



Efficient recovery of copper from aqueous solutions with pyridine extractants (oxime, ketone) and their quaternary pyridinium salts



Aleksandra Wojciechowska, Karolina Wieszczycka*, Irmina Wojciechowska

Poznan University of Technology, Institute of Chemical Technology and Engineering, Berdychowo St. 4, 60-965 Poznan, Poland

ARTICLE INFO

Article history:

Received 24 January 2017

Received in revised form 27 April 2017

Accepted 5 May 2017

Available online 12 May 2017

Keywords:

Reactive extraction

Copper(II)

Pyridine extractant

Cu(II) recovery

ABSTRACT

In this research, 1-(3-pirydy)undecan-1-one, 1-propyl-3-undecanoylpyridinium bromide and 1-propyl-3-undecanoylpyridinium chloride, as well as, 1-(3-pirydy)undecan-1-one oxime with its chloride and bromide salt were designed as new extraction agents for the copper recovery. It was found that the increasing chloride ions concentration positively affected the copper(II) extraction. The discussion also includes the speciation of the complexes transported into the organic phase and the selectivity of the quaternary bromide salts (K-3PC10-PrBr and Ox-3PC10-PrBr) towards iron ions. Moreover, the laboratory-scale experiments indicate that 3-[1-(hydroxyimine)undecyl]-1-propylpyridinium bromide is efficient and selective in the copper extraction and it can be proposed to copper removal from the solution obtained in the chloride leaching of copper sulfides.

© 2017 Elsevier B.V. All rights reserved.

1. Introduction

The success of the hydrometallurgical technique for extraction of copper in the processing of oxide ores and various wastes has induced interest in applying this technology to copper recovery from other raw materials [1–4]. One of the processes, which produce large amounts of wastewater, is the chemical and electrochemical copper plating and etching unnecessary copper layers. Wastewater remaining as a result of that process must be treated before discharge into the sewer, which is associated with the need to meet standards for wastewater discharge [5].

There are numbers of methods for removing of copper(II) from industrial effluents, such as precipitation as metal sulfides, by using an ion exchange, membrane method, electrocoagulation or basing on a mechanism of complexation reaction between metal ions and appropriate ligand (tartaric acid, EDTA) to obtain copper complexes, which are insoluble in water [5–10]. Another method based on the mechanism of a complex formation is a reactive solvent extraction, which is one of the most important techniques in hydrometallurgical operations to recover, separate and to purify the pay-metals. In recent years much attention has been focused on the leaching of chalcopyrite by oxidizing agents, the most common being ferric ion as a sulfate or chloride ferric salts. Moreover, it was found that ferric chloride is much more reactive to chalcopyrite than ferric sulfate [11]. The recovery studies of copper(II) ions

from chloride solutions concern not only on the extraction from solutions obtained by effective leaching the copper concentrates with ferric chloride but also with cupric chloride solutions [12–14]. Concentrated solutions, containing up to 60 g/L Cu and 4–8 mol/L Cl^- , cannot be efficiently converted by solvent extraction process, in which chelating reagents are used [1]. An example of a reactive extractant designed for industry to remove of copper (II) from chloride solutions was Acorga® CLX-50 with an active compound *bis(isodecyl) pyridine-3,5-dicarboxylate* [14]. The extraction with Acorga® CLX-50 and its derivatives depends on many factors, from which the most important are: extractant concentration, chloride ions concentration, water activity and pH [14–17]. Another type of pyridine extractants are hydrophobic pyridine ketoximes, which extraction abilities to copper(II) depend on the extractant structure, type of organic diluents and composition of an aqueous feed [18–20]. The most interesting extractant is 1-(2-pirydy)tridecan-1-one oxime, which, as a strong complexing agent, has ability to extract copper(II) efficiently even at low concentrations of chloride ions. However, the very high stability of the complexes with copper(II) is also a disadvantage of the extractant, the stripping requires a strong receiving agent such as oxalic acid.

1-(3-pirydy)undecan-1-one oxime and its quaternary salts have been successfully evaluated as potential extractants of Zn (II) [21–23]. Studies have demonstrated that using these compounds the extraction is fast, selective towards iron ions and regardless of the acidity and after stripping, the regenerated organic phase can be used repeatedly maintaining the extraction

* Corresponding author.

