

Ion Exchange of Cs Ion in Acid Solution with Potassium Cobalt Hexacyanoferrate

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Abstract—Potassium cobalt hexacyanoferrate (KCoFC) was synthesized for removal of Cs ions in acid waste solution. The synthesized KCoFC was stable in nitric acid solution of pH=1 and showed high selectivity for Cs ion over Sr and Na ions. The $K_{d,Cs}$ for 0.01 N Cs ion solution at pH=2 was about 3.6×10^3 mL/g in the presence of the same concentrations of Sr and Na ions, respectively. In the binary ion exchange system, both the Dubinin-Polanyi model and Langmuir model fit the experimental data, although the Dubinin-Polanyi model fit more correctly than the Langmuir model. However, in the multi-component system, only the modified Dubinin-Polanyi model, which is a semi-empirical equation, fit the experimental data accurately. The ion exchange capacity of KCoFC for Cs ion obtained by the Dubinin-Polanyi equation was 1.72 meq/g.

Key words: Ion Exchange, Cesium Ion, Potassium Cobalt Hexacyanoferrate, Distribution Coefficient, Separation Factor, Radioactive Liquid Waste

INTRODUCTION

For the first 50 to 100 years after SNF (spent nuclear fuel) is discharged from a reactor, the cesium and strontium are the primary sources of decay heat. These two fission products decay away with about a 30-year half life. In order to dispose of these radionuclides safely, an appropriate method to separate ^{137}Cs and ^{90}Sr from high level liquid waste should be introduced. In this regard, many inorganic ion exchangers have been applied for the selective removal of Cs and Sr ions [Huckman et al., 1999; Liang and Hsu, 2001; Marageh et al., 1999; Mardan et al., 1999; Mimura et al., 1994, 1995, 1997, 1998; Moon et al., 2000, 2002; Perona et al., 1995; Sinha, et al., 1995].

Especially, insoluble hexacyanoferrates of transition metals or transition and alkali metals such as nickel hexacyanoferrate (NiFC), potassium nickel hexacyanoferrate (KNiFC) are reviewed as selective for Cs ion. For this reason, they have been employed for the removal of Cs ion in radioactive waste solution. Mimura et al. [1997, 1998] prepared KNiFC by precipitation method and evaluated the ion exchange performance for practical treatment of Cs ion from radioactive waste solutions. Another type of cesium-selective hexacyanoferrate, KCoFC (potassium cobalt hexacyanoferrate), was prepared by Prout et al. [1964]. They proved its chemical stability and adsorption performance in a binary system. However, little is known about ion exchange performances for multi-component acid waste solution.

In this study, we prepared a KCoFC powder which is not commercially available, and assessed its ion exchange behaviors for cesium ion in multicomponent acid waste solution.

EXPERIMENTAL

1. Preparation of KCoFC

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Potassium cobalt hexacyanoferrate (KCoFC) was prepared by adding one volume of potassium ferrocyanide trihydrate ($\text{K}_4\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$) to 2.4 volumes of cobalt nitrate hexahydrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) as described in reference [Prout et al., 1964]. A slurry of KCoFC was stirred for 1 hr at room temperature and then washed with deionized water. The resulting solids were dried at 115 °C for 24 hrs. The granules were ground to fine powders, washed with deionized water and redried. The stability test in acid solution was performed in the range of pH 1-4 at 25 °C for 72 hrs, then the solids were washed with deionized water before being dried at 115 °C for 24 hrs. The crystal structure of the KCoFC was confirmed by XRD (Rigaku. Co.) and its particle size and morphology were observed by using scanning electron microscope (JEO. Co., JSM 5200).

