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Competitive adsorption of Li, K, Rb, and Cs ions onto three ion-exchange resins

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ABSTRACT

Adsorption is one of the effective methods to recover or remove alkali metal ions from aqueous solutions. Current studies on the adsorption of alkali metal ions are mainly focused on the adsorption of one alkali metal ion. However, under natural conditions, alkali metal ions are usually coexisted. During separation processes, they compete with each other. In this study, competitive and noncompetitive adsorption of Li, K, Rb, and Cs ions onto three ion-exchange resins (D001, LSC-100, and LSC-500) of sodium form was investigated in batch experiments at 25°C. Compared with the noncompetitive adsorption, competitive adsorption of different alkali metal ions present with larger differences, in general. The adsorption from single and multiple solutions presents similar preference. Under both the noncompetitive and competitive adsorption conditions, for D001 resin, the separation factor was found to follow the order of $\beta_{\mathrm{Cs/Li}} > \beta_{\mathrm{Rb/Li}} > \beta_{\mathrm{K/Li}}$, on the contrary, for both LSC-100 and LSC-500 resins, it is $\beta_{\mathrm{Cs/Li}} < \beta_{\mathrm{Rb/Li}} < \beta_{\mathrm{K/Li}}$. The affinity sequence was explained by considering the hydration energy changes, the electrostatic attractions and complexation between the alkali metal ions and the resins. The results obtained would be helpful for the understanding of the competitive adsorption processes and the recovery or removal of one or more alkali metal ions from aqueous solutions.

Keywords: Alkali metal ion; Ion-exchange resin; Competitive adsorption; Separation factor

1. Introduction

Alkali metal elements, especially Li, Rb, and Cs, are of great importance for both material and environmental sciences. Lithium has been used in many areas, such as glasses, ceramics, batteries, rubbers, lubricants, pharmaceuticals, nuclear materials, etc. [1–3]. Lithium is found in brines, minerals, clays, seawater, and oil residues. In China, there are many salt lakes containing a large amount of lithium and recovering lithium from these salt lakes is of great importance.

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Rubidium has been considered for use in glasses, catalysts, thermoelectric devices, vacuum tubes, photocells, etc. It is also extensively studied as a potential heat transmission material in space vehicles, as fuel in motors of ionic propulsion, as electrolyte in low-temperature alkaline batteries, etc. Cesium is, of comparatively high average value used in the production of pharmaceuticals, photoelectronic conversion elements, optical crystals, optical glass, etc. As natural resources, rubidium and cesium are widely distributed as elements accompanying other alkali metals, but is not very abundant in the Earth's crust.

Cesium is also of great environmental concern. ^{137}Cs and ^{135}Cs are fission products that are typically present in nuclear wastes. Because of their long half-lives and high solubility, these radionuclides are considered among the most hazardous in the spent nuclear fuel [4,5].

Adsorption is one of the effective methods to extract or remove alkali metal ions from aqueous solutions. Current studies of the adsorption of alkali metal ions are mainly focused on the adsorption of one kind of alkali metal ion, especially Li or Cs ion. However, under natural conditions, alkali metal ions usually coexist. And, the adsorption of a particular alkali metal ion will be affected by the presence of other alkali metal ions. Therefore, it is necessary to study the competitive adsorption behavior of the alkali metal ions in aqueous solutions.

2. Experimental

In the adsorption experiments, three resins of sodium form were used (Table 1), and 0.3 g of the wet resins was mixed with 10 mL of metal ion solutions. In the single-element systems, the metal concentration was 0.01mol/L. In multi-element systems, each Li, K, Rb, and Cs metal ion concentration was 0.0025 mol/L (i.e. total metal concentration was 0.01 mol/L). All the adsorption experiments were carried out at 25℃ in a SHA-C shaking water bath (Changzhou Guohua Co., Ltd., China) with a shaking speed of 100 rpm.

