Synthesis of Amidoxime Chelating Resin and Its Adsorption of Gallium in Bayer Spent Liquor

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Abstract

Gallium is an important strategic resource, and currently more than 90 % of the world's primary gallium is recovered from the spent liquor of alumina production. Amidoxime chelate resin can be used for separation and recovery of metal ions because it contains both oxime group (-N-OH) and amine group ($-NH_2$) in the structure, and oxygen atoms on oxime group and nitrogen atoms on amine group can form coordination bonds with metal ions. The large pore chelating resin PAO was prepared by suspension polymerization of acrylonitrile and divinylbenzene and used for the adsorption of gallium in spent liquor. The structure and functional groups of the samples were characterized by FTIR, and SEM. The infrared spectra of PAO showed an amino absorption peak at 3473 cm^{-1} near the hydroxyl absorption peak at 3432 cm^{-1}, indicating that the amidoxime reaction successfully converted cyanide group to amidoxime group. The adsorption rate of gallium in spent liquor by resin can reach 82 %, which provides a new direction for separating and recovering gallium from spent liquor.

Keywords: Gallium, Spent liquor, Synthetic resin, Ion exchange.

1. Introduction

Gallium is a rare metal found mainly in bauxite, and sometimes is accompanied by sphalerite, ferrotitanium and coal mines [1]. At present, gallium is mainly extracted from the production process of alumina, with a small amount recovered from the zinc smelting process and fly ash [2]. Due to its unique physical properties, gallium is considered an important strategic resource and has been widely used in fields such as semiconductors, photovoltaic materials, magnetic materials, chemicals, medicine, and national defense [3].

In the bauxite dissolution process, gallium and aluminum dissolve together and exist in the solution in the form of sodium galliate [$NaGa(OH)_4$]. Gallium can be recovered after continuously circulating and accumulating to a certain concentration, with the Al_2O_3/Ga content in the circulating solution is typically around 450 [4].

At present, the main methods for recovering gallium from spent liquors include mercury leaching, step precipitation, extraction, and ion exchange. Due to its high cost and potential health and environmental issues, the mercury method has been banned. The step precipitation method has a long process, high consumption, and the residue generated in the process is difficult to handle. The extraction method has strong selectivity and easy to operate, but its expensive price has become an obstacle to industrial application. The ion exchange method has become the most popular method for extracting gallium due to its advantages such as good selectivity and a simple process.

A. Riveros [5] studied the adsorption behavior of ion exchange resin ES-346 for gallium in spent liquor, and found that the resin can simultaneously adsorb gallium and vanadium. As the concentration of alkali in the solution increases, the adsorption rate of vanadium on the resin decreases, while the effect on gallium is not significant. However, in actual Bayer spent liquor adsorption, the alkali concentration of the solution cannot be adjusted, so the kinetic difference between gallium and vanadium can be utilized to achieve the separation of gallium and vanadium by controlling the contact time.

Rao et al.[6] used ion exchange resin Kelex-100 to recover gallium, and the experiment also found a difference in kinetics between gallium and vanadium: the resin had better adsorption kinetics for gallium than vanadium. By shortening the adsorption time and increasing the alkali concentration of the solution, the resin can preferentially adsorb gallium. After the resin adsorption is saturated, rinsed with distilled water, desorption with 1.5 mol/L HCl, it continues to adsorb. After 20 cycles, the adsorption of gallium reaches 7 g/L. The repeated extraction - elution cycle indicates the stability of the resin, but due to the recycling of the stripping liquid, the effectiveness of the stripping liquid deteriorates. In addition, Kelex-100 can only be prepared through multi-step synthesis, making it very expensive. In production, it is necessary to regularly replace the deteriorated resin according to the production situation, leading to a significant impact on the cost.

Teng Yu [3] uses DHG type chelating resin to recover gallium, which can selectively adsorb gallium ions in spent liquor without any other impurities being adsorbed, thus realizing the separation of gallium from other impurities. The saturated resin is rinsed with low concentration NaOH to complete the washing of the spent liquor residue in the resin and the rinsing of impurities in the resin, avoiding harmful components from entering the rinsing stage. A leaching agent that can effectively leach gallium under alkaline conditions is used to leach saturated resin containing gallium. This method effectively separates gallium from other impurities, but the service life of the resin still needs to be improved.