2. Ion Exchange Behaviors

2-1. Determination of Distribution Coefficient

Distribution coefficients of the KCoFC powder were determined for Cs ion. In determining distribution coefficients, Cs ion concentration was fixed at 0.01 N, while solution pHs were varied in the range of 2 to 5.6. The KCoFC powders were contacted with 20 mL/g of 0.01 N CsNO_3 solution for 3 days. Distribution coefficient, K_d (mL/g), was calculated by following equation:

$$K_d = \frac{C_s}{C_L} \quad (1)$$

where, C_s =equilibrium concentration in solid phase (meq/g)

C_L =equilibrium concentration in liquid phase (meq/mL)

The effect of coexisting ions such as Sr and Na ions on the $K_{d,Cs}$ was investigated. The concentrations of coexisting strontium and sodium ions were fixed at 0.01 N, respectively.

2-2. Determination of Ion Exchange Isotherm

The ion exchange isotherms of the KCoFC powder for cesium ion were obtained in a binary and multicomponent system. 0.1 g of the KCoFC powder was contacted with 10 mL of solution for 72 hrs. The initial solution pH was fixed at 2 and the concentrations of cesium were varied between 0.0002 and 0.2 N. In multicomponent

system, strontium and sodium ions were fixed at 0.01 N, respectively. The equilibrated samples were decanted using 0.2 μm syringe filter and then analyzed by AAS (Perkin-Elmer, Model 1100B). The tests were performed in triplicate and averaged to obtain one equilibrium point.

RESULTS AND DISCUSSION

1. Preparation of KCoFC

The KCoFC powder was prepared by precipitation method. The crystal structure of the synthesized KCoFC was confirmed by X-ray diffraction analysis as shown in Fig. 1, which represents the corresponding XRD pattern of the standard KCoFC. The shape of the synthesized KCoFC was shown in Fig. 2 and the particle size distribution was represented in Fig. 3, which shows the mean diameter of 8.48 μm .

In order to confirm the chemical stability of the synthesized KCoFC powder against nitric acid solutions, the KCoFC samples were immersed into the acid solutions in the pH ranges 1 to 4 for 72 hrs, and then the samples were analyzed by XRD and observed by

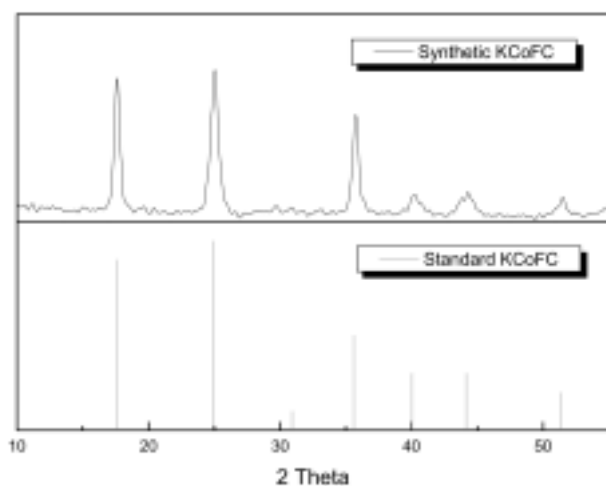


Fig. 1. Comparison of XRD pattern of the synthetic KCoFC and the standard one.

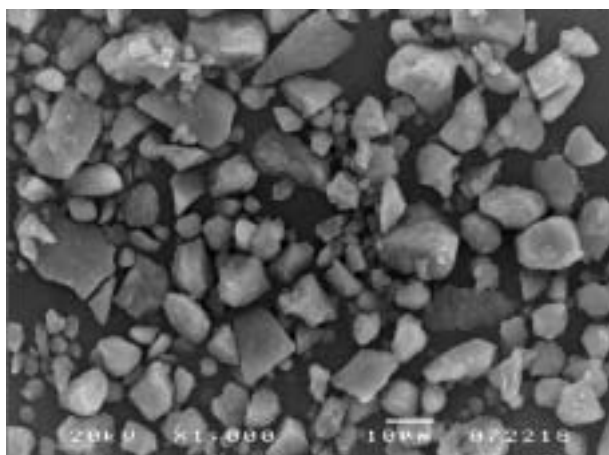


Fig. 2. SEM image of the synthetic KCoFC powder.

