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Separation of tungsten and molybdenum using macroporous resin: Competitive adsorption kinetics in binary system

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ABSTRACT

The method using macroporous resin has great potential in separating mixed solution containing a high concentration of both W and Mo. The competitive adsorption kinetics of W and Mo onto the macroporous weak base resin D301 was studied in the present work. Accordingly, the effect of several factors such as concentration, particle size and temperature was assessed on the adsorption kinetics and separation of these two metals. Backscattering SEM and EDS line scan were performed to study the competitive adsorption behavior of W and Mo, particularly. The macroporous resin D301 exhibits a better selectivity towards W than Mo in the near-neutral solution. The decrease of resin particle size and the increase of temperature are found to increase the adsorption rate and reduce the time required for obtaining the optimum separation results. Furthermore, the adsorption kinetics of W can be expressed by the pseudo-second order model. Such model was successfully modified to describe the Mo adsorption kinetics which is significantly affected by W polyions. Diffusion process was identified as the mechanism controlling the rate of W and Mo adsorption.

1. Introduction

The chemical properties of W and Mo are extremely similar due to the influence of lanthanide contraction, and their separation from each other has always been a challenge (Lassner and Schubert, 1999). Presently, kinds of untraditional resources such as Mo-rich scheelite, scheelite–powellite and Ni–Mo black shale-hosted deposits have to be utilized with the continuous consumption of the high-grade tungsten and molybdenum ores. The content of W and Mo in these resources usually has no obvious differences from each other and is even comparative in some cases (Zhao et al., 2011). As a result, the separation of feed solutions containing a high concentration of both W and Mo has been increasingly important.

So far, many technologies have been developed for the separation of W and Mo (Blokhin, 2001; Ning et al., 2009; Talla et al., 2010; Xiao et al., 2001; Zelikman et al., 1976; Zhao et al., 2012a). However, these technologies are only suitable for the removal of microamounts of W or Mo from the mixed solution. Once these methods are applied to the solutions containing a high concentration of these two metals, the separation result will get worse due to the decreased efficiency and the high reagent consumption. Hence, it's urgent to develop easy, effective and economic methods for treating such solutions.

Any technique used for the separation of similar elements must take advantage of the small differences between them (Zhao et al., 2013a). In fact, there still exists certain difference in the tendency to polymerize between W and Mo (Jiang et al., 1990). In detail, most of the monotungstate ions WO_4^{2-} are transformed to polymeric ions in the pH range of 6.5–7.5, while Mo still presents as the form of MoO_4^{2-} in such solution (Zhang et al., 2013). The W polyions have a higher electrovalence than the monomeric MoO_4^{2-} ions, so they can be preferentially adsorbed from the W–Mo solution by the anion adsorbents. Based on this principle, we proposed a new separation method using macroporous weak base resin in our previous study (Zhao et al., 2013b). It showed that the macroporous weak base resin exhibited a larger capacity and a better selectivity towards W than Mo from the near-neutral mixed solution. This approach has several advantages such as low cost and high separation efficiency, hence it is especially suitable for the separation of W and Mo from the solution containing a high concentration of these two metals.

However, despite using macroporous resin with the porous and macroporous structure, the adsorption rate of W polyions is slow due to their high electrovalence and large size. Additionally, our previous work indicated that it would take at least 10 h to reach the adsorption equilibrium. Hence, the separation efficiency of this method depends to a great extent on the kinetic adsorption behavior of the two metals under certain conditions. Unfortunately, the relevant works were limited and mainly focused on the kinetics for the adsorption from the single solute of W or Mo (Hu, 2007; Zhao et al., 2012b). When both of them are present simultaneously, due to the interference and competition with each other, the kinetic behavior of W and Mo will be more complex

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Table 1
Physical and chemical properties of the resin D301 used in this study[a].

Properties	D301
Structure	Macroporous styrene–divinylbenzene copolymers
Functional groups	$-N(CH_3)_2$
Physical form	White or light yellow spherical grain
Ionic form	Cl^-
Water retention capacity (%)	55.00–65.00
Mass total capacity (mmol/g dry resin)	≥4.80
Bulk density (g/mL)	0.65–0.72
Operating pH range	1–9
Maximum operating temperature (°C)	90

[a] Obtained from the manufacturer.

than that in the single system. As a result, it is imperative to investigate the competitive adsorption kinetics of W and Mo using macroporous resin in the binary system. Then the obtained kinetic information can be employed in further optimizing the operation process and designing column reactors for large-scale treatment of the industrial mixtures.

The aim of the present work was to investigate the competitive adsorption kinetics of W and Mo onto macroporous resin in the binary system. Therefore a study was conducted to investigate the effect of several factors that may influence the adsorption kinetics and separation of these two metals, namely concentration, particle size and temperature. Additionally, two kinetic models were used to fit the experimental data and the associated constants were evaluated. In particular, back-scattering SEM and EDS line scan were performed to study the competitive adsorption behavior of W and Mo.

