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Use of Waste Palm Cooking Oil for Cu (II) Ion Extraction from Aqueous Solution.

Siu Hua Chang[1*], Alif Azwan Abdul Wahab[1], and Ayub Md Som[2].

[1]Faculty of Chemical Engineering, Universiti Teknologi MARA (UiTM) Malaysia, 13500 PermatangPauh, Penang, Malaysia
[2]Faculty of Chemical Engineering, Universiti Teknologi MARA (UiTM) Malaysia, 40450 Shah Alam, Selangor, Malaysia

ABSTRACT

This work aimed to explore the possibility of extracting Cu(II) ions from aqueous solution using waste palm cooking oil (WPCO). Three different samples of WPCO ranging from yellow to brown were examined for their physicochemical properties (density, viscosity, free fatty acid (FFA) content and acid value) and extraction efficiencies. The latter was determined by a series of shake-out tests. The findings were compared with those obtained using fresh palm cooking oil (FPCO). Extraction efficiencies of WPCO loaded with an extractant and/or a phase modifier were also investigated. It was found that various WPCO and FPCO samples showed similar densities but different viscosities, FFA contents and acid values. Although cooking oil alone, either WPCO or FPCO, did not extract Cu(II) ions efficiently, WPCO loaded with 85 mM of di-2ethylhexylphosphoric acid (extractant) and 60 mM of tributylphosphate (phase modifier) was found to attain the highest percentage of extraction of 96% with a good phase separation.

Keywords: *Cu(II) ion, di-2ethylhexylphosphoric acid, extraction, physicochemical properties, waste palm cooking oil*

***Corresponding author**
Email: shchang@ppinang.uitm.edu.my

INTRODUCTION

The rapid economic growth and industrialization have caused severe water pollution everywhere. This is resulting mainly from the excessive discharge of industrial wastewater loaded with nutrients, organic matters and heavy metals into waterways by unscrupulous industries. Heavy metals are particularly toxic to human health and environment owing to their toxicity at low concentrations, bioaccumulation tendency and persistency in nature [1]. Cupric (Cu(II)) ion is one of the toxic metal ions discharged abundantly by industries such as printed board manufacturing, metal finishing and plating, semiconductor manufacturing, petrochemicals and refineries [2]. Various detrimental impacts of Cu(II) ions to human health and other living organisms in the environment are well-documented in the literature [3].

Liquid-liquid extraction (LLE) is one of the effective separation methods for Cu(II) ions from aqueous solution due to its outstanding characteristics such as simplicity of design, ease of maintenance, high efficiency, high selectivity and ability to operate in a fast and continuous manner [4]. However, one of the major disadvantages of this method is the use of a large amount of petroleum-based organic solvents such as carbon tetrachloride [5], chloroform [5], toluene [5] and benzene [6] which are toxic and harmful to human health. Since these solvents are non-renewable, they could be extremely expensive due to their limited resources. Recently, fresh cooking oil has been used successfully as a green solvent in removing toxic pollutants such as phenol [7], dyes [8], and metal ions [9-10] from aqueous solution. However, the use of fresh cooking oil as organic solvent in large amounts would impose a serious threat to the global food security since it is a limited food commodity. The counterpart of fresh cooking oil, namely, waste cooking oil, is a better option in this context.

Waste cooking oil is the used cooking oil produced abundantly by household kitchens, fast food restaurants and other food processing facilities. Being a waste material, it is much cheaper when compared to fresh cooking oil. However, waste cooking oil has been subjected to thermal degradation resulting from several reactions like hydrolysis, polymerization and oxidation during frying, particularly repeated frying, at high temperature [11]. This may change the physicochemical properties of waste cooking oil and affect its performance as organic solvent in LLE processes. Therefore, the aim of this work was to explore into the possibility of using waste palm cooking oil (WPCO) to extract Cu(II) ions from aqueous solution. The physicochemical properties and extraction efficiencies of different WPCO samples were investigated and their findings were compared with those of fresh palm cooking oil (FPCO). Extraction efficiencies of WPCO loaded with an extractant and/or a phase modifier were also explored.