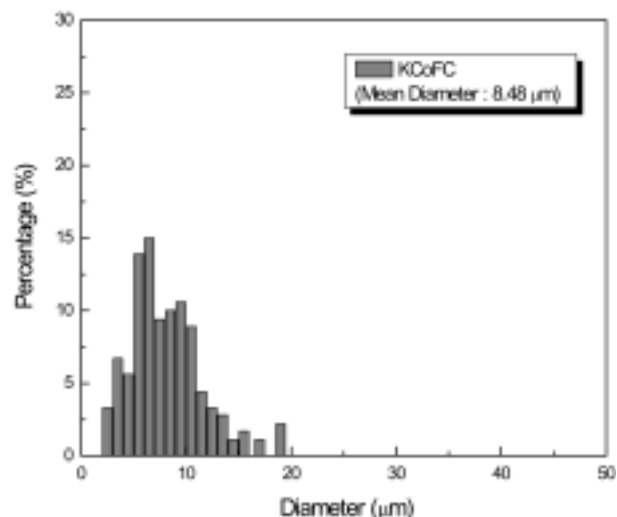


Fig. 3. Particle size distribution of the KCoFC powder.

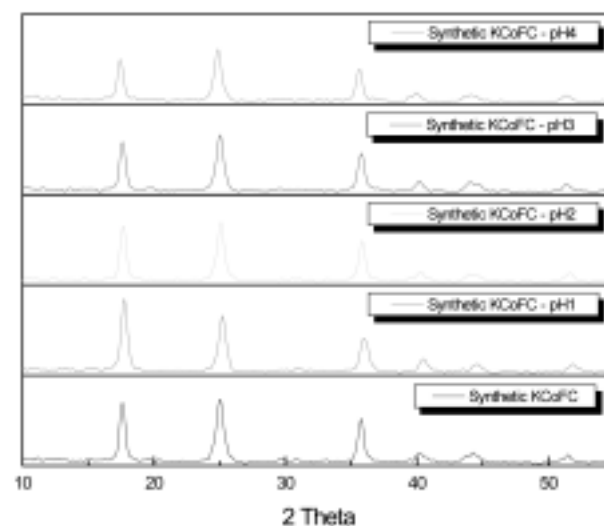


Fig. 4. XRD pattern of the KCoFC treated with nitric acid.

using SEM. As shown in Fig. 4, the XRD patterns of the tested samples are the same as the original one, indicating that the synthesized KCoFC powder is stable in the acid solutions above pH=1. SEM images as in Fig. 5 also showed no morphology changes. Therefore, the synthesized KCoFC ion exchanger is considered to be possibly used in the acid waste solution.

2. Ion Exchange Behaviors

2-1. Distribution Coefficients

The ion exchange behavior of cesium ion was studied in binary and multi-component systems. The distribution coefficient for cesium ion ($K_{d,Cs}$) was measured with the pH variation from 2 to 5.6 as in Fig. 6. It shows that the distribution coefficients are slightly increased proportionally to the solution pH-value. $K_{d,Cs}$ is about 4.6×10^3 mL/g at pH=2 and about 1.0×10^4 mL/g at pH=5.6. The obtained distribution coefficient at pH=2, taking into account the acidity of the solution, is considered rather high.

