

## Preparation of An Extractant-Impregnated Resin Containing 4-tert-butyl-2-( $\alpha$ -methylbenzyl) phenol and Its Adsorption for Cs<sup>+</sup>

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**Abstract.** The adsorption of Cs<sup>+</sup> by a novel extractant-impregnated resin (EIR), was studied using batch adsorption experiments. The new EIR was prepared by impregnating 4-tert-butyl-2-( $\alpha$ -methylbenzyl) phenol (*t*-BAMBP) onto AB-8 macroporous resin beads. Thermogravimetric analysis (TG) and the Fourier Transform Infrared Spectroscopy (FTIR) were used to characterize the EIR. The effects of extraction time, pH values, metal ion concentration, and temperature were investigated. The adsorption results showed that the adsorption amount of Cs was increasing with the pH values and Cs concentration and decreasing with the temperature of the solution. The effect of co-existing ions Na<sup>+</sup> and K<sup>+</sup> on the adsorption was not obviously. Regeneration and recycling of the resin indicated the EIR can be used for continuous cycles.

### 1. Introduction

Cesium is one of the rare metals and plays increasingly important roles in the fields of new energy, new materials, night-vision equipments, fiber optic telecommunication systems and metal-ion catalysts [1,2]. Cesium exists widely in many large hinterland salt lakes worldwide but often at trace concentrations (about 0-20 mg/L). K<sup>+</sup>, Na<sup>+</sup>, Mg<sup>2+</sup>, Li<sup>+</sup> and other ions also coexist in salt lake brine, the concentrations of which are thousands or even hundreds of thousands times that of Cs<sup>+</sup> [3].

Several methods have been used to enrich and separate low-concentration Cs<sup>+</sup> from the aqueous solutions. Among these methods, ion-exchange by resins and solvent extraction were considered as the most useful methods and had been extensively studied by many researchers [4-6]. The substituted phenols, such as 4-sec-butyl-2( $\alpha$ -methylbenzyl) phenol (BAMBP) and 4-tert-butyl-2( $\alpha$ -methylbenzyl) phenol (*t*-BAMBP), are often used as the extractants for Cs<sup>+</sup> due to high selectivities and easy stripping [3, 7-9]. However, the main drawback of solvent extraction process lies in the loss of extractant into aqueous solution, which may cause environmental hazards and economic limitations [10-12]. Compared with solvent extraction, ion exchange is much simpler. Nonetheless, the low selectivity to metal ions is its main problem [13-16].

To solve these problems, extractant-impregnated resins (EIRs, also known as solvent impregnated resins, SIRs) technology has been researched and considered as an alternative process that combines the easy management of ion-exchanger and the high efficiency and selectivity of readily available extractants[17]. EIRs can be prepared by a most common process, which consists in the impregnation of the resin with the extractant previously diluted in an appropriate solvent. The solvent will be removed by evaporation after complete wetting of the resin with the impregnation solution. In recent years, a number of extractants and resins have been used for the preparation of EIRs [18-20].

Here in this work, a novel extractant-impregnated resin, EIR, was prepared by impregnating 4-tert-butyl-2-( $\alpha$ -methylbenzyl) phenol (*t*-BAMBP) onto AB-8 macroporous resin beads. And the adsorption behaviors for Cs<sup>+</sup> from solutions were investigated using batch method. Thermogravimetric analysis (TG) and the Fourier Transform Infrared Spectroscopy (FTIR) were used to characterize the EIR. The effects of extraction time, pH values, metal ion concentration, and

temperature were investigated.

## 2. Experiments

### 2.1 Preparation of EIR

The extractant-impregnated resin was prepared using a dry impregnation method. A known amount of AB-8 support was immersed in 100 mL of *t*-BAMBP-sulfonated kerosene solution. The mixture was stirred for 24 h at 25°C. Then the EIR was separated from solution through filtration and dried in a vacuum oven.

### 2.2 Characteristics of EIRs

TG curve of the EIR was recorded on a TGDTA92 (SETARAM, France) apparatus in N<sub>2</sub> with a heating rate of 10°C/min. FTIR spectrum of the EIR was taken following the usual KBr pellet technique on a Nexus FTIR spectrometer (Thermo-Nicolet, USA). Spectral resolution was 4 cm<sup>-1</sup> and the spectra were obtained using 64 scans.