E-mail address: karolina.wieszczycka@put.poznan.pl (K. Wieszczycka).

efficiency at a constant high level. While these reagents are very suitable to apply as metals extractants from chloride solutions, its application to recovery of copper(II) has not been proposed so far. Therefore, the aim of this work is to study the extraction behaviour of Cu(II) from chloride solution by 1-(3-pyridyl)undecan-1-one, 1-(3-pyridyl)undecan-1-one oxime and their quaternary salts: 1-propyl-3-undecanoylpyridinium bromide, 1-propyl-3-undecanoylpyridinium chloride, 3-[1-(hydroxyimine)undecyl]-1-propylpyridinium bromide and 3-[1-(hydroxyimine)undecyl]-1-propylpyridinium chloride. The key experimental conditions, such as shaking time, pH, chloride and copper ions concentrations, as well as extraction agent concentration were studied

2. Experimental

2.1. Reagents

Aqueous solutions were prepared from $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (p.a., POCH, Poland) or $\text{Cu}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ (p.a., POCH, Poland). NaCl (p.a., POCH, Poland) was used to adjust the chloride ions concentration. HCl (p.a., POCH, Poland), HNO_3 (p.a., POCH, Poland), lithium nitrate (p.a., Sigma Aldrich, Germany) and sodium nitrate (p.a., Sigma Aldrich, Germany) were used to maintain a water activity. Toluene (p.a., Chempur, Poland) and decan-1-ol (p.a., Sigma Aldrich, Germany) were used to compose the organic phase.

Examined reagents were prepared using 3-cyanopyridine (98%, Sigma Aldrich), propyl bromide (95%, Sigma Aldrich), propyl chloride (98%, Sigma Aldrich, Germany), decyl bromide (98%, Sigma Aldrich, Germany), acetonitrile (p.a., Sigma Aldrich, Germany), chloroform (p.a. POCH, Poland), hydroxylamine hydrochloride (p.a., Chempur, Poland), ethanol (99.8%, POCH, Poland), sodium hydroxide (p.a., POCH, Poland) and sodium bicarbonate (99%, Sigma Aldrich).

2.2. Synthesis of extractants

The studied reagents were synthesized according to a procedure described elsewhere [21,22]. Scheme of the synthesis was illustrated in Fig. 1.

2.3. Extraction procedure

Extraction was carried out in a test tube using organic to aqueous volume ratio (O/W) equal to 1. Both phases were shaken for 30 min at room temperature (23–25 °C) using a laboratory shaker Bio-Mix BWR04 (BioMix, Poland) with a constant agitation speed (800 rpm). Each experiment was carried out at least in duplicate, and the results agreed within 5%. The effects of various process parameters were studied: chloride and copper(II) ions concentrations in the aqueous feed solution and the extractant concentration in the organic phase. Chloride feed solutions were prepared by dissolving $\text{Cu}(\text{NO}_3)_2 \times 6 \text{H}_2\text{O}$ or $\text{CuCl}_2 \times 6 \text{H}_2\text{O}$ (at 4 M Cl^-), NaCl, NaNO_3 and LiNO_3 (studies conducted at constant ionic strength $I = 4 \text{ mol/L}$ and at a constant water activity $a_w = 0.835$) [24]. The pH of the aqueous solutions was adjusted using Mettler Toledo T50 Titrator to a value of 3.5 by adding 0.2% HCl or HNO_3 solution. The influence of HCl concentration in the aqueous feed solution on Cu(II) extraction was also examined.

The organic phase was prepared by dissolution of synthesized compounds in toluene with a 10% (v/v) addition of decan-1-ol. The concentration of each extractant in the organic phase was changed from 0.1 to 1.0 mol/L.

The structure and purity of the obtained compound were confirmed by spectroscopic methods (FT-IR, ^1H and ^{13}C NMR, ESI-MS).

1-(3-pyridyl)undecan-1-one (**K-3PC10**) FT-IR [cm^{-1}]: 2890, 1690, 1730, 1450. ^1H NMR (CDCl_3 , DMSO) δ in ppm: 9.15 (Py-2, 1H, s); 8.75 (Py-6, 1H, dd, $J_1 = 3.17 \text{ Hz}$, $J_2 = 6.36 \text{ Hz}$); 8.23 (Py-4, 1H, dd, $J_1 = 3.18 \text{ Hz}$, $J_2 = 12.47 \text{ Hz}$); 7.4 (Py-5, 1H, t); 2.96 (2H, t); 1.73 (2H, qw); 1.37–1.24 (14H, m); 0.86 (3H, t); ^{13}C NMR (CDCl_3) δ in ppm: 198.7 (C=O); 152.8 ($\text{C}_{\text{py}}(2)$); 149.1 ($\text{C}_{\text{py}}(6)$); 134.8 ($\text{C}_{\text{py}}(4)$); 131.7 ($\text{C}_{\text{py}}(3)$); 123.0 ($\text{C}_{\text{py}}(5)$); 39.1 (CH_2); 38.4 (CH_2); 37.4 (CH_2); 35.2 (CH_2); 31.3 (CH_2); 29.0 (CH_2); 28.8 (CH_2); 23.5 (CH_2); 22.1 (CH_2); 13.6 (CH_3) (ESI-MS) m/z : 247.38 (M+H) $^+$.