Figs. 7 and 8 represent the effect of coexisting ions on the distribution coefficients of cesium ion ($K_{d,Cs}$). Even at high strontium

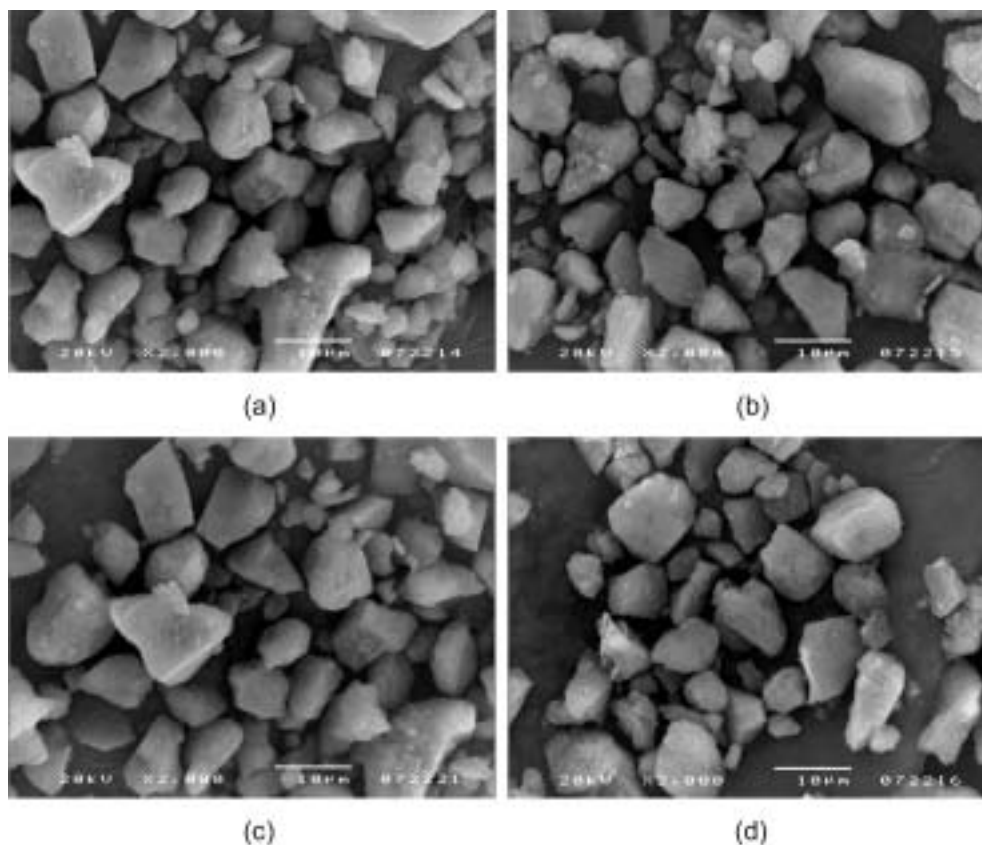


Fig. 5. SEM images of the KCoFC powder treated with nitric acid. (a) pH 1, (b) pH 2, (c) pH 3, (d) pH 4

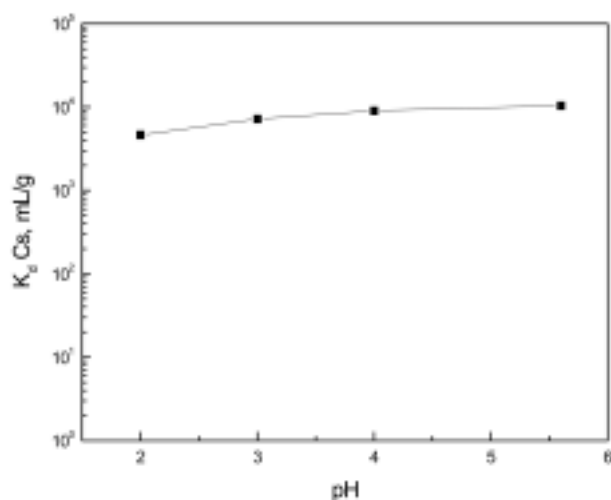


Fig. 6. Effect of pH on the distribution coefficient of Cs ion in KCoFC-Cs system.

