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Synthesis of ion imprinted polymeric nanoparticles for selective pre-concentration and recognition of lithium ions

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Abstract

This work reports the preparation of lithium ion-imprinted polymer material using benzo-12-crown-4 as a selective crown ether, methacrylic acid (MAA) as the functional monomer, ethyleneglycol dimethacrylate (EGDMA) as the crosslinker, and 2,2’-azobisisobutyronitrile (AIBN) as the radical initiator. The imprinted lithium ion was removed from the polymeric matrix using a 1.0 mol L\(^{-1}\) HNO\(_3\) solution. The resulting sorbent was characterized using scanning electron microscopy (SEM), Brunauer–Emmett–Teller (BET) theory, X-ray diffraction (XRD) and IR spectroscopy. The prepared particles have a diameter of 50-60 nm which results in fast recognition of lithium ions. The maximum adsorption capacity and pre-concentration factor of prepared particles were 1019.27 µmol g\(^{-1}\) and 100, respectively. The Li\(^+\)-imprinted sorbent was reused ten times without a significant decrease in binding affinity. The relative standard deviation (RSD %) and limit of detection were evaluated as 2.1 % and 3.29 µg L\(^{-1}\), respectively. Finally, the resulted IIP particles showed high selectivity toward lithium ion over some foreign metal ions with selectivity coefficients above 18.5.

Keywords: Ion-imprinted polymeric nanoparticles, Li\(^+\) ion, B12C4, Flame photometry
1. Introduction

In recent years, molecularly imprinted polymers (MIPs) have attracted extensive research interest due to their outstanding advantages, such as stability, low cost of preparation and capable of molecular recognition. Ion imprinting polymers (IIPs) are similar to MIPs, but they recognize metal ions after imprinting offer all the benefits derived from MIPs and a high capacity for recognizing ions. Currently, different methods had been reported for metal ion imprinted polymers, such as bulk polymerization, suspension polymerization and precipitation polymerization. In all cases, after ion imprinting polymerization, the imprint metal ion is removed from the polymeric particles by leaching with mineral acid that leaves cavities or “imprinted sites” in the polymeric particles that are complementary in shape and size of the imprint metal ion. Ion imprinted materials have been used in various fields, including chromatography, sensors and solid phase extraction.

Since the first synthesis of crown ether compounds by Pedersen and his observation of their selective ion bonding properties, a great deal of research work has been done on crown complexes with inorganic and organic cations and with neutral molecules. Crown ethers (CEs) exhibit themselves as very useful model compounds capable to function as do more complex chemical structures. These unique properties of crown ethers make them very attractive molecules that permit a detailed analysis of interactions that are thought to be important in analytical chemistry. It is well known that the stability and selectivity of the metal ion complexes with cyclic ligands (such as crown ethers) increase very significantly in comparison with their corresponding open chain analogues, the so-called “macrocyclic effect”. The efficiency of interaction may also be affected by the nature of the metal ion and by the number, distance and orientation of the donor atoms of the ligand that are structurally accessible to the complexed cation. We have previously reported the use of macromolecule crown ether derivatives in the various fields of membrane transport, solid-phase and supercritical fluid extraction of metal ions and construction of ion selective membrane potentiometric and optical sensors.

In this study, ion-imprinted polymer particles were used for selective extraction and pre-concentration of lithium ion from aqueous samples. We selected B12C4 as a selective metal complexing agent for Li⁺ ions. The IIP was synthesized via precipitation copolymerization of
Li\textsuperscript{+}-B12C4 template using methacrylic acid (MAA) and ethyleneglycol dimethacrylate (EGDMA) as functional and cross-linking monomers, respectively, in the presence of 2,2\textprime; azobisisobutyronitrile (AIBN) as radical initiator. After removal of lithium ions, the characterization of the synthesized polymer and the adsorption behavior of analytes on the imprinted polymers were investigated in detail. Finally, the ability of polymer to separate and pre-concentrate of Li\textsuperscript{+} ions from water samples was tested by using flame photometric method.

2. Experimental

2.1. Reagent and materials

Methacrylic acid (MAA), ethyleneglycol dimethacrylate (EGDMA) and 2,2\textprime; azobisisobutyronitrile (AIBN) were obtained from Aldrich (St. Louis, MO, USA). Benzo 12-crown-4 was purchased from Fluka (Buchs, Switzerland). All solvents were supplied by Merck (Darmstadt, Germany). Reagent grade LiClO\textsubscript{4} and nitrate or chloride salts of other cations were of reagent grade from Merck chemical company (Darmstadt, Germany) and used without any further purification. Solutions of metal ions were prepared in sixth distilled water. Lithium standard solution (Spectro ECON) was purchased from the Chem-Lab NV of Belgium.

