Adsorption Behaviours for Strontium and Cesium Ions Using Composite Ion Exchangers

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SUMMARY

PAN-4A composite ion exchanger was more selective for Sr ion than other cations and PAN-KCoFC composite ion exchanger has much higher ion exchange capacity for Cs ion than other cations. The ion exchange capacities obtained from Dubinin-Polanyi equation were 3.93 meq/g for Sr ion and 1.50 meq/g for Cs ion using PAN-4A and PAN-KCoFC ion exchangers, respectively. The modified Dubinin-Polanyi model fit the experimental data accurately in multi-component system. The effective surface diffusivities ($D_{s,eff}$) for Sr and Cs ions of PAN-4A and PAN-KCoFC ion exchangers were slightly increased with the different particle sizes.

INTRODUCTION

Of the fission products present in the nuclear stream, cesium-137 and strontium-90 are reportedly the most predominant, hazardous and difficult to handle and store safely[1-4]. To remove and recover cesium and strontium selectively, several researchers have studied PAN-based composite adsorbents. Sebesta et al. [5] conducted chemical and radiation stability tests for PAN-AMP(ammonium molybdophosphate) beads and proved that they had no limitation by no chemical and radiation decomposition. John et al. [6] conducted dynamic leaching tests of 137-Cs from cesium loaded cemented PAN-NiFC (nickelferrocyanate) composite ion exchanger. They proved that the leachability was much lower than that from simply cemented samples. We also sucessfully prepared PAN-potassium titanate and PAN-nickel hexacyanoferrate composite adsorbents and performed for the removal of heavy metal ions and radionuclides [7]. In spite of some sucessful results on the preparation of PAN-based composite adsorbents and adsorption behavior for radionuclides, there are not enough data on equilibrium, uptake performance.

In this study, sorption properties of the composite ion exchangers were evaluated for equilibrium isotherms, adsorption uptake rates in batch reactor, and adsorption behaviors in column.

EXPERIMENTAL

Ion exchange equilibrium isotherms of PAN-4A and PAN-KCoFC composite ion exchangers were obtained for strontium, cesium, nickel, and barium ions in batch reactor. The dosage of composite ion exchangers and solution pH were held at 10mL/0.1g and 2, respectively. The solution concentrations were varied between 0.002 ~ 0.2 N in single and multi-component system, respectively. The composite ion exchangers were contacted with the ion exchangers were contacted with the ion exchange solutions for 72 h at 25 ℃ and the ion exchange capacity tests were performed in triplicate to obtain each isotherm points. In ion exchange kinetic tests, 1 g of ion exchange adsorbent was added to the reactor, which contained 100 mL of the solution under the stirrer at 700 rpm. Then the samples were decanted by using 0.2㎛syringe filter and analyzed by atomic absorption spectrophotometer (AAS, Perkin-Elemer, Model 1100B). The adsorption experiments in fixed bed were carried out using a glass column of 0.025 m inside diameter and 0.2 m in length. 12 g of PAN-4A sample were soaked in deionized water for 48 h at 25 ℃ and then packed into the column. The strontium concentration of the feed solution on the influence of flow rate on the adsorption of strontium on the column was fixed in 0.02 N. The flow rate was changed in the range of 3 to 6 mL/min using peristaltic pump. The temperature during the adsorption was kept at 25 ℃.

RESULTS AND DISCUSSION

Equilibrium Isotherms

Ion exchange equilibrium isotherms of PAN-4A and PAN-KcoFC composite ion exchangers were obtained for Sr, Cs, Ni and Ba ions. The experimental data following from equilibrium isotherms determination were fitted to Langmuir model and Dubinin-Polanyi model in order to determine maximum ion exchange capacity and respective equilibrium constants. Langmuir equation[8] is written as follows :

$$q = \frac{q_s bc}{1 + bc} \tag{1}$$

The Dubinin-Polanyi equation[8] is given by

$$q = q_s \exp[-kR^2 T^2 \{\ln(c_s / c)\}^2] \tag{2}$$

where q (meq/g), q_s (meq/g), c (meq/mL) and c_s(meq/mL) are the equilibrium and saturation concentrations in solid and liquid phases, respectively. Symbols b and k stand for stand for characteristic constants. R and T are molar gas constant and absolute temperature

(K), respectively. The solubility of salts obtained from the literature were 11.4 meq/mL for $CsNO_3$, 6.7 meq/mL for $Sr(NO_3)_2$, 26.4 meq/mL for $Ni(NO_3)_2$, and 0.77 meq/mL $Ba(NO_3)_2$, respectively. The experimental data and the results of fitting for Sr, Cs, Ni, and Ba ions of PAN-4A and PAN-KcoFC composite ion exchangers were shown in Figure 1 and 2, respectively.

