



Solvent Extraction of Copper (II) Ions Using Unmodified and Aromatic Amine Modified Red Onion Skin Extract

Uche John Chukwu^{1*} and Gervais Manizabayo¹

¹Department of Pure and Industrial Chemistry, University of Port Harcourt, Nigeria.

Authors' contributions

This work was carried out in collaboration between both authors. Author UJC designed the study, performed the statistical analysis, wrote the protocol and wrote the first draft of the manuscript. Author GM managed the analyses of the study and the literature searches. Both authors read and approved the final manuscript.

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ABSTRACT

This study investigated the use of unmodified red onion skin extract (UROSE), aniline modified red onion skin extract (AmROSE) and 2-aminophenol modified red onion skin extract (APmROSE) for the extraction of copper (II) ions from aqueous media. The effect of pH, agitation time, ligand concentration and metal ion concentration on the percentage extraction were explored. The stoichiometric coefficients of the metal ions and the ligands (UROSE, AmROSE and APmROSE) in each extraction experiment were determined using slope analysis. The results revealed that the percentage extraction of copper (II) ions increased with increasing ligand concentration and agitation time and decreased with increasing initial concentration of copper (II) ions. The optimum pH for the extraction of copper (II) was found to be 6.77, 6.10 and 2.57 for UROSE, AmROSE and APmROSE respectively, while slope analysis showed that UROSE, AmROSE, and APmROSE ligands reacted with the metal ion in 1:1 molar ratio.

Keywords: Copper (II) ions; ligand; red onion skin extract; slope analysis; solvent extraction.

*Corresponding author: E-mail: Lydiuche@gmail.com, uche.chukwu@uniport.edu.ng;

1. INTRODUCTION

The occurrence of heavy metals in wastewater is one of the major threats to the environment due to their non-biodegradability and toxicity to many forms of life [1-6]. It has been reported that heavy metals such as copper, lead, cadmium, zinc, nickel and chromium in drinking water have adverse impacts on human health such as allergies, hyper pigmentation, skin lesions and cancer, neurological effect, hypertension, cardiovascular disease and pulmonary disease [3,7,8].

Over the years, solvent extraction has been broadly applied as an effective technique for the purification, concentration and extraction of metal ions from aqueous solutions using different types of ligands [9-11]. Solvent extraction is an analytical technique that is used to separate a substance from mixtures by selectively dissolving it in a suitable solvent [12]. This technique involves agitation of two immiscible liquids, one containing the "solute" or substance to be extracted, the other containing the extracting ligand [13,14]. The ligand used to extract a particular metal ion must have a high extracting power and optionally be selective to a particular metal or metals [15]. Thus, the choice of the extractant (ligand) often determines the success of the extraction process [16].

Research [17] has shown that onion skin extract contains the largest concentration of quercetin and other polyphenolic compounds which can be used as a ligand for the extraction of copper and other metal ions from aqueous media. Quercetin is a polyphenolic molecule with five hydroxyl groups at 3, 3', 4', 5 and 7 positions and one C=O group at position 4 (See Fig. 1). This quercetin is found in almost all fruits and vegetables [18-20]. However, the highest amount of quercetin is found in red onion skin as reported [17].

In addition to its pharmacological properties such as antioxidant, anti-inflammation, anti-cancer, antiviral and neurological effects [19], studies have shown that quercetin is a good metal chelator [18,21]. Research also revealed that quercetin has three chelating sites: the 3-hydroxy and 4-keto groups, 5-hydroxy and 4-keto groups, 3'-hydroxy and 4'-hydroxyl groups [22]. The presence of these functional groups gives quercetin the ability to bind with heavy metals at these sites forming stable complexes.

The metal chelation property of quercetin can be enhanced further by increasing the number of electron donating atoms in the structure. In this study, the azo group (N=N) was introduced into the red onion skin extract (ROSE) through diazotization and coupling processes as previously reported [23]. This modified "quercetin-rich" red onion skin extract was then used to investigate the extraction of copper (II) ions from aqueous solution and results compared to extraction of same metal ion (copper) using the unmodified ROSE.