2.2. Apparatus

A flame photometer Corning 410 was used for determination of lithium and atomic absorption spectrometer, Shimadzu 680 was applied to the determination of other ions. The IR spectra were measured by Bruker spectrometer (Germany). A model 728 digital pH meter (Metrohm, Germany) was used for the pH value adjustments. The SEM images were taken on a Philips XL30 instrument using a gold film for loading the dried particles on the instrument. The X-ray diffraction (XRD) patterns were obtained using Cu K\textalpha\ X-ray source and Inel EQUINOX3000 diffractometer (France). The surface area analysis was carried out by using Quantachrome autosorbe-1 surface area analyzer (USA).

2.3. Preparation of lithium-imprinted polymers
The Li\textsuperscript{+}-imprinted polymers were prepared by precipitation polymerization technique according to our previous publications \textsuperscript{10}. For this purpose, a mixture of B12C4 (0.2 mmol) and LiClO\textsubscript{4} (0.2 mmol) were dissolved in 20 mL of acetonitrile at room temperature with continuous stirring for 20 min. Then EGDMA (4 mmol) MAA (1 mmol) and 25 mg of AIBN were added to the first step solution and stirred at room temperature. The polymerization mixture was purged with N\textsubscript{2} for 5 min, sealed and thermally polymerized in an oil bath at 60°C while stirring for 24 h. After polymerization the polymer was filtered to remove the excess amount of solvent. Then, the resulting powder material was washed with methanol repeatedly, in order to remove the un-reacted materials. The polymer particles were leached with 1 mol L\textsuperscript{-1} HNO\textsubscript{3} until the wash solution was free from Li\textsuperscript{+} ions. Finally, the sorbent was washed with six times distilled water until neutral pH is reached. The resulting powder material was dried overnight before sorption studies. The non-imprinted polymer (NIP) materials were prepared in the same way but without the addition of lithium salt. A schematic representation for the synthesis of Li\textsuperscript{+}-ion imprinted polymer is shown in Fig. 1.

Fig. 1 Schematic representation of the synthesis of the ion-imprinted polymer.
2.4. Sorption and desorption procedure

The sorption studies of the Li$^+$ ions by the ion-imprinted and non-imprinted polymer particles were carried out in the batch procedures as follows. In the batch experiment, 15 mg of sorbent was added to a 10 mL solution of 1 µg mL$^{-1}$ lithium ion. The pH of the solution was maintained to 9.0 by adding Tris buffer solution. After centrifugation (5 min, 5000 rpm) the supernatant solution was removed and the Li$^+$ ions pre-concentrated onto sorbent were then eluted by using 4 mL of 0.5 mol L$^{-1}$ HNO$_3$, while stirring for 15 min. Finally, the resulted solution was used for determining its lithium content by flame photometer. The percentage of metal ion adsorbed on the sorbent was determined by comparing its initial, $C_i$ (µg mL$^{-1}$), and equilibrium concentrations, $C_e$ (µg mL$^{-1}$), as

$$\% E = \frac{(C_i - C_e)}{C_i} \times 100 \quad (1)$$

The sorption capacity (µmol g$^{-1}$) of the IIP particles relative to the imprint metal ion was calculated by:

$$Q = \frac{(C_i - C_e)V}{mM} \quad (2)$$

where V is the volume of initial solution (mL), m is the mass of IIP materials (g), and M is the atomic mass of lithium (g mol$^{-1}$).

3. Results and discussion

3.1. Sorbent characterization

In this study the new sorbent based on the [Li-B12C4] was characterized by IR spectroscopy and scanning electron microscopy (SEM). In the IR spectra (Fig. 2), the absorptions due to C=O stretch (1735 cm$^{-1}$), C-O stretch (1161 cm$^{-1}$), C-O bend (1263 cm$^{-1}$), C-H stretch (2993 cm$^{-1}$), CH$_3$ and CH$_2$ bends (1390 and 1459 cm$^{-1}$, respectively) were observed. Similarities between the
IR spectra of unleached and leached ion-imprinted materials suggested that the leaching process does not affect on given different groups in the polymeric network.

The morphology of the polymers, produced by the precipitation method, was assessed by SEM (Fig. 3). It was observed that the size of particles of polymer was in the range of 50-60 nm which are slightly irregular in shape.
Fig. 3 Scanning electron micrograph of the Li$^{+}$-imprinted polymeric nanoparticles obtained via precipitation polymerization method.

The XRD patterns of leached and un-leached ion-imprinted polymers are presented in Fig. 4. As can be seen, the XRD of leached IIP is similar to corresponding XRD patterns of un-leached ion-imprinted polymer, except for the peak corresponding to lithium ion. This behavior confirms complete removal of lithium ion after leaching process. Moreover, according to the Debye-Scherrer formula$^{29,30}$, the particle size of the sorbent was determined to be 50 nm.
The specific area of the sorbent was determined using Brunauer–Emmett–Teller (BET) theory whereas the pore volume and average pore diameter were derived by the Barrett–Joyner–Halenda (BJH) theory (Fig. 5). BET theory aims to explain the physical adsorption of gas molecules on a solid surface and serves as the basis for an important analysis technique for the measurement of the specific surface area of a material. The surface area, BJH adsorption cumulative pore volume and BJH adsorption average pore diameter of the prepared lithium imprinted polymer were found to be 98.03 m$^2$g$^{-1}$, 0.336 cm$^3$g$^{-1}$ and 2.317 nm, respectively. These data indicate that polymer materials with nano-pore and excessive surface area have been prepared.
Fig. 5 BET, BJH and adsorption/desorption isotherms plots of the prepared lithium imprinted sorbent.

