Solvent extraction recovery and separation of cadmium and copper from sulphate solution

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ABSTRACT

In this study solvent extraction process has been used for separation of cadmium and copper from sulphate solution. A phosphoric acid extractant (D2EHPA) and an oxime extractant (MEX) in kerosene diluent were used as cadmium and copper extractants, respectively. The results showed that 1 g/L cadmium could be extracted by 30–35% (v/v) D2EHPA at the pH of 3.5–4. Cadmium separation factor over copper with D2EHPA was calculated 4.04 in best condition of pH (=2). On the other hand 3% MEX separated 1 g/L copper over cadmium optimally at the pH of 3.5 and under this condition of pH, copper separation factor is calculated 4495.5. Loading capacity studies showed that copper existence in cadmium aqueous solution reduces cadmium extraction with D2EHPA up to 10% whilst copper extraction percentage with MEX does not vary considerably in the presence of cadmium.

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Introduction

Elimination of heavy metals from industrial wastes at the point of environmental aspects was always important. Furthermore there is an attitude toward the recovery of precious metals from low-grade or complex ores, secondary resources and industrial wastes because of the reduction of world's high grade resources and metals high prices.

Generally, hydrometallurgical route (leaching–solvent extraction–electro winning) is found suitable to process lower grade ores, wastes such as slag, tailings and recycled solutions [1]. Solvent extraction is now a very well-established process in hydrometallurgy. It is used for the hydrometallurgical processing of copper, nickel, cobalt, zinc, uranium, molybdenum, tungsten, vanadium, rare earths, zirconium, hafnium, niobium, tantalum, indium, gallium, germanium, the platinum group metals, boron, reprocessing nuclear fuels, purification of wet process phosphoric acid, nitric acid recovery, etc. [2].

In this study recovery and separation of cadmium and copper were considered. Cadmium and its compounds are toxic and poisoning occurs through inhalation and ingestion. In spite of its toxicity, it is used in different industries such as electroplating, pigments, synthetic chemicals, ceramics, metallurgical and photographic products, electronics and other industries [3]. Cadmium is

extracted from the by-products of zinc metallurgy among which copper–cadmium slag, cadmium–rich dust and also from the spent Ni-Cd batteries. Pure cadmium can be recovered through solvent extraction, electrolysis refining or vacuum distillation [4].

Among the available processing alternatives, solvent extraction is a technique that not only meets the strict environmental regulations but also high purity value added products could be produced. Acidic extractants, including carboxylic acids, dialkyl phosphoric and dialkyl phosphinic acids, can be used to extract cadmium (II). The extraction of cadmium (II) is selective in the presence of Zn(II), Ni(II), Co(II), Mn(II), Fe(II), Ca(II) and Mg(II) with $\Delta pH_{0.5}(Me/Cd) = 1.5$ where Me = Zn (II), and not less than 2.5 for the remainder of these cations. However, copper (II) and lead (II) can be co-extracted [5]. Different kinds of extractant were used to extract cadmium from aqueous solution and a comprehensive literature about them are available [3,6].

Among phosphoric acids, (Di(2-ethylhexyl)) phosphoric acids (D2EHPA) which is successfully used as cadmium extractant in several industrial and experimental works, is used in this study and the extraction mechanism of the metal ion (in this case cadmium) with D2EHPA which is diluted in kerosene may be expressed as follows [7]:

$$M^{n+} + \frac{n+p}{2}(H_2A_2)_{org} \rightleftarrows (MA_n(HA)_p)_{org} + nH^+ \qquad (1)$$
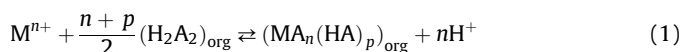
where (H_2A_2) is extractant in dimeric form, M is metal, n is valence of the metal or metal complex ion and $(n + p)$ number of molecules of extractant engaged in reaction. Working with concentrations

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lower than or equal to 0.2 mol L^{-1} (22.48 g/L) of cadmium in the organic phase, according to the literature [8], the chemical reactions can be expressed as:

$$Cd^{2+} + 2(H_2A_2)_{org} \rightleftarrows CdA_2(H_2A_2)_{org} + 2H^+ \qquad (2)$$
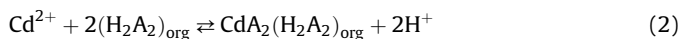
In addition of zinc processing residues cadmium and copper co-existence is seen in different metal processing plants. For instance the dense fumes, which come from smelters of metal bearing ores, are rich in metallic pollutants, such as Cd, Cu, Pb, and Zn [9]. A study which was done in the vicinity of Sarcheshmeh (the largest porphyry copper deposit in Iran) copper smelting plan showed that Sarcheshmeh soil samples are enriched in As, Cu, Mo, Zn, Cd, and Pb [10]. Whereas copper solvent extraction is a well-established route in copper processing plants, copper extractants can also be considered useful in the separation of cadmium and copper. The copper-specific extractants used to extract copper from other base metals in acidic sulphate liquors are known as *hydroxyoximes*, and the interaction is known as *chelation*. The basic structures of modern oxime extractants are shown in Fig. 1 and the complexation of copper by these extractants is shown schematically in Fig. 2. Today modified aldoximes and aldoxime–ketoxime mixtures are the most widely used copper extractant systems [11]. In this study a cadmium common extractant compared with a copper extractant at the point of their ability in selective separation of cadmium and copper and also on their loading capacity toward each and both of these elements.

