



## Removal of tungsten and vanadium from molybdate solutions using ion exchange resin



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**Abstract:** The removal of tungsten (W) and vanadium (V) from molybdate solutions was studied using the poly hydroxyl chelating resin D403 in batch and column experiments. The batch experiments indicated that tungsten and vanadium could be preferentially adsorbed by the D403 resin for 4 h in molybdate solution at a pH of approximately 9.25. Separation factors,  $\alpha_{\text{Mo}}^{\text{V}}$  and  $\alpha_{\text{Mo}}^{\text{W}}$ , were above 45 and 18, respectively, when the molar ratios of Mo/V and Mo/W in the solution exceeded 40. Elution tests illustrated that vanadium and tungsten could be easily eluted from the resin with 1 mol/L sodium hydroxide solution in only 1 h. To further explore the sorption mechanism of the resin, the experimental equilibrium isotherm data of the three metals fitted well with the Freundlich model. The column experiments confirmed the adaptability of the D403 resin in the production of sodium molybdate with a removal rate of tungsten surpassing 90% and that of vanadium of 99.4%.

**Key words:** tungsten; vanadium; removal; ion exchange; molybdate

### 1 Introduction

Molybdenum has strategic and industrial importance with extensive applications in many fields [1]. Due to the rapid consumption of conventional molybdenum sources, the recovery of molybdenum from low-grade and complex ores has become increasingly essential. Raw molybdenum resources, such as Ni–Mo ore from Lower Cambrian Shale, contain molybdenum and a certain amount of valuable metals, such as tungsten and vanadium [2,3]. The recovery of these valuable metals from secondary sources has become increasingly more desirable. These sources, for example, spent residue catalysts, alloys or steel scraps [4,5], usually contain certain amounts of vanadium, tungsten and molybdenum. However, impurities in molybdate extracts must be strictly restricted [6]. Hence, it is extremely important to separate tungsten and vanadium from molybdate solutions so that these molybdenum resources can be effectively utilized.

Due to their similar chemical properties in solution, it is difficult to isolate tungsten, vanadium and molybdenum from each other [7,8]. Many researchers have proposed various methods for the separation of

vanadium and molybdenum in aqueous solution, such as precipitation [9], adsorption with activated carbon [10], ion exchange [11,12] and solvent extraction [13–15]. In terms of separation of tungsten from molybdate solution, methods like extraction [8] and ion exchange [16,17] have also been carried out. However, few studies have considered the simultaneous removal of vanadium and tungsten from molybdate aqueous solutions.

In previous studies, a poly-hydroxyl chelating resin, D403, containing a meglumine function group (i.e.,  $-\text{CH}_2\text{N}(\text{CH}_3)\text{CH}_2(\text{CHOH})_4\text{CH}_2\text{OH}$ , which contains a ternary amino group and a poly hydroxyl group) has been found to selectively remove tungsten from molybdate solutions in alkaline systems [16]. Furthermore, because vanadium predominantly occurs as polymeric ions ( $\text{H}_2\text{V}_3\text{O}_7^{3-}$ ) [18] in weak basic aqueous solutions (approximately pH 9.0) and because molybdenum exists as monomeric ions due to its lower polymerizing tendency [19], poly-vanadate ions have higher electrovalence than monomeric molybdenum ions. Thus, vanadium is preferentially adsorbed and removed from weak alkaline molybdate aqueous solutions with certain adsorbents, i.e., those that contain amine functional groups, such as AG1-X8 [20], D296 [18] (quaternary amino group), and D314 [21] (tertiary amino

group). Thus, the D403 resin, which contains a ternary amino group, could be utilized to remove vanadium from molybdate solutions. Compared with the other separation methods mentioned, use of D403 resin could simultaneously remove tungsten and vanadium from molybdate solutions without using other chemical reagents.

In this work, a poly-hydroxyl chelating resin is used to remove tungsten and vanadium in molybdate aqueous solutions. Batch experiments and column experiments were carried out to investigate the adsorption and elution behaviors of tungsten and vanadium and to further understand the sorption mechanism on the resin. Equilibrium isotherm experiments were also explored.

