**Polyacrylonitrile/crown ether composite nanofibres with high efficiency for adsorbing Li(I): experiments and theoretical calculations**

**Tao Ding a, Qian Wu****b\*, Mianping Zheng b, Zhen Nie b\*, Min Li c, Suping Peng a，Yunsheng Wang b, Xudong Yu d, Cheng Qian b, Si Tang c, Mingliang Wang b**

*a College of Geosciences and Surveying Engineering, China University of Mining and Technology, Beijing 100083, China*

*b MLR Key Laboratory of Saline Lake Resources and Environments, Institute of Mineral Resources, Chinese Academy of Geological Sciences, Beijing 100037, China*

*c School of Chemistry and Chemical Engineering,* *Chongqing University of Science and Technology, Chongqing 401331, China*

*d College of Materials and Chemistry & Chemical Engineering, Chengdu University of Technology, Chengdu 610059, China*

Co-corresponding author: Qian Wu and Zhen Nie, E-mail: wuqian0516@163.com; nieezhen518@163.com, phone number: +86 10 6899 2231

**Text S1.** List of chemicals

**Text S2.** Characterization

**Text S3.** Sorption experiments

**Text S4.** Computational method

**List of Figures**

**Fig. S1** Adsorption kinetics of Li(I) ions onto PAN-CE@SiO2, pseudo-first-order (a) and pseudo-second-order kinetics(b).

**List of Table**

**Table S1** Elements contents in the real saltlake brine Li(I) in this work.

**Table S2** The calculated parameters for the adsorbents before and after adsorption

**Text S1.** List of chemicals

SiO2, Lithium chloride, Sodium hydroxide, Potassium chloride, KH560, N,N-dimethyl formamide (DMF), 2M12C4, ethanol, Sodium chloride, Magnesium chloride and Polyacrylonitrile (PAN) were all purchased from Sinopharm Chemical Reagent Co., Ltd., China. All other reagents were of analytical grade and received from Beijing Chemical Plant, China.

**Text S2.** Characterization

The surface morphologies of the obtained compounds were examined using scanning electron microscopy (SEM, Hitachi S4800, Japan). The surface functional groups were detected via Fourier-transform infrared (FTIR) spectroscopy (TENSOR-27, Germany). Inductively coupled plasma atomic emission spectrometry (ICP-AES, Perkin-Elmer-7000DV, USA) was employed to determine the concentrations of metal ions in the solutions. The elemental compositions were determined by X-ray photoelectron spectroscopy (XPS, ESCALAB 250, Thermo, USA) using monochromatic Al Kα radiation and normalized energy.

**Text S3.** Sorption experiments

**(1)** Batch sorption experiments

The stock solutions of Li(Ι), Mg(II), K(Ι), Na(Ι), and Ca(II) were prepared by dissolving LiCl, MgCl2, KCl, NaCl and CaCl2 in double distilled water, respectively. Solutions with different concentrations were obtained through dilution of the stock solutions followed by pH adjustment with either 0.1 mol·L-1 HClor 0.1 mol·L-1 NaOH solutions. All water samples were filtered using a 0.22 μm membrane before determination. In all adsorption experiments, the concentrations of metallic ions were determined by ICP-AES.The adsorption capacity was calculated according to Eq. (1):

where *q* represents the adsorption capacity (mg·g-1), *ci* and *cf* are the initial and final concentrations of metal ions (mg·L-1), respectively, *V* is the volume of the solution (L) and *m* is the mass of the adsorbent (g).

Static adsorption studies of Li(Ι) ions were carried out via a batch method in constant-temperature oscillator at a stroke speed of 50 r/min. To evaluate the effect of pH studies, 25 mg of adsorbent was added into four capped conical flasks containing 50.0 mL of 100 mg·L-1 Li(Ι) solutions at 298 K and different pH values in the range of 2–10. The kinetic studies were conducted by adding 25 mg adsorbent into 50.0 mL of 100 mg·L-1 Li(Ι) solutions at 298 K at variable contact times from 0 to 25 min. The adsorption isotherms were obtained by adding 25 mg adsorbent into 50.0 mL of Li(Ι) solutions at different concentrations ranging from 10 to 100 mg·L-1 for 12 h to ensure the establishment of adsorption equilibrium.

The selectivity of PAN-CE@SiO2 towards target ions was evaluated by means of competitive adsorption experiments. To this end, 25 mg of adsorbent was added to 50.0 mL of binary metal mixed aqueous solutions containing 100mg·L-1 of Li(Ι)/Mg(II), Li(Ι)/Na(Ι), Li(Ι)/K(Ι), and Li(Ι)/Ca(II), respectively, at pH 3,6 and 9 under constant stirring. After reaching adsorption equilibrium, the metal ions concentrations were determined using ICP-AES. The distribution coefficient (*Kd*) selectivity coefficient (*K*), and selectivity coefficient (*K*) were calculated using Eqs. (2) and (3), respectively:

 (2)

 (3)

where *ci* and *ce* are the initial and equilibrium concentrations of M (mg·L-1, M represents the metal ions), *V* is volume of the solution (mL), *m* is mass of adsorbent (g), *Kd*(In) and *Kd*(M) are the distribution coefficients of Li(Ι) ions and other metallic ions, respectively, and *K* is selectivity coefficient of competitor metal ions M with respect to Li(Ι) ions. Note that a larger value of *K* indicates a stronger selectivity for Li(Ι) ions.

