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Adsorption behavior of zirconium and molybdenum from nitric acid medium using low-cost adsorbent

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ABSTRACT

The highly radioactive waste liquors from the processing of nuclear reactor fuels contain zirconium and molybdenum, which occur among the fission products. Treatment of wastewater by economical and effective methods is very crucial in the area of development and technological advancements. In the present work, the adsorption behavior of Zr(IV) and Mo(VI) on charcoal from nitric acid medium was investigated using batch technique. Variations of the distribution coefficients as a function of HNO_3 concentration in the range 0.05–3.0 M were presented. Some of the separation possibilities were pointed out. The obtained results indicate that the selectivity of Zr(IV) is higher than Mo(VI) at high acidities. The adsorption kinetics data following the pseudo-second order model indicated that the rate-controlling step is chemical adsorption. The data also followed the Langmuir, Freundlich and Dubinin–Radushkevich (*D–R*) isotherms. The values of enthalpy and entropy changes show that the overall adsorption process was endothermic ($\Delta H > 0$) and increasing entropy ($\Delta S > 0$), and it was spontaneous ($\Delta G < 0$). This study shows that the low-cost adsorbent, charcoal, is an effective adsorbent for the retention of Zr(IV) and Mo(VI) species from nitric acid medium. The feasibility of the removal of ^{95}Zr and ^{99}Mo from simulated intermediate level waste solutions was tested.

1. Introduction

Zirconium is used in nuclear reactor technology in the form of zircaloys as cladding material for the uranium fuel and for other reactor internals. Due to ageing effect of reactor vessels, erosion starts and leads to contamination of the coolant water with radioactive species of zirconium, thus posing hazards to the systems and environment [1]. Zirconium and its compounds are also extensively used in chemical industries, steel and cast manufacturing, surface agent on satellites, lamp filaments, welding fluxes, in vacuum tubes, preparation of water repellent textiles, dyes pigments, ceramics, glass and abrasives. It is, therefore, important to decontaminate the reactor coolant water from radioactive zirconium and from other industrial effluents, before their safe disposal into water bodies [1,2].

Molybdenum has strategic and industrial importance due to its various applications, e.g., as an alloying agent in steels and cast iron, solid lubricants, reactor vessels, and in special batteries. High concentrations of molybdate (>5 ppm) cause environmental problem, which makes the removal of molybdenum ion from wastewater and ground water a task of great significance from the environmental point of view [2]. Molybdenum-99 is the most important radionuclide used in nuclear medicine practice [3]. Molybdenum is one of the fission products and is present in significant concentration in the High Level Waste of Purex reprocessing process. Due to the complex chemical properties of molybdenum, it forms soluble and insoluble complexes which give rise to various problems, mainly in concentration, storage and solidification of high level waste [3].

High-level radioactive liquid waste generated from the extraction cycle in fuel reprocessing by PUREX process, contains fission products, actinides, lanthanides, corrosion products, various chemical additives and etc. [4]. In order to minimize an adverse impact of high-level radioactive liquid waste on the environment, a variety of extraction processes have been developed in recent years to separate harmful radionuclides from high level radioactive liquid waste [5]. Solvent extraction with *n*-octyl(pheny1)-*N*,*N*-diisobutylcarbamoylmethylphosphine oxide (CMPO) was found to be effective extractant for the actinides and fission products from a concentrated HNO_3 solution. Since CMPO shows excellent chemical-stability in nitric acid medium and is a commercially available compound for actinide partitioning from high level radioactive liquid waste [4,5]. Alkyl phosphoric acids were also used to separate zirconium from molybdenum in presence of long-lived fission products ^{90}Sr, ^{99}Tc, ^{106}Ru, ^{137}Cs, ^{144}Ce and ^{147}Pm [6].

In the partitioning process, the short lived elements (Zr, Mo, etc.), transuranium elements, platinum group metals, and Cs/Sr can be separated by solvent extraction methods [4]. However, these partitioning processes essentially utilize liquid–liquid extraction technology by a mixture of an organic extractant and a hydrocarbon diluent. A large

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quantity of so-called secondary-waste liquid containing the hydrolytic and radiolytic degradation products of organic compounds can thus be generated [4]. Furthermore, a great number and large scale of equipments are often required in the extraction processes. Therefore, a separation technique which utilizes minimal organic solvents and compact equipment is very desirable for the high level radioactive liquid waste partitioning [4]. Thus, it is important to explore some new separation systems or methods superior to the current separation process which has been widely applied to uptake zirconium and molybdenum.

Adsorption has been found to be superior to other techniques for wastewater treatment due to low-cost, flexibility and simplicity of design, ease of operation, insensitivity to toxic pollutants and for avoiding the formation of secondary-waste [7]. A number of laboratory-scale studies were performed to investigate the potential application of commercial carbonaceous material as adsorbent for the removal of uranium and heavy metal ions and organic materials from different wastewaters [7–13]. The results indicated that this material is a very suitable adsorbent in wastewater management. Furthermore, high chemical, radiation, and thermal stability, rigid porous structure, and mechanical strength impart present considerable advantages over polymeric materials [13]. However, few studies have been done on the use of charcoal for the adsorption of heavy metals and radionuclides from nitric acid medium.