Materials and methods

Reagent

The aqueous feed solution containing cadmium and copper was prepared by dissolving appropriate amount of their sulphate salt in distilled water. Sulphuric acid (H$_2$SO$_4$) and sodium hydroxide (NaOH) solutions were used in order to maintain desired equilibrium pH of the solution during extraction. All chemicals used were analytical reagent grade. All inorganic reagents were purchased from Merck. "MEX" reagent from SOIL Company was used for solvent extraction of copper. This extractant based on aldoxime and ketoxime molecules: 5-nonylsalicylaldoxime, 5-nonyl-2-hydroxyacetophenone oxime. Di-(2-ethylhexyl) phosphoric acid (D2EHPA), from the Luoyang Zhongda Chemical Co. Ltd. was of chemical reagent quality with a purity >95.0%, was used as cadmium extractant. Commercial grade kerosene was used as diluent for organic extractant.

Procedure

Experimental studies were carried in two steps. At first, optimum condition of pH and extractant concentration for extracting of cadmium with D2EHPA and copper with MEX from their pure sulphate solution of each metal were determined. In this stage we have investigated the extraction process in order to obtain optimum conditions of pH and extractants concentrations
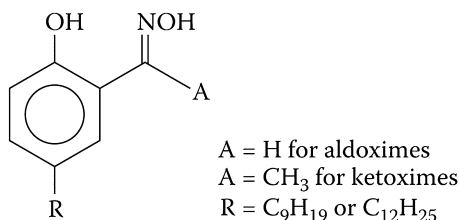

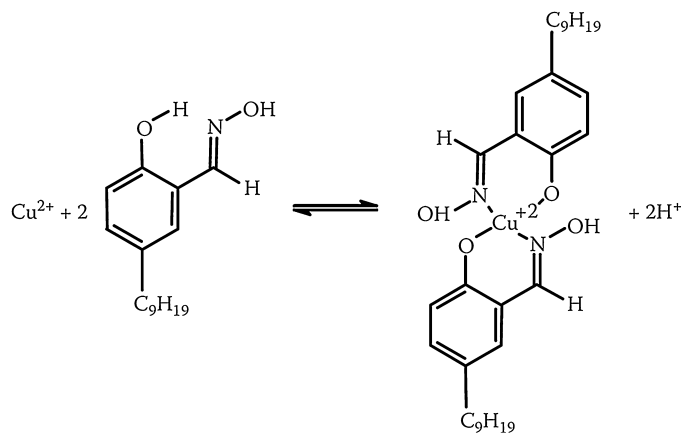Fig. 1. Modern oxime extractant.

Fig. 2. Complexation of copper with oxime extractants.

([HA]), whereas optimum condition of each desired parameter (pH or [HA]) was determined by varying that parameter whilst all other parameters kept fixed. The condition at which highest extraction percentage happened, were chosen as optimum condition.

After that, a solution of both metals was prepared and contacted with organic phases (extractant which diluted in kerosene). Metals concentrations in all aqueous phases were 1 g/L. Equal volumes (25 mL) of aqueous and organic phase were shaken using incubator shaker (stirring rate: 100 rpm) for 20 min in each test. Aqueous solution pH was varied from 1 to 4.5 and all tests were carried in room temperature.

After extraction process organic and aqueous phases were separated using separatory funnel. The solutes (Cd or Cu), which initially was dissolved in aqueous phase (with initial concentration of [A$_0$]$_{aq}$) distributes between the two phases. Sample was taken from aqueous phase and its metal content ([A$_1$]$_{aq}$) was measured using Unicam 939 atomic absorption spectrophotometer. The flame conditions were those recommended by the instrument manufacturer (wavelengths 324.8 nm and 228.8 nm, respectively, for copper and cadmium). The quantification limits were 0.096 mg/L and 0.03 mg/L and the detection limits were 0.29 mg/L and 0.01 mg/L for copper and cadmium, respectively.

The distribution ratio of the solute can be calculated as following:

$$D = \frac{[A_{eq}]_{org}}{[A_{eq}]_{aq}} = \frac{[A_0]_{aq} - [A_1]_{aq}}{[A_1]_{aq}}$$
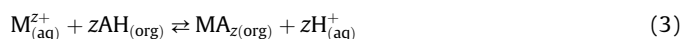
For practical purposes, as in industrial applications, it is often more popular to use the percentage extraction %E (sometimes named the extraction factor), which is given by:

$$\%E = \frac{100D}{1 + D}$$

Results and discussion

Determination of optimum pH and extractant concentration

Acidic extractants include simple reagents such as carboxylic acids and organophosphorus acids, as well as chelating acids, extraction occurs by a change of the acidity in solution; thus, increasing the pH of solution increases extraction. Acidic extractants extract metals generally according to the following equilibrium reaction:

$$M^{z+}_{(aq)} + zAH_{(org)} \rightleftarrows MA_{z(org)} + zH^+_{(aq)} \qquad (3)$$