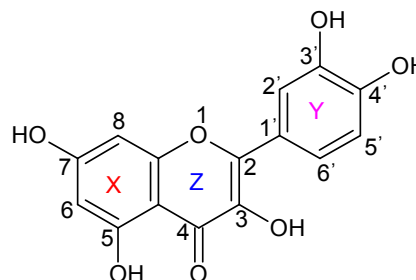


Fig. 1. Structure of quercetin a major component in ROSE [17]

2. METHODOLOGY

2.1 Extraction of Red Onion Skins

The red onion skins (ROS) were collected from oil mill and fruit garden markets in Port Harcourt, Nigeria. The skins were carefully selected, thoroughly washed with distilled water, air dried at ambient temperature, and pulverized into powder form using an electric grinder. The pulverized ROS was sieved to generate ROS particles of diameter 125 μm . Extraction of the ROS was then carried out using 300 mL of 50% acetone/water mixture at room temperature. The ROS was agitated in the acetone/water mixture and left for 48hrs before filtration. Thereafter, the filtrate was evaporated in a water bath at 60°C to obtain the unmodified red onion skin extract (UROSE). The experimental procedure for the modification of ROSE using aniline and 2-aminophenol diazonium salts is as earlier reported [23] and discussed below.

2.2 Modification of ROSE

ROSE was modified using two aromatic diazonium salts, namely, benzenediazonium chloride and 2-hydroxybenzenediazonium salt. These salts were synthesized via diazotization reaction of aniline and 2-aminophenol separately

with hydrochloric acid as described. Approximately 1 mL (0.01 mol) of aniline and 1.09 g (0.01 mol) of 2-aminophenol, were each dissolved into 45 mL of distilled water in two different 250 mL beakers labeled A and B respectively. To each beaker, 12 mL of 11.4 M hydrochloric acid was slowly added while stirring. The resulting solutions were cooled in an ice bath at 0–5°C. To each of the aromatic amine solutions at 0–5°C, 5 mL of cold NaNO₂ (0.01 mol, 0.7 g) was added drop wise while stirring at a constant rate. The reaction mixtures were then stirred for another 2–3 min. The resulting solutions were benzenediazonium chloride (beaker A) and hydroxybenzenediazonium chloride (beaker B). This was then used for the modification of ROSE [23,24,25].

Modification of ROSE (AmROSE and APmROSE) was carried out as follow: An alkaline solution of ROSE was first prepared by dissolving 3.02 g of ROSE into 30 mL of 10% sodium hydroxide solution in a 250 mL beaker. The resulting solution was cooled in an ice bath at 0°C–5°C. The first modification, namely, aniline-modified ROSE (AmROSE), was prepared by slowly adding benzenediazonium chloride solution to the alkaline solution of ROSE while stirring at a constant rate. The reaction mixture was stirred for another 15 min to ensure completion of the reaction. The resulting precipitate was filtered using a suction filtration apparatus, washed with small amount of cold water, and dried at ambient temperature for 5 days. Similarly, the second modification 2-aminophenol-modified ROSE (APmROSE) was obtained following the same procedure but with the use of hydroxybenzenediazonium chloride. The modified and unmodified products of ROSE were then used for solvent extraction studies of copper (II) ion.

2.3 Solvent Extraction of Cu (II) ion and Stoichiometric Analysis

A stock solution of Cu²⁺ (500 mg/L each) was prepared by dissolving 0.314 grams of CuSO₄·5H₂O into 20 mL of distilled water in a 250 mL volumetric flasks. The mixture was stirred until all the salts dissolved. Afterwards, it was made up to mark using distilled water.