MATERIALS AND METHODS

Materials

Three WPCO samples ranging from yellow to brown, denoted as Samples 1 to 3 in Figure 1, were collected from a local restaurant and an FPCO sample, denoted as Sample 4 in Figure 1, was bought from a local department store. The WPCO samples were filtered with cheesecloth before use while the FPCO sample was used as received. Copper sulphatepentahydrate ($Cu2SO4.5H2O$) (> 99.6% purity, R&M Chemical), di-2-ethylhexylphosphoric acid (D2EHPA) (> 95% purity, Merck), tributylphosphate (TBP) (> 99% purity, Merck), sodium sulphate ($Na2SO4$) (> 99% purity, QRëC), phenolphthalein (98% purity, Merck), potassium hydroxide (KOH) (≥ 85% purity, Merck), 2-propanol ($C3H8O$) (99.7% purity, QRëC), sodium hydroxide (NaOH) (> 99% purity, QRëC) and sulphuric acid ($H2SO4$) (> 98% purity, Fisher Scientific) were analytical grade reagents which were used as received.

Figure 1: WPCO (Samples 1-3) and FPCO (Sample 4) samples used in this work

Methods

Measurement of density and viscosity

The measurement of oil density started with weighing an oil sample on an analytical balance. Next, the sample was placed in a cylindrical cell of the gas pycnometer(Micromeritics, AccuPyc II 1340) which measured the oil volume by employing the Archimedes' principle of fluid displacement and gas expansion (Boyle's law) [12]. The oil density was then calculated by dividing the mass of oil with its volume measured. To determine the viscosity of an oil sample, a spindle of the viscometer (Brookfield, DV-I Prime) was immersed in the oil and the spindle was rotated at a specific speed until the reading of viscometer was constant. All measurements of oil density and viscosity were repeated three times at room temperature (25 ^{o}C) and their average values were calculated.

Determination of FFA content and acid value

The free fatty acid (FFA) contents of all oil samples in this work were determined according to the standard PORIM test method [13] which has been used widely by numerous researchers. This method involves an acid-base titration where a specific amount of oil sample was titrated to a phenolphthalein endpoint with a standard 0.1 M KOH in neutralized 2-propanol solution. The amount of KOH consumed during the titration was used to determine the %FFA in the oil sample by [14]:

$$\%FFA=28.2VM/W \qquad (1)$$

Where V is the volume of KOH used (mL), M is the standardized molarity of KOH (M) and W is the weight of oil sample (g). The acid value of oil sample was then calculated by multiplying the corresponding %FFA with 1.99 [14].

Extraction procedure

The extraction experiments were carried out by a series of shake-out tests. It began with preparation of 100 mg/L of Cu(II)-containing aqueous solution and a cooking oil-based organic solvent. The former was prepared by dissolving an appropriate amount of $Cu_2SO_4.5H_2O$ in 250 mM Na_2SO_4 solution, whereas the latter was prepared by mixing WPCO or FPCO with or without 85 mM D2EHPA (extractant) and/or 60 mM TBP (phase modifier). The prepared aqueous solution and organic solvent were then mixed in 1:1 volume ratio in a glass stoppered bottle at 100 rpm for 3 minutes by using an orbital shaker. Next, the mixture was allowed to settle for approximately 10 minutes until two distinct phases were formed. The pH of the aqueous phase was then examined and adjusted with 1 M H_2SO_4 or 1 M NaOH if the desired equilibrium pH of 4.5 was not obtained. The mixture was mixed for another 3 minutes and the pH of the aqueous phase was checked and adjusted again. This process continued until the desired equilibrium pH was obtained. The mixture was then transferred to a separating funnel for phase separation and, finally, a sample was collected from the aqueous phase for analysis with ICP-OES (PerkinElmer, Optima 7000). The percentage of extraction (%E) of Cu(II) ions was determined from [15]:

$$\%E = \frac{Cu_{i,aq} - Cu_{f,aq}}{Cu_{i,aq}} \times 100\% \qquad (2)$$

Where $Cu_{i,aq}$ is the initial Cu(II) ion concentration in the aqueous phase before extraction (mg/L) and $Cu_{f,aq}$ is the final Cu(II) ion concentration in the aqueous phase after extraction (mg/L). All extraction experiments were conducted in duplicate at room temperature ($25^{o}C$) and the relative standard deviation between replicate samples was less than 3%.

