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Extraction of lanthanides by polysulfone microcapsules containing EHPNA. I. Piercing method

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Abstract: Since the conventional liquid-liquid extraction method suffered from a series of problems such as inefficiency of one stage extraction, vast device occupation and severe emulsification, we adopted microcapsule (MC) technique to change the former liquid-liquid extraction to liquid-solid extraction. Firstly, the piercing method was performed to prepare the empty polysulfone (PSF) microcapsules, which was easy to implement and control. Secondly, the ultrasonic approach was utilized to prepare the functional microcapsules containing 2-ethylhexylphosphonic acid mono-2-ethylhexyl ester (EHPNA). We focused on a key factor of the molar ratio of PSF over 1-Methyl-2-pyrrolidinone (NMP), attaining a loading ratio as high as 7.21 g-EHPNA/g-PSF. Thirdly, we examined the kinetics and thermodynamics of extraction. Kinetic results demonstrated that equilibrium was reached within two hours, with an extraction rate of Sm^{3+}≈Er^{3+}>La^{3+}; Thermodynamic results showed that the extraction of lanthanides complied with the Langmuir law, with an extraction capacity of 0.25–0.30 mmol/g-microcapsule. Fourthly, stripping experiment indicated that three hours were required to accomplish equilibrium for La^{3+} and Sm^{3+} while longer hours for Er^{3+}. Finally, seven extraction-stripping cyclic experiments were performed for three mixed elements, the results of which revealed that Sm^{3+} and Er^{3+} maintained constantly high extraction amount whilst La^{3+} leveled off at approximately 50%. This proposed polysulfone microcapsule containing EHPNA is suitable to be applied to extraction and concentration of rare earth metals.

Keywords: extraction; microcapsule; rare earths; EHPNA

The separation of lanthanides is extremely difficult to perform due to the similarity in physical and chemical properties[1]. The widely used method to extract rare earths (REs) in large scale by saponated 2-ethylhexylphosphonic acid mono-2-ethylhexyl ester (EHPNA)[2,3] suffers from some drawbacks, such as the extractant loss and high energy consumption. As the height equivalent to a theoretical plate (HETP) is relatively high during the extraction process of REs, the conventional mixer-settler device usually occupies large space[4,5]. If EHPNA can be impregnated into the microcapsules[6], the former liquid-liquid extraction can be transformed to a liquid-solid system which better addresses the abovementioned issues, especially for dilute RE solutions[7]. Moreover, functionalized microcapsule is convenient to be applied in the extraction or ion exchange column devices[8–11], which can expand mass transfer area as well as improve mass transfer coefficient. Hence, more theoretical stages and higher efficiency can be achieved without the repetitive input of energy.

Currently, the preparation of microcapsules can be generally categorized into three paradigms[12], namely chemical method[13,14], physical method (e.g., solvent evaporation[15–17], solvent extraction[18,19], spray drying) and polymerization method (e.g., *in situ* polymerization, interfacial polymerization). One of the most influential reports of the third methodology was divinylbenzene homopolymeric microcapsules with highly porous membranes by *in situ* polymerization by Yoshizawa et al.[20]. Using these microcapsules, hydrochloric acid could be sufficiently extracted from aqueous solution. Subsequently, the polymerization method was extensively reported in literatures, however, only a few groups have reported on lanthanide separation. The extraction of lanthanides such as Sm^{3+}, Er^{3+}, Pr^{3+}, Nd^{3+} and Y^{3+} was studied by adopting microcapsules containing bis(2-ethylhexyl) phosphoric acid[21]. The separation of La^{3+} and Ce^{3+} by using microcapsules was explored via *in situ* microencapsulation process[22]. The large size microcapsules containing tri-n-octylamine by *in situ* polymerization in combination of a gel inclusion method were prepared for acetic acid extraction[23]. Recently, the metal extraction dynamics into microcapsules have been investigated[24–26].

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Inherent drawbacks also exist in the polymerization method. For instance, some polymerization reactions required a few hours with low reaction rate. Additionally, reaction apparatuses were used with high costs and an enormous amount of extractant was lost during the synthetic process. Thus it is reasonable to present an easier and handier method for industrial applications. Solvent evaporation method is easy to control while the surface of microcapsules tends to be usually compact which is adverse to mass transfer. Likewise, the solvent extraction method is also easy to control and can produce porous microcapsules. Polysulfone enjoys the advantages of strong strength, anti-wear, non-toxic, anti-acid or anti-alkali and anti-heat with the available temperature of –100–150 ℃, which makes it fit for wall material of microcapsules. In previous works[18,19,27], we succeeded in preparing for the polysulfone microcapsules containing 1-octanol for caprolactam extraction by adopting one-step and two-step methods. The former referred to production of functionalized microcapsules in one step by mixing the wall material and the extractant; the latter represented the preparation of empty microcapsules in the first step and the encapsulation with extractant afterwards. Nonetheless, the extraction process was complicated when EHPNA reacts with lanthanides, quite different from the physical dissolution of 1-octanol and caprolactam. Accordingly, the research into the lanthanides extraction by microcapsules is of great significance both academically and practically.

