A green method for extracting molybdenum (VI) from aqueous solution with aqueous two-phase system without any extractant

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ABSTRACT

An aqueous two-phase system (ATPS) of TX-100 + $(NH_4)_2SO_4$ + H_2O without using any extractant was reported for the selective extraction and separation of molybdenum (VI) from aqueous media. The effects of aqueous pH, initial molybdenum concentration, phase-forming ammonium sulfate and TX-100 concentration, extracting temperature on the extraction of molybdenum were investigated. The experimental results indicate that the extraction rate and distribution coefficient of molybdenum have remarkable relationship with molybdenum species in aqueous phase and reach the maximum of 97% and 75 at pH = 3.00. The extraction rate of molybdenum decrease with increasing temperature within 298.15–343.15 K, and its distribution coefficient decrease with increasing temperature within 303.15–343.15 K, and the thermodynamic analysis of extracting process indicates that polymolybdate anion transferring from salt-rich phase to TX-100-rich micellar phase is a spontaneous and exothermic process. The high distribution coefficient and extraction rate of molybdenum are obtained in the broad initial molybdenum concentration range of 0.1–30 g L^{-1} in aqueous phase. The extraction mechanism reveals that there is no significant interaction between polymolybdate anion and ethylene oxide unit in TX-100 molecule by Fourier Transform Infrared Spectroscopy (FT-IR) and zeta potential of TX-100 micellar phase slightly changes from positive to negative after extracting polymolybdate anion, and from negative to positive again after adding charge modifier making for separation of molybdenum and metal cations by Dynamic Light Scattering (DLS), which can be deduced that polymolybdate anion is extracted into TX-100 micellar core depending on salting-out effect of phase-forming ammonium sulfate and relatively high hydrophobic nature of polymolybdate anion by micelle solubilization. The stripping rate of molybdenum can be easily achieved to 95% in single stage stripping. Some metal cations (Fe(III), Co(II), Ni(II), Cu(II), Zn(II)) are remained in salt-rich phase and separated from molybdenum under the suitable conditions by adding charge modifiers.

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1. Introduction

Molybdenum and its compounds have many important industrial applications such as steel and iron, catalyst, electronic components, and fertilizer. The common methods to extract and separate molybdenum from its aqueous solutions include the solvent extraction [1–5] and ion exchange & adsorption [6,7].

Compared with traditional organic solvent liquid-liquid extraction, aqueous two-phase system (ATPS) is a new green method, which has the advantage of no toxic, nonflammable, low-cost [8].

The possibilities of linear scale up, ease of use and rapid phase separation without the formation of stable emulsions are other advantages of the ATPS technique [9]. The APTS have been widely used in extracting and separating bioactive substance [10–12], organic small molecule [13–15] and metal cations [16–19]. However, only a few outcomes have been reported in the extraction and separation of metal anion by ATPS. Rogers [20–24] studied the distribution performance of TcO_4^- and ReO_4^- with ATPS composed of PEG-salt-H_2O and ionic liquid-salt-H_2O without any extractant, showing that two solutes could be extracted into polymer-rich or ionic liquid-rich phase with high distribution coefficient under the presence of WO_4^{2-} and MoO_4^{2-} in aqueous solution, and WO_4^{2-} and MoO_4^{2-} were hardly extracted in wide concentration range. The preference of TcO_4^- and ReO_4^- for

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polymer-rich phase or ionic liquid-rich phase has been attributed to their large relatively hydrophobic nature. Mu [25] achieved the extraction and separation of ReO_4^- from aqueous media containing ReO_4^- and MoO_4^{2-} by masking MoO_4^{2-} with tartrate as masking agent under the condition of basicity by ATPS composed of PEG-salt-H_2O. Sali [26] studied extraction mechanism of Cr(VI) anion on APTS composed of tetrabutylammonium bromide and $(NH_4)_2SO_4$ mixture.

To the best of our knowledge, there has been no report about extraction and separation of molybdenum (VI) anion by ATPS. The purpose of our study is to develop a new green method, where ATPS is composed of TX-100 + $(NH_4)_2SO_4$ + H_2O without any extractant for extracting and separating molybdenum (VI).

2. Experiments

2.1. Reagents

Triton X-100(TX-100, $CH_3(CH_2)_7C_6H_4O(CH_2CH_2O)_{10}H$), with an average molar mass 646.85 g mol^{-1}, ammonium sulfate, sodium molybdate, ferric sulfate, cobalt sulfate, nickel sulfate, copper sulfate, zinc sulfate, sulfuric acid, ammonium hydroxide were all purchased from Guangfu fine chemical engineering research institute. Octadecyl amine ethoxylate ether (1815), with an average molar mass of 1591 g mol^{-1} and a composition of $CH_3(CH_2)_{17}N(CH_2CH_2-O)_{30}H_2$, was brought from Haian Chemical Plant, Jiangshu, China. All reagents are analytical grade. The used water is distilled water in all experiments.

2.2. Experimental procedure

2.2.1. Extraction

Both TX-100 and $(NH_4)_2SO_4$ aqueous stock solution have the same concentration (400 g L^{-1}). The stock solutions of 100 g L^{-1}, 20 g L^{-1} and 1 g L^{-1} molybdenum were prepared by dissolving sodium molybdate in distilled water, respectively. The stock solution of 1 g L^{-1} mixed ions containing Fe(III), Co(II), Ni(II), Cu(II), Zn (II) was prepared by dissolving their salt sulfate or salt nitrate in distilled water.