1-propyl-3-undecanoylpyridinium bromide (**K-3PC10-PrBr**): FT-IR [cm^{-1}]: 2890, 1680, 1735, 1450, 860. ^1H NMR (CDCl_3 , DMSO) δ in ppm: 9.20 (Py-2, 1H, s); 8.60 (Py-6, 1H, dd, $J_1 = 3.16 \text{ Hz}$, $J_2 = 6.34 \text{ Hz}$); 8.20 (Py-4, 1H, dd, $J_1 = 3.16 \text{ Hz}$, $J_2 = 12.30 \text{ Hz}$); 7.45 (Py-5, 1H, t); 3.66 (N- CH_2 ; 2H, t); 2.96 (2H, t); 1.75 (2H, qw); 1.36–1.23 (18H, m); 0.83 (6H, t); ^{13}C NMR (CDCl_3) δ in ppm: 200.1 (C=O); 148.1 ($\text{C}_{\text{py}}(2)$); 146.0 ($\text{C}_{\text{py}}(6)$); 145.6 ($\text{C}_{\text{py}}(4)$); 141.2

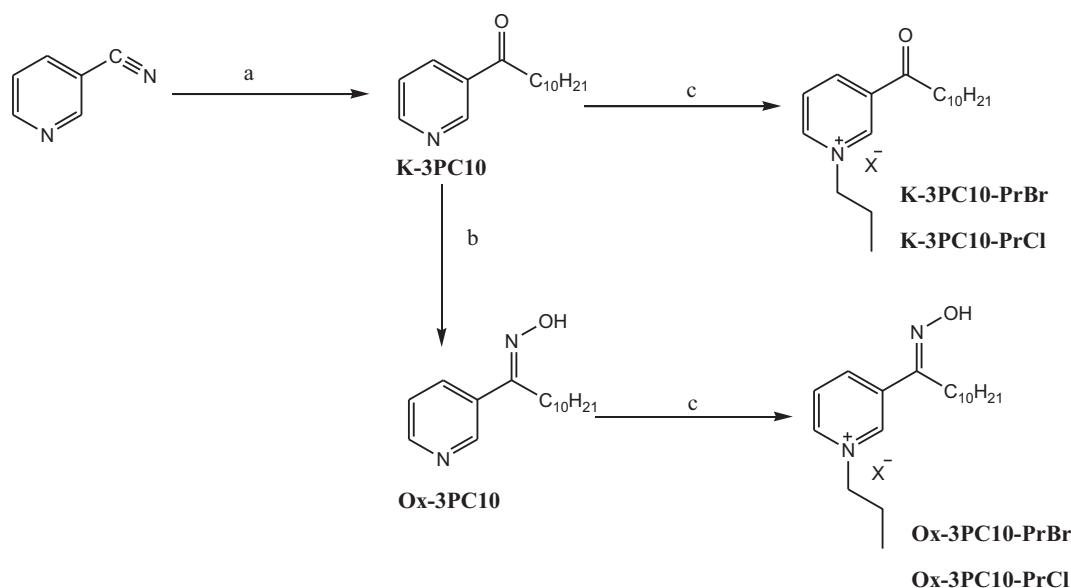


Fig. 1. Scheme of synthesis of studied reagents: (a) (1) $\text{C}_{10}\text{H}_{21}\text{MgBr}$, diethyl ether, (2) H_2O , H^+ , pH = 7–8, reaction time: 48 h, (b) $\text{NH}_2\text{OH} \cdot \text{HCl}$, NaOH/ethanol, reaction time: 2 h and (c) 1-chloropropane or 1-bromopropane in ethanol, reaction time: 12 h; $\text{X}^- = \text{Cl}$ or Br.

Download English Version:

<https://daneshyari.com/en/article/4989635>

Download Persian Version:

<https://daneshyari.com/article/4989635>

[Daneshyari.com](https://daneshyari.com)