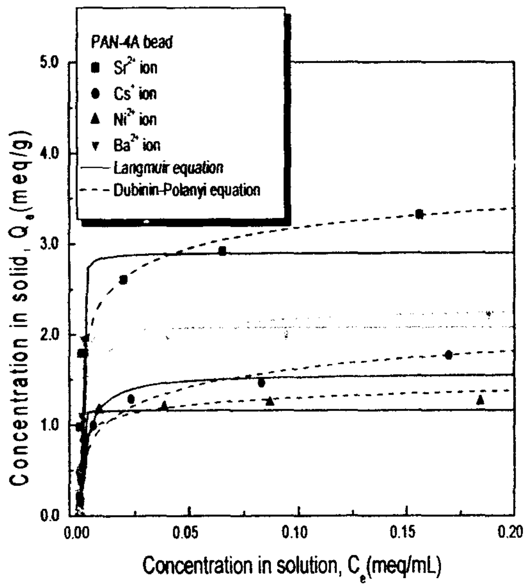

Figure 1. Experimental data and equilibrium isotherms fitted by Langmuir and Dubinin-Polanyi equations using PAN-4A composite ion exchanger.

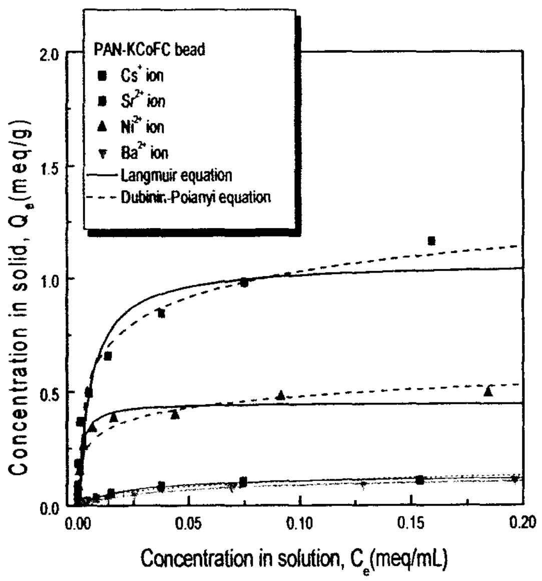

Figure 2. Experimental data and equilibrium isotherms fitted by Langmuir and Dubinin-Polanyi equations using PAN-KCoFC composite ion exchanger.

Figure 1 indicates that PAN-4A composite ion exchanger has much higher ion exchange capacity for Sr ion than other cations and has the following selectivity order Sr>Ba>Cs>Ni. As shown in Figure 2, the results show that PAN-KcoFC composite ion exchanger has much higher ion exchange capacity for Cs ion than other cations and has the following selectivity order Cs>Ni>Sr>Ba. The coefficients and R^2 values for each equilibrium isotherm model are summarized in Table 1 and 2. The results represent that Dubinin-Polanyi model fit the experimental data more correctly. The ion exchange capacities of the PAN-4A and PAN-KcoFC composite ion exchangers obtained for strontium and cesium ions using Dubinin-Polanyi model were 3.93 meq/g and 1.50 meq/g, respectively.

Table 1. Equilibrium parameters for Sr, Cs, Ni, and Ba ions modelled by Langmuir and Dubinin-Polanyi equations using PAN-4A composite ion exchanger.

Model	Coefficient(unit)	Ions			
		Sr	Cs	Ni	Ba
Langmuir	q_s [meq/g]	2.90	1.57	1.16	2.08
	b [mL/meq]	4808.9	334.78	18002.4	2163.33
	R^2	0.96	0.97	0.96	0.95
Dubinin-Polanyi	q_s [meq/g]	3.93	2.47	1.65	2.30
	k	3.39×10^{-8}	5.39×10^{-8}	2.21×10^{-8}	3.99×10^{-8}
	R^2	0.98	0.98	0.98	0.98

Table 2. Equilibrium parameters for Sr, Cs, Ni, and Ba ions modelled by Langmuir and Dubinin-Polanyi equations using PAN-KCoFC composite ion exchanger.

Model	Coefficient(unit)	Ions			
		Sr	Cs	Ni	Ba
Langmuir	q_s [meq/g]	0.13	1.07	0.45	0.12
	b [mL/meq]	44.87	179.35	639.45	23.48
	R^2	0.98	0.92	0.97	0.98
Dubinin-Polanyi	q_s [meq/g]	0.21	1.50	0.73	0.12
	k	1.14×10^{-8}	4.73×10^{-8}	3.86×10^{-8}	2.34×10^{-8}
	R^2	0.98	0.98	0.98	0.99

A modified version of the Dubinin-Polanyi equation was tested to overcome some limitations in multi-component system[9]. The modified Dubinin-Polanyi model is given by

$$q_i = \exp[b_0+b_1\times\ln(c_i)+b_2\times\{\ln(c_i)\}^2] \qquad (3)$$

This modified Dubinin-Polanyi equation was solved for for b_0, b_1, and b_2. The results were represented in Figure 3 and 4 and the fitting results were summarized in Table 3 and 4. As shown in Figures, modified Dubinin-Polanyi model fit the experimental data accurately. The modified Dubinin-Polanyi isotherm equation is semi-empirical, but it is theoretically sound since equation that can be modelled with a minimum amount of experimental data.