## 2 Experimental

### 2.1 Materials

A macro poly-hydroxyl D403 chelating resin, purchased from Jiangsu Suqing Industrial Co., Ltd., was used in this study. Prior to experiments, the resin was alternately pre-treated with 5% NaOH and 5% HCl aqueous solutions, and washed to near-neutral pH. All chemicals used in this work were of analytical grade, and all concentrations of tungsten (W), vanadium (V) and molybdenum (Mo) were detected using an inductively coupled plasma-atomic emission spectrometer (ICP-AES, Thermo Electron Corporation, USA).

### 2.2 Batch experiments

The experiments were carried out by varying adsorption conditions, such as pH value, contact time and Mo/V or Mo/W molar ratios. The ternary mixed solution was prepared in the laboratory. For each experiment, the testing solution was adjusted to a specific pH value with hydrochloride acid before the adsorption process. These solutions were set to stand for 1 h. Then, 10 mL D403 resin and 50 mL prepared solution were mixed. Samples were agitated for 4 h at ambient temperature (stirring speed of 300 r/min), and the loaded resin was separated by filtration at the end of sorption.

The effects of the eluent concentration and contact time were investigated in desorption experiments, which were conducted by mixing 10 mL loaded resin and 60 mL eluent solutions in a water bath for certain duration. The prepared saturated loading resin was washed with distilled water before desorption.

### 2.3 Column experiments

For the column-loading experiments, prepared solutions were directly passed through glass column (13 mm in diameter and 1010 mm in height) at a flow rate of approximately 48 mL/h ( $0.7V_B h^{-1}$ ). The bed

volume ( $V_B$ ) of the resin was 66.5 mL. An auto sampler was used to collect a number of 20 mL effluent samples, which were subsequently analyzed. After the adsorption process, the saturated loading resin was drip washed with distilled water until tungsten was not detected in the effluent. Subsequently, the eluent was analyzed. First, the effluent was obtained at a flow rate of approximately 93 mL/h ( $1.4V_B h^{-1}$ ), and an auto sampler was used to collect a number of 25 mL effluent samples.

### 2.4 Adsorption isotherm experiments

In the adsorption isotherm experiments, 10 mL D403 wet resin was mixed with a series of volume solutions containing different concentrated compounds in a water-bath shaker for 4 h at room temperature. The pH values of all the solutions were adjusted to be 9.25 with hydrochloric acid.

Like other chemical processes, the ion exchange equilibrium was characterized by corresponding equilibrium isotherms. In this case, the adsorption equilibrium between W, Mo and V is simulated with Henry model [22], Langmuir model [23] and Freundlich model [24]. These three models are as follows:

Henry model

$$Q_e = K_H C_e \quad (1)$$

Freundlich model

$$\ln Q_e = \ln K_F + \frac{1}{n} \ln C_e \quad (2)$$

Langmuir model

$$\frac{C_e}{Q_e} = \frac{C_e}{Q_m} + \frac{1}{bQ_m} \quad (3)$$

where  $Q_e$  is the equilibrium adsorption capacity of the wet resin (mg/mL);  $C_e$  is concentration of the equilibrium solution after the exchange process (g/L);  $Q_m$  is the maximum adsorption capacity of the resin (mg/mL);  $K_H$ ,  $K_F$ ,  $b$  and  $n$  are the corresponding constant parameters of these models.

The adsorption ratio ( $\varphi$ , %), the separation factor for W over Mo ( $\alpha_{Mo}^W$ ), the separation factor for V over Mo ( $\alpha_{Mo}^V$ ), the capacity of the resin ( $Q_e$ , mg/mL), the elution ratio ( $\phi$ , %) and the removal ratio in each column experiment ( $\omega$ , %) are calculated as follows:

$$\varphi = \frac{C_0 - C}{C_0} \times 100\% \quad (4)$$

$$\alpha_{Mo}^W = \frac{\bar{X}_W X_{Mo}}{\bar{X}_{Mo} X_W} \quad (5)$$

$$\alpha_{Mo}^V = \frac{\bar{X}_V X_{Mo}}{\bar{X}_{Mo} X_V} \quad (6)$$

$$Q_e = \frac{(C - C_0)V}{V_R} \quad (7)$$

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