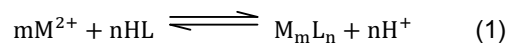
The extraction of copper (II) ions was carried out by agitating 2 mL of the aqueous phase of known pH containing the metal ion and 2 mL of the ligand solution. The ligand solutions were prepared using ethyl acetate as the organic

solvent. After agitation, the two phases were allowed to settle and 1 mL aliquot pipetted from the lower (aqueous) phase. The aqueous raffinate was further diluted with distilled water and the concentration of the metal ion determined using Varian SpectrAA 100 Atomic Absorption Spectrophotometer (AAS). The concentration of the metal ion extracted by the ligand was determined by difference as reported by previous authors [9,26].

The percentage extraction of copper (II) ions at different pH, agitation time, ligand concentration and initial metal ion concentration were determined. The slope analysis [9,25] was carried out by plotting the results of log D vs [Cu (II)] and log D vs [HL] where D and [HL] are the distribution ratio and ligand concentration respectively.

3. RESULTS AND DISCUSSION

The extraction of copper (II) ions (designated as M²⁺) with the ligand (UROSE, AmROSE and APmROSE) designated as HL may be described by the following equilibrium equation as reported by previous authors [9,26,27]



Where HL represents the ligand (UROSE, AmROSE and APmROSE) and M²⁺ represents copper (II) metal ion. The extraction constant K* is written as equation (2)

$$K^* = \frac{[M_mL_n][H^+]^n}{[M^{2+}]^m [HL]^n} \quad (2)$$

While the distribution ratio D is written as equation (3):

$$D = \frac{m[M_mL_n]}{n[M^{2+}]} \quad (3)$$

Substituting equation (2) into equation (3), we get equation (4) and D becomes:

$$D = \frac{m K^* [M^{2+}]^m [HL]^n}{n [M^{2+}] [H^+]^n} \quad (4)$$

Applying log on both sides of the equation, equation (4) can be rewritten as equation (5)

$$\log D = \log K^* + \log m + (m - 1) \log [M^{2+}] + n \log [HL] + n \text{pH} - \log n \quad (5)$$

Where the distribution coefficient, D, is defined as the ratio between the concentration of the

metal ion in organic phase designated by org and aqueous phase designated by aq.

The slope analysis on differentiating log D with respect to ligand concentration [HL] gives the number of mole(s) of the ligand involved in the reaction as (n) according to equation (6):

$$\frac{d[\log D]}{d[\log HL]} = n \quad (6)$$

Also, the slope analysis on differentiating log D with respect to metal ion concentration $[M^{2+}]$ gives the number of mole(s) of the metal involved in the reaction as (m-1) according to equation (7).

$$\frac{d[\log D]}{d \log[M^{2+}]} = m - 1 \quad (7)$$

The equilibrium slope method has been used to analyze the experimental data for each extraction system. The stoichiometric coefficients of the metal and the ligands were determined on the basis of equation (6) and (7) respectively. The percentage extraction of copper (II) ion was calculated using equation (8).

$$\% E = \frac{D}{D+1} \times 100 \quad (8)$$

3.1 Extraction Study of Cu^{2+} Using UROSE, AmROSE and APmROSE

The extraction of Cu^{2+} was carried out at different pH values ranging from 1.15 to 9.20, and the results presented in Fig. 2. The results show that the percentage extraction of copper using 0.01 M APmROSE increased rapidly from 67.4% at a pH of 1.15 to the maximum of 96.8% at a pH of 2.57 and then started dropping. Similarly, the percentage extraction of Cu^{2+} using 0.01 M UROSE increased from 25.4% to 99.4% when the pH increased from 1.40 to 6.77. On the other hand, 0.01 M AmROSE had relatively low percentage extraction of Cu^{2+} with optimum percentage extraction of 35.9% at pH 6.10. Extraction of Cu^{2+} using APmROSE was more favorable in acidic medium while extraction using UROSE and AmROSE was better at neutral pH.

