STOICHIOMETRY OF CU(II) ION EXTRACTION WITH DI-2-ETHYLHEXYLPHOSPHORIC ACID DISSOLVED IN WASTE PALM COOKING OIL

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ABSTRACT

This study was aimed to determine the reaction stoichiometry between Cu(II) and di-2-ethylhexylphosphoric acid (D2EHPA) in Waste Palm Cooking Oil (WPCO). The stoichiometry was computed based on the following experimental methods, namely slope analysis, loading test and Job's method. Slope analysis was used to measure the variation of the distribution coefficient D to the concentration of Cu(II) ions and D2EHPA. Besides that, the loading test and Job's method are used to determine and confirm the complexation reaction between D2EHPA and Cu(II) ions. It was found that, the reaction stoichiometry for the Cu(II) to D2EHPA was 1:2 in Cu(II) organic complexes. Therefore, the chemical equation can be determined and it will be a useful information in the reaction mechanism of Cu(II) with D2EHPA in WPCO.

Keywords: Cu(II) extraction; D2EHPA; Reaction mechanism; Stoichiometry; Waste palm cooking oil

1. INTRODUCTION

Stoichiometry is an important aspect in chemical reactions. It comes from two Greek words, namely *stoicheon,* which means "element" and *metron,* which means "to measure" (Christian, 2007). Literally, stoichiometry can refer to the study or measurement of the chemical equation and formulas (Christian, 2007; Hill, 2005; Russo & Silver, 2001). Reaction stoichiometry is usually used to estimate the amount of reactant to produce a product or it can be interpreted the other way around, which is the amount of product to be expected from a certain amount of reactant (Hill, 2005; Russo & Silver, 2001; Rydberg et al., 2004), since all the information about the structural relations between reactants and products are needed. Thus, with this definition, stoichiometry can be simply described as a tool to understand the existence and strength of atomic mass and the law of conservation of mass (Renny et al., 2013).

Many methods are available to determine the reaction stoichiometry, such as slope analysis (Liu et al., 2014), loading capacity and loading test (Talebi et al., 2015), continuous variation method (Job's method) (Baba et al., 2012), ligand number method (Rydberg et al., 2004), numerical method (Chang et al., 2011), volumetric method (Pisarello et al., 2010) and infrared spectroscopy (Bidari et al., 2014). Out of those prominent methods, slope analysis, loading test and Job's method which consists of an experimental approach. These methods are the most

preferred methods used by numerous researchers (Baba et al., 2012; Ohto et al., 2006; Talebi et al., 2015). Slope analysis is a measurement of the variation of the distribution coefficient D for a component at a time (Liu et al., 2014; Rydberg et al., 2004). On the other hand, the loading test is the measurement of the maximum capacity of complexation and decomplexation of the reaction (Baba et al., 2012; Talebi et al., 2015) while Job's method is used to measure the amount of product obtained in a solution that contains the same amount of components, but at a different ratio (Renny et al., 2013). In general, all these methods are used to determine the reaction stoichiometry in the various fields of chemical reaction, especially for metal-organic complexes in the solvent extraction.

Solvent extraction is a well-known method in the field of extraction, separation and purification of heavy metals. The extractant is used to form a selective metal-organic complex with the metal .ion in the aqueous phase in order to facilitate the transport process to the organic phase (Kislik, 2009; Manuel, 2008). A number of extractants have been used in this context, and one of them is organophosphorous acid. Many related works have been reported to determine the stoichiometry of metal-complexation with organophosphorous acid, such as scandium-N-[N,N-di(2-ethylhexyl) aminocarbonylmethyl] glycine (D2EHAG) complex (Baba et al., 2012), nickel-di-2-ethylhexylphosphoric acid (D2EHPA) complex (Talebi et al., 2015) and gallium-octyl phenyl acid phosphate (OPAP) complex (Mihaylov & Distin, 1995). However, most of these are using petroleum-based organic solvents, such as n-dodecane (Baba et al., 2012), benzene (Azzoug et al., 2014) and kerosene (Mihaylov & Distin, 1995; Talebi et al., 2015), which are harmful, flammable and toxic to environment (Talebi, 2012). Thus, more eco-friendly solvents, such as WPCO need to be considered. Therefore, in this study, the stoichiometry of extraction of Cu(II) with D2EHPA in WPCO is determined and analysed by using slope analysis, loading test and Job's method. Thus, this analysis will provide useful information to determine the mechanisms and the rate of extraction of Cu(II) ions.