### 2.3 Batch adsorption experiments

In the batch method, 1.0 g portions of adsorbent, EIR, weighed into the 100-mL plastic bottles, and thoroughly mixed with Cs solutions (40 mL) of the different initial concentrations and pH was adjusted to the desired value. The suspension in flask was shaken for equilibrium in a thermostatic bath. After phase separation, the concentration of Cs<sup>+</sup> ion in the aqueous phase was analyzed by the ICS-1100 ionic chromatograph (Dionex Corporation). The amount of metal ions adsorbed by the adsorbent was determined by mass balance. The adsorption capacity, *q* (mmol/g), was calculated with the following equation:

$$q = \frac{(C_0 - C_e)V}{m} \quad (1)$$

In this equation, *C*<sub>0</sub> and *C*<sub>*e*</sub> are the initial and equilibrium concentrations (mmol/L) of metal ions in solution, respectively. *V* is the volume of solution (mL) and *m* is the weight of the adsorbents used (g).

2.0 mol/L HCl was used for desorption of Cs<sup>+</sup> from the EIR after adsorption and the regeneration performance of the EIR was studied.

## 3. Results and discussion

### 3.1 Characterization of EIR

Thermogravimetry analysis curves in Fig.1 show thermal stability of AB-8 support and EIR. AB-8 support was used for the reference material, and its weight loss started at 350°C, which means that it has good thermal stability and can be used as the matrix material. The weight loss between 150°C and 320°C for the EIR is due to the fracture of the organic chain of impregnated extractant, and the content of the extractant in pore structure of the EIR can be calculated, which is about 46%. The second obvious mass loss in TG curves of EIR was observed from 320°C, which resulted from decomposing of the matrix material AB-8. The thermal stability indicated that EIR could meet the requirement for adsorbing metal ion.

Fig.2 shows the infrared spectra of the prepared EIR and with free AB-8, there are some additional bands. As observed in Fig.3, the bands of 1270 cm<sup>-1</sup> is the band speak of the phenolic hydroxyl group which can confirm that the impregnation process has been performed through a physical adsorption pathway.

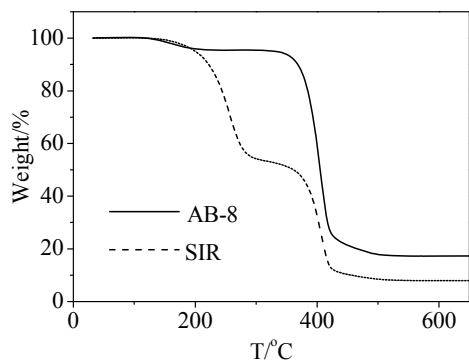


Fig. 1 TG curves of EIR and AB-8

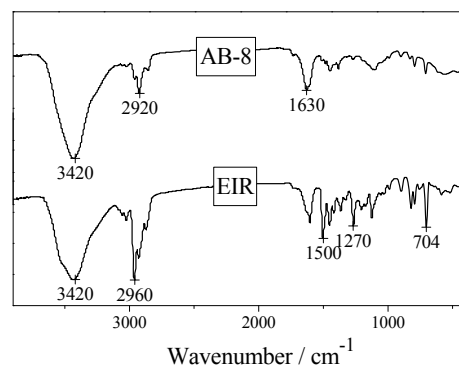


Fig. 2 FTIR of EIR and AB-8

### 3.2 Effect of pH on adsorption

Solution pH is known as one of the most important factors that can affect the protonation of the functional groups on the adsorbent surface as well as the metal chemistry [21]. The reaction between the substituted phenol *t*-BAMBP and  $\text{Cs}^+$  only occurs under alkaline conditions. In order to investigate the effect of pH on the adsorption of  $\text{Cs}^+$  on the EIR, the adsorption experiments were carried out by varying the initial pH of the solution over the range of 7-13, and results are shown in Fig. 3. The adsorption of  $\text{Cs}^+$  could be negligible by AB-8 resin, and increased with the increasing of pH by EIR. That is consistent with the react of extraction between  $\text{Cs}^+$  and *t*-BAMBP [3].