(i) The effect of pH on extraction performance: 20 mL TX-100 stock solution, 10 mL $(NH_4)_2SO_4$ stock solution, 1 mL molybdenum stock solution (100 g L^{-1}) and 9 mL distilled water were mixed in a 100 mL beaker. The ATPS was composed of 200 g L^{-1} TX-100, 100 g L^{-1} $(NH_4)_2SO_4$ and 5 g L^{-1} molybdenum. The pH values of mixture solutions detected by acidometer (PHS-3C, Shanghai, China) were adjusted to 1.00, 2.00, 3.00, 4.00, 5.00, 6.00, 7.00, respectively, with a little 9 mol L^{-1} sulfuric acid. The mixtures were stirred for 20 min under 303.15 K by the constant temperature heating magnetic stirrer (DF-101S, Yuhua Instrument Company Limited, Gongyi, China) and settled for 12 h under 303.15 K in the thermostat water bath (HWS12, Yike Instrument Company Limited, Shanghai, China). After complete phase separation, two phase volume was recorded accurately. The molybdenum in salt-rich phase was appropriately diluted with distilled water (within 50–100 times) and analyzed by inductively couple plasma atomic emission spectrometry (ICP-AES 6300 Radial, Themo Scientific, USA). Ammonium sulfate concentration in aqueous phase after dilution was below 10 g L^{-1} and didn't affected precision of molybdenum measured by control experiment. The two parallel experiments have a standard deviation less than ±5%. The concentration in Triton X-100-rich micellar phase was determined with material balance method based on phase volume (Eq. (1)). The distribution coefficient and extraction rate of molybdenum were calculated according to Eqs. (2) and (3).

$$c_{At} = \frac{m - V_b c_{Ab}}{V_t} \tag{1}$$

$$D = \frac{c_{At}}{c_{Ab}} \tag{2}$$

$$E = \frac{m - V_b c_{Ab}}{m} \times 100\% \tag{3}$$

c_{At} is the molybdenum concentration in TX100-rich micellar phase (g L^{-1}), c_{Ab} is the ending molybdenum concentration in salt-rich phase (g L^{-1}), m is the added molybdenum mass (g), V_b is the volume of salt-rich phase (L), V_t is the volume of TX100-rich micellar phase (L), D is the distribution coefficient of molybdenum, E is the extraction rate (%) of molybdenum.

(ii) Other experimental parameters: effect of temperature on extraction performance: the extracting and phase-separating temperatures were 298.15, 303.14, 313.15, 323.15, 333.15 and 343.15 (K), respectively. Effect of TX-100 concentration on extraction performance: the quantity of pure TX-100 added to the ATPS was 0.4, 2, 4, 6 and 8 mL, respectively. Effect of ammonium sulfate concentration on extraction performance: the quantity of ammonium sulfate stock solution added to the ATPS was 1, 5, 10, 15, 20 and 30 mL, respectively. Effect of initial molybdenum concentration on extraction performance: the molybdenum concentration of the ATPS was 0.01, 0.1, 1, 5, 10, 15, 20, 30 gL^{-1}, respectively. The other unspecified parameters、analysis and calculation methods were the same as (i).

2.2.2. Stripping

The 30 g extraction phase and 10 g $(NH_4)_2SO_4$ aqueous solution were added to a 100 mL beaker. The pH of mixture solutions was adjusted to 9.0 by 6 mol L^{-1} ammonium hydroxide. The time of stirring and phase-separating was 20 min and 12 h, respectively. The effects of temperature (313.15, 323.15, 333.15, 343.15 and 353.15 K) and ammonium sulfate concentrations (8, 12, 15 and 20%) on stripping performance were investigated. The stripping rate was calculated by Eq. (4).

$$E_{strip} = \frac{V_{bs} c_{Abs}}{m_0} \times 100\% \tag{4}$$

E_{strip} is the stripping rate (%), V_{bs} is the volume in stripping salt-rich phase (L), c_{Abs} is the molybdenum concentration in stripping salt-rich phase (g L^{-1}), m_0 is the molybdenum mass in added extraction phase (g).

2.2.3. Separation

0.4 mL mixing ions stock solution was added into a 100 mL beaker. Every kind of final cation concentration was 20 mg L^{-1} in salt-rich phase. Then, 10 mL ammonium sulfate stock solution, 1 mL 100 g L^{-1} molybdenum stock solution, and 20 mL TX-100 stock solution were added into the beaker. The distilled water was added to keep the total volume 40 mL. In addition, the charge modifier 1815 was added to another sample with the same composition according to n(1815):n(Mo) = 1:8 (distilled water amount was decreased to guarantee total system volume unchanged). The pH of two mixtures was adjusted to 2.0 by 9 mol L^{-1} sulfuric acid. The mixtures were composed of 200 g L^{-1} TX-100, 100 g L^{-1} ammonium sulfate according to total system volume, 5 g L^{-1} molybdenum and 20 mg L^{-1} other metals according to salt-rich phase volume. The mixtures were stirred and allowed to settle for 20 min and 12 h under the conditions of 303.15 K, respectively. The analytical and calculation methods of concentration of molybdenum and metal cations were the same as before. The separation factor among molybdenum and metal cations was calculated according to Eq. (5).