Extraction of Cu(II) from aqueous solutions by vegetable oil-based organic solvents

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Abstract: - Various types of vegetable oil-based organic solvents (vegetable oils without extractant, vegetable oils loaded with di-2-ethylhexylphosphoric acid (D2EHPA) and vegetable oils loaded with tributylphosphate (TBP)) were investigated into their potentialities as greener substitutes for the conventional petroleum-based organic solvents to extract Cu(II) from aqueous solutions. Percentage extractions (%E) of Cu(II) with different types of vegetable oil-based organic solvents were determined and the pH-extraction isotherms of Cu(II) using various vegetable oils loaded with D2EHPA were investigated. All types of vegetable oils studied show a similar extractability for Cu(II). Vegetable oils loaded with D2EHPA were found to be the most effective vegetable oil-based organic solvents for Cu(II) extraction and thus, are potential greener substitutes for the petroleum-based organic solvents.

Key-Words: - Extraction, Cu(II), vegetable oil, di-2-ethylhexylphosphoric acid (D2EHPA), tributylphosphate (TBP), extractant

1 Introduction
Solvent extraction is widely acknowledged as one of the effective methods to remove heavy metals from aqueous solutions [1] among other methods like chemical precipitation [1-2], coagulation-flocculation [1-2], flotation [1-2], ion exchange [1-2], electro-oxidation [1-2], membrane filtration [1-2] and bisorption [2-3]. It is a process that involves the removal of a solute from one liquid to another liquid in which the two liquids must be practically immisible, for instance aqueous solutions and organic solvents [4]. The organic solvents used are usually composed of an extractant and a diluent [5-6]. Each of these substances plays an important role in the extraction processes where the former acts as an active component to extract specific metal ions whereas the latter controls the solvent conditions, such as the hydrophobicity or water content of the region around the extractant molecules, which can affect the extractability of the extractant molecules [5-6]. Nowadays, a wide variety of effective extractants and diluents have been commercialized for the hydrometallurgical processes [7]. Among all the extractants, D2EHPA has been reported as one of the highly effective extractants for the separation of Cu(II) from aqueous solutions [8-9]. TBP, on the other hand, is normally used as a phase modifier [10]. These extractant and phase modifier are usually diluted in the petroleum-based organic diluents such as kerosene [11], chloroform [12], dichloromethane [13], n-dodecane [14], isododecane [15], n-decanol [16], n-heptane [17], n-hexane [18] and cumene [19]. These petroleum-based diluents, which form the bulk components in the organic phase, are usually toxic, non-renewable, non-biodegradable, flammable and volatile in nature. Consequently, they are difficult to handle and will result in ecological hazard to the aquatic systems in case of solvent loss due to entrainment in the aqueous phase [5]. Hence, it is essential to find a greener replacement for the conventional petroleum-based organic solvents in order to curb this environmental problem. Vegetable oils, which are derived from an assortment of fruit and seeds of plants such as soybeans, palm oil fruit, palm kernels, rapeseeds, sunflower seeds, cotton seeds, coconuts, corns, peanuts, rice grains etc, have created a great deal of interest as greener substitutes for the conventional solvents owing to their outstanding characteristics such as nontoxicity, inflammability, nonvolatility, renewability and biodegradability [20]. In addition, the unlimited
bioresources, as well as relatively simpler processing steps and technologies involved, make the vegetable oils way cheaper than the conventional solvents. In this work, various types of refined vegetable oils were investigated into their potentiality to extract Cu(II) from aqueous solutions. Effect of various vegetable oils loaded with D2EHPA or TBP on Cu(II) extraction was also investigated.

2 Experimental

2.1 Reagents

Refined vegetable oils like corn, canola, sunflower and soybean oils (100% purity) were supplied by Soon Soon Oil Mill Sdn. Bhd., Malaysia and they were used without further purification. Copper sulphate pentahydrate (CuSO₄·5H₂O) (R&M Chemicals, 99.6% purity), D2EHPA (Aldrich, 97% purity), tributylphosphate (TBP) (Merck, 99% purity), sulphuric acid (H₂SO₄) (Merck, 98% purity), sodium hydroxide (NaOH) (Merck, 99% purity) and sodium sulphate (Na₂SO₄) (Merck, 99%) were used as received.