2. MATERIALS, EQUIPMENT AND METHODS

2.1. Materials
A sample of WPCO (FFA: 5.73%, viscosity: 51.5cP) was collected from local restaurant and filtered by using cheesecloth before use. Chemicals, namely copper sulphate pentahydrate ($Cu_2SO_4.5H_2O$) (>99.6%, R&M chemical), sodium sulphate (Na_2SO_4) (>99% purity, Qrëc), di-2-ethylhexylphosphate (D2EHPA) (>95% purity, Merck), tributylphosphate (TBP) (>99% purity, Merck), nitric acid (HNO_3) (>65% purity, Fisher Scientific), hydrochloric acid (HCl) (>37%, Fisher Scientific), sulphuric acid (H_2SO_4) (>98% purity, Fisher Scientific) and sodium hydroxide (NaOH) (>99% purity, Qrëc) were analytical grade reagents, which were used as received from the supplier.

2.2. Equipment
A pH meter (Eutech Instruments, pH 2700) was used to measure the pH of the aqueous phase, whereas the A bench top orbital shaker (Jeio Tech, SK 300) was used to mix up the two phases, namely the aqueous and organic phases. On the other hand, an inductively coupled plasma optical emission spectrometry (*ICP-OES*) (PerkinElmer, Optima 7000) was used to measure the concentration of Cu(II) ions in the aqueous phase before and after extraction and stripping at a wavelength of 327.393 nm.

2.3. Methods
2.3.1. Preparation of aqueous and organic phases
The aqueous phase contained various concentrations of Cu(II) ions (30–5700 mg/L (0.5–90 mM)), which was prepared by dissolving a specific amount of $Cu_2SO_4.5H_2O$ in 250 mM Na_2SO_4 solution. The solution was prepared and fixed according to the pH_{eq} 4.5, except for the

pH study in the slope analysis (2.5–6.0 were applied). Meanwhile, the organic phase was prepared by mixing WCPO with D2EHPA (extractant) and TBP (phase modifier). The concentrations of D2EHPA and TBP in the organic phase were fixed at 85 and 60 mM, respectively, for all extraction experiments, except D2EHPA concentrations for the extractant concentration study in slope analysis (varied from 10–100 mM), the loading test (fixed at 8.5 mM) and Job's method (varied from 10–90 mM). All the values for pH_{eq} (4.5), D2EHPA (85 mM) and TBP (60 mM) concentrations were determined from our previous work (Chang et al., 2010).

2.3.2. Extraction and stripping procedures

The prepared aqueous phase of Cu(II) and the prepared organic phase was mixed with an equal volume at a ratio 1:1, using glass stoppered bottle. A top orbital shaker was used to mix both phases at 100 rpm for 3 minutes. Then, the mixture was allowed to settle for 10 minutes until two distinct phases were observed. The pH of the aqueous phase was checked and adjusted to the desired value by using 1M H_2SO_4 or 1M NaOH. Then, the sample was mixed and the pH was checked and adjusted again. The process continued until the aqueous phase obtained the desired pH_{eq}. After that, both phases were separated by using separatory funnels and finally the aqueous phase will be further analysed by using ICP-OES. The percentage of Cu(II) extraction can be determined from Equation 1, shown below:

$$\%E = \frac{Cu_{i,aq} - Cu_{f,aq}}{Cu_{i,aq}} \times 100\%$$

(1)

where $Cu_{i,aq}$ is the initial Cu(II) concentration in the aqueous phase and $Cu_{f,aq}$ is the final Cu(II) concentration in the aqueous phase after extraction. The same procedures were applied on the stripping experiments except without pH adjustment. The percentage of Cu(II) stripped into stripping phase can be calculated as shown in Equation 2:

$$\%S = \frac{Cu_{f,strip}}{Cu_{i,aq} - Cu_{f,aq}} \times 100\%$$

(2)

where $Cu_{f,strip}$ is the final Cu(II) concentration in stripping phase. All the experiments were conducted at room temperature (25°C).