Table 1
Resins used for the adsorption experiments

Resin	D001	LSC-100	LSC-500
Matrix	Styrene-DVB	Styrene-DVB	Styrene-DVB
Functional group	$–SO_3^-$,	$–N(CH_2COO^-)_2$	$–NHCH_2PO_3^{2-}$
Particle diameter (mm)	0.4–0.7	0.4–1.0	0.4–1.0
Water content (%)	48.6	56.7	55.2
Adsorption capacity (mmol/g)	⩾4.35	⩾5.5	⩾5.5

Metal ion concentrations were determined using an ICS-1100 ionic chromatograph (Dionex). The adsorption amount of the alkali metal ions onto the resins was calculated by a mass–balance relationship:

$$q = \frac{V(C_0 - C)}{m} \tag{1}$$

where q is the adsorption amount of metal ions onto the resins (mmol/g) at time t, V is the volume of the solution (L), m is the mass of the dry resins (g), and C_0 and C are metal ion concentrations in solutions at beginning and time t (mmol/L).

3. Results and discussion

3.1. Noncompetitive and competitive adsorption results

The results for the noncompetitive and competitive adsorption are shown in Figs. 1 and 2. respectively. In all the experimental conditions, the adsorption reaches equilibrium in about 30 min.

In order to have a total comparison for the adsorption, separation factors were calculated according to the following equations based on the adsorption data at 2 h:

$$\text{Separation factor } \beta_{M/Li} = (q_M/C_M)/(q_{Li}/C_{Li}) \tag{2}$$

where M denotes K, Rb, or Cs. The results are listed in Table 2 and shown in Fig. 3.

As shown in Figs. 1–3 and Table 2, the general adsorption comparison results could be summarized as follows:

(1) Compared with the noncompetitive adsorption, competitive adsorption of different alkali metal ions present larger differences, in general.
(2) For D001 resin, the separation factor was found to follow the order of $\beta_{Cs/Li} > \beta_{Rb/Li} > \beta_{K/Li}$ under both the noncompetitive and competitive adsorption conditions. The order of preference for the adsorption is $Cs^+ > Rb^+ \sim K^+ >> Li^+$.
(3) For both LSC-100 and LSC-500 resins, the separation factor was found to follow the order of $\beta_{Cs/Li} < \beta_{Rb/Li} < \beta_{K/Li}$ under both the noncompetitive and competitive adsorption conditions. For