Since transactinide elements ($Z > 103$) are characterized by short half-lives, studies of their chemical properties require the use of fast and efficient radiochemical methods and techniques involving sorption offer these advantages [14–17]. Moreover, analogies in the behavior of Zr and Rf ($Z = 104$), as well as of Mo and Sg ($Z = 106$) have unambiguously been demonstrated [14–17]. In order to reach a better understanding of the chemical properties of the first transactinide elements i.e. Rf and Sg, experiments involving sorption process was conducted with their homologues [14–17].

To the best of our knowledge, the application of charcoal in sorption of Zr(IV) and Mo(VI) ions from nitric acid media has not been reported in the literature. To achieve a better understanding of the adsorption mechanism of Zr(IV) and Mo(VI) ions from HNO_3 medium onto the charcoal and to find an effective separation method of these ions from High-level radioactive liquid waste in the MAREC (Minor Actinides Recovery from HLLW by Extraction Chromatography) process, the adsorption behavior of Zr(IV) and Mo(VI) ions with charcoal in a broad range of HNO_3 concentration was examined.

2. Experimental

2.1. Materials and chemicals

$ZrOCl_2 \cdot 8H_2O$ and $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ were used as sources for Zr(IV) and Mo(VI), respectively. Various concentrations of Zr(IV) and Mo(VI) with given concentration of HNO_3 were prepared as needed. All the chemicals used were of analytical reagent (AR) grade and supplied by Merck or Aldrich, except charcoal activated which was supplied by Loba Chemical (India), and all the chemicals were used as received.

2.2. Radioactive isotopes

The radioactive isotopes ^{95}Zr ($t_{1/2} = 64.4$ d) was artificially produced through the irradiation of spec-pure $ZrOCl_2.8H_2O$ powder while ^{99}Mo ($t_{1/2} = 66.0$ h) was produced from ^{235}U nuclear fission as a fission product at the 2nd Egyptian Research Reactor at the Inshas site.

2.3. Instrumentation

Shimadzu UV–Visible Recording Spectrophotometer (UV-160A) manufactured and supplied by Shimadzu Kyoto, Japan was used for estimation of Zr(IV) and Mo(VI) concentration.

The adsorbent was characterized with respect to its pore structure and surface area using nitrogen adsorption/desorption at 77 K which was conducted using a gas sorption analyzer (Quantachrome, NOVA 1000e series, USA), FTIR spectrum of the charcoal sample was recorded using a Nicolet spectrometer from Meslo, USA to identify the functional groups.

Simultaneous differential thermal and thermogravimetric analyses (DTA/TGA) of activated carbon were carried out using DTA and TGA with sample holder made of platinum using a Shimadzu DTG-60/60H thermal analyzer, Japan. It was used for the measurements of the phase changes and weight losses of the sample at heating rate of 10 °C/min in presence of nitrogen gas to avoid thermal oxidation of the adsorbent sample. The sample was heated in a platinum crucible from room temperature to 1000 °C.

2.4. Distribution studies and capacity

Accurate and reliable knowledge of the distribution coefficients of the metal ions between the solution and charcoal is needed in adsorption study to estimate their transport rates. Both distribution coefficient determinations and capacity measurements were performed by batch technique at constant volume to mass ratio of 100 mL/g. A mixture of charcoal (0.1 g) and the solution (10 mL) of either separate Zr(IV) or Mo(VI) was allowed to stand overnight in a shaker thermostat adjusted at room temperature with shaking to ensure establishment of equilibrium. The solid adsorbent was then separated from its solution by filtration, and the concentrations of Zr(IV) and Mo(VI) in filtrate were assayed by spectrophotometric methods using Alizarin red S and alcoholic ammonium thiocyanate as chromogenic reagents [18]. The distribution coefficient (K_d mL/g) values for the individual Zr(IV) and Mo(VI) were determined at different nitric acid concentrations using the equation [19]:

$$K_d = \frac{C_o - C_e}{C_e} \times \frac{V}{m} (\text{mL/g}) \tag{1}$$

2.5. Separation factor (α)

The separation factor is a guiding measure of the ability of the adsorption system to separate two metal ions (such as Zr and Mo) of equal concentration. The separation factor is sometimes also called the 'selectivity'. It is used as a measure of possibility of chromatographic separation and is also expressed as the ratio of the distribution coefficients of the ions to be separated. If the Zr(IV) is preferred for the adsorbent the value of α^{Zr}_{Mo} is > 1. The opposite is true, i.e., $\alpha^{Zr}_{Mo} < 1$ means that Mo(VI) is preferred [20].

$$\text{Separation factor } (\alpha^{Zr}_{Mo}) = \frac{K_d(\text{Zr})}{K_d(\text{Mo})}, \tag{2}$$

where K_d(Zr) and K_d(Mo) are the distribution coefficients of the two competing Zr(IV) and Mo(VI) species in the adsorption system.

2.6. Equilibrium studies

Sorption onto the charcoal was studied using 0.1 g, 10 mL of solution at 0.1 M nitric acid concentration, and different initial metal ion concentrations (20–400 mg/L for Mo and 50–400 mg/L for Zr). The solutions were shaken until equilibrium was reached. The experimental data obtained from this experiment were evaluated using Langmuir and Freundlich isotherm models.

The uptake efficiency (% R) and amount of Zr(IV) and Mo(VI), q_e (mg/g) retained on the charcoal were calculated using the following