3.   RESULTS AND DISCUSSION

3.1.   Equilibrium Slope Analysis

Equilibrium slope analysis was used to investigate and estimate the reaction stoichiometry of Cu(II) with D2EHPA in WPCO. In general, D2EHPA was found in dimeric form due to intermolecular hydrogen bonding when it was diluted in non-polar organic solvent (Chang et al., 2011; Mellah & Benachour, 2006; Shiri-Yekta et al., 2009). Therefore, in this study, Cu(II) ions will be presumed to form complexation metal with D2EHPA in dimeric form in WPCO. Thus the general equation for that extraction reaction can be expressed as shown in Equation 3:

$$Cu_{aq}^{2+} + ([2+n]/2)\, H_2R_{2(org)} \overset{K_{ex}}{\longleftrightarrow} Cu(R_2)(HR)_{n(org)} + 2H_{aq}^+$$

(3)
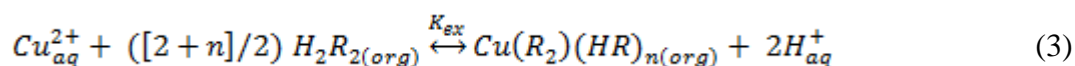
where H_2R_2 is the D2EHPA in dimeric form and n is the number of D2EHPA molecules that are involved in the reaction. By referring to Equation 3 above, the equilibrium constant of the reaction can be denoted as K_{ex}. K_{ex}, which can be defined as the function of molar

concentration as in Equation 4 below as long as the ionic strength of the aqueous solution remains constant (Juang & Chang, 1993; Shiri-Yekta et al., 2009). This process was performed by introducing an excess of inert salt (Na$_2$SO$_4$) into the system (Chang et al., 2011), as shown in Equation 4:

$$K_{ex} = \frac{\left[Cu(R_2)(HR)_{n(org)}\right]\left[H_{aq}^+\right]^2}{\left[Cu_{aq}^{2+}\right]\left[H_2R_{2(org)}\right]^{([2+n]/2)}} \tag{4}$$

By taking the distribution coefficient D equal to the ratio of Cu(II) concentration in the solvent phase to the concentration of Cu(II) in the aqueous phase at equilibrium (Chang et al., 2011; Mellah & Benachour, 2006; Shiri-Yekta et al., 2009), Equation 4 can be elucidated as shown in Equation 5:

$$D = \frac{K_{ex}\left[H_2R_{2(org)}\right]^{([2+n]/2)}}{\left[H_{aq}^+\right]^2} \tag{5}$$

Therefore, the relation of K_{ex} to distribution coefficient D can be expressed in logarithmic terms as shown in Equation 6:

$$logD = logK_{ex} + \left(\frac{2+n}{2}\right)\log(HR)_2 + 2pH \tag{6}$$

The experiment was conducted by varying the pH of the aqueous phase (2.5–6.0) and the concentration of D2EHPA (10–100 mM) with an initial concentration of 100 mg/L of Cu(II) ions. A graph of $logD$ vs pH_{eq} was plotted as in Figure 1 and the slope value can be determined as 1.8, which supports the divalent structure of Cu(II) i.e. 2. Thus, it indicated that the experimental data was well-suited to Equation 6. In order to compute the value of n, the linear function graph of $logD$ vs $\log(HR)_2$ was plotted as shown in Figure 2. The slope obtained was 1.12 which corresponds to the $(2+n)/2$ in Equation 6, thus the value of n can be determined as 0.12. Therefore, the result of $(2+n)/2$ is approximately 1 and by assuming D2EHPA present as a dimeric form in WPCO, the extraction stoichiometry can be rewritten back as shown in Equation 7;

$$Cu_{aq}^{2+} + H_2R_{2(org)} \overset{K_{ex}}{\longleftrightarrow} Cu(R_2)_{org} + 2H_{aq}^+ \tag{7}$$
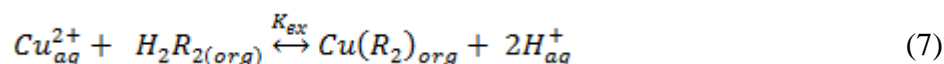
which shows the extraction of Cu(II) is treated with a solvation of 2 molecules of D2EHPA or 1 dimeric form of D2EHPA to form $Cu(R_2)_{org}$ complexes, where the complexes are not associated with each other.