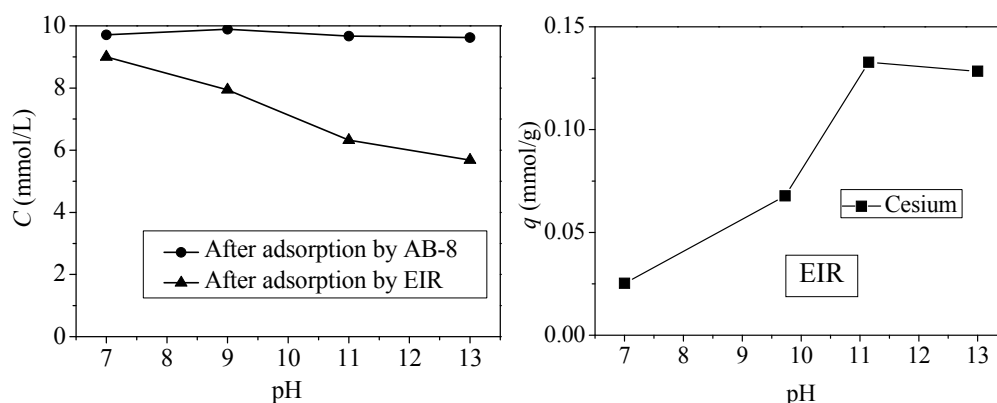


Fig. 3 Effect of pH on the adsorption

### 3.3 Adsorption kinetics

Fig. 4 shows the adsorption capacity of the EIR at different time intervals for different initial concentrations varying from 5 to 20 mmol/L. As can be seen, for all initial concentrations of 5, 10, 15 and 20 mmol/L, the removal amount of  $\text{Cs}^+$  increased rapidly during the initial few hours, and then increased slowly until the equilibrium state was reached after about 2 hours. Also, Fig. 4 shows the effect of initial concentration on the adsorption of  $\text{Cs}^+$  on EIR. With increase in the initial concentration from 5 to 20 mmol/L, the amount of Cs adsorption (adsorption capacity;  $q_e$ ) was increased from 0.1 to 0.2 mmol/g.

The effect of temperature is important in adsorption systems since change in temperature can cause the change in the equilibrium constant and adsorption capacity of the adsorbent for a particular solute. As shown in Fig. 4, the adsorption capacity of EIR was decreased with increasing the temperature, indicates that adsorption is exothermic nature.

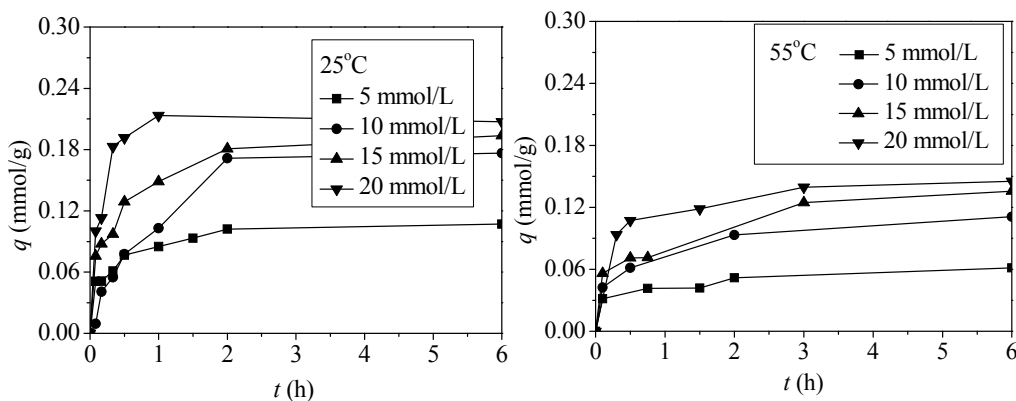


Fig. 4 Effect of  $\text{Cs}^+$  concentration and temperature on the adsorption kinetics

### 3.4 Adsorption isotherms

The initial concentration of  $\text{Cs}^+$  was varied in the range 2.5-25 mmol/L, and the adsorption isotherms at two different temperatures are shown in Fig. 5. Equilibrium was reached within 4-6 h: the time required to reach equilibrium slightly increased with decreasing metal concentration. In general, the adsorption amount at equilibrium decreases with increasing temperature, and increases with the increase in  $\text{Cs}^+$  concentration. Based on the adsorption isotherms, the adsorption capacities for EIR were found to be 0.23 and 0.14 mmol/g in 25°C and 55°C, respectively.