RESULTS AND DISCUSSION

Physicochemical Properties

The physicochemical properties of cooking oil like density, viscosity, FFA content and acid value are vital in determining its suitability as organic solvent for LLE processes. Density provides a good understanding with regard to the configuration of aqueous and organic phases in an LLE system, while viscosity measures the resistance of oil to flow which influences the mass transfer rate across the LLE system [16]. The FFA content and acid value, on the other hand, determines the amount of acidic protons present in the oil. The acidic protons are deemed to have the tendency to extract metal ions from aqueous into organic phase by a cation exchange process [17]. Table 1 summarizes the physicochemical properties obtained for different oil samples studied in this work. It was found that the densities (~0.9 g/cm^3) of different WPCO samples did not vary much among themselves and nor did they differ greatly from that of FPCO sample. This suggests that all oil samples, regardless of WPCO or FPCO, would float on aqueous solution in an aqueous-organic system. Other properties like viscosity, FFA content and acid value, however, were found to vary considerably among the oil samples. As shown in Table 1, when the colour of WPCO gets darker from Sample 1 to 3, the viscosity, FFA content and acid value of WPCO get higher. The darkness of the colour of WPCO was associated to the amount of compounds like FFA, monoglycerides, diglycerides, glycerol, oxidized monomers and dimers, carbonyl compounds and polymers present in WPCO. These compounds were produced from the hydrolytic, oxidation and polymerization reactions during frying at high temperature when WPCO was exposed to the moisture from the foodstuff and oxygen from the atmosphere [18]. In general, the darker the colour of WPCO, the greater the amount of these compounds in WPCO, and thus the higher the viscosity and acid value of WPCO were observed. Accordingly, FPCO showed the lowest viscosity, FFA content and acid value due to its lightest colour among the oil samples studied. These findings are consistent with those obtained by other similar previous works [18-19]. The FFA contents in different oil samples were further verified by the FTIR spectra as shown in Figure 2. It reveals a gradual increment in the percent transmittance of the C=O and C-O stretching bands of carboxylic acid (i.e. functional group of FFA) at 1760-1690 cm−1 and 1320-1000 cm-1 [20], respectively, from the lightest yellow colour of FPCO (Sample 4 (Figure 1)) to the darkest brown colour of WPCO (Sample 3 (Figure 1)).

Table 1: Physicochemical properties of different oil samples studied in this work

Oil Samples*	Physicochemical properties			
	Density (g/cm^3)	Viscosity (cP)	FFA (%)	Acid Value
1	0.9100	50.4	2.33	4.64
2	0.9075	51.5	5.73	11.40
3	0.9101	56.5	6.42	12.78
4	0.9078	46.5	0.60	1.19

*Samples 1-3 are WPCO samples and Sample 4 is the FPCO sample as shown in Figure 1