$$y = 1.8031x - 6.3152$$
$$R^2 = 0.9533$$

Figure 1 Log D vs pH_{eq}

$$y = 1.1237x + 2.7211$$
$$R^2 = 0.9873$$
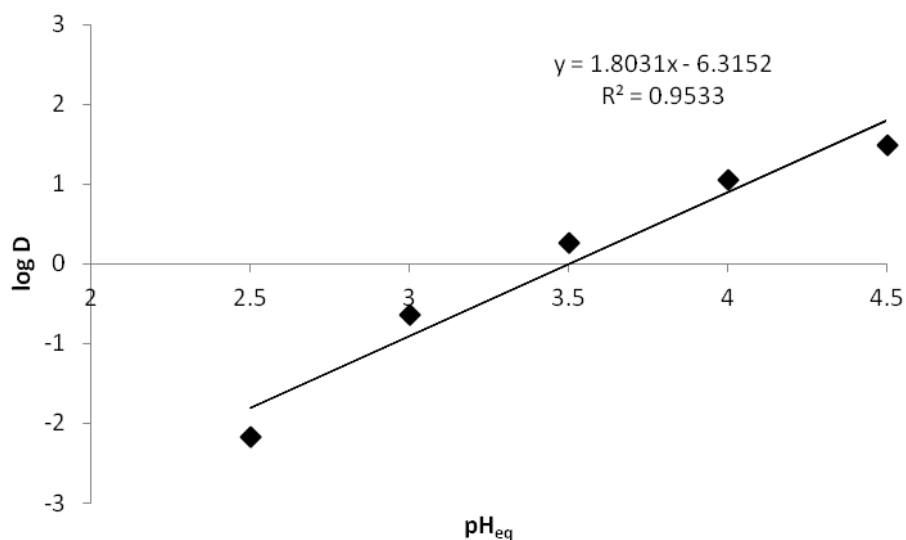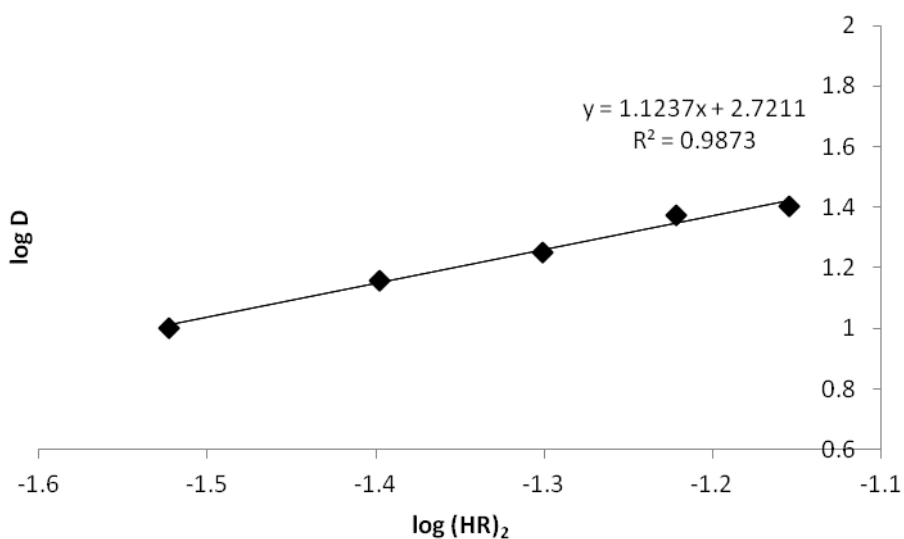
Figure 2 log D vs log $(HR)_2$

3.2. Loading Test

The reaction stoichiometry was further verified by using a loading test as shown in Figure 3 in the loading test, the ratio of an initial concentration of D2EHPA (8.5 mM) to the loading of Cu(II) ions in the organic phase was plotted as a function of the various initial concentrations of Cu(II) (30–350 mg/L (0.5–5.5 mM)) in the aqueous phase. The trends decreased with an increasing value of the initial concentration of Cu(II) ions and these reached a constant value approximately at 2. This result supported the earlier finding that Cu(II) ions were extracted with 2 molecules of D2EHPA.
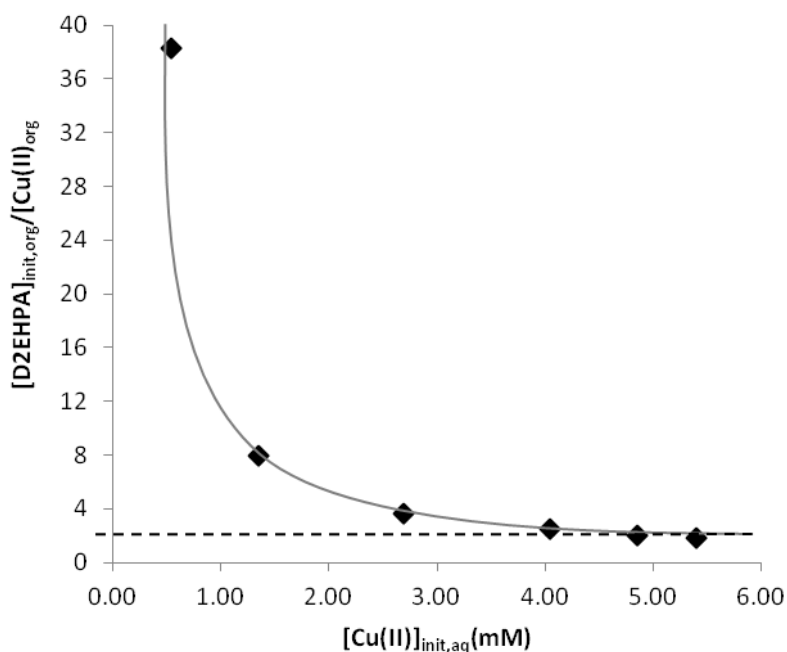
Figure 3 Binding stoichiometry estimation between D2EHPA and Cu(II)

