Efficient Adsorption Performance of Lithium Ion onto Cellulose Microspheres with Sulfonic Acid Groups

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Abstract: The separation of Li\(^+\) from an aqueous solution has received much attention in recent years because of its wide application in batteries and nuclear energy. A cellulose microsphere adsorbent with sulfonic acid groups (named as CGS) was successfully prepared by the pre-irradiation-induced emulsion graft polymerization of glycidyl methacrylate onto cellulose microspheres through subsequent sulfonation and protonation. The adsorption performance of Li\(^+\) onto the CGS adsorbent is investigated in detail. The as-prepared CGS adsorbent exhibited fast adsorption kinetics and a high adsorption capacity of Li\(^+\) (16.0 mg/g) in a wide pH range from 4 to 10. The existence of K\(^+\) and Na\(^+\) was found to have the ability to affect the adsorption capacity of Li\(^+\) due to the cation-exchange adsorption mechanism, which was further confirmed by X-ray photoelectron spectroscopy (XPS). The column adsorption experiment indicated that the adsorption capacity of CGS agreed well with the batch adsorption, and a fast desorption could be obtained in 10 min. It is expected that CGS has potential usage in the adsorption separation of Li\(^+\) from an aqueous solution.

Keywords: Li\(^+\) adsorption; cellulose microsphere adsorbent; radiation synthesis; ion-exchange mechanism

1. Introduction

Lithium has been widely studied in recent decades due to its wide applications in lithium secondary batteries [1], catalysts [2], and nuclear energy [3]. It is important to separate lithium from brine and to recover lithium from a spent solution by using an environmentally-friendly, simple, and low cost method [4]. Among the processes for lithium separation, such as adsorption, solvent extraction [5,6], precipitation [7] and electrochemical methods [8,9], the adsorption process is considered to be a promising method to separate lithium at a large scale with a high efficiency.

Several adsorbents such as lithium manganese oxides (LMOS), ion sieves, H\(_2\)TiO\(_3\) [10], and ion-imprinted polymers [11] have been prepared for the adsorption of lithium. Among them, the most common inorganic adsorbents are the LMOS [12–14] and ion sieves, which have good adsorption capacities and selectivities [15]. However, these adsorbents with powder forms cannot be practically used due to the loss of adsorbents in their applications [16,17]. To overcome this disadvantage, an ion-sieve powder has been immobilized onto polymers such as membranes [16], foams [18], fibers and spheres [19] by using poly(vinyl chloride), polyacrylonitrile, poly(vinylidene fluoride)
and polyacrylamide as binders. Nevertheless, these materials still have some weaknesses such as slow adsorption kinetics, complicated synthetic routes and non-biodegradability, which limit their practical application.

Thus, it is important to develop an environmentally-friendly adsorbent with a high adsorption capacity, fast adsorption kinetics, good biodegradability, and reusability. A microcrystalline cellulose microsphere (CMS) is a suitable substrate for adsorbents due to its good biodegradability, renewability, low cost [20], and spherical morphology. However, due to the low adsorption capacity of Li\(^+\) onto raw cellulose, some functional groups should be introduced to enhance its adsorption performance. Radiation-induced graft polymerization is a convenient way to modify polymer materials with a certain shape [21–23] and has been proven as a green, fast, effective, and environmentally-friendly method in the modification of cellulose [24–29]. Some research about the radiation grafting of glycidyl methacrylate (GMA) onto cellulose has been reported in literatures [26,28,30]. Recently, cellulose microspheres that contained crown-ether groups were synthesized via gamma-radiation-induced grafting in our previous work, and this crown-ether modified CMS could be used to selectively separate lithium-ions and their isotopes [31]; however, the adsorbent in this method has a low adsorption uptake for Li\(^+\) in an aqueous solution. In order to separate the Li\(^+\) from an aqueous solution, we used a cellulose microsphere adsorbent with sulfuric acid (named CGS) [27] that was prepared through the pre-irradiation-induced emulsion grafting of the GMA onto the CMS, followed by a sulfonation and protonation reaction. We found that the cations of ionic liquids can be efficiently adsorbed onto CGS by an ion exchange mechanism [27]. Thus, CGS is expected to be good adsorbent for Li\(^+\). In this work, the kinetics and isotherm of the adsorption of Li\(^+\) onto CGS in an aqueous solution are investigated and compared with the commercial cation exchange resin, DIAION SK1B resin. Additionally, the effects of the solution’s pH and the presence of various cations and anions on the adsorption performance are studied in detail. Furthermore, the adsorption mechanism was investigated by X-ray photoelectron spectroscopy (XPS), the reusability of the CMS adsorbent was studied in five consecutive circles, and column adsorption was measured to test its feasibility in column separation of Li\(^+\) from the aqueous solution, the results of all of which are analyzed herein.