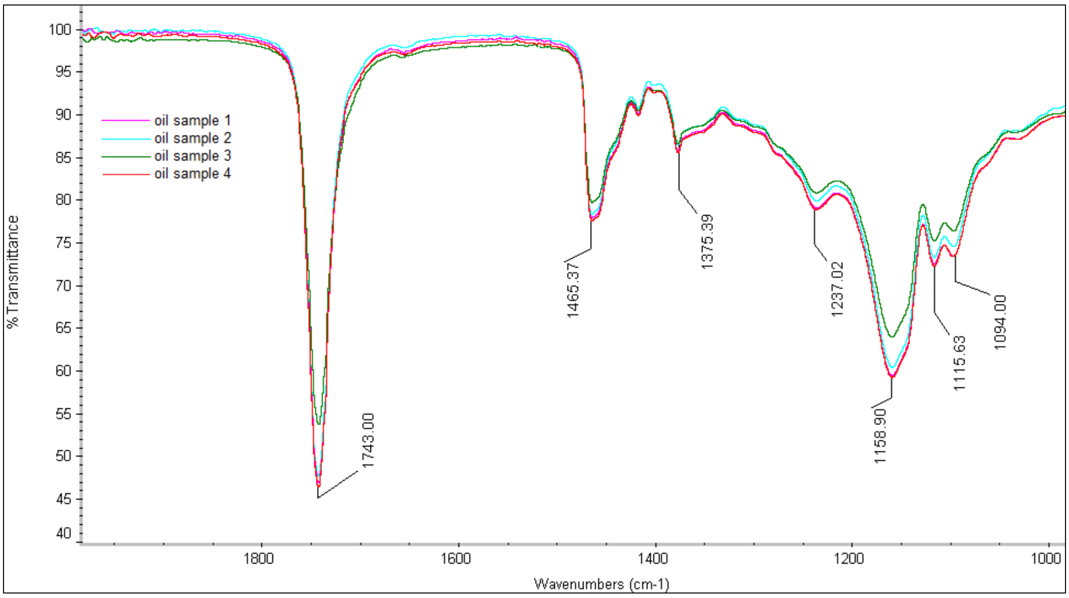

Figure 2: FTIR spectra of WPCO (Samples 1-3 (Figure 1)) and FPCO (Sample 4 (Figure 1)) samples

Extraction Efficiency

To evaluate the efficiencies of different oil samples, they were used to extract Cu(II) ions from aqueous solution and the results obtained are shown in Figure 3. It was found that %E increased appreciably from Sample 1 to 3 which could be deduced from the increasing FFA content in the WPCO samples (Table 1 and Figure 2). The %E of Sample 4 (FPCO), however, was found to be very close to that of Sample 1 (WPCO) even though the FFA content in Sample 4 was much lower. This could be explained by the smaller viscosity of FPCO (Table 1) which enhanced the transport of Cu(II) ions from one phase to another. Although Sample 3 achieved the highest %E among all oil samples, its value was about 6% only which was just slightly (< 2 %) different from the %E attained by other oil samples. The low %E achieved by different oil samples was attributed to their non-polar nature [16] which did not dissolve polar Cu(II) ions readily based on the popular aphorism of 'like dissolves like' [21]. Hence, it can be concluded that both WPCO and FPCO functioned as diluents during Cu(II) ion extraction from aqueous solution and this is consistent with the findings obtained by other researchers [22].

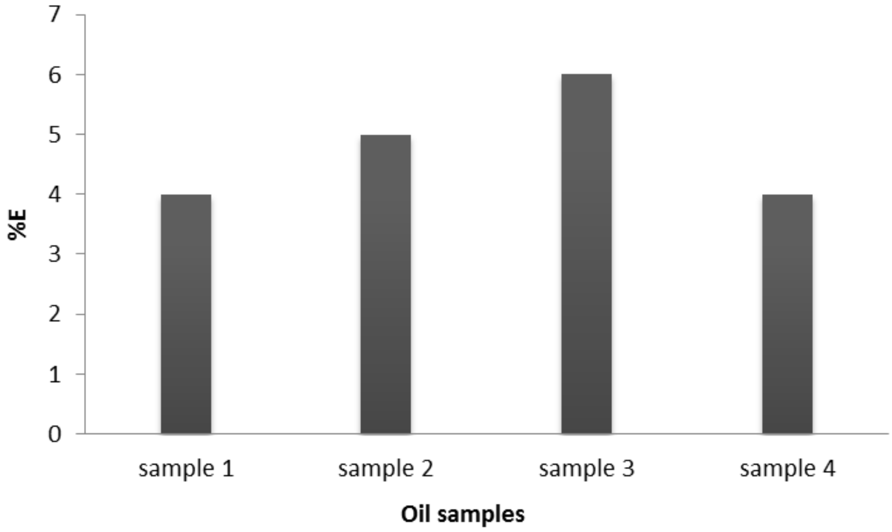

Figure 3: Extraction of Cu(II) ions from aqueous solution by using WPCO (Samples 1-3 (Figure 1)) and FPCO (Sample 4 (Figure 1))

