Kinetic evaluation of simultaneous waste cooking oil hydrolysis and reactive liquid-liquid Cu extraction from synthetic Cu-containing wastewater: Effect of various co-contaminants

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ABSTRACT

Combination of oil hydrolysis reaction and reactive liquid-liquid extraction of Cu^{2+} from wastewater offers economic and environmental advantage than running two processes separately. To give better insight on the application of the proposed process to treat real wastewater, the effects of other pollutants (acid/base, chelating agents, organic solvent, anions) present in the synthetic Cu-containing wastewater were studied. The reaction was carried out in a batch reactor using a water/acylglycerides molar ratio of 30:1 at 225 °C up to 8 h to understand the effect of the studied parameters during the reaction time course. It was found that pH influenced acid/base balance, which governs catalysis and Cu-soap formation in sub-critical water. Chelating agents formed strong complexation with Cu^{2+} that changed Cu removal mechanism from cation exchange reaction to that of conventional solvent extraction. The presence of organic solvents affected the dielectric constant of water that shifted the equilibrium of cation exchange reaction towards lipophilic Cu soap formation. Different anion type produced different type of acid by means of the cation exchange mechanism that influenced acid catalysis and Cu-soap formation. Other heavy metal cations expressed the same cation exchange mechanism and catalysis ability as that of Cu^{2+}.

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1. Introduction

Among all waters in the world, fresh water only occupies 2.8% with only around 0.63% available as potable surface and ground waters [1]. Based on that fact, fresh water is a very limited resource for the increasing global population. Wastewater reuse and recycling are one way to alleviate the water shortage issue. Reuse and recycle of wastewater require a good understanding on the composition and characteristics of wastewater.

Pollutants in wastewater are classified as organic and inorganic. Although both classes can impose certain level of hazard to the environment, a class of inorganic pollutants named heavy metals possess lethal toxicity and strong persistency to human, animals, and even microorganisms, which has to be removed before the

recycle and reuse of wastewater [2]. Various techniques are available for treating heavy metals in wastewater such as membrane filtration, solvent extraction, chemical precipitation, ion exchange, adsorption, and electrochemical deposition [3]. Nevertheless, all these methods are limited by some factors such as expensive capital cost, material fabrication, and material regeneration, which overall hinders its application for treating large volume of industrial wastewater [3,4].

Copper (Cu) is a heavy metal that commonly exists in wastewater from various industries such as printed circuit board, metal plating, battery manufacturing, electronic, mining, and metallurgical [3,5–7]. Moreover, the amount of Cu-containing wastewater generated is undoubtedly increasing with increasing production of electronics in this modern era. Other pollutants may exist in Cu-containing wastewater. For example, Fe, Zn and Ni may exist together with Cu in the drainage of acid-treatment of ores [8,9]. In the plating and printed circuit board manufacturing, chelating agent and organic solvents also are present [10]. The existence of those pollutants may inhibit the recovery and removal of Cu from the wastewater. Due to those contaminants, Cu removal was required to pass a series of treatments, such as pH-controlled

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solvent extraction with different carrier agent [11], a combined microbial desalination cells and electro-dialysis system [12], and combination of advanced oxidation-chemical precipitation [7,13] to remove each pollutant separately allowing Cu to be removed effectively.

Recently, a study reported the utilization of artificial Cu-containing wastewater for hydrolysis of waste cooking oil under subcritical water state, which offers a promising way to directly reuse wastewater [14]. Direct reuse of Cu-wastewater for waste cooking oil hydrolysis process also brings revenue by producing fatty acids (FAs) instead of simply remove Cu^{2+} and dispose the waste cooking oil. This strategy is critical to overcome the economic uncertainty in the realization of wastewater reuse [15]. Moreover, the process was demonstrated to possess remarkably higher Cu removal (5 times) from wastewater without adding carrier agent compared to the use of refined vegetable oil alone in the solvent extraction process, which reflected high aspect of economic and environmental sustainability [16]. In that study, free Cu^{2+} was described to undergo an exchange with two *in situ* generated FA molecules, producing a molecule of a mineral acid catalyst and Cu-soap, where the latter is soluble in the oil phase and provides a slight degree of water-in-oil emulsification. However, the use of artificial wastewater in the previous studies often did not cover the effects of other organic and/or inorganic compounds that co-exist with Cu ion in the wastewater [11,14]. Overlooking the presence of these compounds may surprisingly alter the Cu exchange mechanism and catalysis of oil hydrolysis reaction, hence leading to the rising of uncontrolled aspects when real wastewater is dealt with. In this study, the effect of possible co-contaminants in the Cu-containing wastewater, such as acid-base, chelating agent, organic solvents, and anion type on FA concentration and Cu removal percentage was thoroughly evaluated by kinetic modeling developed from the previously studied basic reaction mechanism. Different divalent heavy metals sulfate salts were also assessed to illustrate the utilization of a wider range of heavy metal-containing wastewaters.

2. Experimental

2.1. Chemicals

Waste cooking oil was donated by a local restaurant in Taipei, Taiwan. The oil was kept in a sealed amber glass bottle to avoid air oxidation. The oil was used without further pretreatment. KOH (85%, Acros Organics, USA) and HCl (37% purity, Acros Organics, USA) were used for pH adjustment and acid-base titration analysis. Anhydrous $CuSO_4$ (97%, Shimakyu, Japan), $CuNO_3 \cdot 3H_2O$ (99%, Acros Organics, USA), $CuCl_2 \cdot 2H_2O$ (Sigma Aldrich, USA), $Cu(CH_3-COO)_2 \cdot H_2O$ (J.T. Baker, USA), $FeSO_4 \cdot 7H_2O$ (99%, Shimakyu, Japan), $NiSO_4 \cdot 6H_2O$ (99%, Shimakyu, Japan), $ZnSO_4 \cdot 7H_2O$ (99% Sigma Aldrich, USA), H_2SO_4 (95–97%, Scharlau Chemical, Spain), ethanol (95%, Echo Chemical, Taiwan), and oxalic acid dihydrate (≥99%, Kokusan Chemical Co. Ltd., Japan) were reagent grade. Analytical reagent grade anhydrous citric acid (99.5%, Acros Organics, USA) and anhydrous ethylenediaminetetraacetic acid (EDTA, 98.5%, Sigma Aldrich, USA) were used in the experiment on chelating agent effect. Acid-base titration indicator used was phenolphthalein (Sigma Aldrich, USA) dissolved in ethanol. All solutions were made by dissolving the corresponding salts with deionized water into a concentration of 25,000 mg metal (II)/kg. HNO_3 (90%, May and Baker, UK) was diluted by deionized water to form 10% v/v solution for copper ion extraction from the oil hydrolysate. A mixed standard solution (solution IV, 1000 mg/L, Merck Chemicals, USA) was used to obtain Cu, Fe, Ni, and Zn calibration curves in the inductively coupled plasma (ICP) measurement.

