



Study of molybdenum extraction by trioctylamine and tributylphosphate and stripping by ammonium solutions



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ABSTRACT

The extraction of molybdenum from an aqueous solution by a tertiary amine extraction system was experimentally studied in this work. The organic phase is composed of trioctylamine (TOA) as the extractant, tributylphosphate (TBP) as the modifier, and kerosene as the diluent. The effects of various parameters including the concentrations of TOA and TBP, initial pH of aqueous phase, phase ratio of organic/aqueous, contact time of phases, type of diluent, and concentration of metal ions in the aqueous phase on the extraction of molybdenum were investigated. At the same time, stripping of molybdenum from the molybdenum-loaded organic phase using an ammonium hydroxide solution as stripping reagent was studied. The results showed that an extraction of 99.9% was obtained with the extraction system composed of 4 vol.% TOA, 12 vol.% TBP, and 84 vol.% kerosene at a phase ratio of 1, initial pH = 1, and contact time = 600 s. The difficulties in separating aqueous and organic phases were successfully obviated through addition of TBP to TOA extractant.

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1. Introduction

Molybdenum is known as a strategic metal which has an extensive usage in the fabrication of radios, thermocouples, and anticathode of X-ray tubes. It is also used in the production of alloys of special steels. High contents of various metals such as U, V, W, Re, Al, Ni, Cu, and Co also exist in molybdenum resources (Keshavarz Alamdari et al., 2012; Wang et al., 2009).

The conventional method for the production of molybdenum involves the extraction from molybdenite (MoS₂) concentrates or ores. The industrial method used for the extraction of Mo from its sulfide mineral molybdenite includes the following steps: roasting of the MoS₂ concentrate, purification of the generated calcine either by a hydrometallurgical method or distillation and, eventually, hydrogen reduction of the trioxide to molybdenum. During the roasting process, a substantial amount of SO₂ is generated which is a major source of environmental pollution (An et al., 2009; Cao et al., 2010). Therefore, because of strict environmental regulations, the hydrometallurgical route becomes more attractive especially for low-grade and complex ores. Electrooxidation is one of the best methods that can be used as an alternative method for the roasting process. In the latter method, the molybdenite (MoS₂) is first oxidized in the electrolysis bath by NaClO solution. An aqueous solution is then produced that molybdenum must be extracted from this solution (Cao et al., 2010).

Several authors have studied the extraction of molybdenum from the aqueous solutions by various methods including supported liquid membranes (Marchese et al., 2004), ion exchange (Kononova et al., 2003), precipitation (Yatirajam et al., 1975), and solvent extraction (Banda et al., 2012; Karagiozov and Vasilev, 1979; Saberyan et al., 2003). Each of these extraction techniques has its own advantages and drawbacks. Among these techniques, solvent extraction is one of the well-established unit operations in hydrometallurgy for its commercial production of high purity metals. Advantages of solvent extraction include ease of continuous operation, improved economics, high throughputs, and suitability for extraction of a variety of metal solutions from various sources (Zeng and Cheng, 2009).

A number of extractants have been utilized for the extraction of molybdenum from aqueous solutions. The most commonly used extractants are organic phosphoric acids, such as PC-88A (Sato et al., 1989), tributylphosphate (Alamdari and Sadrnezhaad, 2000), Alamine 304-I (Parhi et al., 2011), di-(2-ethylhexyl) phosphoric acid (D2EHPA) (Qingyuan and Huihao, 1986), oxime and amines.

A number of extractants, including TBP, have been also considered as modifiers for the extraction of some metal ions such as zinc, cobalt, and nickel (Haghshenas Fatmehsari et al., 2009; Nash and Choppin, 1977). On the other hand, the synergistic effect of an extractant mixture for the solvent extraction of molybdenum by trioctylamine and tributylphosphate has not been reported so far. Thus the present work focuses on the study of extraction of Mo(VI) by a mixture of extractants from the leach liquor. The studied variables include pH of aqueous solution, concentration of extractants, kinetics of extraction, concentration of NH₄OH as the stripping phase, phase ratio (O:A), and the effect of a

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number of diluents. A thorough study was conducted to determine the optimum conditions for the extraction of Mo(VI) from aqueous solutions. Extraction and stripping isotherms were also developed from equilibrium data obtained in this study.

2. Materials and methods

2.1. Apparatus

An inductive coupled plasma optical emission spectrometer (ICP-OES) model Liberty 220 from Varian, a pH meter from Precisa (pH 900), and a FTIR analyzer from Nicolet (model 870) were used for analytical purposes. A mechanical shaker was also used to contact the phases.

2.2. Materials

Aqueous solutions of molybdenum at various concentrations were prepared by dissolving sodium molybdate ($\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$) in distilled water. Hydrochloric acid and sodium hydroxide were used for adjusting pH of solutions. Ammonium hydroxide, obtained from Merck, was used as a stripping reagent. Distilled kerosene (obtained from Tehran refinery) was used as a diluent to prepare the organic phase. Trioctyl amine (TOA), an anionic extractant, obtained from Fluka, was used for the extraction of molybdenum. Tributyl phosphate (TBP) was used as a modifier. All chemicals were used as-received without any further purification.

