



Novel geochemistry-inspired method for the deep removal of vanadium from molybdate solution



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HIGHLIGHTS

- A geochemistry-inspired method was developed for removal of V from molybdates.
- Magnetic separation of the Fe_3O_4 adsorbent took 10 s.
- Vanadium can be deeply removed in 5 min at pH of 7.0–11.0.
- Fe_3O_4 adsorbent has excellent V selectivity and reusability.
- A flowchart is presented for Mo/V separation in the leachate of spent HDS catalyst.

GRAPHICAL ABSTRACT



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ABSTRACT

Separation of vanadium from molybdates is an essential task for processing the leaching solution of hazardous spent hydrodesulphurization (HDS) catalyst. In this study, the difference in the main naturally occurring mineral forms of Mo and V inspired us to develop a method for the deep removal of V from molybdate solution using Fe_3O_4 as an adsorbent. First, the adsorbent was synthesized with coprecipitation method, and then it was characterized by XRD, TEM, and VSM. The synthesized material consisted of pure Fe_3O_4 nanoparticles that exhibited paramagnetic property, with a saturated magnetization of 68.6 emu g^{-1} . The V removal efficiency was investigated using batch adsorption experiments in varying conditions. Results indicated that V could be deeply removed from various concentrations of molybdate solution at pH of 7.0–11.0 within 5 min. A slight decrease was found in the adsorption ratio after the adsorbent had been reused for 4 cycles. The resulting molybdate solution contained less than 0.02 g L^{-1} of V, which satisfies the requirement for preparing high-quality products. Finally, a process flowchart is presented for the separation of Mo and V from the leaching solution of spent HDS catalyst, based on the excellent V removal performance and rapid separation rate of the Fe_3O_4 adsorbent.

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1. Introduction

Presently, the use of hydrodesulphurization (HDS) catalyst in the petroleum refining industry accounts for about 30% of total global catalyst consumption [1]. The catalyst deactivates with time and spent catalyst is discarded. More than 100,000 tons of spent HDS catalyst is discarded annually [2]. Such a large amount of hazardous solid waste presents a serious threat to ecological systems and human health [3]. This waste has therefore been listed in the latest edition of hazardous wastes published by the Chinese government. In addition, HDS catalyst is rich in valuable rare metals, such as Mo, Ni, Co, and micro amounts of V, supported on an alumina carrier [4,5]. Due to depletion of the traditional mineral resources of these metals, spent HDS catalyst has become an important resource [6]. Therefore, proper treatment and metal recovery from spent HDS catalyst is imperative from the stance of both resource preservation and environmental protection [7].

Metals in spent catalyst wastes are usually present as a mixture of metal sulfides and oxides. As a result, oxidation roasting or sodium salt roasting followed by leaching have been common treatment processes [8,9]. Aqueous solutions of inorganic acids (HCl, H₂SO₄, etc.), water, and alkalis have been used to leach the roasted catalysts [10,11]. All valuable metals can be dissolved by acid leaching; however, the subsequent separation process is quite complex and difficult to control [12]. Alkali leaching or sodium salt roasting with water leaching can be used to selectively dissolve Mo and V [13]. They also dissolve some aluminum, but leave nickel and cobalt in the solid residue [14]. This leaching strategy may reduce subsequent separation steps to obtain pure metal products, but the separation of V from molybdate solution is an inevitable task.

However, separation of Mo and V is very difficult because of their similar physicochemical properties. Ammonium salt precipitation is the most commonly used and simplest method to treat molybdate solution containing a relatively high concentration of V [15,16]. After the separation process, almost all of the V can be precipitated as solid NH₄VO₃, but frequently about 0.1–0.5 g L⁻¹ of V remains in the molybdate filtrate [17]. If the mass ratio of V to Mo exceeds 0.001 in the molybdate solution, high purities (>99%) of Mo products cannot be obtained [18,19]. Therefore, much effort has been made to remove micro amounts of V from molybdate solution, for instance by using solvent extraction [20–22], ion exchange [23,24], or adsorption [25,26]. In the first two methods, the solution pH needs to be pre-adjusted to a narrow range (7.0–8.5) before separation, resulting in a large amount of acid consumption. Among these methods, adsorption is most convenient for scale up, due to the simplicity of the required equipment and its operation. Zhao [25] proposed a method in which Mn(VII) salt and some reductants were first added to molybdate solution, and then micro amounts of V could be selectively adsorbed by the nascent MnO₂ generated through the redox reaction. Another similar method presented by Chen [26] demonstrated favorable results for V removal using Fe(OH)₃ produced in situ as an adsorbent. However, in these two adsorption methods, impurities such as Mn or Fe were introduced to the solution simultaneously with the soluble reagents. Furthermore, the subsequent solid/liquid separation was quite slow because of the generated colloidal hydrated oxide.