2. Materials and Methods

2.1. Materials and Reagents

CMSs with an average particle size of 230 µm were obtained from Asahi Kasei Chemicals Corporation, Japan. DIAION SK1B resins (a commercial cation exchange resins containing a sulfonic group) were obtained from Mitsubishi Chemicals Corporation, Japan. Glycidyl methacrylate, LiSCN, and LiCl (purity >99%) were purchased from J&K Company (Beijing, China). All the other chemicals were analytical grade and used without further purification, and tri-distilled water was used throughout the experiments.

2.2. Instruments and Characterization

The content of S in CGS was obtained in an elemental analyzer (Thermo Flash EA 1112, Waltham, MA, USA). Micro-FTIR analyses of the CMS, CGG (cellulose microspheres grafted by GMA) and CGS were performed with a Nicolet (Magna-IR 750, Waltham, MA, USA) spectrometer. The spectra were recorded in the absorbance mode in the wavenumber range of 4000–600 cm\(^{-1}\). XPS experiments were carried out on an AXIS-Ultra instrument (Krato Analytical, Manchester, UK) with the use of monochromatic Al K\(\alpha\) radiation (225 W, 15 mA, and 15 kV) and low energy electron flooding for charge compensation. All data were analyzed with the CASA XPS software. The morphology of the dried CMS, CGG and CGS samples were observed with scanning electron microscopy (SEM) (Hitachi S-4800, Tokyo, Japan) at an accelerating voltage of 1 kV after gold coating.
2.3. Preparation of CGS

The adsorbent was prepared according to our previous work [27], and its synthetic route is illustrated in Scheme 1.

![Scheme 1. The synthetic route of the CGS (cellulose microsphere adsorbent with sulfuric acid) adsorbent.](image)

2.3.1. Radiation-Induced Emulsion Grafting of GMA onto Cellulose Microspheres

In the grafting step, 1.0 g of a dried CMS was irradiated in air with gamma ray from a $^{60}$Co source (Peking University, Beijing, China) at a dose rate of 380 Gy/min for 20 kGy (which was traced by a Fricke dosimeter). Then, the irradiated CMS was immersed into a 5 wt% GMA aqueous emulsion (with 0.5 wt% Tween 20). After being bubbled with Ar to get rid of O$_2$, the grafting reaction was carried out in a shaker at 50 °C and 140 rpm for a period of time. The residual monomer and homo-polymer were removed by washing with acetone and water for three times, respectively. The as-prepared microspheres were then dried in a vacuum at 45 °C for 4 h. The resulting samples were washed with distilled water, followed by acetone. Finally, the CGS microspheres were then dried in a vacuum oven.

The sulfonated microspheres were separated and washed with water three times. The protonation of the microspheres was then carried out by using 50 mL of 2 mol/L H$_2$SO$_4$ in a shaker (120 rpm) at 50 °C for 4 h. The resulting samples were washed with distilled water, followed by acetone. Finally, the CGS was obtained by drying to a constant weight in a vacuum oven.