The effect of agitation time on the percentage extraction of Cu^{2+} using UROSE, AmROSE and APmROSE was studied at constant pH (6.77 for UROSE, 2.57 for APmROSE and 6.10 for AmROSE) and the results are displayed in Fig. 3. The results show that the percentage extraction of Cu^{2+} using UROSE, AmROSE and APmROSE

increased when the agitation time increased from 10 to 50 minutes. The percentage extraction when using UROSE increased from 87.7% to 94.2%, while for AmROSE, it increased from 90.3% to 98.2% and for APmROSE, it increased from 93.2%, to 99.8%. The same observation of increase in agitation time giving a corresponding increase in percentage extraction has been reported by previous authors [1,8,24,28,29], and can be attributed to increase in collision frequency. Overall, APmROSE ligand showed the highest percentage extraction of Cu^{2+} , followed by AmROSE and UROSE respectively.

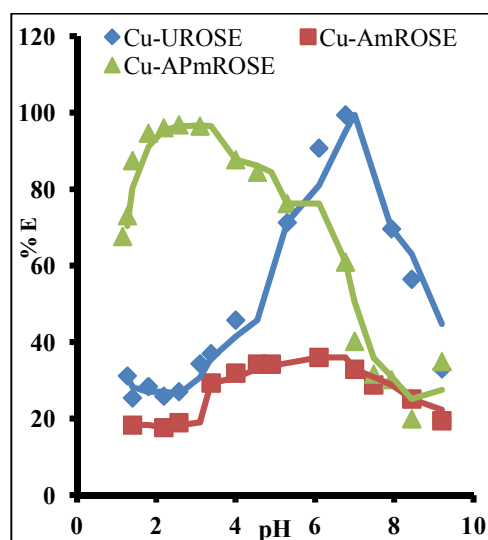


Fig. 2. Effect of pH of the percentage extraction of Cu (II) using UROSE, AmROSE and APmROSE

Studies on the effect of initial metal ion concentration at constant pH (6.77 for UROSE, 2.57 for AmROSE and 6.10 for APmROSE), and agitation time (50 mins) using UROSE, AmROSE and APmROSE are displayed as plots in Fig. 4. The results demonstrated that the percentage extraction of Cu^{2+} using UROSE, AmROSE and APmROSE decreased as the initial concentration of Cu^{2+} increased from 10 ppm to 50 ppm. A similar observation has been reported by previous authors [1,8]. This decrease in percentage extraction may be attributed to the saturation of the active sites of the ligands as their concentrations increased.

Investigation of Cu^{2+} extraction at different ligand concentrations (UROSE, AmROSE and APmROSE) under room temperature was equally studied and results presented as plots in

Fig. 5. The results demonstrated that the percentage extraction of Cu^{2+} using the ligands increased gradually when their concentrations increased from 0.001 M to 0.02 M. A similar trend was reported by [30,31,32]. This increase in percentage extraction of Cu^{2+} while increasing

the ligand concentrations may be attributed to the presence of more coordination sites available for binding of the metal ions [30,33]. Overall, UROSE ligand showed the least percentage extraction for Cu^{2+} , followed by AmROSE and APmROSE.

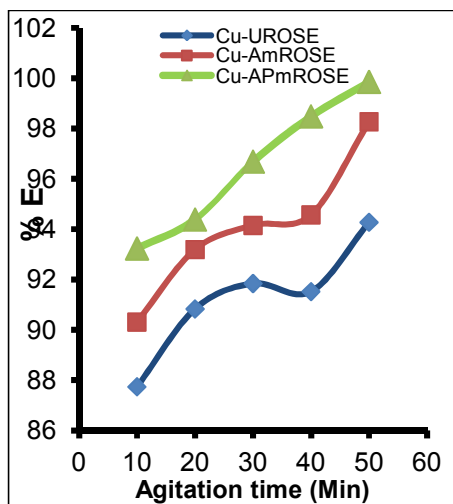


Fig. 3. Effect of agitation time on the extraction of Cu (II) ion using UROSE, APmROSE and ABmROSE ligands