ion concentration of 0.01 N, the $K_{d,Cs}$ value was about 3.7×10^3 mL/g at pH=2, which gives the separation factor ($\alpha_{Cs/Sr} = K_{d,Cs}/K_{d,Sr}$) about 7.4×10^2 mL/g. This value is considered much higher than that of other inorganic ion exchangers such as Cs-selective zeolites. In acid solution containing strontium and sodium ions together with Cs ions, $K_{d,Cs}$ and $\alpha_{Cs/(Sr+Na)}$ were about 3.6×10^3 and 3.0×10^2 mL/g, respectively. The results indicate that the KCoFC ion exchanger is highly

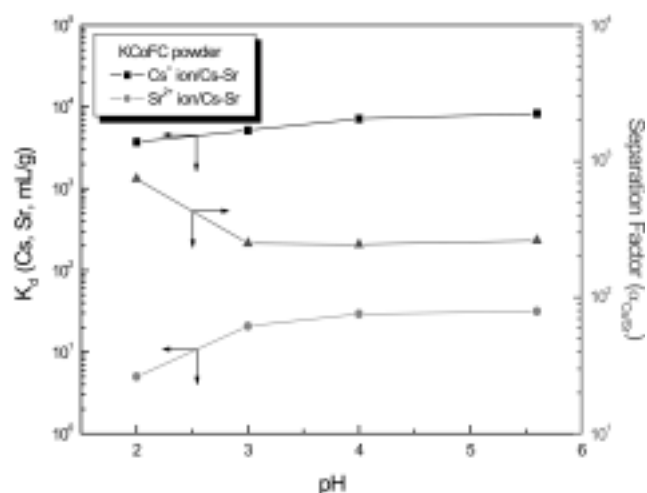


Fig. 7. Effect of pH on the distribution coefficients of Cs, Sr ions in KCoFC-Cs-Sr system.

selective for cesium ion and can be used effectively for separation of cesium ion from mixed solution of Cs, Sr, Ni ions in acid waste.

2-2. Ion Exchange Equilibrium Isotherm

Ion exchange equilibrium isotherms were obtained to evaluate the ion exchange capacity and the equilibrium constant. Experimental data were modeled by Langmuir and Dubinin-Polanyi equations [Robinson, 1993; Moon et al., 2000, 2002; Rengaraj et al., 2004] given by

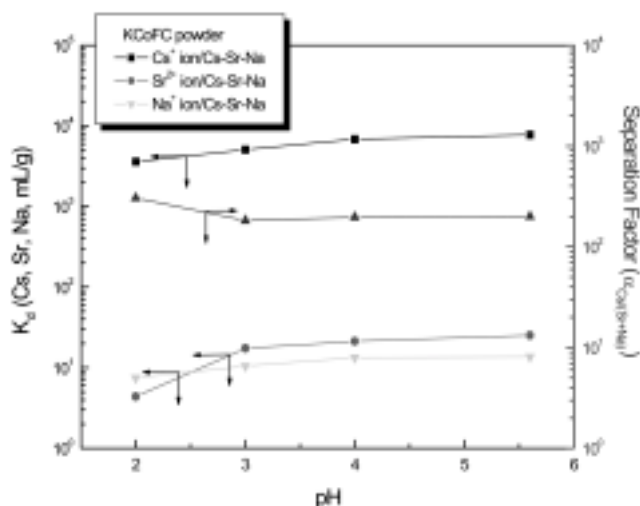


Fig. 8. Effect of pH on the distribution coefficients of Cs, Sr and Na ions in KCoFC-Cs-Sr-Na system.

$$q = \frac{q_s b C}{1 + b C} \quad (2)$$

$$q = q_s \exp[-k R^2 T^2 \{\ln(C_s/C)\}^2] \quad (3)$$

where q (meq/g), q_s (meq/g), c (meq/mL) and c_s (meq/mL) are the equilibrium and saturation concentrations of metals in solid and liq-