The Li$^+$ concentration was analyzed at a certain time interval by inductively coupled plasma-mass spectrometry.

The degree of grafting (DG) was calculated as follows:

$$DG(\%) = \frac{W_g - W_0}{W_0} \times 100$$  \hspace{1cm} (1)

where $W_0$ and $W_g$ are the weights of the initial cellulose microspheres and dried grafted cellulose microspheres, respectively.

CGGs with different DG values (26% and 63%) were prepared with varying reaction times and used for further chemical modification.

2.3.2. Chemical Modification of CGG

Typically, 1.0 g of the CGG was added into a solution containing 1.26 g of Na$_2$SO$_3$, 1.89 g of 2-propanol, and 9.45 g of H$_2$O, and the reaction was carried out in a shaker (120 rpm) at 50 °C for 20 h. The sulfonated microspheres were separated and washed with water three times. The protonation of the microspheres was then carried out by using 50 mL of 2 mol/L H$_2$SO$_4$ in a shaker (120 rpm) at 50 °C for 4 h. The resulting samples were washed with distilled water, followed by acetone. Finally, the CGS was obtained by drying to a constant weight in a vacuum oven.

CGGs with DG values of 26% and 63% were used for sulfonation and protonation, and the corresponding products were named as CGS-I and CGS-II, respectively.

2.4. Adsorption of Li$^+$ onto CGS Adsorbents and DIAION SK1B Resin

Adsorption experiments were carried out in a flask that contained 20 mg of adsorbents and 20 mL of the Li$^+$ solution. The flask was then placed in a shaker at 30 °C and 140 rpm for a period of time.
The Li\(^+\) concentration was analyzed at a certain time interval by inductively coupled plasma-atomic emission spectrometry (ICP-AES, Prodigy, America) at 30 °C. The standard deviation of the test results given by the ICP-AES was within 3%. The Li\(^+\) uptake was calculated as follows:

\[
\text{Li}^+\text{uptake} = (c_0 - c_e) \times \frac{V}{m} \tag{2}
\]

where \(c_0\) and \(c_e\) are the Li\(^+\) concentrations before and after adsorption, respectively; \(V\) is the volume of the aqueous solution used for adsorption; and \(m\) is the weight of the added CGS adsorbents.

The adsorption time was set as 12 h except for the samples in the kinetics study, and the concentration of the Li\(^+\) was fixed at 140 ppm except for the samples in the adsorption isotherm, where the concentration was varied. The lithium salt was LiCl unless otherwise stated. A solution with pH of 10 was used in all experiments except for the study of the influence of pH.

2.5. Regeneration of the Adsorbent

After adsorption, the residual solution was removed, and 20 mL of a 1 mol/L HCl solution was added to the flask, followed by 24 h of shaking in the shaker at 30 °C and 140 rpm. Then, the adsorbents were washed three times with water. The adsorption and desorption experiments were conducted in five consecutive circles. The adsorption experiments were carried out by a very similar procedure to that shown in Section 2.4.

2.6. Column Adsorption

The column adsorption was carried out at 25 °C. 1.30 g of CGS-II was swelled in water and then poured into a glass column (\(l = 101\) mm, \(d = 5.32\) mm). In the absorption experiment, an Li\(_2\)SO\(_4\) solution (\(C_i = 19.8\) ppm Li) was pumped into the column at 2.0 mL/min. The Li\(^+\) concentration of the effluent (\(C_t\)) was measured by using ICP-AES at a premeditated schedule to get a complete breakthrough curve. In the desorption experiment, the Li-loaded column was first washed with deionized water to remove unbound Li\(^+\), followed by the addition of 1 mol/L HCl at 2.0 mL/min to get the desorption curve.