2.2. Waste cooking oil hydrolysis

A mixture of waste cooking oil and $CuSO_4$ solution (500 mg $CuSO_4$/kg solution = 3.13 mmol Cu^{2+}/L, pH 5.0) with a triacylglycerides to water molar ratio of 1:30 was introduced into a stainless steel reactor. The reactor apparatus is comprised of a 200 mL glass chamber, a 316-grade stainless steel autoclave body, a K-type thermocouple, a PID temperature controller, a pressure gauge, a magnetic stirrer, and an external electric heater (Fig. S1). After the reactor was closed tightly, trapped air was purged out by nitrogen. The reactor was then heated to 225 °C and held at that temperature up to 8 h to reach equilibrium according to the previous study [14]. After the reaction, the reactor was cooled to 50 °C. Aqueous phase was separated prior to washing to remove trapped glycerol in the product for monitoring the change of aqueous pH. Washing step was carried out twice using warm deionized water. Separation was performed gravitationally in a separation funnel overnight. The recovered oil product was weighed and analyzed for its acid value (AV) and Cu content.

The effect of the initial pH of the copper solution was studied at pH 4.0 and 6.0 by addition of 0.1 N of H_2SO_4 or KOH. Adjustment of pH by KOH was stopped at pH 6.0 to avoid Cu precipitation. EDTA and citric acid were introduced to the $CuSO_4$ solution (1:1 molar ratio) at pH 3.0–9.0 to study the effect of chelating agent. Meanwhile, 0.25–1.0% aqueous ethanol or acetone solution was used to dissolve and dilute $CuSO_4$ to obtain 500 mg $CuSO_4$/kg solution used in the experiments on the effect of organic solvents. Ethanol and acetone were picked as the model solvents in cleaning metals with the concentration simulated based on total organic carbon content of printed circuit board wastewater in other studies [7,10]. Anion type was evaluated by changing $CuSO_4$ solution into $CuNO_3$, $CuCl_2$ or $Cu(CH_3COO)_2$ solution with an equimolar concentration of Cu^{2+} (3.13 mmol Cu^{2+}/L). Fe, Zn, and Ni solutions (3.13 mmol metal (II) ions/L) were also used to substitute $CuSO_4$ solution to study the effect of divalent metal types. Experiments involving different pH, chelating agents, organic solvents, anion, and other divalent metal cations were carried out at the same temperature and acylglycerides/water molar ratio. All experiments were performed in triplicate.

2.3. Oil analysis

AV was analyzed by KOH titration according to ASTM D1980-87 method and calculated by using Eq. (1).

$$AV \ (mg \ KOH/g \ oil) = \frac{V_{KOH} \ (mL) \times C_{KOH} \ (N) \times 56.1}{wt. \ of \ sample \ (g)} \tag{1}$$

Saponification value (SV) was determined titrimetrically (ASTM D5558-95) to know the maximum obtainable fatty acid from the waste cooking oil. SV was calculated by using Eq. (2).

$$SV \ (mg \ KOH/g \ oil) = \frac{V_{HCl} \ of \ blank - sample \ (mL) \times N_{HCl} \ (N) \times 56.1}{wt. \ of \ sample \ (g)} \tag{2}$$

Ester value (EV) and average molecular weight of waste cooking oil (MW_{av}) as pure triacylglycerides can be calculated from Eqs. (3) and (4), respectively. MW_{av} was used to estimate the amount of oil required to fulfill 30:1 water/triacylglycerides molar ratio.

$$EV \ (mg \ KOH/g \ oil) = SV \ (mg \ KOH/g \ oil) - AV \ (mg \ KOH/g \ oil) \tag{3}$$

$$MW_{av} = \frac{1000 \times 56.1 \times 3}{EV_{oil \ feed} \ (mg \ KOH/g \ oil)} \tag{4}$$

To provide more detailed concentration profile of acylglycerides for kinetic evaluation purpose, gas chromatography (GC) analysis was carried out as described in the previous study [14]. The results were then used in Eqs. (5)–(8) to obtain average molecular weight of triacylglycerides (TG), diacylglycerides (DG), monoacylglycerides (MG), and free fatty acids (FA). SV was defined as the total theoretical amount of saponifiable FA and the identity of acylglycerides as the ester of glycerol (G) and FA.

$$\frac{\text{SV (mg KOH/g oil)}}{\text{MW}_{\text{KOH}}} = 1000 \frac{\text{mg oil}}{\text{g oil}}$$
$$\times \left(3 \frac{\text{wt.\% TG}}{\text{MW}_{\text{TG}}} + 2 \frac{\text{wt.\% DG}}{\text{MW}_{\text{DG}}} + \frac{\text{wt.\% MG}}{\text{MW}_{\text{MG}}} + \frac{\text{wt.\% FA}}{\text{MW}_{\text{FA}}} \right) \tag{5}$$

$$\text{MW}_{\text{TG}} = \text{MW}_{\text{G}} + (3 \times \text{MW}_{\text{FA}}) - (3 \times \text{MW}_{\text{H}_2\text{O}}) \tag{6}$$

$$\text{MW}_{\text{DG}} = \text{MW}_{\text{G}} + (2 \times \text{MW}_{\text{FA}}) - (2 \times \text{MW}_{\text{H}_2\text{O}}) \tag{7}$$

$$\text{MW}_{\text{MG}} = \text{MW}_{\text{G}} + \text{MW}_{\text{FA}} - \text{MW}_{\text{H}_2\text{O}} \tag{8}$$

Analysis results revealed that waste cooking oil comprised 84.1 ± 1.27 wt.% TG, 9.25 ± 0.67 wt.% DG, 0.29 ± 0.03 wt.% MG, and 6.29 ± 0.59 wt.% FA with SV and AV of 200.73 ± 2.70 and 13.58 ± 1.18 mg KOH/g oil, respectively. Molecular weights obtained were 839.66, 590.47, 341.28, 267.21, and 595.96 g/mol for TG, DG, MG, FA, and $Cu(FA)_2$, respectively.