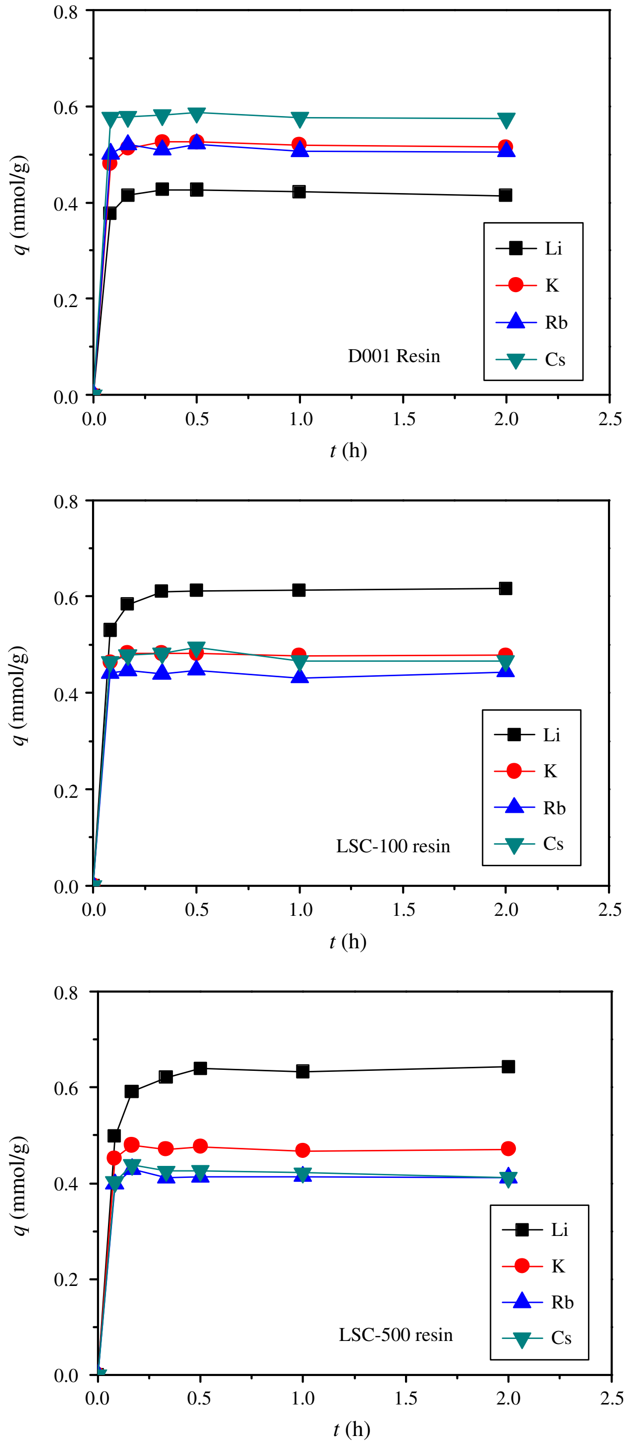

Fig. 1. Comparison of noncompetitive adsorption in single component solutions.

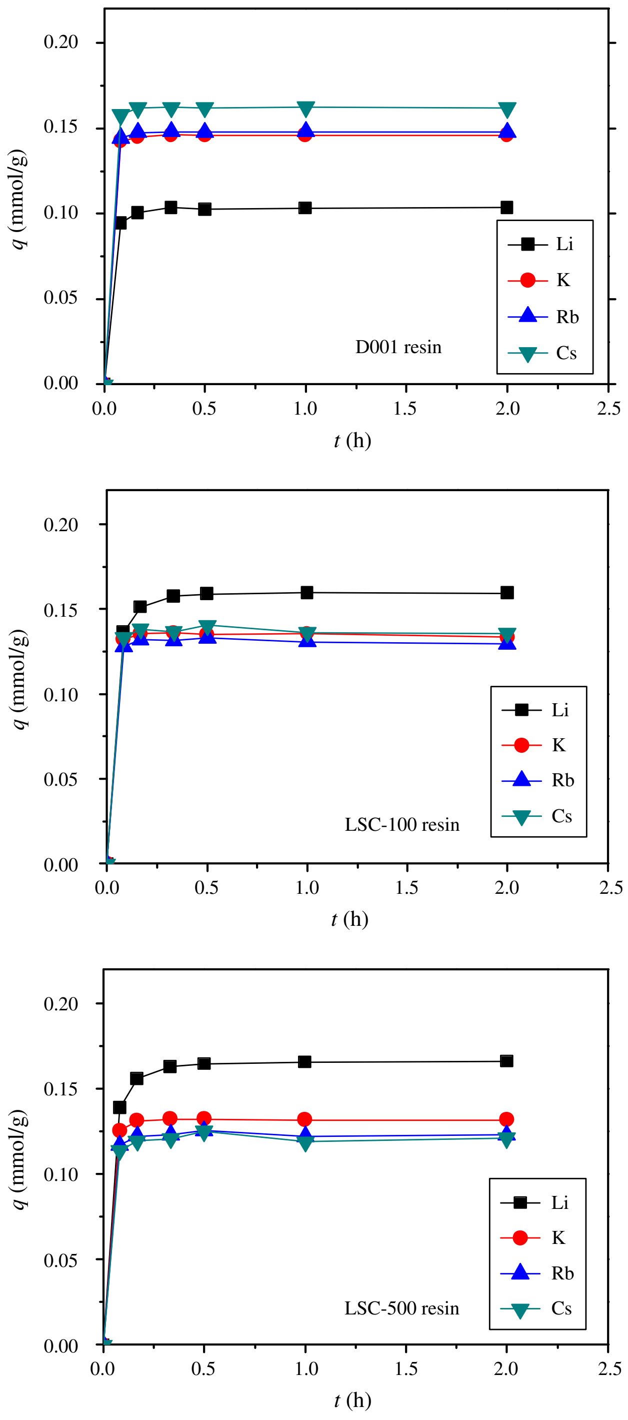

Fig. 2. Comparison of competitive adsorption in multi component solutions.

