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Critical Metals Removal via Sustainable Solvent Extraction Technique from Metal Scrap Recycling Waste

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Abstract **-** Metals from the critical raw material list play a key role in the successful transition to more sustainable practices in any sectors now. However, there could be partial loss of them due to insufficiency of waste management practices. In this paper, the proof-of-concept of an environmentally friendly technique utilizing a choline-based deep eutectic solvent (DES) as an alternative option to conventional solvents is presented for the extraction of copper and zinc from dust after the mechanical metal scrap process.

Keywords**:** deep eutectic solvent, choline chloride, metal scrap, metal extraction.

1. Introduction

The main economic driving force for the recycling of metal scrap is the recovery of valuable and/or critical metals [1]. Critical raw materials (CRM), particularly metals, have a constantly increasing demand due to their high usage in renewable energy technologies, metallurgical manufacturing, and electronic devices [2], [3]. Recovering metals from various waste streams can be more sustainable yet more challenging than the conventional mining of rapidly depleting virgin sources due to differences in chemical behavior of the matrixes containing the CRM. The waste streams themselves and chemicals used in recovery processes could pose a serious risk to both human and environmental health [2], [4], [5]. However, often such waste streams contain valuable metals in a higher concentration than what is found in ores, making them an important secondary resource of valuable and/or critical metals [6]. Recycling and metal recovery can provide security of raw materials supply for places with limited or non-existing ore and assist in the global transition into a more circular economy [5, 6].

Copper, cobalt, nickel, and manganese have all been classed as critical raw materials by the European commission in their latest report [7]. 38% of Ni and 19% of Cu used in the EU are sourced from within its borders, while the rest are mainly sourced from abroad [7]. Cu is an essential component in the renewable energy industry and can be found basically in any electronic devices e.g., rechargeable batteries, electrical wiring, cathode-ray tube screen, and charging stations [5], [8]. Waste from Electrical and Electronic Equipment (WEEE) streams contain Cu in a significantly higher concentration when compared to primary ore found in conventional mining operations [5]. This coupled with the predicted increase in Cu demand, depleting resources, environmental, and humanitarian problems associated with mining operations [8] may make recycling of WEEE a more sustainable option than conventional mining.

The most popular recycling method of metal scrap throughout the globe is mechanical recycling [9]. This method separates waste fractions by the differences in the physical attributes of the different components in the waste which can be achieved through different ways such as dismantling, crushing, magnetic separation, shredding, and sieving [1], [9], [10]. The low costs and easy operation are the main advantages of mechanical recycling [1].

Hydrometallurgical recycling processes involve different methods such as chemical leaching, acid/alkali leaching, solvent extraction, and bioprocessing [3], [10], [11]. Generally, there are three main processes that are present in hydrometallurgy: metal dissolution (leaching), concentration and purification, and finally, metal recovery [12]. Hydrometallurgical recycling processes are often considered more environmentally friendly than pyrometallurgical processes due to easier operation, lower operating temperatures, lower emissions, and higher metal separation efficiency [1], [4], [9]. However, hydrometallurgical processes have some major drawbacks such as high consumption of often harmful solvents such as cyanide and aqua regia, and the production of waste which is difficult to dispose and are often discarded directly into waterbodies [1], [2], [13], [14]. Ionic liquids (ILs) and deep eutectic solvents (DESs) are considered a greener alternative to the organic solvents traditionally used in hydrometallurgical processes due to their high chemical/thermal stabilities, high solvent capacity, negligible vapor pressure, non-flammability, and their good metal extraction capability [12], [15]. In this study, we demonstrate proof-of-concept for the metal extraction technique from metal scrap residues, utilizing choline-based DES.

2. Materials and Methods

2.1. Materials

Choline chloride (ChCl, AR, ≥ 98%), ethylene glycol (EG, AR, ≥99%), urea (UA, ultra-pure, ≥99%) as well as oxidants and acids, such as hydrogen peroxide 30% (w/w), hydrochloric and nitric acids were purchased from VWR Chemicals. The waste residue was obtained from the local metal scrap recycling company. The sample was sieved into two fractions <250µm and 250µm – 4mm. Additionally, the size distribution of waste material was determined on Hosokawa Alpine. X-ray fluorescence spectroscopy (XRF, PanAnalytical Minipal 4) and flame atomic-adsorption spectroscopy (FAAS) were used to analyze the elemental compositions in solid and liquid phases. A powder X-ray diffraction method (XRD, a PANnalytical X´Pert PRO MPD diffractometer, Co Kα radiations generated at 40 kV and 40 mA, step width of 0.02°, Highscore software 3.0) was used to define the mineralogical composition.