The amount of metals transferred into the oil phase was determined by acid extraction as reported in a previous study with slight modification [17]. Oil sample (5 g) was mixed with 20 mL 10% (v/v) HNO_3 at 60 °C for 4 h under magnetic stirring (500 rpm). After the extraction was finished, the mixture was left to separate. The oil layer was cooled in a refrigerator and then filtrated using a 5-μm filter paper (Advantec Grade No. 2). Aqueous layer was analyzed by an ICP-AES (Horiba Jobin Yvon 2000–2). Metal removal percentage was expressed as number of metal ions transferred into the oil phase to total metal ions put in the reaction system as showed in Eq. (9).

8.8 (Aspen Technology Inc., 2015). Due to high resemblance between the measured densities of oil and oleic-oil mixture at 25 °C (0.919 g/mL vs. 0.908 g/mL), the density of the studied waste cooking oil was predicted to be 0.807 g/mL at 225 °C (Fig. S2). Properties of pure water at the working temperature and pressure (225 °C and 2.94 MPa), particularly specific volume of water and steam was estimated from online calculator provided by Moscow Power Engineering Institute [20]. Liquid mass fraction (ω^l) of the total amount of water introduced into the reactor ($\hat{V}$) then can be found through calculations using Eqs. (10) and (12) [21].

$$\hat{V} \ (\text{m}^3/\text{kg}) = \frac{\left(2 \times 10^{-4} - \frac{m_{\text{oil}}}{\rho_{\text{oil}}} \right)}{m_{\text{aqueous}}} \tag{10}$$

$$\hat{V} \ (\text{m}^3/\text{kg}) = \omega^v . \hat{V}^v + (1 - \omega^v) . \hat{V}^l \tag{11}$$

$$\omega^l = (1 - \omega^v) \tag{12}$$

where moil and maqueous are mass of oil and metal solution (assumed as pure water), respectively. Superscript v and l refer to the vapor and liquid phase of water in the reactor with a volume of 2×10^{-4} m³. For temperature and pressure used in the experiments, calculation showed that 95.24 wt.% of the aqueous phase remained as liquid.

Initially H_3O^+ came from water self-ionization [22], unless the system was acidified by H_2SO_4. The added amount of H_3O^+ in moles can be traced by the difference of pOH to normalize the effect of metal ions as Lewis acid in the original Cu solution. In terms of base addition, added OH^- appears to subtract the amount of H_3O^+ from water self-ionization. Initial concentration of H_3O^+ was calculated by Eq. (13)

$$[H_3O^+] = \frac{\frac{\text{added } H_3O^+}{V} + \sqrt{\frac{\text{added } H_3O^+}{V} + 4 \cdot K_W}}{2} - \frac{\text{added } OH^-}{V} \tag{13}$$

where $[H_3O^+]$ and KW are concentration of the liberated proton and the self-ionization constant of water, respectively.

$$\text{Removal (\%)} = \frac{\text{Metal}_{\text{oil product}} \ (\text{mg/kg}) \times m_{\text{oil product}} \ (\text{kg}) - \text{Metal}_{\text{oil feed}} \ (\text{mg/kg}) \times m_{\text{oil feed}} \ (\text{kg})}{C_{\text{metal solution}} \ (\text{mg metal cations/kg}) \times m_{\text{metal solution}} \ (\text{kg})} \times 100\% \tag{9}$$

2.4. Kinetic modeling

In this study, several assumptions were made:

- Total volume of liquid water and oil was constant at the given temperature and pressure, which was the volume of the reaction system (V). Concentration of species was expressed as mol/L.
- Thermodynamic properties of metal solution can be approached by those of pure water.
- Density of oil and water were constant regardless of the transfer of glycerol and change of oil composition [18].
- Reaction between diffusing metal ions and FA as the ion exchanger is instantaneous [19]. The reaction of metal ions and FA can be described as $M^{2+} + 2FA + 2H_2O \leftrightarrow M(FA)_2 + 2H_3O^+$, where M is the metal.

Density of oil (mixture of TG, DG, MG and FA) was approached by the density of mixture of triolein, diolein, monoolein and oleic acid, which was simulated by NRTL-Rackett model in Aspen Plus

Reaction rate equations can be expressed as follows:

$$\frac{dTG}{dt} = -k_{TG}.TG.H_2O + k_{-TG}.DG.HFA \tag{14}$$

$$\frac{dDG}{dt} = k_{TG}.TG.H_2O - k_{-TG}.DG.FA - k_{DG}.DG.H_2O + k_{-DG}.MG.FA \tag{15}$$

$$\frac{dMG}{dt} = k_{DG}.DG.H_2O - k_{-DG}.MG.FA - k_{MG}.MG.H_2O + k_{-MG}.G.FA \tag{16}$$

$$\frac{dG}{dt} = k_{MG}.MG.H_2O - k_{-MG}.G.FA \tag{17}$$

$$\frac{dCu(FA)_2}{dt} = \frac{1}{2}.\frac{dH_3O^+}{dt} = -\frac{dCu^{2+}}{dt} = k_{Cu}(Cu^{2+} - Cu^{2+}_{\text{interface}}) \tag{18}$$

$$Cu^{2+}_{\text{interface}} = \frac{Cu(FA)_2.(H_3O^+)^2}{K_{Cu(FA)_2}.(FA)^2.(H_2O)^2} \tag{19}$$

$$-\frac{dH_2O}{dt} = \frac{dFA}{dt} = k_{TG}.TG.H_2O - k_{-TG}.DG.HFA + k_{DG}.DG.H_2O$$
$$- k_{-DG}.MG.FA + k_{MG}.MG.H_2O - k_{-MG}.G.FA$$
$$- 2.k_{Cu}(Cu^{2+} - Cu^{2+}_{interface}) \qquad (20)$$

These equations were numerically solved using Euler method programmed in Excel (Microsoft Office 2007) with a step size of 0.5 min. All hydrolysis rate constants (L/moles.min), Cu^{2+} mass transfer coefficient (1/min), and apparent equilibrium constant of Cu-soap formation (L/moles) were estimated by the assistance of Solver Add-In to minimize the objective function (OF).

$$OF = \sum_{i=1}^{n} \left(\frac{Y^{ex} - Y^{cal}}{Y^{ex}} \times 100 \right)^2 \qquad (21)$$

where Y is the data of AV and metal removal percentage found by experiments (ex) and fitting (cal), which are Eqs. (22) and (23) using concentrations found in the simulation.