LSC-100 resin, the order of preference for the adsorption is $Li^+ >> K^+ \sim Rb^+ \sim Cs^+$. For LSC-500 resin, the order of preference for the adsorption is $Li^+ >> K^+ > Rb^+ \sim Cs^+$.

Generally speaking, LSC-100 and LSC-500 resins present with the same preference, on the contrary, D001 resin presents with the reverse preference.

Table 2
Separation factors for the adsorption under different conditions

Resin	Single component solution			Multi component solution		
	$\beta_{K/Li}$	$\beta_{Rb/Li}$	$\beta_{Cs/Li}$	$\beta_{K/Li}$	$\beta_{Rb/Li}$	$\beta_{Cs/Li}$
D001	3.30	3.38	3.91	3.55	4.19	5.28
LSC-100	0.25	0.19	0.17	0.12	0.11	0.10
LSC-500	0.19	0.13	0.10	0.094	0.077	0.062

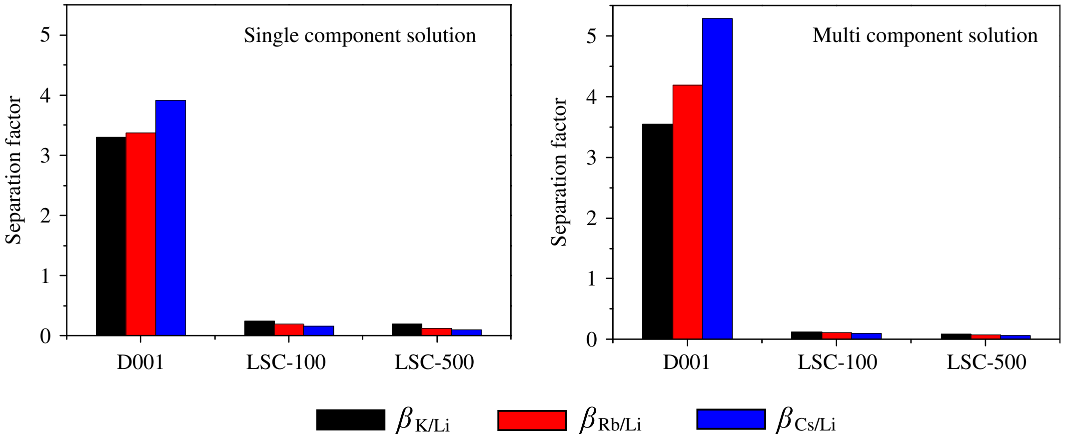

Fig. 3. Comparison of the separation factors under different adsorption conditions.

3.2. *Some information and explanation about the above adsorption results*

3.2.1. *The hydration of alkali metal ions and its relationship with the adsorption*

In aqueous solutions, metal ions interact with water to form clusters of $M^{x+}(H_2O)_y$. That is, metal ions associate with water molecules to form geometrically-defined hydration shells. Water molecules around metal ions exchange very quickly. For alkali metal ions, the exchange time of water molecules is longer around Li^+ ions and decreases with an increase in the ionic radius [6]. Metal ions with higher charge densities can bind larger water clusters more strongly than those with lower charge densities [7]. The strength of hydration shells also depends on the solution's ionic strength, pH, and temperature [8]. Alkali metal cations form a sequence known as the Hofmeister series. The Hofmeister series of Cs^+, K^+, Na^+, Li^+ orders cations from the least-hydrated to the most-hydrated [9].

Larger metal ions have softer hydration shells, while smaller ions have harder hydration shells. When metal ions transfer from an aqueous solution into another phase or environment, the metal ions may be able to rearrange or lose waters of hydration. During transport through the membrane, due to shear stress created by trans-membrane pressure, metal ions with relatively weak hydration potential may temporarily rearrange the water molecules in the hydration shells [8]. Studies with gel sieving chromatography have shown that small monovalent cations, for example, Li^+, Na^+, etc. flow through the gel matrix with water molecules attached, whereas the large monovalent cations including K^+, Rb^+, Cs^+, etc. adsorb to the nonpolar surfaces of the gel, a process which requires partial dehydration of the cations indicating that these cations bind the immediately adjacent water molecules weakly [7]. For the adsorption of alkali metal ions by muscovite, Li^+ ions are more likely to form outer-sphere complexes, on the contrary, K^+ and Cs^+ ions from inner-sphere complexes. That is, Li^+ ions are adsorbed with their original hydration shells. The water molecules around Cs^+ ions that were adsorbed to muscovite surfaces that seemed to avoid coordinating with Cs^+ ions on the surfaces [6].