**(2)** Fixed-bed sorption

The fixed-bed adsorption experiments were carried out in glass columns of 6 mm internal diameter and 100 mm height. Real saltlake brine samples containing Li(Ι) ions were supplied from China Zhabuye saltlake. The effluent was collected after 5.00 mL of the solution had passed through the column. All column experiments were performed at room temperature and pH 7.8. Regeneration experiments were also carried out by fixed-bed, whereby 1 g PAN-CE@SiO2 was packed into the column and 100 mg·L-1 Li(Ι) solution was pumped upwards through it at steady flow rate 0.50 mL·min-1 using a peristaltic pump. After the adsorbent in the column was exhausted, regeneration of PAN-CE@SiO2 and desorption of Li(Ι) ions were carried out. Desorption of Li(Ι) ions from the loaded material was performed using double distilled waterat constant flow rate of 0.25 mL·min-1. The reusability of PAN-CE@SiO2 was tested over 60 consecutive adsorption–desorption cycles. Finally, a fixed-bed comprised of 1.5 g PAN-CE@SiO2 was employed to selectively separate and recover Li(Ι) ions from real saltlake brine using the same procedures as for fixed-bed experiments.

**(3)** The pseudo-first- and pseudo-second-order models

The kinetics data were analyzed using pseudo-first-order and pseudo-second-order models. Note that pseudo-first-order kinetic model assumes that the rate of change solute uptake with time is directly proportional to difference in saturation concentration. By comparison, the pseudo-second-order kinetic model considers that adsorption process is controlled by surface reaction. The pseudo-first- and pseudo-second-order models are represented by Eqs. (4) and (5).

 (4)

 (5)

where *qt* (mg·g-1) and *q*e (mg·g-1) are the adsorption capacities of Li(Ι) ions at any time *t* and at equilibrium, respectively. *k*1 (min-1) and *k*2 (min-1·g·mg-1) represent the rate constants of the pseudo-first-order and pseudo-second-order models, respectively.

 **(4)** The Langmuir and Freundlich models

The relationship between the amount of Li(Ι) in liquid phase and that adsorbed at equilibrium can be represented by an adsorption isotherm. The experimental adsorption isotherm data were fitted by the Langmuir and Freundlich models ( Eqs.(6) and (7)). (6)

 (7)

where *q*e corresponds to the amount of Li(Ι) ions adsorbed per gram of adsorbent (mg·g-1) and *c*e represents the equilibrium concentration of Li(Ι) ions in the solution. *q*m and *K*L denote the Langmuir constants related to the maximum adsorption capacity (mg·g-1) and adsorption energy (L·g-1), respectively, *Kf* and (1/*n*) are rough indicators of the adsorption of adsorption intensity, respectively.

**Text S4 Computational method**

Natural bond orbital (NBO) analysis was carried out at B3LYP/6–311++ G(d,p)//B3LYP/6–311+G(d,p) (LANL2DZ for lithium ions) to demonstrate the interaction mechanism between functional group and lithium ions. The adsorption energies and were the net charge calculated with the following equations[Eqs.(8) and (9)], respectively.

 (8)

 (9)

where *E*complex, *E*adsorbent and *E*ilithium ions represent the calculated total energies of complex, functional groups selected fragment and indium ions, respectively. The value of *E*ad is less than 0, indicates that the chemical adsorption is stable. Mulliken chargeafter and Mulliken chargebefore are the charges of functional groups after and before adsorption, respectively. A negative value of the net charge means the capacity of getting electrons.

**Fig. S1**





Fig. S1 Adsorption kinetics of Li(I) ions onto PAN-CE@SiO2, pseudo-first-order (a) and pseudo-second-order kinetics(b).

**Table S1**

Elements contents in the real saltlake brine Li(I) in this work.

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| Elements | Li | K | Mg | Ca | Na |
| Concentration(ppm) | 1085 | 25376 | 20.5 | 0.32 | 118593 |

Table s2 The calculated parameters for the adsorbents before and after adsorption

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| adsorbent | bond distance(Å) |  | bond angle(°) | Cavity Sizea |
| C2-O10 | C7-O11 | C13-O18 | C27-O25 | O10-M | O11-M | O18-M | O25-M |  | C2-O10-C26 | C13-O18-C19 | C20-O25-C27 | O11-M-O25 | O10-M-O18 |  |
| Functional group | 1.36 | 1.39 | 1.42 | 1.42 |  |  |  |  |  | 118.29 | 117.15 | 114.31 |  |  | 3.44(4.55) |
| Li(I) complex | 1.43 | 1.43 | 1.44 | 1.44 | 2.16 | 2.06 | 2.20 | 1.99 |  | 117.25 | 115.07 | 116.55 | 116.23 | 141.51 |

a The cavity size is the minimum distance between two oxygen atoms in the opposite position, and the values in parentheses are the cavity size of the free crown ether.