AV^{cal} (mg KOH/g)

$$= \frac{1000 \times FA \times MW_{KOH}}{FA \times MW_{FA} + MG \times MW_{MG} + DG \times MW_{DG} + TG \times MW_{TG} + Cu(FA)_2 \times MW_{Cu(FA)_2}} \qquad (22)$$

$$Removal^{cal} \ (\%) = 100 \times \left(1 - \frac{Cu^{2+}(at\ t)}{Cu^{2+}(t=0)} \right) \qquad (23)$$

3. Results and discussion

3.1. Effect of pH

Acid and base addition enhanced the reaction rate of FA production as showed in Fig. 1. Regardless of considerable difference in the formed Cu-soap amount, FA concentration of acidic system was found as high as that in the alkalinized Cu solution system, which suggests a unique catalysis by H_2SO_4 produced in the ion exchange reaction rather than the Cu-soap. Production of H_2SO_4 was confirmed in both acidified and alkalinized system from the final pH of the aqueous phase (2.4–2.6). Since the stoichiometric ratio of water to the acylglycerides in the system are fixed in this study, FA concentration obtained at equilibrium in the acidified and alkalinized system remained similar (approximately 170 mg KOH/g oil), which is also in agreement with the concept of catalysis, where the catalyst is unable to alter the reaction stoichiometry.

Addition of base to $CuSO_4$ solution was not simply spiking up Cu removal percentage by eliminating the net amount of protons in the reaction system. This enhancement was observed at the early stage of reaction since the amount of KOH added was not enough to overcome the initial acidic species to form either K-soap or K_2SO_4 from the reaction between FA or $CuSO_4$. Considering the effect of subcritical water, certain extent of OH^- from self-ionization of water may be stabilized by the K^+ present in the system [23]. A previous study showed a possible formation of soap with FA in the oil phase, which is called acid soap [24]. Similar mechanism to the cation exchange reaction between Cu^{2+} and FA [25] may explain the subcritical water effect to cause KOH formation from K^+, which further transformed into K-soap in the presence of FA. K-soap tends to dissolve in the aqueous phase to form oil-in-water emulsion, which may help hydrolysis of non-polar compound such as TG.

Kinetic rate constants in Table 1 show higher TG transformation rate in the acidified and alkalinized Cu solution system. The increase in the reverse reaction rate constant of MG hydrolysis indicates that acid and alkaline treatments are not selective towards FA formation. Remarkably high reverse reaction rate constant than that of the forward reaction can be explained by a lower water amount used in this study (oil:water = 2:1 v/v) than in the studies with a negligible reverse reaction that used oil:water = 1:1–1:4 v/v [26,27]. Although the molar amount of water was excessive, only certain excessive amount of water could sufficiently dilute the formed glycerol and gave an impression of no reverse reaction in the system. From the same theory on the presence of K-soap, a higher reverse MG hydrolysis rate in the base-added system was due to the better transfer of glycerol from the aqueous phase in addition to the non-selectivity of H_2SO_4 catalysis.

Table 1
Kinetic rate constants of waste cooking oil hydrolysis using Cu solution with different initial pH.

Kinetic rate constant	Initial pH		
	4.0	5.0 (original Cu solution)	6.0
k_{TG}	9.72×10^{-4}	7.94×10^{-4}	1.00×10^{-3}
k_{DG}	9.98×10^{-3}	9.98×10^{-3}	9.98×10^{-3}
k_{MG}	1.82×10^{-3}	9.55×10^{-4}	1.91×10^{-3}
k_{-TG}	0	0	0
k_{-DG}	0	0	0
k_{-MG}	9.90×10^{-3}	7.94×10^{-3}	1.05×10^{-2}
$K_{Cu(FA)2}$	1.66×10^{-10}	2.16×10^{-9}	2.93×10^{-8}
k_{Cu}	3.80×10^{-3}	3.74×10^{-1}	5.69×10^{-3}
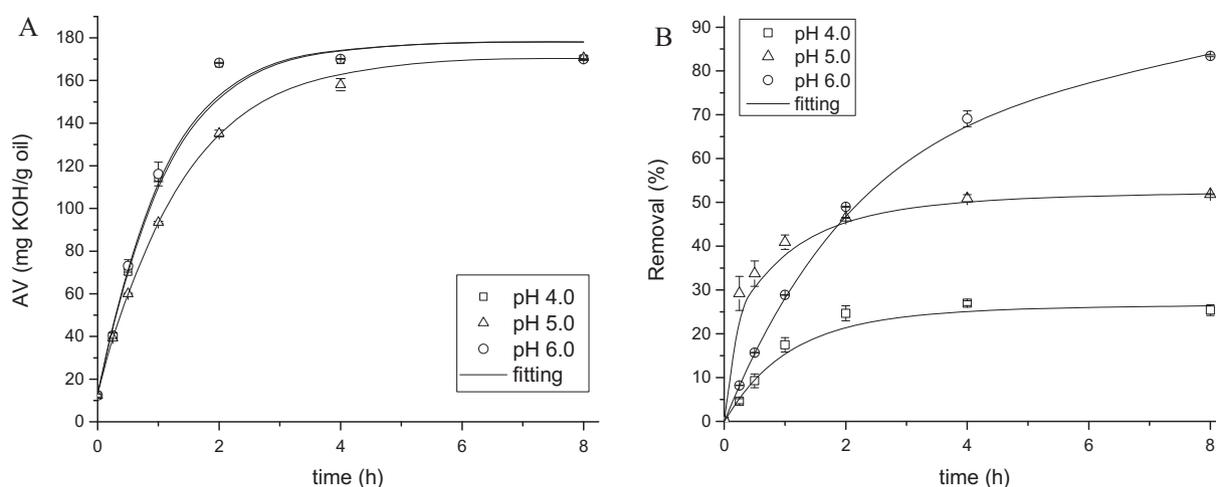
Fig. 1. Effect of initial pH of Cu solution on the (A) AV and (B) Cu removal percentage.

