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ORIGINAL RESEARCH

Cross-linked polyvinyl amidoxime fiber: a highly selective and recyclable adsorbent of gallium from Bayer liquor

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Abstract
Gallium, a scarce metal produced mainly from Bayer liquor, is widely used in semiconductors. Ion-exchange method is currently considered as the most effective method to recover gallium from Bayer liquor. In this article, fibrous amidoxime adsorbents are introduced to recover gallium from Bayer liquor. In addition, hydrazine cross-linked polyvinyl amidoxime (HPAO) fibers have been prepared. The structure of the as-prepared fibers was ascertained by FTIR, elemental analysis and weight gain rate. The adsorption kinetics, adsorption isotherm and recycling performance were investigated by batch method. Cross-linking duration was studied and it turned out to be an important factor to optimize the adsorption capacity and recycling performance. After 1.5 h cross-linking time, the fiber showed the highest gallium adsorption capacity of 14.83 mg/g in Bayer liquor. After 3 h cross-linking time, the fiber showed the best recycling performance, which retained 82.9% of the initial adsorption ability after four cycles. Adsorption capacity of vanadium was lower than 1 mg/g for all samples. HPAO displayed very fast adsorption kinetics with an equilibrium at 60 min. The EDS results confirmed the low extraction of aluminum and vanadium provided by HPAO fibers. The gallium-loaded fiber could be effectively eluted by acidified thiourea. With proper control of the cross-linking duration by hydrazine, HPAO fiber with high selectivity towards gallium, high adsorption capacity and good recycle performance could be obtained, which is promising for recovering gallium needed for industrial applications.

Keywords Amidoxime · Chelating fiber · Gallium recovery · Bayer liquor · Kinetics

Introduction

Gallium is predominantly used in semiconductors in electronics. In the US, gallium arsenide (GaAs) and gallium nitride (GaN) wafers are used in integrated circuits (ICs) and optoelectronic devices which account for about 75% of domestic gallium consumption [1]. With the rapid development of consumer electronics and low-carbon technologies such as solid-state lighting and photovoltaics [2], there has been a steep rise in the demand of gallium. According to the United States Geological Survey Mineral Commodity Summaries, the estimated worldwide primary gallium production in 1999 was 75 metric tons, while that of 2015 increased dramatically to 730 metric tons [1, 3]. Gallium is a scarce material and is produced as a byproduct of aluminum and zinc. The largest resource of gallium is Bayer liquor [4, 5], which is used to dissolve bauxite in the Bayer process to produce aluminum.

Bayer liquor is a strongly alkaline, thick and dense solution containing large amounts of sodium hydroxide, aluminum, sodium carbonate and traces of gallium, vanadium and iron. Gallium (III) stays in Bayer liquor as tetrahedral hydroxo complex $Ga(OH)^{-}_{4}$ [6]. There are several methods of extracting gallium from Bayer liquor, including fractional precipitation, electrochemical methods, solvent extraction and ion exchange. In the fractional precipitation process, chemicals (lime or CO_2) are added to the aluminate solution which, therefore, cannot be reintroduced into the cycling process without further treatment [5]. The electrolytic amalgamation method is inefficient and expensive, besides generating environmental problem [7]. The major problems of

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