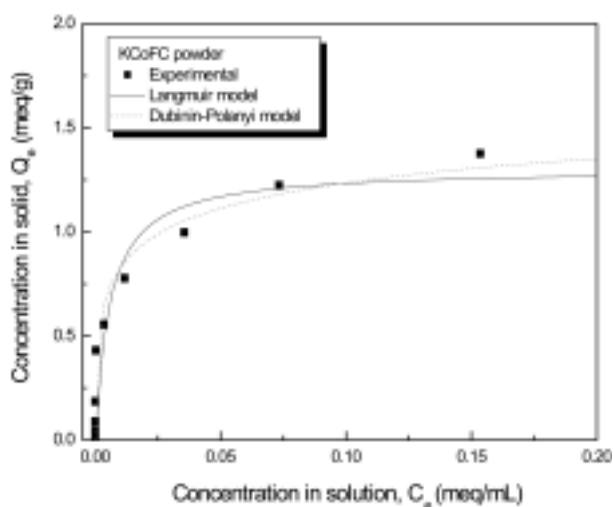


Fig. 9. Binary ion exchange equilibrium isotherm and modeling examples for Cs ion exchange with KCoFC powder.

Table 1. Model parameters for Cs ion exchange isotherm with KCoFC

Model	Coefficient	
Langmuir	q_s (meq/g)	1.303
	b (mL/meq)	174.33
	R^2	0.98
Dubinin-Polanyi	q_s (meq/g)	1.720
	k	4.21×10^{-7}
	R^2	0.98

uid phases, respectively. Symbols b and k stand for characteristic constants. R and T are gas constant (cal/gmol K) and temperature (K), respectively. The solubilities of the respective salts as taken from the literature [Broul, 1981] make for $c_s[\text{CsNO}_3]=11.4$ meq/mL and $c_s[\text{Sr}(\text{NO}_3)_2]=6.7$ meq/mL. The experimental data and fitting results for binary system were represented in Fig. 9 and Table 1. Although both models fit experimental data qualitatively, the Dubinin-Polanyi isotherm is more accurate evidently. Using this isotherm, the following maximum sorption capacity of KCoFC ion exchanger was calculated: $q_s[\text{CsNO}_3]=1.72$ meq/g.

The parameters obtained from the binary ion exchange isotherm were applied to the multicomponent equations, which are extended from the binary Eqs. (2) and (3) in a logical manner to describe multicomponent system, given by

$$\frac{q_i}{q_m} = \frac{b_i C_i}{1 + \sum_{j=1}^m b_j C_j} \quad (4)$$

for Langmuir model,

$$\sum q_i = \exp[b_0 + b_1 \ln(\sum C_i) + b_2 \ln(\sum C_i)^2] \quad (5)$$

$$b_0 = \ln(q_s) - k R^2 T^2 [\ln(C_s)]^2 \quad (6)$$

$$b_1 = -2k R^2 T^2 \ln(C_s) \quad (7)$$

$$b_2 = -k R^2 T^2 \quad (8)$$

for the Dubinin-Polanyi model, respectively. The experimental data and the modeling results are represented in Fig. 10.

As shown in the figure, the multicomponent Langmuir and Dubinin-Polanyi models did not accurately predict the experimental data. These results indicate that the multicomponent data cannot be predicted by using the parameters obtained from the binary isotherms, obviously due to the nonideality of the multicomponent systems. The same results were reported by Robinson et al. [1993] and Moon et al. [2000] in the multi-component ion exchange study using zeolites and potassium titanate ion exchangers, and they were reportedly successful in treating multi-component ion exchange equilibria by using the modified version of Dubinin-Polanyi model given by,