During separation processes, the selectivity of metal ions has been suggested to relate with the hydration behavior of the metal ions. It was realized that when metal ions are confined within nanopores (biochannels, inorganic nanopores, etc.), the ionic hydration is much different from that in bulk solutions and has important effects on the ionic selectivity [10]. K^+- or Na^+-selective environments can be obtained if the coordination numbers of water molecules around the K^+ or Na^+ ions are constrained to be of the same value as that of bulk water [10]. The selectivity of K^+ over Na^+ ions for KcsA channel was suggested to relate with the hydration of the two cations in the nanochannel [11]. MacKinnon and his co-workers observed that K^+ ions have to lose part of their surrounding water molecules in the filter of KcsA channel. And this stripping of the coordination shell is important for the high K^+-selectivity of this channel [12]. Hydration has been suggested to play a role in the selectivity of 18-crown-6 towards K^+ ions [11]. The K^+ and Na^+ ions confined in the 18-crown-6/cation complexes are hydrated by the two nearest water molecules, one above and the other below the 18-crown-6/cation plane [11]. Na^+-zeolite-A has ion-exchangeable Na^+ ions that occupy six-membered and eight-membered oxygen rings. Within the rings, the Na^+ ions are accompanied by two or three water molecules. During ion-exchange reaction processes, each type of ring exhibits different affinities for the entering cations [13].

In this study, all the alkali metal ions present as hydrated ions in aqueous solutions, with Li^+ ions being the most hydrated and Cs^+ ions, the least hydrated. During ion-exchange processes with Na^+ ions on the resins, Li^+, K^+, Rb^+, and Cs^+ ions may change their hydration states or degrees, and such changes may be related with the ion-exchange selectivity.

3.2.2. *Effect of surface properties of adsorbents on adsorption*

Adsorbent surfaces are always to some extent, hydrated in aqueous solutions and the structure of the interfacial water is fundamentally different from that in the bulk solutions. James and Healy have developed a thermodynamic model of ion adsorption at oxide–solution interfaces. A distinction was made between the adsorption behavior of oxides with a low dielectric constant and those with a high dielectric constant [14]. The model demonstrated that low-dielectric oxide surfaces, such as quartz surfaces ($\varepsilon = 4.6$) will preferentially interact with less-hydrated cations, while strongly-hydrated ions will not as easily adsorb on such surfaces. Thus, the affinity of alkali metal cations towards the quartz surfaces follow a sequence of $Cs^+ > K^+ > Na^+ > Li^+$, the same sequence as their crystallographic radii. Cesium cations adsorb at the quartz–solution interfaces in higher quantities than lithium cations [9]. H^+ forms titanium silicate, $H_2Ti_2O_3SiO_4{\cdot}1.6H_2O$, also exchanges preferably large cations and exhibit a selectivity sequence of $Cs^+ > K^+ >> Na^+ > Li^+$ [15].

In this study, D001, LSC-100, and LSC-500 resins have the same Styrene-DVB Matrix, but different functional groups of $-SO_3^-$, $-N(CH_2COO^-)_2$, and $-NHCH_2PO_3^{2-}$, respectively. They should have different hydration behavior due to different functional groups. And, the differences in their hydration behavior will result in differences in their affinity towards different alkali metal ions.

3.2.3. *Explanation about the affinity sequence*

Hydrated radius (or effective radius) has been used to explain the ion selectivity. A larger hydrated radius means that the cationic center of the charge is farther from the surface. And therefore, the adsorbent–cation electrostatic interactions would be weaker [8,16]. However, selectivity by this mechanism alone assumes that the adsorbed cations are fully hydrated (i.e. as hydrated as they would be in aqueous phase), which may be valid on the surfaces which are in contact with the aqueous phase, but may not be valid in the interior regions of the solid phase. Xu and Harsh theoretically demonstrated that the hydrated radius may not be a good predictor of cation-exchange selectivity [17]. For example, the hydrated radius of Li^+ is larger than that of Na^+, however, there is no significant difference in the selectivity of montmorillonites (clay) for Li^+ vs. Na^+ [8,17].