2.2 Analytical instrument and apparatus

A flame atomic absorption spectrophotometer (FAAS) (Shimadzu, AA-6800) was used to measure the concentration of Cu(II) in the aqueous phase after extraction. Orbital shaker (Fisher Scientific, SSL1), pH meter (Mettler Toledo, Delta 320), glass-stoppered bottles (Pyrex, 250 mL) and separatory funnels (Pyrex, 250 mL) were used to mix the aqueous and organic phases, measure the pH of aqueous phase, hold the mixture of organic and aqueous phases during mixing and to settle out the organic and aqueous phases after mixing, respectively.

2.3 Preparation of aqueous and organic phases

Aqueous phase containing a fixed initial concentration of Cu(II), i.e. 100 mg/L (1.576 mM), was prepared by dissolving an appropriate amount of CuSO₄·5H₂O in distilled water. The ionic strength of the aqueous phases was maintained constant by addition of 200 mM Na₂SO₄. Different organic phases such as vegetable oils without extractant, vegetable oils loaded with 100 mM D2EHPA and vegetable oils loaded with 100 mM TBP were prepared.

2.4 Extraction procedures

The prepared organic solvent was mixed with the prepared Cu(II)-containing aqueous solution at 5:1 aqueous to organic volume ratio in a glass-stoppered bottle. The bottle was shaken by an orbital shaker at 200 rpm. After 10 minutes of mixing, the mixture was allowed to stand for 5 minutes to separate. A syringe with a small tube on the tip was used to take about 20 mL sample from the aqueous phase, and its pH was measured with a pH meter. If the pH measured was higher or lower than the desired pH, the 20 mL sample was returned back to the bottle and its pH was adjusted with 1 M H₂SO₄ or 1 M NaOH. After mixing for another 10 minutes, the mixture was allowed to separate and the pH was measured and adjusted again. The test was continued until the desired equilibrium pH of solution was obtained. Next, the mixture was transferred into a separatory funnel for phase disengagement and finally, about 10 mL sample was taken from the aqueous phase for chemical analysis with an AAS. All experiments were carried out at room temperature (25 °C). The percentage extraction (%E) of Cu(II) was calculated based on Eq. (1):

\[
\%E = \frac{[\text{Cu}]_{f,aq} - [\text{Cu}]_{o,aq}}{[\text{Cu}]_{o,aq}} \times 100\%
\]

Where \([\text{Cu}]_{o,aq}\) = initial Cu(II) concentration in the aqueous phase and \([\text{Cu}]_{f,aq}\) = final Cu(II) concentration in the aqueous phase.

3 Results and Discussion

3.1 Effect of vegetable oil-based organic solvents on Cu(II) extraction

Refined vegetable oils such as corn, canola, sunflower and soybean oils were investigated into their potentialities to extract Cu(II) from aqueous solutions. The \([\text{Cu}]_{o,aq}\) and equilibrium pH (pHₑq) were fixed at 100 mg/L (1.567 mM) and 4.5, respectively. Three different types of vegetable oil-based organic solvents had been studied: vegetable oil without any extractant, vegetable oil loaded with 100 mM D2EHPA and vegetable oil loaded with 100 mM TBP. Fig. 1 shows the %E obtained for Cu(II) extraction with different vegetable oil-based organic solvents.