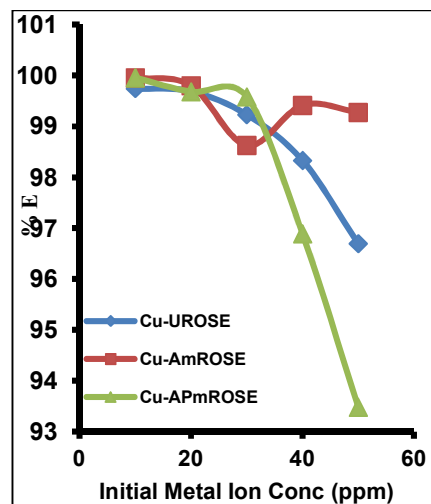


Fig. 4. Effect of initial metal ion concentration on the extraction of Cu (II) ion using UROSE, AmROSE and APmROSE ligands at room temperature

Table 1. Stoichiometric coefficients for the metal ion and ligands

	Cu-UROSE	Cu-AmROSE	Cu-APmROSE
m-1	-0.0298	-0.0311	-0.0471
m	0.9702	0.9689	0.9529
n	0.8838	1.0851	0.6727

m: Number of mole of copper (II) ion; n: number of mole of UROSE, AmROSE or APmROSE

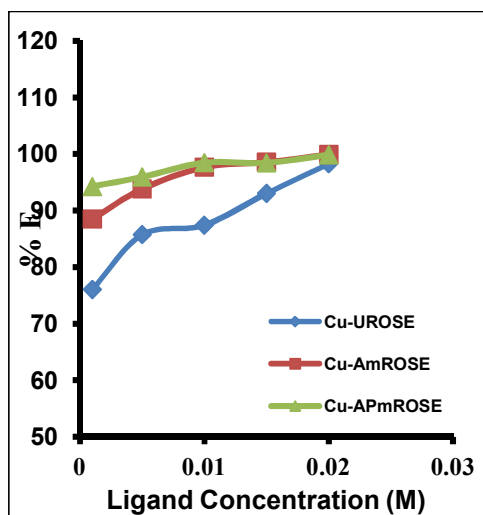


Fig. 5. Effect of UROSE, AmROSE and APmROSE concentration on the extraction of Cu (II)

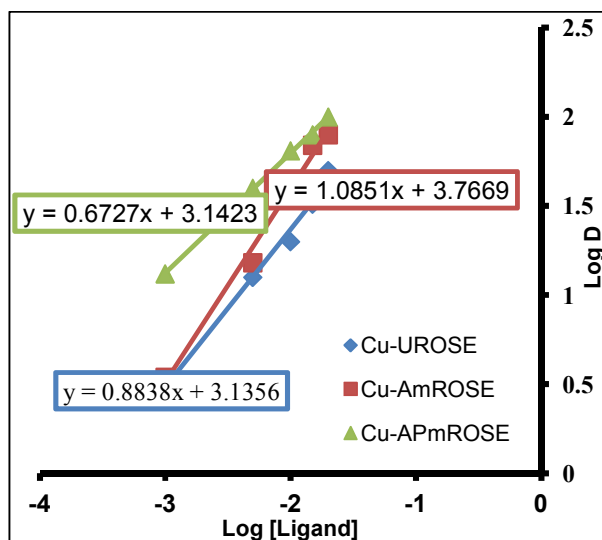


Fig. 6. Graph of log D versus log concentration of UROSE, AmROSE, APmROSE ligands for the extraction of copper (II) ion

