Sorption of tungsten on alumina in dynamic conditions

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The sorption of tungstate anions on alumina from aqueous solutions of sodium chloride was investigated in dynamic conditions. The breakthrough curves as the function of W and NaCl concentrations, pH and the flow rates were determined. The breakthrough capacities, the capacities at \( C/C_0 = 0.5 \), the total column sorption capacities and the utilization degrees or column efficiencies, were determined. The obtained tungstate anion sorption data fit with a Langmuir-type isotherm. The values of the breakthrough capacity, \( Q_{0.9}^{\text{max}} \), the Langmuir equilibrium constant or affinity parameter, \( K_L \), and the free energy change, \( \Delta G \), of tungsten sorption were also determined.

Introduction

In principle, in the natural radioactive decay, parent and daughter radioisotopes have different atomic numbers. Therefore, their separation is based on the differences in chemical properties. The devices in which this separation occurs are called generators.

The first generator, designed for the separation of \(^{222}\text{Rn} \) from its parent \(^{226}\text{Ra} \), was patented by F AILA1 in 1920. Since then, the interest for the biomedical generators with the emphasis on nuclear medicine is growing.

Now, the most important is the \(^{99}\text{Mo}^{/99m}\text{Tc} \) generator2 for the production of \(^{99m}\text{Tc} \) (\( T_{1/2} = 6 \) h). It is the main diagnostic radioisotope applied in about 80% of all nuclear medicine procedures.

In the last decade \(^{188}\text{W}^{/188}\text{Re} \) became very attractive in the therapeutic nuclear medicine. To ensure sufficient activities of this radioisotope, intense investigations are devoted to the development and optimization of \(^{188}\text{W}^{/188}\text{Re} \) generator.3,4

There are several similarities between these two generators. The most suitable method for the separation of the daughter radioisotopes is ion-exchange. In principle, the solid support, onto which the parents are bound, could be either organic or inorganic sorbent. For example, the first \(^{188}\text{W}^{/188}\text{Re} \) generators used Dowex-1 in chloride form.5 The elution of \(^{188}\text{Re} \) was performed by 1.5M HCl.

However, inorganic sorbents such as alumina, are better suited for radionuclidic generators. Besides good selectivity, the important advantages are high stability against ionizing radiation and the resistance against microbial contamination.4 So, the best and, therefore, the most often used type of \(^{99}\text{Mo}^{/99m}\text{Tc} \) generator applies alumina with sorbed \(^{99}\text{Mo} \). Technetium-99m is eluted by NaCl solution. Consequently, the most efforts are devoted to the development of a similar generator for the separation of \(^{188}\text{Re} \) from \(^{188}\text{W} \).6,7

In order to optimize the performances of the \(^{188}\text{W}^{/188}\text{Re} \) generator, a detailed investigation of tungsten sorption processes is needed. The present paper is a contribution to the understanding of the sorption of tungstate anions on alumina from NaCl solutions in dynamic conditions. The main parameters, such as the breakthrough and saturation capacities and column efficiencies were determined.

Experimental

Reagents

All chemical were of reagent grade. Sodium tungstate \( \text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O} \) (Fluka) was dissolved in hot conc. NaOH solution and acidified by addition of HF. The sorbent is alumina for column chromatography (grain size 40–140 \( \mu\text{m} \) without pretreatment) (Alumina N-Super I, ICN Biomedicals).

Chemical analyses

The concentrations of tungsten in the solutions were determined by direct current argon arc plasma atomic emission spectroscopy (DCP-AES) with aerosol supply. U-shaped DC arc was used as the excitation source and a 2-meter plane grating spectrograph PGS-2 (Carl Zeiss) with laboratory-made attachment for photoelectric detection was used as the monochromator. The Bausch and Lomb echelle grating with 316 grooves/mm, blaze angle 63° 26 and order sorter were used. The solution were sprayed into the plasma using Babington type nebulizer supported by a peristaltic pump. Potassium was added as a spectrochemical buffer into all samples to the final concentration of 67mmol KCl/l.8,9

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For the measurement of tungsten, the most sensitive atomic line W I 400.88 nm was used. The limit of detection LOD was 5.4·10⁻⁷ mol W/l.

**Dynamic (on column) experiments**

The experiments were performed in a glass column of 8 mm internal diameter. For each experiment the column was filled with 1.0 g Al₂O₃. The height of the sorbent layer was 2.8 cm and its volume 1.4 ml. To avoid air bubbles the bed was carefully packed under distilled water. Prior to the experiment the bed was washed with the corresponding NaCl solution. Constant flow rates of the solution through the column were achieved by using Masterflex C/L pump (Cole-Palmer Instrument Co.). In the sorption experiments the concentrations of tungsten were 5.4, 16.3 and 54.4 mmol/l, respectively. The concentrations of NaCl solution were 0.12, 0.15 and 0.20 mol/l, respectively. The pH values were 2, 4 and 6 (±0.2), respectively. The desired pH was adjusted by diluted HCl. For the experiments only freshly prepared solutions were used. The flow rates of the solution in the downward direction were 1, 3, 5 and 10 ml/min. Samples of the initial solutions and of the successive fractions (10 ml) were taken for the chemical analyses.

The experiments were conducted at room temperature (22±2 °C).

**Results and discussion**

The breakthrough curves of tungstate anions on alumina were determined as the function of W and NaCl concentrations, pH and the flow rates. A typical example of the results obtained for various flow rates is shown in Fig. 1. Figure 2 presents the breakthrough curves obtained for various tungsten concentrations.