Teppen and Miller [16] explained the cation-selectivity based on energy changes. For two cations of equal valence, the more weakly hydrated one will tend to partition into the subaqueous phase. Cations with lower hydration energies can reduce the water molecules in hydration shells relatively easier, hence can enter into the subaqueous phase more easily [16]. Cations with smaller entropies have a higher packing density of water molecules within their hydration shells and are able to hold their hydration shells more strongly exhibiting hard hydration shells. For the adsorption of cesium by synthetic clay–organic matter complexes, the strong affinity for cesium is due to the small hydration energy of the cation allowing it to lose its hydration water on adsorption [18].

In this study, for D001 resin, the separation factor was found to follow the order of $\beta_{Cs/Li} > \beta_{Rb/Li} > \beta_{K/Li}$ under both the noncompetitive and competitive adsorption conditions. The order of preference for the adsorption is $Cs^+ > Rb^+ \sim K^+ >> Li^+$. This is probably dominated by the electrostatic attractions between the $-SO_3^-$ groups of the D001 resin and the cations. From Cs^+ to Li^+ ions, their hydrated radius increases gradually, during adsorption, Cs^+ ions can reach to the D001 resin negative surfaces more closely, and therefore, there are stronger electrostatic attractions between Cs^+ ions and the D001 resin surfaces.

For both LSC-100 and LSC-500 resins, the separation factor was found to follow the order of $\beta_{Cs/Li} < \beta_{Rb/Li} < \beta_{K/Li}$ under both the noncompetitive and competitive adsorption conditions. For LSC-100 resin, the order of preference for the adsorption is $Li^+ >> K^+ \sim Rb^+ \sim Cs^+$. For LSC-500 resin, the order of preference for the adsorption is $Li^+ >> K^+ > Rb^+ \sim Cs^+$. Electrostatic attractions and hydration energy changes could not explain the observed affinity sequence of LSC-100 and LSC-500 resins. This affinity sequence is probably dominated by the complexation between alkali metal ions and the functional groups of $–N(CH_2COO^-)_2$ and $–NHCH_2PO_3^{2-}$, since they are stronger ligands than water and $–SO_3^-$ groups for complexation with metal ions.

4. Conclusions

Competitive and noncompetitive adsorption of Li, K, Rb, and Cs ions onto three ion-exchange resins (D001, LSC-500, and LSC-100) of sodium form was investigated in batch experiments at 25°C. The results could be summarized as follows:

(1) In all the experimental conditions, the adsorption reached equilibrium in about 30 min.
(2) Compared with the noncompetitive adsorption, competitive adsorption of different alkali metal ions present larger differences, in general.
(3) For D001 resin, the separation factor was found to follow the order of $\beta_{Cs/Li} > \beta_{Rb/Li} > \beta_{K/Li}$ under both the noncompetitive and competitive adsorption conditions. The order of preference for the adsorption is $Cs^+ > Rb^+ \sim K^+ >> Li^+$. This affinity sequence is probably dominated by the electrostatic attractions between the $–SO_3^-$ groups of the D001 resin and the cations.
(4) For both LSC-100 and LSC-500 resins, the separation factor was found to follow the order of $\beta_{Cs/Li} < \beta_{Rb/Li} < \beta_{K/Li}$ under both the noncompetitive and competitive adsorption conditions. For LSC-100 resin, the order of preference for the adsorption is $Li^+ >> K^+ \sim Rb^+ \sim Cs^+$. For LSC-500 resin, the order of preference for the adsorption is $Li^+ >> K^+ > Rb^+ \sim Cs^+$. This affinity sequence is probably dominated by the complexation between alkali metal ions and the functional groups of $–N\ (CH_2COO^-)_2$ and $–NHCH_2PO_3^{2-}$.

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