The present paper is organized as follows. The experimental section elaborated on the preparation of empty polysulfone microcapsules by employing piercing method. The section 2.1, 2.2 and 2.3 described the detailed the crucial properties of microcapsules. The section 2.4 and 2.5 dealt with kinetic and thermodynamic extraction performance of light (La^{3+}), medium (Sm^{3+}), heavy (Er^{3+}) RE and their mixture, respectively. Cyclic experiments of the extraction-stripping for the functionalized microcapsules were conducted to evaluate the stability of microcapsules in the section 2.6.

1 Experimental

1.1 Materials

Polysulfone (PSF) (average MW=35,000) was purchased from Aldrich Co., Ltd. N-Methyl-2-pyrrolidone (NMP) (>99.5 %), ethanol (>99.7 %) were purchased from Sinopharm Chemical Regent Beijing Co., Ltd. The extractant, 2-ethylhexylphosphonic acid mono-2-ethylhexyl ester (EHPNA) (>95%) was purchased from Luoyang Aoda Chemical Co., Ltd. $LaCl_3·7H_2O$, $SmCl_3·6H_2O$ and $ErCl_3·6H_2O$ (>99.99%) were purchased from the Biam Alloys Co., Ltd., Beijing Institute of Aeronautical Materials of AVIC. All the reagents were used without further purification.

1.2 Preparation of microcapsules containing EHPNA

The preparation methods of microcapsules can be divided into two categories: one-step and two-step method. In this paper, microcapsules were prepared by the two-step process: (1) prepare empty microcapsules and (2) load extractant (EHPNA). For the first step, the experimental scheme is illustrated in Fig. 1. Polymer solution was firstly prepared by dissolving the desired amount of PSF in NMP. Then the polymer solution was pumped through a nozzle (SNA-22G-50) by a syringe pump (LSP01-1BH, Longer, China) with a flow rate of 200 μL/min. The outer and inner diameter of the nozzle was 0.73 and 0.41 mm. The polymer drops were solidified in a solidification solution (500 mL ethanol and 1500 mL deionized water). In order to keep a good shape of microcapsules, the addition of ethanol is necessary to reduce the density and surface tension of the solidification solution. The formed microcapsules were kept in the solidification solution for more than one hour, and then filtrated and washed five times by using deionized water. Finally, the empty microcapsules were obtained after being dried under 120 ℃ for six hours. For the second step, EHPNA was introduced into the empty microcapsules by using the ultrasound method.

In addition, we further performed one-step preparation for microcapsules. The main procedure was as follows: (1) to dissolve the certain amount of EHPNA (extractant) and PSF (wall material) in NMP to obtain the polymer solution; (2) to solidify the microcapsules by utilizing a nozzle (SNA-22G-50). Nevertheless, one-step method failed in the preparation, which will be discussed below.

1.3 Characterization of microcapsules

The outer diameter of microcapsules could be obtained through the camera (Cannon, 600D). The concrete procedure is as follows. Microcapsules were initially placed onto a ruler to be photographed. Then the pixel coordinates of the diameter could be measured by aiding software. Finally, the diameter of the microcapsules

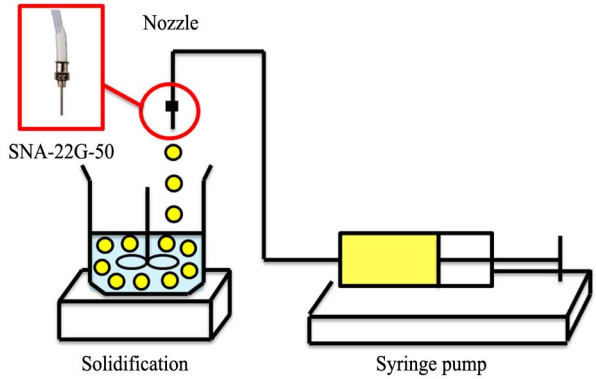

Fig. 1 Experimental scheme of microcapsule preparation using the piercing method