3. Results and Discussions

3.1. Preparation of the CGS Adsorbents

When the CMS was irradiated by \(^{60}\)Co gamma ray in air, trapped free radicals were generated in the crystalline area of cellulose, and peroxides were also formed in the amorphous phase of cellulose due to the presence of oxygen [32], which is very suitable for the grafting of a monomer [24]. When heated at 50 °C, the radicals trapped inside the crystalline phase of cellulose migrated to the surface and initiated the graft copolymerization of the GMA, forming the grafting chains on the cellulose microspheres. The CGGs with DG values of 26% and 63% were prepared by controlling the grafting reaction time.

3.2. Characterizations of the CGS Adsorbents

3.2.1. FTIR and XPS Analysis

Both FTIR and XPS were used to investigate the change in the chemical structures of different samples. The micro-FTIR spectra of the CMS, CGG and CGS are shown in Figure 1A. After the pre-irradiation-induced emulsion grafting of GMA, a strong peak at wavenumber 1731 cm\(^{-1}\) in the CGG was found that corresponded to the characteristic absorption peak of a C=O group in the poly(glycidyl methacrylate) (PGMA). Moreover, the bands at 1258 and 909 cm\(^{-1}\) were also attributed to the epoxy group in the PGMA, indicating a successful grafting of the PGMA onto the CMS. For the CGS, a new peak at 1043 cm\(^{-1}\) appeared that was assigned to the S=O group, and the intensity of the epoxy group at 909 cm\(^{-1}\) decreased, thus indicating the ring-opening reaction of the PGMA in the
CGG. The results were similar to those of our previous report [27]. Micro-FTIR results confirmed a successful synthesis of the CGG and the CGS.

![Micro-FTIR spectra](image)

Figure 1. (A) Micro-FTIR spectra of (a) CMS (microcrystalline cellulose), (b) CGG cellulose microspheres grafted with GMA (glycidyl methacrylate), and (c) CGS; (B) XPS (X-ray photoelectron spectroscopy) diagram of (a) CMS, (b) CGG (degree of grafting (DG) = 63%), and (c) CGS-II.

The XPS patterns of the CMS, CGG and CGS are shown in Figure 1B. For the CMS, only peaks of C 1s and O 1s could be observed in XPS. Since the elements in the PGMA were similar with those of the CMS, no new peaks beside C 1s and O 1s were observed in the CGG. In contrast, after sulfonation and protonation, new peaks of S 2s and S 2p at 229 and 165.5 eV, respectively, appeared, and it further identified the successful sulfonation; the XPS analysis agreed well with the micro-FTIR results.

3.2.2. SEM Observation

The morphology of the adsorbent is of great importance for the adsorption properties of microspheres. SEM images of the CMS, CGG and CGS are shown in Figure 2. For the CMS, the average diameter was about 230 µm. For the grafting of the PGMA onto the CMS, the diameter of the CGG increased to 340 µm, and it had a DG value of 63%, indicating the grafting of the PGMA on the surface of the CMS. Finally, the diameter of the microspheres was increased to 390 µm after sulfonation and protonation, and the surface of the CGS became rougher than that of the CGG. This was attributed to the chemical modification of the PGMA on the surface of the CGG. The change in the SEM images of the microspheres after the grafting, the sulfonation, and the protonation also confirmed the success of the modification process from the CMS to the CGS. After the grafting and chemical
modification, the resultant microsphere still kept its spherical morphology, which showed its potential use in column adsorption [29].

![Figure 2. SEM images of different samples. (A) CMS; (B) CGG (DG = 63%); (C) CGS-II.](image)

### 3.3. Adsorption Performance of Li⁺ onto CGS Adsorbents

Both the batch and column adsorption performance of Li⁺ onto the resultant CGS adsorbents were investigated for evaluating the adsorption capacity of the CGS adsorbent for Li⁺.