For Cu^{2+} mass transfer, acid/base addition inhibited mass transfer through the formation of dense ionic barrier with a larger decrease of magnitude for more organized barrier of H^+ in acidified system. Although cation exchange equilibrium constant ($K_{Cu(FA)2}$) is supposed to be independent of pH, it was found that the $K_{Cu(FA)2}$ in alkalinized system was higher than in acidified system. This indicates that the acquired constant is the apparent equilibrium constant. An investigation of the change in equilibrium constant resulted in surprisingly comparable results with initial pH difference, which is about $10^{-1.11}$ and $10^{1.13}$ for acid- and base-added system, respectively. This finding revealed a hidden mechanism involving HSO_4^-, a type of inorganic ligand that could inhibit ion exchange reaction. Accordingly, the possible reason for a higher apparent equilibrium constant in the alkalinized system is the suppressed SO_4^{2-} protonation by KOH formed in subcritical water. Since K-soap formation also involved consumption of a proton from FA, the theory of ion exchange facilitation by K-soap is interchangeable with the prevention of SO_4^{2-} protonation.

3.2. Effect of chelating agent

Chelating agent stabilizes metal ions to be precipitated in water by hindering metal-hydroxide precipitate formation. In the electroless Cu-plating, chelation of Cu is mandatory since the pH of the bath has to be adjusted to 13.5 for the oxidation of formaldehyde to occur [28]. However, the presence of chelating agent leads to difficult heavy metal removal process since the stability of metal in wastewater becomes very high [29,30].

By observation, aqueous solution of Cu-EDTA and Cu-citric acid possessed an acidic pH of 3.0, which later changed into very slightly more acidic after reaction (pH 2.9–3.0). Interestingly, same pH value of 4.8 was observed in the aqueous phase of non-catalytic system (oil and water only) as well as Cu-EDTA and Cu-citric acid with an initial pH of 5.0–9.0. These indicate unchanging H^+ concentration in the chelated-Cu system that further reflects different mechanism for Cu transportation. Rather than ion exchange mechanism, van der Waals interaction of carbon backbone of chelating agents with oil phase may facilitate Cu-complex extraction to the oil phase in the form of dimer or polymer [31,32]. Since Cu-EDTA could form polymeric structure, removal percentage of Cu-EDTA complex was higher than dimeric Cu-citrate complex (Fig. 2B). This finding changed the model of Cu removal into Eq. (24).

$$-\frac{dCu_{complex,aq}}{dt} = k_{Cu-complex}(Cu_{complex,aq} - Cu_{complex,lip}) \quad (24)$$

Cu-EDTA and Cu-citric acid complexes were found to be stable in subcritical water [33–35]. Hence, concentration of Cu-complex in the aqueous phase ($Cu_{complex,aq}$) was assumed to be the same as Cu^{2+} introduced into the system. Although some Cu^{2+} seen in Fig. S3 for Cu-citric acid system was at pH 3.0, the assumption still may be valid at high reaction temperature due to the increase of chelating stability of Cu-citrate complex, which has endothermic nature [36]. Fitting was employed to find mass transfer rate ($k_{Cu-complex}$) and maximum concentration of Cu complex in the oil phase ($Cu_{complex,lip}$).

Surprisingly, FA concentration in the system with chelating agents was slightly higher than chelating agent-free system. With significantly lower Cu removal percentage, the results indicate that Cu complex also induced catalytic ability in the reaction system. Neevel [37] mentioned that metal complexes are able to catalyze the reaction as long as some coordination sites are free from the ligand blocking. Fully occupied structures of Cu complex with studied ligands are given in Fig. S4. Based on the speciation diagram in Fig. S3 [38,39], free coordination sites are available only at pH lower than 5.0 for Cu-EDTA system and in the whole studied pH range of this work (2.0–9.0) for Cu-citric acid complex. FAs deprotonation can provide slight acidification to pH 4.8 and possibly changed the Cu-complex species [40]. Moreover, exothermic nature of Cu[EDTA]$^{2-}$ complex as the fully occupied coordination complex of Cu with EDTA indicates its less proportion under high hydrolysis temperature [36].

On the other hand, dihydrate bridged Cu-complex structure could improve water transportation into the oil phase besides improving complex stability in the water [31,32]. Both Cu-EDTA and Cu-citrate have the same capability to form hydrogen bonding, given that the ability comes from the metal ion nature and not the ligand. Double function of chelated-Cu as catalyst and water vehicle resulted in a comparable FA concentration in contrast to the combination of acid catalyst (H_2SO_4) and $Cu(FA)_2$ as water-in-oil emulsifier in the free-chelating agent system [14] even with limited amount of chelated-Cu in the oil phase.