2. Materials and methods

2.1. Ion-exchange resin

The macroporous weak base anion exchange resin D301 (analog to Amberlite IRA-94, Hangzhou Zhengguang Industrial Co., Ltd., Hangzhou, China) was used in the study. Some properties of the resin D301 are given in Table 1. The resin in the wet form was pretreated with 5% NaOH solution, and then transformed to Cl-type with 5% HCl solution. After being washed adequately with deionized water, the resin was dried in a vacuum oven at 323 K for 12 h. Finally, the weighed pretreated resin was swelled and stored in 10% NaCl solution. In the particle size experiments, the pretreated resin was sieved to obtain the following three size fractions: the fraction with a size between 0.45 and 0.63 mm, between 0.63 and 0.9 mm, and between 0.9 and 1.2 mm.

2.2. Chemicals

Standard stock solutions of W and Mo were obtained by dissolving the commercial salts ($Na_2WO_4 \cdot 2H_2O$ and $Na_2MoO_4 \cdot 2H_2O$, analytical grade) in ultra pure water. Appropriate concentrations of each metal

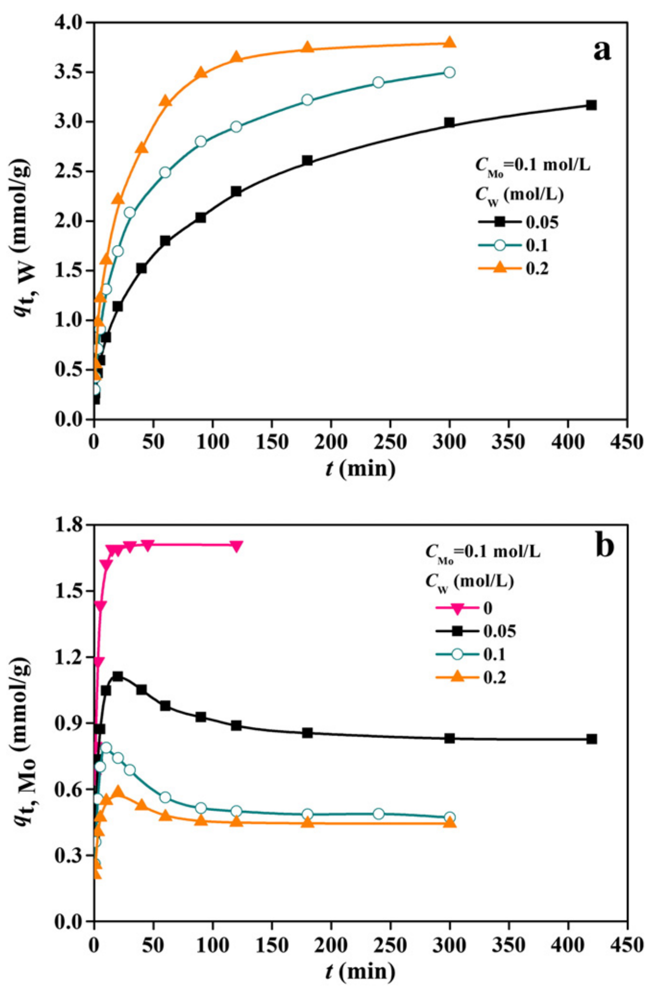

Fig. 1. Adsorption kinetics of W (a) and Mo (b) in the binary system by D301 at different concentrations of W ($T = 20$ °C).

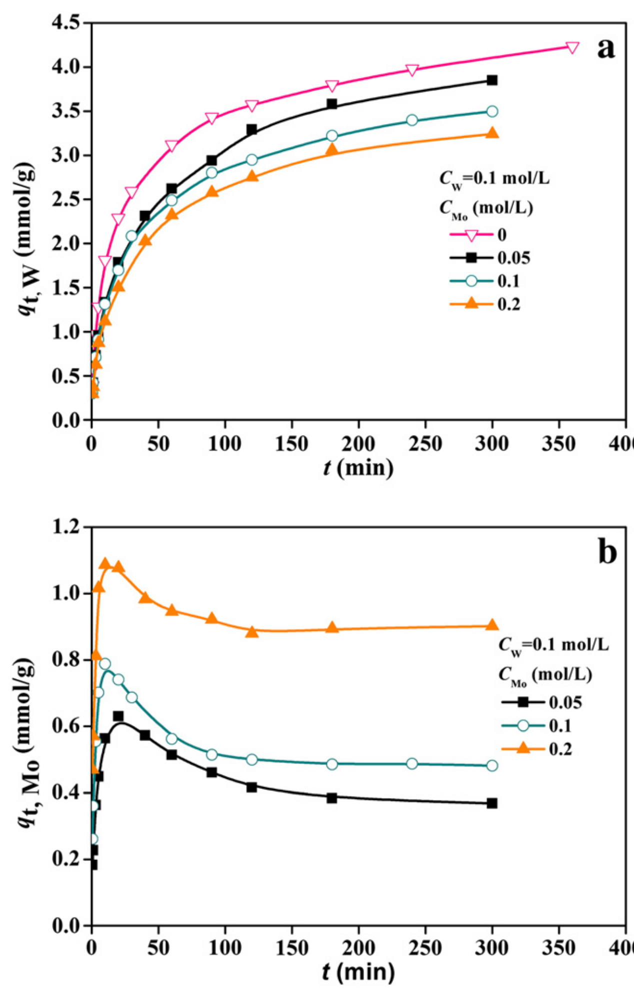

Fig. 2. Adsorption kinetics of W (a) and Mo (b) in the binary system by D301 at different concentrations of Mo ($T = 20$ °C).