Fig. 1: %E of Cu(II) obtained with different vegetable oil-based solvents

It was discovered that when using a vegetable oil, either corn, canola, sunflower or soybean oil, without any extractant as organic solvents, only about 10% of Cu(II)
was extracted. This implies that vegetable oils are poor extractants for Cu(II). This is in good agreement with the poor extractability of coconut oil for Cu(II) as reported by [21]. The extractability of oils for Cu(II) is governed by the relative solubility of Cu(II) salts in both oil and aqueous phases [4]. A popular aphorism used for predicting solubility is ‘like dissolves like’ which indicates that polar solvents dissolve polar compounds best and non-polar solvents dissolve non-polar compounds best [22]. Hence, the non-polarity nature of vegetable oils gives rise to the weak interaction between oil molecules and polar compounds like Cu(II) salts, and thus results in poor extraction. The mild extraction of approximately 10% could be deduced as the extraction by the free fatty acids contained in the oils by cation exchange between copper cations (Cu²⁺) in the aqueous phase and proton (H⁺) in the organic phase. This is on account of the substantial pH drop, i.e. from 5.9 to 4.5, measured from the aqueous phase before and after extraction. Triglycerides, which accounts for approximately 98% of the components in vegetable oils, are naturally occurring long-chain esters that do not carry acidic proton (H⁺) [23]. Hence, it is presumed that the acidic H⁺ was derived from the free fatty acids which are minor components (less than 2%) in vegetable oils [23]. This small quantity of free fatty acids resulted in the low %E of Cu(II) obtained. When vegetable oils loaded with 100 mM D2EHPA were used as organic solvents, however, %E of Cu(II) was increased dramatically to more than 99%. This shows that D2EHPA, an organophosphorus acid, is a highly effective extractant for Cu(II). Similar results are reported by [24]. Conversely, using 100 mM TBP loaded vegetable oils as organic solvents did not increase the %E of Cu(II) but improve the phase separation. This implies that TBP, a phosphorus ester, is a poor extractant for Cu(II) but a good phase modifier.

3.2 pH-extraction isotherms

Fig. 2 shows the pH-extraction isotherms of Cu(II) obtained at different equilibrium pH using 100 mM D2EHPA loaded in various types of vegetable oils as organic solvent. Again, the [Cu]₀,aq was fixed at 100 mg/L (1.576 mM). From Figure 2, a sigmoid curve, which indicates the increase of %E with pHₐq, is obtained for all the pH-extraction isotherms investigated. This finding is consistent with the similar isotherms reported in the literatures [10, 25]. In general, %E is the minimum at pHₐq < 2.0, increasing sharply from pHₐq 3.5 to 4.0, and reaches its maximum at pHₐq > 4.5. This implies that the extractability of D2EHPA for Cu(II) in various types of vegetable oils studied is pH-dependent. This could be deduced from the general extraction equation between divalent metal ions and D2EHPA molecules, as shown in Eq. (2) [4]:

\[
\text{Cu}^{2+} (aq) + n\text{(HR)}_2 (org) \rightarrow \text{CuR}_2\text{(HR)}_{2n-2} (org) + 2\text{H}^+ (aq)
\] (2)

where (HR)₂ is a dimeric form of D2EHPA and n is an equilibrium constant which has a value of 2 for Cu(II) [26]. According to Eq. (2), as the pHₑₐₐₚ increases (decreasing H⁺), the equilibrium position moves to the right and thus, gives rise to the increasing %E. On the contrary, as the pHₑₐₐₚ decreases (increasing H⁺), the equilibrium position shifts to the left and %E decreases. From Figure 2, it is found that %E of more than 99% could be achieved with 100 mM D2EHPA loaded in various types of vegetable oils at pHₑₐₚ > 4.5.

Fig. 2: pH-extraction isotherms of Cu(II) using 100 mM D2EHPA loaded in various types of vegetable oils as organic solvents

4 Conclusion

All the refined vegetable oils investigated such as corn, canola, sunflower and soybean oils, either with or without D2EHPA or TBP, show a similar extractability for Cu(II) from aqueous solutions. Vegetable oils without extractants (D2EHPA or TBP) are poor extractants for Cu(II) wherein only about 10% of Cu(II) was extracted. Vegetable oils loaded with 100 mM D2EHPA, however, are effective extractants where more than 99% of Cu(II) was extracted from the aqueous solutions. Conversely, vegetable oils loaded with 100 mM TBP did not show any appreciably amount of Cu(II) extracted from aqueous solutions, but it greatly improved the phase separation. A sigmoid curve was obtained for all the pH-extraction isotherms of Cu(II) investigated with 100 mM D2EHPA loaded in all types of vegetable oils as organic solvents. It was found that %E of more than 99% could be achieved with 100 mM D2EHPA loaded in various types of vegetable oils at pHₑₐₚ > 4.5. Therefore, it can be concluded that vegetable...
oils-loaded with 100 mM D2EHPA are effective organic solvents for Cu(II) extraction from aqueous solution at pH\textsubscript{eq} \geq 4.5.

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