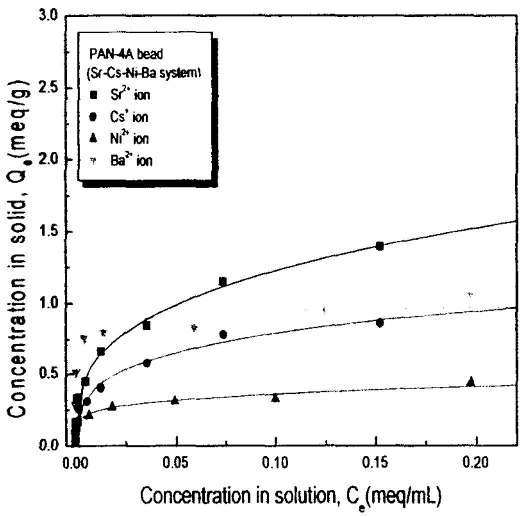

Figure 3. Modified Dubinin-Polanyi models for Sr, Cs, Ni, and Ba ions on PAN-4A composite ion exchanger.

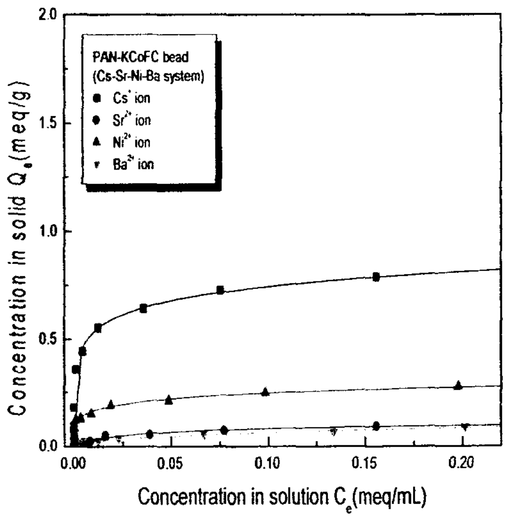

Figure 4. Modified Dubinin-Polanyi models for Sr, Cs, Ni, and Ba ions on PAN-KCoFC composite ion exchanger.

Table 3. Equilibrium parameters for modified Dubinin-Polanyi isotherm equation in Sr-Cs- Ni-Ba system using PAN-4A adsorbent.

Isotherm	Coefficients			
	b_0	b_1	b_2	R^2
Sr	-0.931	0.319	0.001	0.99
Cs	0.297	0.200	-0.014	0.99
Ni	-0.586	0.198	0.003	0.98
Ba	-0.036	-0.026	-0.015	0.98

Table 4. Equilibrium parameters for modified Dubinin-Polanyi isotherm equation in Cs-Sr-Ni-Ba system using PAN-KCoFC adsorbent.

Isotherm	Coefficients			
	b0	b1	b2	R2
Cs	-0.033	0.100	-0.006	0.99
Sr	-2.301	-0.073	-0.076	0.98
Ni	-1.110	0.109	0.009	0.98
Ba	-1.772	0.441	0.009	0.98

Adsorption Kinetics

In single component system, experimental data obtained from the batch reactor were represented in Figure 5 and 6. These figures show Sr ion and Cs ion uptake curves for different particle sizes of PAN-4A and PAN-KcoFC adsorbents, respectively. The uptake for the R_p = 1.25 mm particle of PAN-4A adsorbent was significantly faster than for the R_p = 1.52 mm and R_p = 1.70 mm particles. For PAN-KcoFC adsorbent, the uptake rate for the R_p = 1.47 mm particle of PAN-4A adsorbent was also faster than for the R_p = 1.63 mm and R_p = 2.03 mm particles.