In contrast to the result of free-chelating agent system, chelated-Cu performed catalysis of TG hydrolysis better than H_2SO_4 produced from ion exchange of $CuSO_4$ and FA (Table 2). While catalysis of forward and reverse MG hydrolysis were comparable to those in the free-chelating agent system, chelated-Cu system showed a slower rate of DG hydrolysis due to steric hindrance contribution of the confined structures of chelated Cu. Mass transfer of chelated-Cu was faster than free Cu^{2+} due to its lipophilicity.
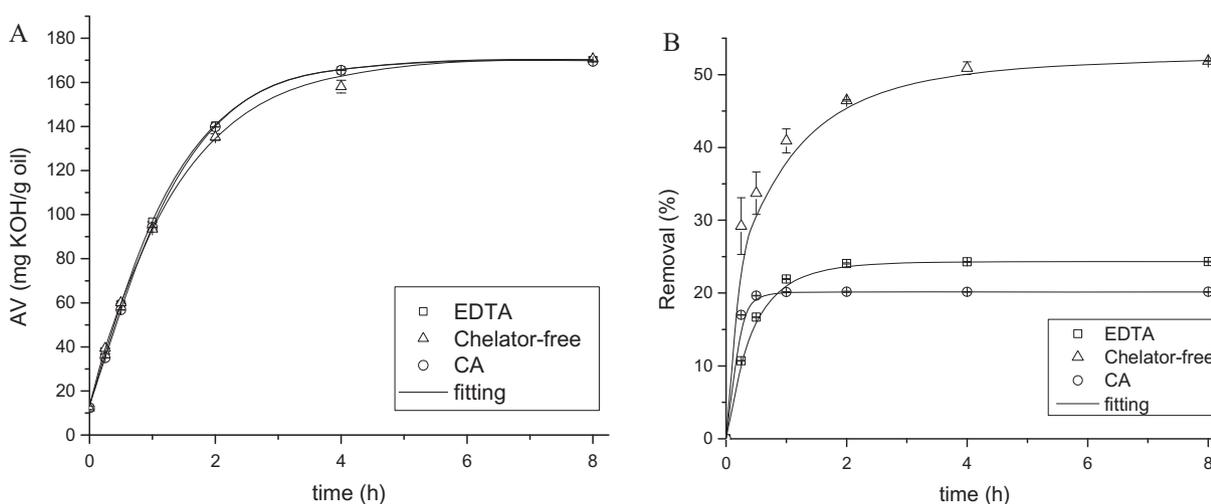

Fig. 2. Effect of chelating agents on (A) FA yield and (B) Cu removal percentage in the Cu-catalyzed hydrolysis of waste cooking oil at 225 °C.

Table 2
Kinetic rate constants obtained from experimental data fitting of waste cooking oil hydrolysis using chelated Cu solution at an initial pH of 5.0.

Constants	Chelating agent	
	EDTA	Citric acid
k_{TG}	9.94×10^{-4}	1.07×10^{-3}
k_{DG}	4.26×10^{-3}	2.80×10^{-3}
k_{MG}	9.38×10^{-4}	9.38×10^{-4}
k_{-TG}	0	0
k_{-DG}	0	0
k_{-MG}	7.99×10^{-3}	8.20×10^{-3}
$k_{Cu\text{-complex}}$	3.83×10^{-2}	1.20×10^{-1}
$Cu_{complex,\ lip}$	7.38×10^{-4}	7.78×10^{-4}

Compared to Cu-citrate complex, Cu-EDTA showed slower transfer due to its larger molecular size. This also explains a smaller k_{TG} and a slightly lower saturation concentration of Cu-EDTA complex in EDTA system due to higher steric hindrance and larger spatial occupation of molecules in the oil phase.

The possibility of K^+ involvement in catalysis as occurred in the base addition was evaluated in the system with a lower pH (Table S1 and Fig. S5). Similar values of k_{TG} and k_{-MG} independent of pH indicate that K-soap did not form as significant as in the free-chelating agent system. Though the system also contained K^+, the presence of negative-charged Cu-complex should be considered as the counter ion that inhibited K^+ from being free in the aqueous phase. By varying pH, mass transfer of Cu-complex into the oil phase increased gradually due to less charge density of complex formed and more K^+ available to neutralize complex charge at higher pH. Saturation concentration values were approximately constant with pH change since the space is limited by the fixed oil mass (volume) only.

3.3. Effect of organic solvent

Organic solvent presents in wastewater may lower down the dielectric constant of water [41], which could affect the formation of Cu-soap [25]. The increase of obtained FA concentration and Cu removal was small since only very small amount of solvents was added. At a glance, Fig. 3 showed comparable effect of the presence of ethanol and acetone. At equilibrium, the effect of solvent concentration on FA production was negligible (Fig. S6). Meanwhile, negligible increase on Cu removal percentage was observed, except for ethanol system at concentrations of 0.75 and 1 wt.%. Thus, in

order to accentuate the effect of organic solvent presence, 1 wt.% solvent concentration was chosen for kinetic modeling.

Due to better association of ethanol than acetone in water by means of the hydroxide group of ethanol, Cu^{2+} mass transfer (k_{Cu}) in aqueous ethanol is faster than that in water-acetone (Table 3). Lower polarity also slightly increased the apparent equilibrium constant of Cu-soap formation. Facilitated mixing between water and oil by solvents was obvious from higher k_{TG} than that of pure $CuSO_4$ solution. More non-polar acetone might give certain interference on the interaction between water and acylglycerides as observed in the slightly lower k_{TG}, k_{MG}, and k_{-MG} than ethanol and pristine Cu solution.

3.4. Effect of anion types

In the previous study, mineral acid was discussed as the main catalyst that increased FA yield significantly [14]. Thus, the anion species may also affect acid catalysis in subcritical water [25]. In this study, equimolar Cu systems with sulfate anion (SO_4^{2-}) was compared with nitrate (NO_3^-), chloride (Cl^-), and acetate (CH_3-COO^-), which are commonly found anions coupling with Cu in the wastewater. Overall, comparable FA yield and Cu removal were achieved for all anion systems (Fig. 4). A pH decrease to 2.3–2.5 was observed in all systems, except for the equilibrium pH of the aqueous phase in Cu-acetate system, which reached 3.63 due to lower deprotonation of acetic acid.

As showed in Table 4, Cu-chloride surpassed the other anion systems in TG hydrolysis. Cu-acetate system was the least among all. In the meantime, Cu mass transfer increased in the following order: Cu-chloride, Cu-nitrate, Cu-sulfate, and Cu-acetate. Since

Table 3
Reaction rate constants of waste cooking hydrolysis using 500 mg $CuSO_4$ in 1 kg of 1 wt.% aqueous ethanol and acetone.