Although the resins mentioned above have a certain degree of adsorption effect on gallium, there are also many problems, such as complex processes, short resin life, and high prices. The amidoxime based chelating resin proposed in this study has fast adsorption kinetics, simple process, and the resin can be reused. Amidoxime chelate resin can be used for separation and recovery of metal ions because it contains both oxime group (-N-OH) and amine group ($-NH_2$) in the structure, and oxygen atoms on the oxime group and nitrogen atoms on the amine group can form coordination bonds with metal ions. In this study, a macroporous amidoxime chelating resin with acrylonitrile (AN) and divinylbenzene (DVB) as the backbone was synthesized by suspension polymerization for the extraction of gallium from spent liquor. The results are of great significance for further development of a high performance gallium extraction resin.

2. Experimental

2.1 Synthetic Adsorption Resin

In this paper, an ion exchange resin was prepared by suspension polymerization which showed excellent adsorption properties and selectivity for gallium. Appropriate amounts of gelatin and $CaCl_2$ solution were added to a three necked flask with a stirring device and stirred until the gelatin dissolved. Then, AN, DVB, cyclohexanone, xylene, AIBN and BPO were added into the flask, and followed by the addition of nitrogen to heat up for reaction. After the reaction, PAN was prepared by repeatedly washing and drying with deionized water and anhydrous ethanol. 10 mL of $NH_2OH \cdot HCl$ and Na_2CO_3 solution were mixed into a flask, to which 1.2 g PAN was added. The reaction was heated to 65–75 °C for 5 h. At the end of the reaction, the adsorption material PAO was washed with deionized water several times and dried. The main synthesis steps are shown in Figure 1.

relatively fast, reaching adsorption equilibrium after 300 minutes of adsorption. When adsorbed for 360 minutes, the adsorption rates of PAO for gallium reached 82 %.

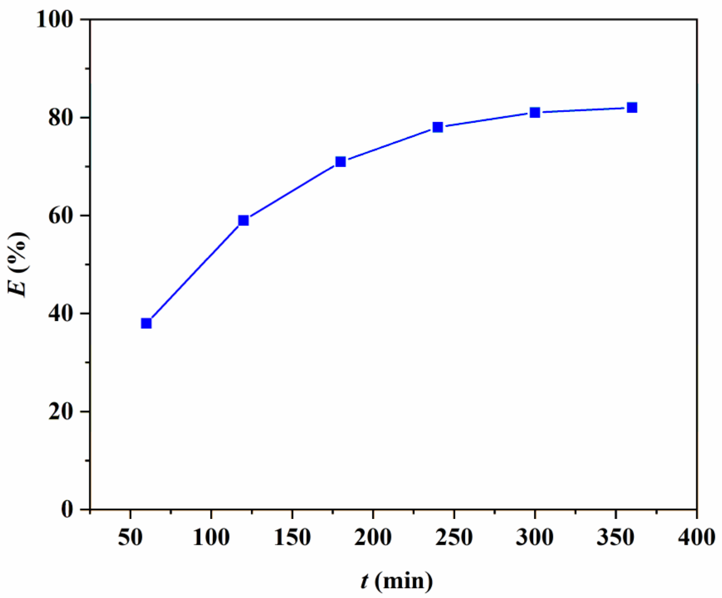

Figure 6. The adsorption effect of PAO on gallium at different times.

4. Conclusion

Amidoxime chelate resin was synthesized from acrylonitrile and divinyl benzene by solution suspension polymerization. The experimental results showed that the cyanide group had been successfully introduced into the material and converted into amidoxime group, and the synthesized material was uniform. Through experiments, it was found that PAO had a faster adsorption kinetics for gallium. When PAO had adsorbed gallium for 300 minutes, it had basically reached adsorption equilibrium. The new resin showed excellent adsorption capacity for gallium, and it is worth further exploring its selectivity for gallium and the rate of resin regeneration. This study has guiding significance for the separation of gallium from Bayer spent liquor using amidoxime based resins.

5. References

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