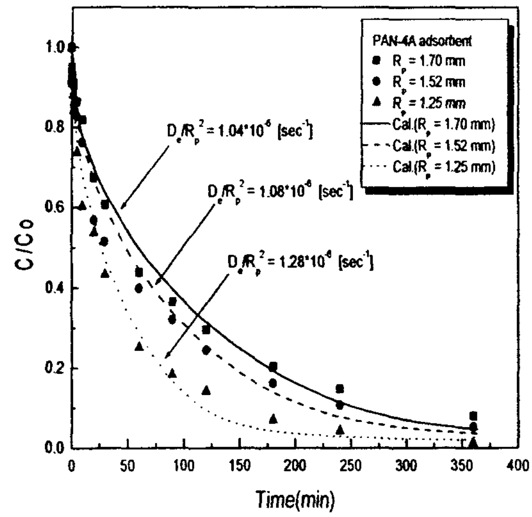

Figure 5. Effect of particle size on the Sr ion uptake rate using PAN-4A ion exchanger.

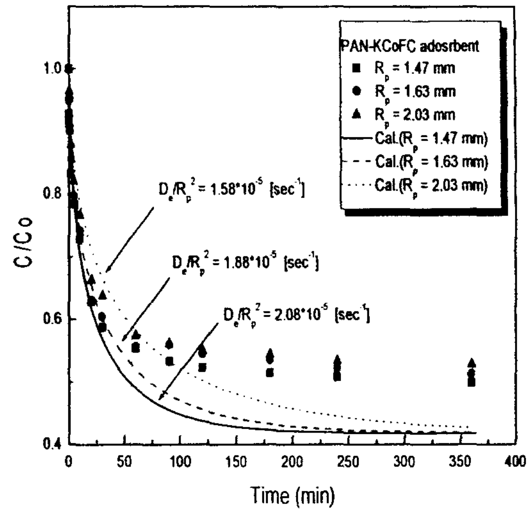

Figure 6. Effect of particle size on the Cs ion uptake rate using PAN-KCoFC ion exchanger.

The homogeneous diffusion model was used to evaluate experimental data and the calculated values for the effective diffusivities were summarized in Table 5. The results showed that the estimated $D_{s,eff}$ values for PAN-4A and PAN-KcoFC ion exchangers were slightly increased with the different particle sizes. These values were on the order of 10^{-8} cm^2/sec for Sr ion using PAN-4A and on the order of 10^{-7} cm^2/sec for Cs ion using PAN-KcoFC ion exchanger. Typical effective micropore diffusivities in liquid systems were in the range of 10^{-6} to 10^{-10} cm^2/sec [10]. Therefore, the calculated effective diffusivities are well within diffusivities reported in the literature.

Table 5. Effective surface diffusivities for Sr and Cs ions using PAN-4A and PAN-KCoFC ion exchangers.

Exchangers	Ions	Particle size [mm]	Ds,eff [cm2/sec]
PAN-4A	Sr	1.25	2.00x10-8
		1.52	2.50x10-8
		1.70	3.00x10-8
PAN-KCoFC	Cs	1.47	4.50x10-7
		1.63	5.00x10-7
		2.03	6.50x10-7

Adsorption in Fixed Bed

The experiments were carried out in the nitric acid solution of pH 2. Figure 7 presents the breakthrough curves for the three different flow rate. The total capacity was about 1.62 meq/g in flow rate of 3 mL/min. This value is about 60% of the saturation capacity obtained from Langmuir equations by batch experiments.

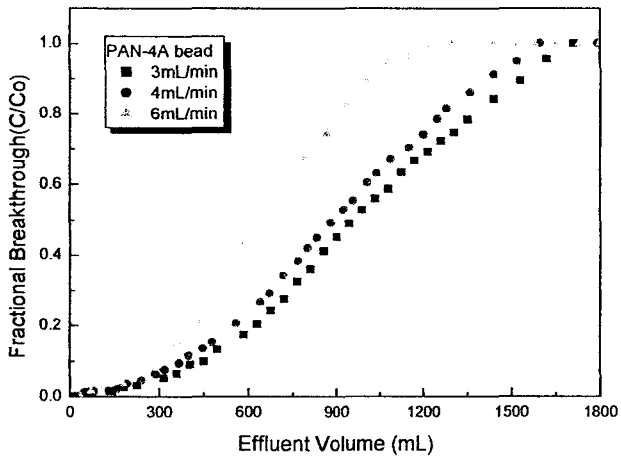

Figure 7. Influence of flow rate on the breakthrough curve.

CONCLUSIONS

PAN-4A composite ion exchanger was more selective for Sr ion than other cations and PAN-KcoFC composite ion exchanger had much higher ion exchange capacity for Cs ion than other cations. The ion exchange capacities obtained from Dubinin-Polanyi equation were 3.93 meq/g for Sr ion and 1.50 meq/g for Cs ion using PAN-4A and PAN-KcoFC ion exchangers, respectively. The modified Dubinin-Polanyi model fit the experimental data accurately in multi-component system. $D_{s,eff}$ values for Sr and Cs ions of PAN-4A and PAN-KcoFC ion exchangers were on the order of 10^{-8} cm^2/sec and 10^{-7} cm^2/sec, respectively.

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