Kinetic rate constant	Aqueous organic solvent	
	Ethanol (1 wt.%)	Acetone (1 wt.%)
k_{TG}	9.36×10^{-4}	9.34×10^{-4}
k_{DG}	9.98×10^{-3}	9.98×10^{-3}
k_{MG}	9.55×10^{-4}	9.16×10^{-4}
k_{-TG}	0	0
k_{-DG}	0	0
k_{-MG}	7.94×10^{-3}	7.25×10^{-3}
$K_{Cu(FA)2}$	2.80×10^{-9}	2.81×10^{-9}
k_{Cu}	3.83×10^{-1}	3.69×10^{-1}
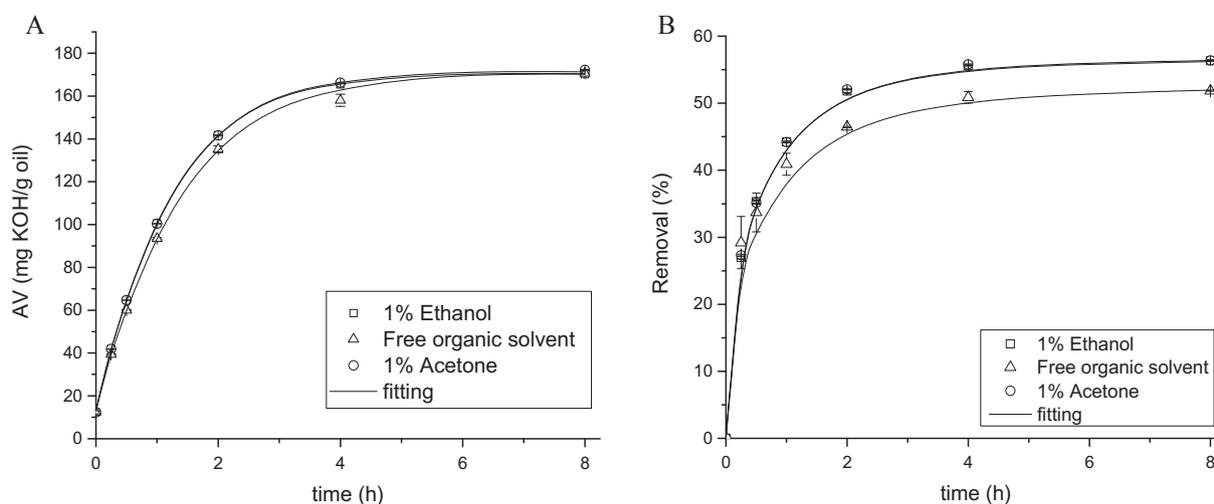
Fig. 3. Kinetic curves of (A) AV and (B) Cu removal percentage in the experiments using Cu solution contaminated with organic solvent.
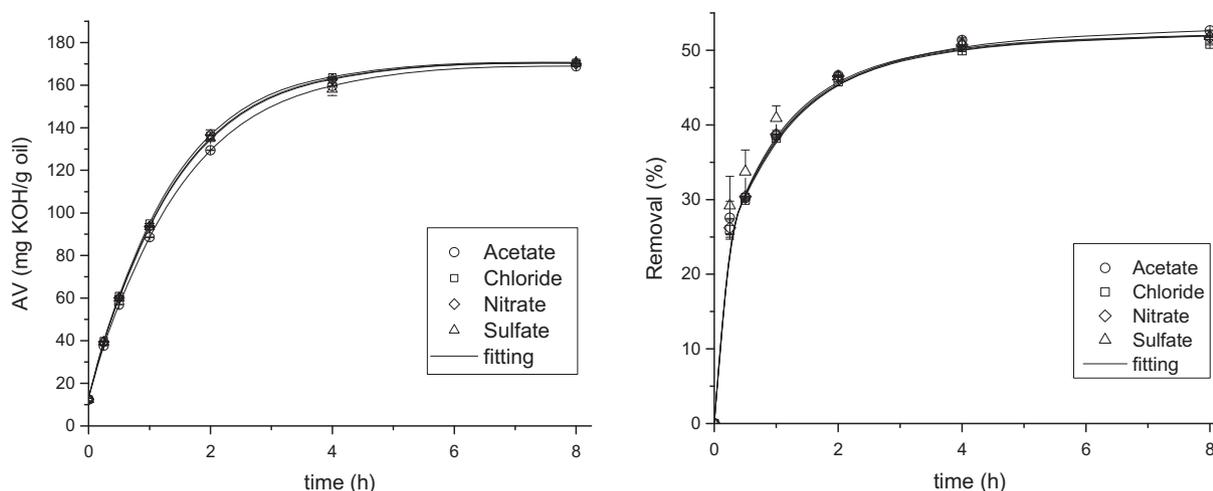
Fig. 4. FA yield and Cu removal percentage in the hydrolysis of waste cooking oil using various anion types.

Table 4
Reaction rate constants of waste cooking hydrolysis using Cu solution with different anion type.

Kinetic rate constant	Anion			
	Acetate	Chloride	Nitrate	Sulfate
k_{TG}	7.34×10^{-4}	8.24×10^{-4}	8.04×10^{-4}	7.94×10^{-4}
k_{DG}	9.58×10^{-3}	9.99×10^{-3}	9.98×10^{-3}	9.98×10^{-3}
k_{MG}	8.65×10^{-4}	9.84×10^{-4}	9.55×10^{-4}	9.55×10^{-4}
k_{-TG}	0	0	0	0
k_{-DG}	0	0	0	0
k_{-MG}	7.62×10^{-3}	8.01×10^{-3}	7.91×10^{-3}	7.94×10^{-3}
$K_{Cu(FA)2}$	2.16×10^{-9}	2.16×10^{-9}	2.16×10^{-9}	2.16×10^{-9}
k_{Cu}	3.75×10^{-1}	3.64×10^{-1}	3.68×10^{-1}	3.74×10^{-1}

an equimolar amount of Cu should produce the same amount of proton, this trend may be the results of the acids dissociation at higher temperature. Negative logarithm of the acid dissociation constant (pK_a) and the enthalpy of acid dissociation are listed in Table S2 [42–44]. HCl as the strongest acid demonstrated the highest hydrolysis rate constants among all acids formed in this study. As the weakest acid, acetic acid gave the lowest forward hydrolysis rate and the least inhibition of Cu^{2+} mass transfer by less ionic barrier made of hydrogen proton. In contrast with HNO_3, sulfuric acid has a smaller amount of proton since dissociation occurs in two steps with considerable weak dissociation at the second step (dissociation of HSO_4^-). With exothermic nature, HSO_4^-

is less deprotonated at high temperature by van't Hoff correlation, which also proved its inhibiting effect on ion exchange reaction in acidified system. The same apparent equilibrium constants indicate the same degree of cation exchange. With unselective nature of the acid catalyst, faster reversible reaction rate of MG hydrolysis was also observed at higher acidity.