#### 3.3.1. Adsorption Kinetics and Isotherms

It is very important to study the adsorption kinetics for practical use. As shown in Figure 3A, a fast adsorption process in the first 30 min was observed for both CGS-I and CGS-II. Then, a slow process occurred from 30 to 40 min, and finally both CGS-I and CGS-II reached an adsorption equilibrium within 40 min, showing a similar behavior when the CGS adsorbents were applied to ionic liquids adsorption [27]. Compared with existing Lithium adsorbents, the CGS was much faster than H₂TiO₃, some ion-sieves [8,33], and the DIAION SK1B ion exchange resin (see Table 1), which is very important for the practical application of adsorbents. The data of the kinetics curves were fitted by the pseudo-first-order and pseudo-second-order models, which are shown in Equations (3) and (4), respectively:

\[
\log (q - q_t) = \log q - \frac{k_1}{2.303} t
\]

\[
\frac{t}{q_t} = \frac{1}{q_i} + \frac{1}{q^2 k_2}
\]

where \(q_t\) and \(q\) are the Li⁺ uptakes at the time \(t\) and equilibrium, respectively; \(k_1\) (min⁻¹) and \(k_2\) (g mg⁻¹ min⁻¹) are the rate constants of the pseudo-first-order and the pseudo-second-order model, respectively. Huang Y. et al. [34] pointed out that \(q\) is not a constant during the adsorption process as the concentration of the solution changes. Here, an initial solution with a high concentration was used in the adsorption kinetics study, and the concentration decreased to less than 10% during the experiment, which could be ignored. Therefore, \(q\) values are considered to be constant in this work.

The linear fits of the kinetic data are shown in Figure 3B, and the fitting results are presented in Table 2. For both CGS-I and CGS-II, the pseudo-second-order model gave better fitting parameters compared to those of the pseudo-first-order model. Furthermore, the \(q\) values of CGS-I and CGS-II obtained from the pseudo-second-order model were closer to the experimental equilibrium value on the curve, indicating that the rate-limiting step could be chemical sorption involving the exchange of ion between the CGS and the Li⁺ [35]. In order to reach an adsorption equilibrium, 12 h was used as the contact time in the experiment.
Figure 3. (A) Adsorption kinetics of the CGS adsorbent for Li\(^+\) adsorption; (B) linear fit of the kinetic data for CGS-I and CGS-II; and (C) adsorption isotherm of the CGS adsorbent for Li\(^+\) adsorption.
Table 1. Time to reach equilibrium and maximum adsorption capacity for some Li$^+$ adsorbents.

| Adsorbents                                    | Equilibrium Time | Maximum Adsorption Capacity (mg/g) | Ref |
|-----------------------------------------------|------------------|------------------------------------|-----|
| H$_2$TiO$_3$                                  | 10 h             | 32.6                               | [10]|
| Iron-Doped Manganese Oxides                   | 6 h              | 28                                 | [33]|
| H$_{1.6}$Mn$_{1.6}$O$_4$/poly(acrylonitrile) | -                | 10.3                               | [36]|
| Lewatit K2629/TP 207/TP 208 resin             | <30 min          | 1.23–2.54                          | [37]|
| DIAION SK1B resin                             | 3 h              | 0.23                               | This work |
| CGS                                           | 40 min           | 16.0                               | This work |

Table 2. Kinetic results of CGS-I and CGS-II for Li$^+$ adsorption (LiCl, pH = 10).

| Sample   | Pseudo-First-Order | Pseudo-Second-Order |
|----------|--------------------|---------------------|
|          | $k_1$ (min$^{-1}$) | $q$ (mg/g) | $R^2$ | $k_2$ (g mg$^{-1}$ min$^{-1}$) | $q$ (mg/g) | $R^2$ |
|----------|--------------------|-------------|------|-----------------|-------------|------|
| CGS-I    | 16.8               | 7.84        | 0.948| 0.0017          | 6.72        | 0.990|
| CGS-II   | 20.7               | 20.1        | 0.970| 0.0082          | 15.6        | 0.987|