2.3. Experimental procedures

Appropriate amounts of sodium molybdate were dissolved in distilled water to prepare aqueous solutions of 11 g/L concentration. The organic phases were prepared by dissolving determined amounts of trioctyl amine and tributyl phosphate in kerosene. TOA was pre-equilibrated with the same volume of a 2 M HCl solution in the absence of metal ions. It was decanted and washed with distilled water until neutral pH. Equal volumes (10 mL) of aqueous and organic solutions of known concentrations were added to a beaker and were thoroughly mixed. The contact time of phases was set to 600 s. The mixture was then poured into a decanter, where the phase separation occurred within about 60 s after the rest. After several minutes, the phases were separated from the decanter and their volumes were measured. The organic phases were collected (for stripping studies), and aqueous phases were analyzed, using ICP, for their molybdenum contents. The extraction percentage was calculated as the mass of metal extracted into the organic phase to the initial mass of metal in the aqueous phase before extraction.

3. Results and discussions

3.1. Extraction of molybdenum

3.1.1. Effect of TBP and TOA concentrations

The influence of TOA and TBP concentrations on the extraction of Mo ions was investigated at an initial pH of 1 and a phase ratio of O:A = 1. The ratio of TBP/TOA was kept constant at 3 throughout the experiments (Zhan-fang et al., 2009). The percentage of Mo extraction at various extractant and modifier concentrations, and constant ratio of 3, was investigated. The percentage of Mo extraction vs. volumetric concentration of TOA is shown in Fig. 1. It is clearly seen that Mo extraction increases from 54.5 to 98.5 % by increasing the extractant concentration from 1 to 4 vol.%.

3.1.2. Effect of contact time

In order to figure out the required duration for the equilibrium extraction of Mo(VI), the effect of contact time (of aqueous and organic phases) on the extraction of Mo(VI) was investigated. An aqueous

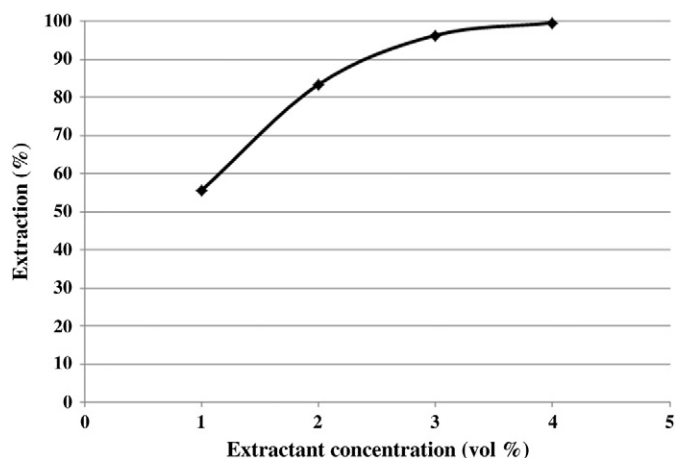


Fig. 1. Effect of extractant concentration on the solvent extraction of molybdenum (TBP/TOA = 3; aqueous phase volume = 10 mL; organic volume = 10 mL; molybdenum concentration = 11 g/L; pH = 1, O/A phase ratio = 1).

solution of molybdenum (11 g/L, 10 mL) was brought into contact with an organic phase containing 4.0 vol.% of TOA and 12 vol.% of TBP in kerosene (10 mL) for a period of 30–600 s. Fig. 2 shows the effect of contact time on the extraction of Mo(VI) from aqueous phase. As it is seen, the equilibration was established after 120 s. Within this period, the extractant molecules are combined with the hydrating water molecules in a short time. The extraction percentage of molybdenum depends on the degree of hydration of the polar and ionic moieties of the extractants, which influences its depth of penetration and concentration in the aqueous phase and, hence, the probability of collision with molybdenum ions. To ensure the maximum extent of extraction, an equilibration time of 600 s was chosen for the subsequent extraction studies (Jung et al., 2008).

3.1.3. Effect of initial pH

To investigate the effect of initial pH of extraction medium on Mo extraction, the pH of the solution was varied in the range of 1–9. The concentration of TOA (4 vol.%) and TBP (12 vol.%) in kerosene, and phase ratio (O:A = 1) were kept constant during the extraction experiments. Based on E-pH diagram at pH values higher than 8 the molybdenum is in the form of molybdate ion and is completely stable (Schweitzer and Pesterfeld, 2009). The percentage of Mo(VI) extraction vs. initial pH is shown in Fig. 3. It is observed that the percentage of Mo extraction decreases from 99 to 0% where the initial pH of solution increases from pH 1 to pH 9. It is also seen that the initial pH of solution has a significant effect on the extraction of Mo. This observation could

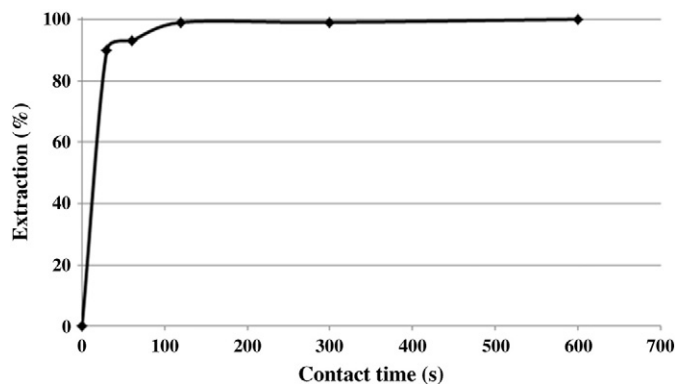


Fig. 2. Effect of contact time on the extraction of molybdenum ions from the aqueous phase (aqueous phase volume = 10 mL; organic volume = 10 mL; molybdenum concentration = 11 g/L; pH = 1.1, O/A phase ratio = 1).

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