3.5. Application of other divalent heavy metal ions

Substitution of $CuSO_4$ by other heavy metal sulfate salts at the same initial metal concentration showed the same equilibrium FA concentration (Fig. 5). Same low equilibrium aqueous phase
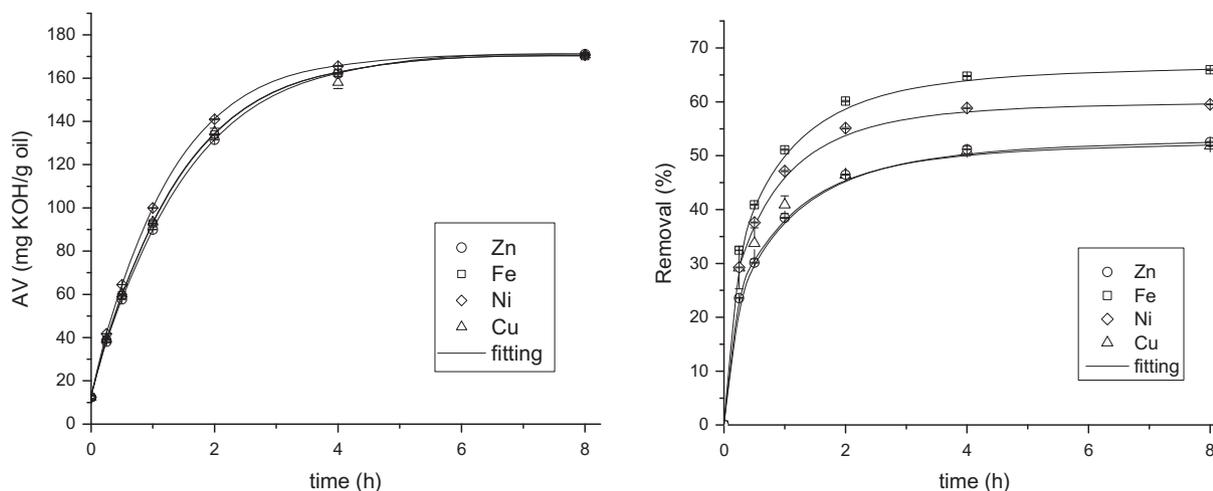

Fig. 5. Kinetic curves of AV and removal percentage in the waste cooking hydrolysis using various metal sulfate solution (3.13 mmol metal (II) ions/L, initial pH 5.0).

Table 5
Kinetic rate constants obtained from the hydrolysis experiments using various metal sulfate solution (3.13 mmol metal (II) ions/L, initial pH 5.0).

Kinetic rate constants	Metal (II) cation			
	Zn	Fe	Ni	Cu
k_{TG}	7.53×10^{-4}	7.89×10^{-4}	9.31×10^{-4}	7.94×10^{-4}
k_{DG}	9.68×10^{-3}	9.98×10^{-3}	9.99×10^{-3}	9.98×10^{-3}
k_{MG}	8.65×10^{-4}	9.46×10^{-4}	9.24×10^{-4}	9.55×10^{-4}
k_{-TG}	0	0	0	0
k_{-DG}	0	0	0	0
k_{-MG}	6.75×10^{-3}	7.82×10^{-3}	7.62×10^{-3}	7.94×10^{-3}
$K_{Cu(FA)2}$	2.16×10^{-9}	5.81×10^{-9}	3.59×10^{-9}	2.16×10^{-9}
k_{Cu}	1.55×10^{-1}	2.04×10^{-1}	4.35×10^{-1}	3.74×10^{-1}

pH, all metals followed the same mechanism and sufficient catalyst was present in all systems. From the hydrolysis rate constants (Table 5), Ni gave the highest acylglycerides conversion. However, considering the same order of magnitude, all metals actually performed quite similar, indicating lower contribution of metal ions and soaps as catalyst species than the produced H_2SO_4.

Apparent equilibrium constants revealed the order similar to the Irving-William series: $Cu \leq Zn < Ni < Fe$, which also serves as a trend of Lewis acidity [45]. Higher Lewis acidity results in less cation exchange due to more solid hydration cage between metal ions and water ligand. However, since the acidity of metal ions is not as strong as the proton from the acid deprotonation, the magnitude of the constants remained similar. In the meantime, Cu^{2+} mass transfer coefficient increased with increasing electronegativity: Ni (1.91) > Cu (1.9) > Fe (1.83) > Zn (1.65). This reflects metal ions attraction towards a free electron pair of species in the oil phase, either oxygen atom of the ester group in acylglycerides or oxygen atom of the deprotonated FA. Coincidentally, increasing TG hydrolysis rates were also showed by the same electronegativity trend. As the miscibility of acylglycerides in water increases as in the case of DG and MG, this trend is diminished by overshadowing catalysis of H_3O^+.

4. Conclusion

The effects of other contaminants in the Cu-containing wastewater on the hydrolysis of waste cooking oil were studied. Overall, the presence of contaminants did not give significant effect on the FA production. However, system acidification and chelating agents remarkably lowered down Cu removal percentage. More ionic species by acid and base addition disturbed Cu^{2+} transfer from aqueous to oil phase by providing ionic barrier at the interface. Subcritical water effect particularly self-dissociation of water molecules had a certain contribution to the enhancement of hydrolysis in the acidified and alkalinized system. Molecular interaction between the organic solvent and water influenced the equilibrium and mass transfer of Cu^{2+} towards the oil phase. Different anions formed different acids by means of cation exchange mechanism that determines the extent of cation exchange and hydrolysis reaction. The studied process also can be applied to other heavy metal ions with removal efficiency depending on the Lewis acidity of the corresponding metal ion.

Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.seppur.2017.06.049.

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