The adsorption isotherm curves of the CGS are presented in Figure 3C. Two typical isotherm models, Langmuir and Freundlich, expressed as Equations (5) and (6), respectively, were used to fit the data, where $q$ (mg/g) is the Li$^+$ uptake at the corresponding Li$^+$ concentration $c$ in the solution and $q_e$ is the adsorption capacity. $K_L$ and $K$ (L/mg) represent the Langmuir and Freundlich constants, respectively, and in the Freundlich model, $1/n$ represents a coefficient connected with heterogeneity.

\[
\text{Langmuir model : } \frac{c}{q} = \frac{c}{q_e} + \frac{1}{K_L q_e} \quad (5)
\]

\[
\text{Freundlich model : } q = K c^\frac{1}{n} \quad (6)
\]

As shown in Table 3, when fitted by the Langmuir model, both CGS-I and CGS-II had much higher $R^2$ values, indicating that the adsorption of Li$^+$ corresponded to a saturated monolayer of cations [38] on the surface of the CGS. The adsorption capacities of CGS-I and CGS-II were 8.02 and 16.0 mg/g, respectively, which was relatively high compared to the other Li$^+$ adsorbents (see Table 1). In addition, for CGS-II, a removal of 6 mg/g of Li$^+$ was still obtained at a low initial concentration of Li$^+$ (11 mg/L), which demonstrated a potential use in the separation of Li$^+$ under low concentrations. Similar isotherm adsorption behavior was also observed in the lithium manganese oxide adsorbent [14]. Furthermore, the adsorption capacity increased with increasing the content of sulfonic acid group in the CGS.

Table 3. Sample information and isotherm results of CGS-I and CGS-II for Li$^+$ adsorption (LiCl, pH = 10).

| Sample   | S Content (%) | Langmuir R$^2$ | $q_e$ (mg/g) | Freundlich R$^2$ | $1/n$ |
|----------|---------------|----------------|--------------|------------------|-------|
| CGS-I    | 5.7           | 0.999          | 8.02         | 0.938            | 0.140 |
| CGS-II   | 8.0           | 0.996          | 16.0         | 0.988            | 0.287 |

3.3.2. Effect of Solution pH

The pH of the solution is an important parameter for the adsorption properties of Li$^+$ [17]. As shown in Figure 4, the Li$^+$ uptake decreased at pH values below 4, which was attributed to the competition of H$^+$ against Li$^+$ for the active sites on the CGS adsorbent. The Li$^+$ uptake also decreased when the pH increased to 11.2 due to the competition between Na$^+$ and Li$^+$. Furthermore, at a pH above 13, OH$^-$ destroys the structure of cellulose microspheres [39], so adsorption under a higher pH
was not tested. However, it should be noted that the CGS had a good adsorption property in a wide pH range from 4 to 10, indicating its potential for usage in the separation of Li$^+$. 

3.3.3. Effect of Different Cations and Anions of Salts

Na$^+$ and K$^+$, which are common coexisting ions with Li$^+$ in aqueous solutions, were both chosen as the models to investigate the influence of the cations on the adsorption of Li$^+$ onto the CGS. As shown in Figure 5A, the adsorption of Li$^+$ decreased with the increase of concentration of Na$^+$ or K$^+$. This was attributed to the competition between Li$^+$ and Na$^+$ or K$^+$. With the increase of size of ions, the effect on adsorption uptake of Li$^+$ increased. The effect of different anions is shown in Figure 5B by using various lithium salts such as LiCl, Li$_2$SO$_4$, LiNO$_3$, LiSCN. Herein, we set the relative capacity, using LiCl as an Li$^+$ salt, as 100%. There was no obvious difference in the adsorption capacities when using LiCl, Li$_2$SO$_4$, LiNO$_3$ and LiSCN as Li$^+$ salts. The influence of cations and anions on the adsorption demonstrated a cation-exchange interaction between Li$^+$ and the CGS during the adsorption.
In order to further study the adsorption mechanism of the CGS towards Li$^+$, the XPS of the CGS before and after the Li$^+$ adsorption as well as after the desorption were measured. As shown in Figure 6A, a peak around binding energy (B.E.) of 55.6 eV occurred after the adsorption of Li$^+$, which was attributed to the Li 1s group \[40\]. Moreover, the B.E. of the O and S groups in the CGS did not change after the adsorption of Li$^+$, indicating that no complexation between O or S and Li$^+$ occurred during the adsorption. After desorption by 1 mol/L HCl, the peak around the B.E. of 55.6 eV disappeared. No new peaks appeared because H$^+$ was exchanged onto the −SO$_3^-$ group. All the above results confirmed the cation-exchange mechanism for the adsorption of Li$^+$ onto the CGS.

