b) High OAc^- concentrations (Begum et al.³⁰)

Begum et al.³⁰ also found out that for nickel extraction, the percentage of extraction increased with increase in acetate ion concentration (0.01 to 0.5M). For the extraction of zinc, the extraction percentage was increased slowly with acetate ions. These facts imply the involvement of OAc^- ion in the copper complex formed in the organic phase. Therefore, in the present studies also is logical to say that there was involvement of OAc^- in the Cu-diketone complex as previously reported especially that the experiments were conducted with at least 5-fold excess amount of the $Cu(OAc)_2$ solution. Others have also reported that stoichiometry depends largely on the concentration of ligand.^{27,31} According to Gerald et al.²⁷ plot of $\log D$ of Co(II) against $\log [1\text{-phenyl-3-methyl-4-(p-nitrobenzoyl)pyrazolone, HPMNP}]$ has a slope of 1.0 at lower concentrations of HPMNP and a slope of 2.0 at higher concentration of HPMNP. It was assumed that Co(II) was initially extracted as $Co(PMNP)^+$ and at higher concentration, the cationic species changes to $Co(PMNP)_2$. Such charged metal complex was also found by Lertlapwasin et al.³² while extracting Cu(II) with ionic liquid combined with 2-aminothiophenol ligand. Furthermore, Begum et al.³⁰ also plotted $\log D$ vs equilibrium pH of the extraction Cu(II), Ni(II) and Zn(II) with Cyanex 272 and observed it was linear with a slope of 1 implying the release of H^+ during the extraction of the metal ions. In addition, β -diketones are known to form neutral complexes by cation exchange.²⁹ Therefore, based on this present studies of the equilibrium slope analysis, a proposed equilibrium for

the Cu(II) extraction with the Htd at these conditions is given below in Equation 2. Such cationic exchange equilibria of extraction of metal with Htd have been similarly reported in other works (Figure 5).^{29,33}



Equation 2 The equilibrium equation for extraction of Cu(II) with Htd

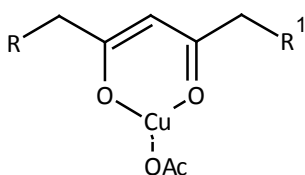


Figure 5 The structure of the product (complex) formed (CuROAc).

Therefore, on the basis of the above stoichiometry (Equation 2), the amount Cu(II) extracted with respect to the theoretical Cu(II) extraction is $38 \pm 2.68\%$ at the equilibrium pH range of 5.3–5.8 with Cu: Htd ratio range of 1:3–1:14. Hence we can say that the biobased (renewable) lipophilic 14, 16-hentriacontanedione is an effective chelator of metals. It can even do better when the pH of the extraction medium is raised. Obviously as the concentration of the β -diketone increases, more of the Cu(II) was extracted.

Effect of pH on the extraction of Cu(II) from Cu(OAc)₂ with Htd

Solvent extraction of metal ions is dependent on the equilibrium pH as well,³¹ because chelators are effective at different pH. Moreover, each metal ion has a peculiar pH value requirement for its extraction. An influence of pH on extraction of Cu(II) from 0.03 M Cu(OAc)₂ solution was studied here at three different pH values (7.40, 6.41 and 3.00) with 0.001M Htd as presented in Figure 4. The ratio of the metal: L is 30:1. Therefore, at pH 6.41 (no adjustment), 32mg/L Cu(II) was removed representing 50% Cu(II) extracted. When the pH was adjusted from 6.41 to 7.41 with NaOH, 426mg/L Cu(II) was quantitatively extracted. The high levels of Cu(II) extracted at pH 7.41 is due to precipitation of Cu(II) ions with OH⁻. Lowering the pH from 6.41 to 3.00 by adding HCl resulted into no extraction. It can also be deduced that, the higher ratio of M:L of 30:1 favors the Cu(II) extraction. When the According to Shigematsu et al.³⁴ Cu(II) ions can be extracted in the pH range of 5-9 using β -diketone. Begum et al.³⁰ found that the pH of 5.3 and 7.45 are optimal for extraction of Cu(II) and Zn(II) using Cyanex 272. The point here is that, the β -diketones are effective chelators under basic condition as it has been reported.^{11,20} Hence, increase in pH favors the extraction of Cu(II) from the Cu(OAc)₂ solution. It has been reported that for the extraction of metal ions from acidic medium, higher concentration of β -diketone is required.³⁵ The effect of concentration, solvent, temperature, effect of contact time, the UV-visible and FTIR spectra of the β -diketonate of the extracted Cu has been earlier published.³⁶ More so further studies on metals recovery are published by Asemave et al.^{23–25} (Figure 6).