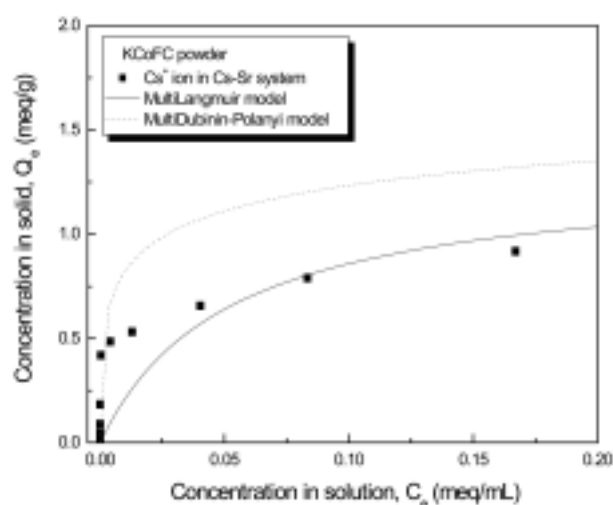


Fig. 10. Equilibrium isotherm and modeling examples for Cs ion exchange in KCoFC-Cs-Sr-Na system.

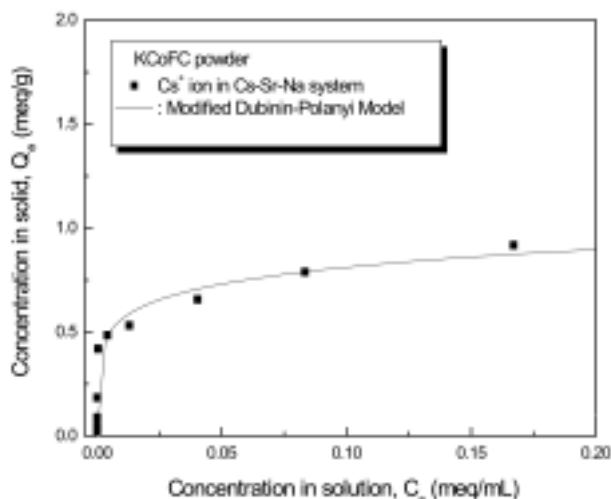


Fig. 11. Modeling results using a modified Dubinin-Polanyi equation for Cs ion exchanges in KCoFC-Cs-Sr-Na system.

Table 2. Model parameters for modified Dubinin-Polanyi isotherm equation for Cs in KCoFC-Cs-Sr-Na ion exchange system

Ions	Coefficients			R ²
	b ₀	b ₁	b ₂	
Cs	0.108	0.127	-0.004	0.98

$$q_e = \exp[b_0 + b_1 \ln(C_e) + b_2 (\ln(C_e))^2] \quad (9)$$

The constants b_0 , b_1 and b_2 were determined by nonlinear regression analysis. If the systems are ideal, the equation should be equal to Eq. (5). In this study we also used this model to describe the multicomponent ion exchange equilibria. The fitting results for experimental data are shown in Fig. 11, and the parameters for this equation are summarized in Table 2. It shows that the modified Dubinin-Polanyi equation fit the data accurately with the least number of experimentally determined coefficients. The modified Dubinin-Polanyi equation is theoretically sound, even though it is semi-empirical, since the Dubinin-Polanyi model has a thermodynamic basis. Furthermore, it is so simple that it can be modeled with a minimum amount of experimental data. Therefore, this model would be applied favorably to describe multicomponent ion exchange equilibria with KCoFC ion exchanger.

CONCLUSIONS

A potassium cobalt hexacyanoferrate (KCoFC) ion exchanger was prepared for removal of cesium in acid waste solution. A chemical stability test showed that the KCoFC was stable in nitric acid solution of pH=1. Ion exchange performance was tested and it showed favorable uptake for Cs ion over Sr and Na ions. $K_{d,Cs}$ and $\alpha_{Cs/(Sr+Na)}$ in the presence of Sr and Na ions together with Cs ion, were about 3.6×10^3 and 3.0×10^2 mL/g, respectively. For binary ion exchange isotherm, the Dubinin-Polanyi equation fit the experimental data more correctly than the Langmuir equation. In a multicomponent system, the modified version of the Dubinin-Polanyi model, which

is semi-empirical equation, fit the experimental data accurately. The ion exchange capacity for Cs ion, obtained for binary system by using the Dubinin-Polanyi equation, was 1.72 meq/g.

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