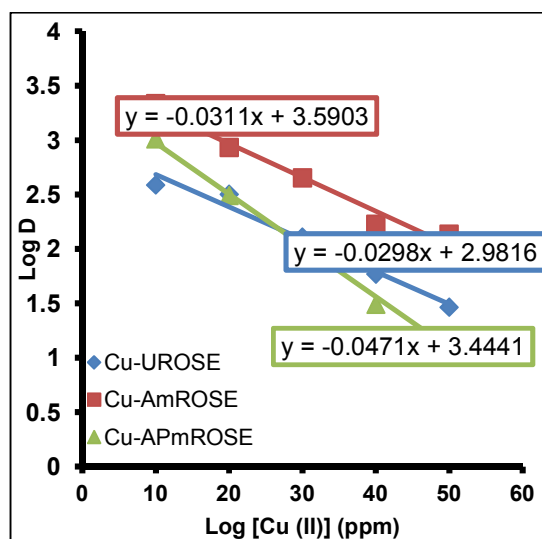


Fig. 7. Graph of log D versus log [Cu (II)] concentration for extraction using 0.1M UROSE, AmROSE, APmROSE ligands

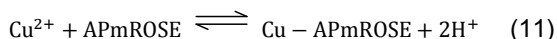
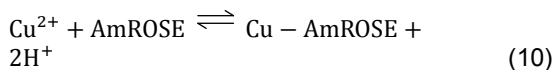
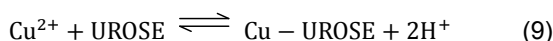
3.2 Slope Analysis for the Extraction of Cu²⁺ Using UROSE, AmROSE and APmROSE

The stoichiometric coefficients between Cu²⁺ and the ligands (UROSE, AmROSE and APmROSE) were determined from plots of log D vs log [UROSE], log D vs log [AmROSE] and log D vs log [APmROSE] as presented in Fig. 6. The slope analysis of these plots using equation (6) gives the values of m as: 0.9702, 0.9689 and 0.9529 for log D vs log [UROSE], log D vs log [AmROSE]

and log D vs log [APmROSE] plots respectively. This reveals that approximately one mole of each of the ligand (UROSE, AmROSE and APmROSE) was involved during the extraction of Cu (II) ion. Table 1 shows all the stoichiometric coefficients for the metal ion and ligands obtained from the slope analysis study.

The graph of log D versus log [Cu (II)] as displayed in Fig. 7, show that the slopes of the plots of log D versus log [Cu (II)] for the extraction of Cu²⁺ with UROSE, AmROSE and

APmROSE are 0.8838, 1.0851, and 0.6727 respectively. According to equation (7), this indicates that approximately one moles of the metal ion (Cu^{2+}) was involved in the extraction using 0.1M UROSE, AmROSE and APmROSE ligand. Therefore, equation (1) can be rewritten as in equation (9 - 11).



4. CONCLUSION

The extraction of copper (II) ion using 0.1M concentration of UROSE, AmROSE and APmROSE has been successfully carried out at room temperature, different pH, varying agitation time and different concentrations of both ligand and metal ion. Optimum percentage extraction of 96.8 %, 99.4 % and 35.9 % were obtained at pH 2.57, 6.77 and 6.10 for APmROSE, UROSE and AmROSE respectively. The percentage extraction increased with increase in agitation time and ligand concentration but decreased with increasing initial concentration of Cu^{2+} . The stoichiometric coefficient between the ligands concentration ([UROSE], [AmROSE] and [APmROSE]) obtained from plots of $\log D$ vs \log [UROSE], $\log D$ vs \log [AmROSE] and $\log D$ vs \log [APmROSE] reveals that approximately one mole of each of the ligand was involved during the extraction process. While plots of $\log D$ versus \log [Cu (II)] metal ion concentration [Cu^{2+}] reveals that one mole of the metal ion was involved in the extraction processes for all the ligands used. Thus, the molar ratio of Cu^{2+} to ligands was found to be 1:1 metal to ligand ratio. Finally, at constant pH, agitation time and metal initial metal ion concentration, the modified ROSE extracts (APmROSE, and AmROSE) displayed higher extraction efficiencies than the unmodified ROSE.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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