In recent years, the integration of different disciplines has led to many innovative theories and methods. Geochemistry is such an interdisciplinary field, combining geology and chemistry. Any method for the separation of similar elements must be based on differences in their physicochemical characteristics. The difference between Mo and V is slight, but is more apparent in the naturally occurring forms that have evolved over many billions of years. According to the geochemical classification, V is a typically siderophile element and frequently occurs in iron oxide minerals [27]. The content of V is higher in magnetite than in the other

common iron oxide minerals, such as hematite, limonite, and specularite [28]. The average V content in the magnetite of China is about 0.2–0.3% [29], a much higher concentration than the average crustal concentration of 135 ppm. This indicates that magnetite is a favorable carrier for V. On the other hand, Mo primarily exists in the mineral form as molybdenite, while it is rare in magnetite due to being a sulphophile [30]. These geochemical phenomena indicate that V may possibly be selectively adsorbed from molybdate solution using magnetic iron oxide as an adsorbent. Moreover, the laden magnetic adsorbent can be separated rapidly from a purified solution using an external magnetic field.

Using this knowledge, we propose a method for the removal of micro amounts of V from molybdate solution using synthesized Fe₃O₄ particles as an adsorbent. In this study, the feasibility of this new method was evaluated and the effects of several variables on the removal efficiency were investigated for developing a technical approach.

2. Materials and methods

2.1. Materials

All chemical agents, including Na₂MoO₄·2H₂O, V₂O₅, FeCl₃·6H₂O, FeCl₂·4H₂O, and NH₃·H₂O, were analytical reagent grade (Sinopharm Chemical Reagent Beijing Co., Ltd, China). The test solutions were prepared by diluting 1 mol L⁻¹ of stock solutions of Na₂MoO₄ and Na₃VO₄. The stock solution of Mo was obtained by dissolving exact quantities of Na₂MoO₄·2H₂O, while the stock vanadate solution was obtained by dissolving V₂O₅ in NaOH solution. Before diluting to volume, the pH of each test solution was adjusted to the required value. The pH measurements were made using a pH meter (PHS-25, Shanghai Leici Instrument Plant, China).

2.2. Preparation of adsorbent

Fe₃O₄ adsorbent was synthesized based on the procedure from Kang [31]. First, FeCl₃·6H₂O and FeCl₂·4H₂O reagents with a Fe³⁺/Fe²⁺ molar ratio of two were dissolved in the ultrapure water with mechanical stirring. Next, 1.5 mol L⁻¹ NH₄OH solution was added slowly with vigorous stirring. When the pH reached 9.0, the stirrer was turned off. The black precipitate was isolated by placing a NdFeB magnet near the vessel, and the supernatant was decanted. Finally, the synthesized gel was washed three times with ultrapure water, to obtain pure and neutral product. For the purpose of moisture content calculation and characterization, part of the clear wet colloidal gel was dried in a vacuum at 60 °C for 6 h. The mass ratio of moisture in the hydrous Fe₃O₄ adsorbent was measured to be 62%–64%.

2.3. Characterization

The morphology of synthesized materials was examined by transmission electron microscopy (TEM, Tecnai G2 F30 S-TWIN, FEI, US). Each sample was prepared by placing a very dilute particle suspension onto a 400-mesh carbon grid coated with Formvar film. The structures of the adsorbents before and after adsorption were determined by an X-ray diffractometer (XRD, RINT-TTR3, RIGAKU, Japan). Magnetic behavior was analyzed using a vibrating sample magnetometer (VSM, PPMS-9, Quantum Design, Inc., US).

2.4. Adsorption experiments

For each experimental run, 25 mL of the solution containing a known concentration of Mo and V was mixed with a known dry weight of fresh hydrous adsorbent in a 50 mL polypropylene

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