Separation and Purification Technology 187 (2017) 184–192

Contents lists available at ScienceDirect

Separation and Purification Technology

journal homepage: www.elsevier.com/locate/seppur

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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ARTICLE INFO

Article history:
Received 24 March 2017
Received in revised form 14 June 2017
Accepted 17 June 2017
Available online 21 June 2017

Keywords:
Hydrolysis
Wastewater reuse
Liquid-liquid extraction
Heavy metal
Waste cooking oil
Fatty acids
Subcritical water

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 subcritical 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+}.

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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http://dx.doi.org/10.1016/j.seppur.2017.06.049
1383-5866/

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), $Cu(CH_3COO)_2{\cdot}H_2O$ (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).

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

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).

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

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.

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

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