To enhance the extraction efficiency of WPCO, Sample 3 of WPCO was loaded with a suitable extractant (85 mM of D2EHPA) and/or a phase modifier (60 mM of TBP) as determined in our previous work [33]. It was discovered that the %E of Cu(II) ions achieved as high as 96% when WPCO was either loaded with D2EHPA alone or with both D2EHPA and TBP. Nevertheless, the %E of Cu(II) ions remained as low as 6% (i.e. same as that obtained earlier when WPCO alone was used (Figure 3)) when WPCO was loaded with TBP only. This agrees well with our previous findings that D2EHPA was an efficient extractant for Cu(II) ions but TBP was not [17]. In fact, D2EHPA has been widely acknowledged as an effective cationic extractant for metal ions which extract metal ions by a cation exchange process [15]. In spite of the poor extraction efficiency of TBP for Cu(II) ions, TBP was found to improve the separation between aqueous and organic phases significantly and two distinct phases were formed much faster when it was loaded in the organic phase. Figure 4 shows the mixtures of aqueous and organic phases with (Figure 4a) and without (Figure 4b) TBP at 10 minutes after mixing. In the case where the organic phase was loaded with TBP, only a thin emulsion layer was observed between the aqueous and organic layers (Figure 4a). However, when TBP was not loaded in the organic phase, a thick emulsion layer was formed (Figure 4b). Therefore, TBP was claimed to be an effective phase modifier in Cu(II) ion extraction with WPCO.

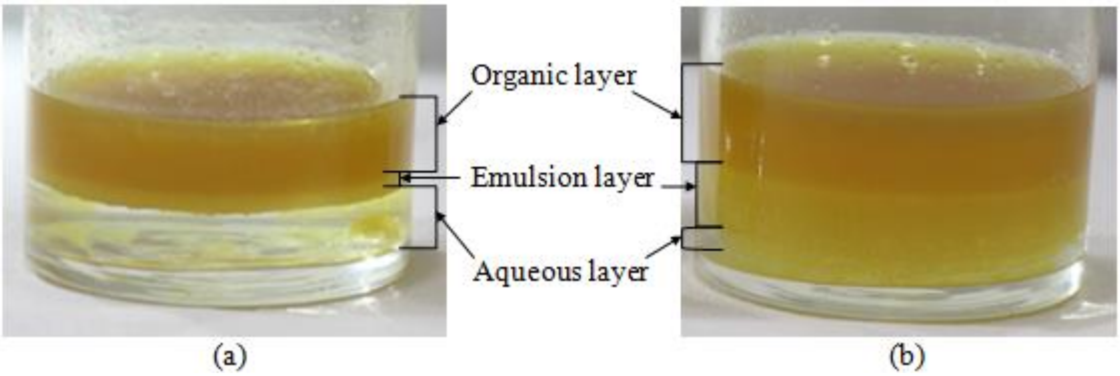

Figure 4: Mixture of aqueous and organic phases with (a) and without (b) TBP at 10 minutes after mixing

CONCLUSIONS

The densities (~0.9 g/cm3) of different WPCO and FPCO samples were found to be similar to each other, while their viscosities (46.5 – 56.5 cP), FFA contents (0.6 – 6.42 %) and acid values (1.19 – 12.78) were found to increase with the darkness of their colours. The latter was due to the presence of the increasing amounts of reaction products from the hydrolytic, oxidation and polymerization reactions during frying at high temperature. The percentage of extraction (%E) of Cu(II) ions achieved by different WPCO and FPCO samples were < 6% only when no extractant and/or phase modifier was loaded in the organic phase. An appreciable increment of %E was observed as the darkness of WPCO colour increased and this could be deduced from the increasing FFA content in the WPCO samples. The highest %E of 96% with a good phase separation was accomplished when WPCO was loaded with 85 mM of di-2ethylhexylphosphoric acid (extractant) and 60 mM of tributylphosphate (phase modifier). Therefore, WPCO is a potential low-cost organic solvent for Cu(II) ion extraction from aqueous solution.

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