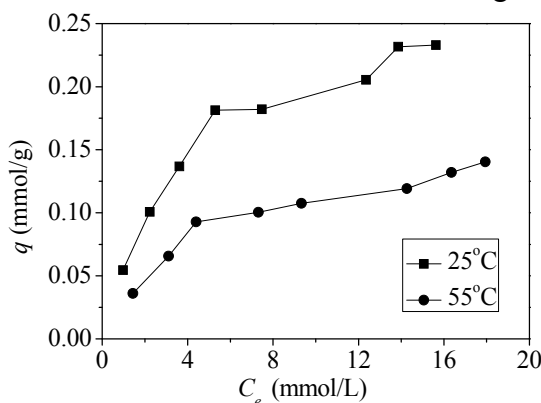


Fig. 5 The adsorption isotherms of EIR

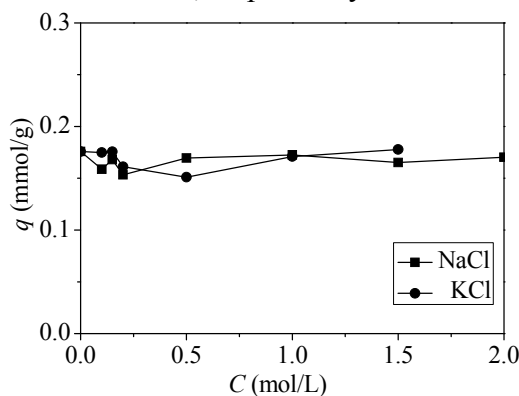


Fig. 6 The effect of co-existing ions  $\text{Na}^+$  and  $\text{K}^+$  on the adsorption

### 3.5 Effect of co-existing ions

The Interference from coexisting ions was studied, 1.0 g of the adsorbent was equilibrated with 40 mL aqueous solution containing 10 mmol/L  $\text{Cs}^+$  and different amount of  $\text{Na}^+$  or  $\text{K}^+$  (2-2.0 mol/L). The results were shown in Fig.6. It demonstrated that both  $\text{Na}^+$  and  $\text{K}^+$  had almost no effect to the adsorption amount of  $\text{Cs}^+$  on the EIR, indicating that the EIR has good selectivity for  $\text{Cs}^+$  in the solution.

### 3.6 Recycle test

To make resins competitive and efficient for metal recovery, it is important to verify their reproducibility and reliability. Therefore, the recycle performance of EIR was investigated through several adsorption-elution cycles. 2.0 mol/L HCl solution was used for desorption of  $\text{Cs}^+$  loaded on the EIR. After desorbed the loaded  $\text{Cs}^+$ , the EIR can be regenerated by washing the beads with water till it is free of  $\text{H}^+$ . Then the EIR can be reused after regenerating. In order to test the reusability and stability of the EIR, successive adsorption-desorption cycles were repeated 4 times by using the same EIR beads. The result was shown in Fig. 7. It shows that after four times adsorption-desorption cycles, the adsorption capacity of EIR was still good for  $\text{Cs}^+$  from the solution.

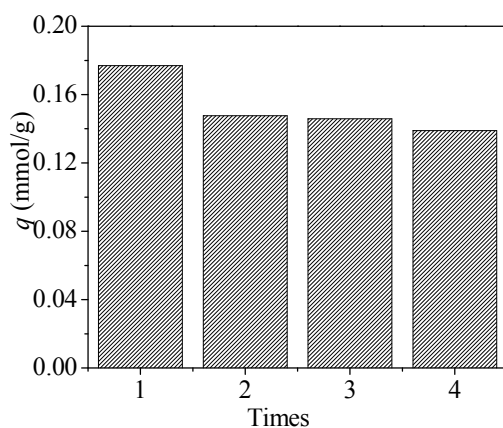


Fig. 7 The recycling performance of EIR

#### 4. Conclusion

A novel extractant-impregnated resin, EIR, was prepared and used to adsorb  $\text{Cs}^+$  from the solution. The TG curves and FTIR analysis exhibited that *t*-BAMBP molecules entered into AB-8 resins by the impregnation process. The results of the adsorption experiments showed that the EIR had good adsorption properties for  $\text{Cs}^+$ . The adsorption amount decreased with the increasing of temperature indicating that adsorption is exothermic nature. Solution pH has a significant effect on the equilibrium adsorption amount. Compared with acidic and neutral solution, in alkaline solution, *t*-BAMBP could react with  $\text{Cs}^+$  more easily. The highest adsorption amount was received at pH~12. Both  $\text{Na}^+$  and  $\text{K}^+$  had almost no effect to the adsorption amount of  $\text{Cs}^+$  on the EIR. The results of effect of coexist ions and adsorption in the simulated brine indicated that the EIR has good selectivity for  $\text{Cs}^+$  in the solution. The EIR is easy to regeneration and has good recycling performance.

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