Effect of ionic strength on extraction of Cu(II) from CuCl₂ solution

Influence of ionic strength was tested by adding KCl as similarly reported in the literature¹⁹ on the removal of Cu(II) with the Htd M:L (5:1). 10.3mg, 20.40mg, 31.01mg and 40.2mg of KCl were

respectively added into 5mL 15mM solution of CuCl₂ and the Cu(II) extracted with 3mM Htd. There was slight decrease in the amount of Cu(II) removed with the Htd as the ionic strength increased in the range of 0.05–0.13M (Figure 7). The levels of Cu(II) removed were between 26mg/L–13mg/L. Other studies of extraction of metals showed that, increase in ionic strength enhances the extraction efficiency³⁷ where the added salt could be acting as salting out agent and weak complexing agents.^{19,38} However, the use of larger amount of metal ions versus chelator ratio (5:1) in the present studies may have brought about the opposite trend of the influence of added KCl during the extraction of the Cu(II) ions.

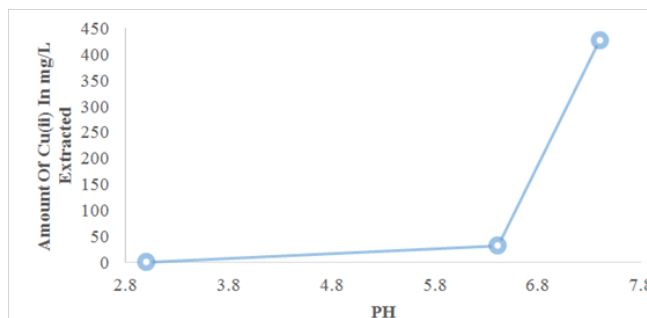


Figure 6 Effect of pH on extraction of Cu(II) from Cu(OAc)₂ solution using the Htd.

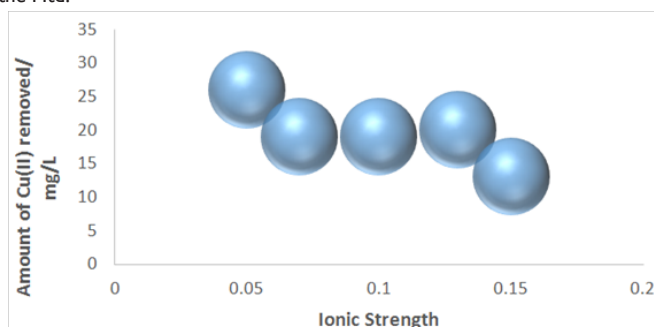


Figure 7 Effect of adding various amount of KCl on removal of Cu(II) from CuCl₂ solution with the Htd at M: L (5:1).

Conclusion

This preliminary investigation emphasises the use of renewable (sustainable) chelators otherwise known as greener chelators (which is currently more desired) for metals recovery. Importantly, the work showcases the application of lipophilic type of greener chelator (14, 16- hentriacontanedione - Htd). Hydrophobic chelator can be readily recycled hence making it to be more economic than the corresponding hydrophilic ones. Hence, in this studies liquid-liquid biphasic Cu(II) extractions from a varying concentrations of synthetic Cu(OAc)₂ solutions with the chelator were demonstrated. The stoichiometry of the extraction of the Cu(II) with the chelator is 1: 1. The results also showed that, the % Cu(II) extracted with respect to the theoretical Cu(II) extraction by the renewable and greener lipophilic β -diketone is efficient at the conditions of the experiment. The results were substantially dependent on concentrations of chelator, Cu: L ratio, pH of the aqueous medium and ionic strength. This biobased renewable chemical can find use as metals chelator and in other allied applications.

Acknowledgments

None.

Conflicts of interest

Authors declare that there is no conflict of interest.

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