3.3. Job's Method

Job's method, as depicted in Figure 4, was conducted to further investigate the influence of Cu(II) ions concentration in the aqueous phase on the extraction of D2EHPA. The plots of Cu(II) concentration in the organic phase reached the maximum value when the ratio of the initial concentration of D2EHPA to the total concentration of Cu(II) and D2EHPA was at the value 0.7. This value was close to 1, thus it confirmed that the stoichiometric ratio of Cu(II) to D2EHPA was 1:2 in Cu(II)–organic complexes. The confirmation of the reaction stoichiometry by using the loading test and Job's method, especially in the extraction of metal ions also had been proposed by Talebi et al. (2015), Chetry et al. (2015), and Baba et al. (2012).
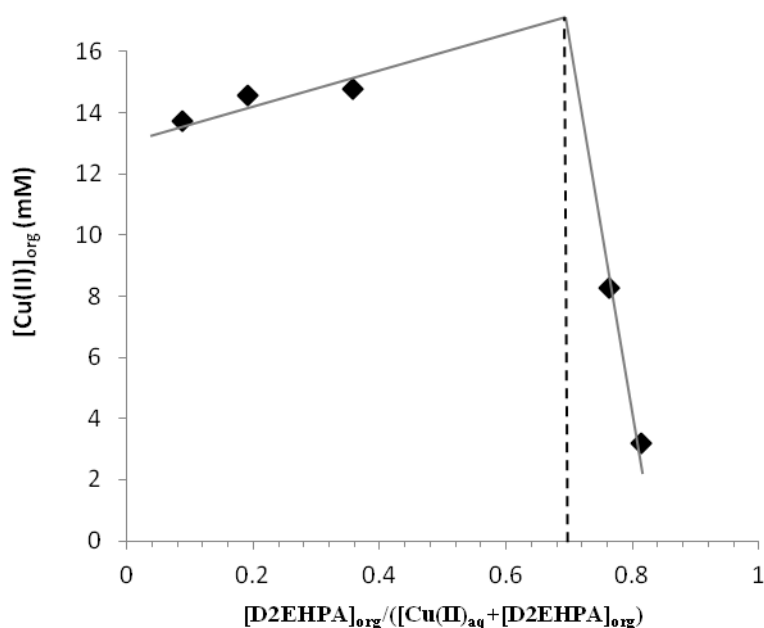

Figure 4 Job's method for estimation of Cu(II) ions in extraction reaction

The above result agreed with the work reported by Venkateswaran et al. (2007) and Juang and Chang (1993) on the Cu(II)–D2EHPA complex in coconut oil and kerosene, respectively. However, the reaction stoichiometry was differently discovered by Chang et al. (2011) by using fresh soybean oil which are at a ratio of 1:4 in Cu(II)–organic complexes for Cu(II) to D2EHPA ratio. This result can be presumed from the different dimerization constant of D2EHPA through coordination and/or substitution of the different types of diluent molecules (Juang & Chang, 1993; Oshima et al., 2015).

4.   CONCLUSION

A sample of WPCO loaded with D2EHPA (extractant) and TBP (phase modifier) was used to extract Cu(II) ions from the aqueous solution. The reaction stoichiometry between Cu(II) and D2EHPA in the complexation reaction were determined from slope analysis, loading test and Job's method. Slope analysis was used to measure the variation of the distribution coefficient D to the concentration of Cu(II) ions and D2EHPA during the extraction reaction. The confirmation of the complexation reaction was determined from the loading test and Job's method. It was found that the extraction stoichiometry of Cu(II) to D2EHPA can be computed as a ratio of 1:2 in Cu(II)-organic complexes. Thus, this result indicated substantial information for the reaction mechanism between Cu(II) ions and D2EHPA in WPCO.

5.   ACKNOWLEDGEMENT

6.   REFERENCES

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