In practical usage, adsorbents should have a good reusability. The as-prepared CGS-II was tested by using five consecutive adsorption—desorption cycles. As shown in Figure 6B, the adsorption performance declined slowly to 89% in the first three cycles. However, CGS-II still maintained 83% of its performance after five cycles. It was illustrated that the resultant CGS had a good stability during the adsorption and desorption process and could be easily reused.
3.3.5. Column Adsorption Study of CGS Adsorbents for Li$^+$

To simulate a practical application, a primary column adsorption experiment was carried out, and the results are shown in Figure 7. The breakthrough curve follows the typical S-shape curve \[41\]. In the first 200 min, no Li$^+$ signal was detected by ICP-AES, which meant that almost all the Li$^+$ was adsorbed by the CGS column. The breakthrough ($C_t/C_i = 10\%$) occurred at 325 min, the saturation ($C_t/C_i = 90\%$) occurred at 456 min, and equilibrium ($C_t/C_i = 100\%$) occurred at about 600 min during the adsorption of Li$^+$ onto CGS-II. Correspondingly, the Li$^+$ adsorption capacities of CGS-II at breakthrough time, saturation time and equilibrium time were determined to be 9.80, 11.5 and 11.8 mg/g, respectively. The equilibrium adsorption capacity agreed well with that obtained in the batch experiment of CGS-II. The desorption curve shows a sharp elution peak. After a period of time, 80\% (9.37 mg/g) of the adsorbed Li$^+$ could be desorbed, showing a reasonable agreement with the regeneration experiment results. It is worth mentioning that 98\% of the desorption capacity was achieved in 10 min, which indicates the good enrichment effect of CGS-II adsorbent towards Li$^+$ in the aqueous solution.

![Breakthrough curve of adsorption of Li$^+$ onto CGS-II. Desorption curve of Li$^+$ from CGS-II. Inset: a magnification of the first 20 min.](image-url)
4. Conclusions

A cellulose microsphere-adsorbent that contained sulfonic acid groups for Li\(^{+}\)—the CGS—was successfully prepared by the pre-irradiation-induced emulsion grafting of GMA onto a CMS, followed by sulfonation and protonation. The adsorption behavior of Li\(^{+}\) onto the CGS was well investigated. The adsorption process of Li\(^{+}\) onto the CGS had faster adsorption kinetics than commercial cation exchange resin and some ion sieves reported in the literatures. The adsorption isotherm agreed well with the Langmuir model, with a lithium adsorption capacity of 16.0 mg/g for CGS-II. The CGS adsorbents had good adsorption properties in a wide pH range from 4 to 10, which covers the pH of brine. The addition of Na\(^{+}\) and K\(^{+}\) led to a decrease in the adsorption capacity of Li\(^{+}\) due to the competition for the active sites, while different anions had little influence on adsorption, indicating that the cation-exchange mechanism was dominant in the adsorption of Li\(^{+}\) onto the CGS. The CGS could be easily regenerated and reused in five adsorption–desorption cycles, and the column adsorption study showed the quick adsorption and desorption of Li\(^{+}\), which illustrates a potential application in the separation of Li\(^{+}\) ions from an aqueous solution. Consequently, this work provides a feasible and low cost route for Li\(^{+}\) removal.

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