2.2. DES preparation and metal extraction

The methodology of the DES preparation and the sample pretreatment was adopted [16] with minor changes. The mixtures of ChCl with urea or ethylene glycol with molar ratios 1:2 were prepared at a temperature of 80°C in the closed vials on the hot plate until the solid sample became transparent and homogeneous. The ChCl or prepared DES was mixed with H_2O_2 (5 wt%), and waste residues (2 fractions) in a liquid-to-solid phase ratio equal 100:1 were agitated on a magnetic stirrer for 1h at ambient temperature.

After the separation of the metal-laden DES phase and solid phase by vacuum-filtration, an excess H_2O_2 was removed by boiling for 5 min on the hot plate. Further, 0.500 g of the metal-containing DES was digested in nitric acid in termoblock, and after dilution analyzed by FAAS to calculate the removal rate for each DES.

3. Results and discussion

The XRF results of two waste fractions are presented in Table 1. The target elements for the leaching test were present at the levels 1-5%, Ni, Mn, and Co were determined as impurities e.g. 0.1-0.3%. Aluminium and silicon oxides as well as calcium and iron oxides were present in significant quantities. The XRD patterns of the waste residues showed the presence of the characteristic diffraction peaks of gypsum, aluminium and silicon oxides (quartz type), Cu0. The amorphous halo located at 20–30◦ was probably attributed to the carbon materials, various alumosilicates, and amorphous iron oxides.

Table 1: Chemical compositions of waste residues from the meal scrap recycling process (α=0,05, *n*=3).

Constituent	Content (wt. %)	
	> 250µm	< 250µm
Na_2O	2.4±0.9	1.5±0.6
Al_2O_3	9.5±0.9	12.5±0.8
SiO_2	23±5	36±6
SO_3	1.8±0.5	1.6±0.2
K_2O	1.1±0.8	1.3±0.2
CaO	16±3	11.5±0.6
Fe_2O_3	26±3	25±3
Cu	1.5±0.8	1.3±0.8
Zn	4.9±0.9	3.5±0.2
Pb	<1	1.1±0.8

Three choline-based DES compositions choline chloride (ChCl), choline chloride-ethylene glycol (ChCl-EG), and choline chloride-urea (ChCl-U) were studied to define their extraction ability towards Cu, Zn, and Pb from the waste residue. The results of Cu removal efficiency in DES with and without the addition of H_2O_2 are listed in Table 2. The metal leaching efficiency was significantly enhanced in the presence of an oxidizing agent, reaching up to 91% for copper and 42% for zinc, respectively.

Table 2: The removal efficiency (%) of metals from waste restudies with choline-based DES (α=0,05, *n*=3).

Fraction / Element	> 250µm			< 250µm		
	ChCl	ChCl-EG	ChCl-U	ChCl	ChCl-EG	ChCl-U
without H_2O_2						
Cu	6.1±0.8	9±1	19±2	9.8±0.7	12±2	23±2
Zn	5±1	16±2	15±2	6.6±0.9	18±2	16±1
with H_2O_2						
Cu	12±2	72±4	66±4	16±3	91±5	85±4
Zn	6.1±0.8	29±3	25±2	9±1	42±4	28±2

Liu et. al (2024) attributed detectable metal leaching in ChCl to its acidic nature [16]. They also emphasize that systems containing both oxidizing and complexing agents could promote solvolysis. Enhanced removal of zinc and copper perhaps might be related to this fact.

4. Conclusion

The present work investigated the extraction of copper and zinc from waste residues after mechanical metal scrap recycling process. Using choline-based DES with complexing properties with and without the addition of oxidizing agent. The studied systems act as the coordination agents and solvents in the leaching process. The study demonstrated a new approach that could facilitate sustainable metal recovery on recycling sites. That would allow the municipalities and the recycling facilities to generate revenues to cover the cost of treatment whilst reducing the environmental burdens caused by long-distance logistics of hazardous waste and conventional disposal.

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