3.2. Study of sorption-desorption properties of Li⁺-IIP

The influences of different parameters affecting the sorption and desorption properties of synthesized nanoparticles were investigated and the results are shown in Fig. 6. The effect of pH on the adsorption of lithium ions was tested in the pH range of 1.0–12 in batch experiments, by equilibrating 15 mg of nanoparticles with 10 mL of solutions containing 1.0 µg mL⁻¹ of Li⁺ ions. As can be seen in Fig. 6A, the binding of template ions increased with increasing pH and reached to maximum at pH 8.0, and remains constant with further increase in pH from 8 to 10. Then, the extraction recovery of lithium ions was decreased at pH > 10. As expected, due to the presence of oxygen as donating atoms in B12C4, the adsorption of lithium ion onto the sorbent is highly dependent on the pH of solution. At lower pHs, the donating oxygen atoms can be protonated and, therefore, negligible amounts of lithium ions are adsorbed to the polymer. When the pH increased, condition became more favorable for complex formation and adsorption of lithium ions. Therefore, the pH was adjusted to 9.0 in all subsequent studies using Tris buffer.

In a typical uptake kinetics test, 15 mg of the sorbent was added to 10 mL of 1 µg mL⁻¹ lithium solution at a pH of 9.0. The suspension was stirred for different periods of time (from 5 to 30 min) using a magnetic stirrer. After leaching of bounded Li⁺ on the IIP particles and the final concentrations of template ion in solutions were determined by flame photometer. The
results indicated that more than 98% lithium uptake was achieved within 15 min (Fig. 6B). This rapid adsorption equilibrium time is most probably due to high affinity between Li\(^+\) ion and the cavities in the polymer network structure.

The effect of desorption time was also investigated in batch experiments. The results showed that the template ions could be quantitatively desorbed from the sorbent with 4 mL of 0.5 mol L\(^{-1}\) HNO\(_3\) during 15 min. Therefore, 15 min was selected as desorption time for subsequent experiments. (Fig. 6C)

In order to choose a proper eluent for leaching the adsorbed Li\(^+\) ion, after its uptake from aqueous media, lithium ion was eluted by different acidic solutions such as HNO\(_3\), HCl, H\(_3\)PO\(_4\) and H\(_2\)SO\(_4\). After leaching of adsorbed lithium using 4 mL of 0.5 mol L\(^{-1}\) of each acid, the effluent lithium was determined by flame photometer. It was found that the template ions could be quantitatively (> 99%) desorbed from the particles with nitric acid. After selecting of HNO\(_3\) as a proper leachant, in order to study its optimum concentration, several 4 mL portions of nitric acid solutions with different concentrations (i.e., 0.001, 0.01, 0.1, 1.0 and 2.0 mol L\(^{-1}\)) were used for leaching of Li\(^+\) ions from the imprinted sites in the polymer network. It was found that a concentration of 0.5 mol L\(^{-1}\) HNO\(_3\) was required to remove the bound Li\(^+\) ion (Fig. 6D). Thus, 4 mL of 0.5 mol L\(^{-1}\) HNO\(_3\) was selected as optimal leachant solution. It is most possibly due to complete protonation of donating hetero-atoms of binding sites in the cavities of sorbent, when 0.5 mol L\(^{-1}\) HNO\(_3\) penetrate into polymeric network.

In the analysis of real samples, the sample volume is one of the important parameters influencing the pre-concentration factor. Therefore, maximum sample volume up to which quantitative Li\(^+\) sorption occurred was determined by varying the sample volume (from 10 to 600 mL) each containing a constant amount of lithium ion. The results indicated that, the maximum sample volume can be up to 400 mL with the recovery >97%. Thus, 400 mL was selected as the maximum sample volume and a pre-concentration factor of 100 can be obtained.

The effect of the polymer particles weight on the quantitative adsorption of Li\(^+\) ion onto the prepared sorbent was studied. The results indicate no difference between 15 and 50 mg of IIP particles in pre-concentration of lithium ions onto active sites of IIP. Thus, 15 mg of particles were used for sorption-desorption studies.
Fig. 6 Effect of different parameters on sorption of lithium ions on nano beads: (A) pH of solution, (B) adsorption time, (C) desorption time, (D) eluent concentration.

3.3. Adsorption capacity

The adsorption capacity of Li$^+$ onto the ion imprinted and non-ion imprinted polymeric particles were investigated by static adsorption method. In several batch experiments, 15 mg portions of the polymer were equilibrated with varying concentrations of lithium ion (initial concentration ranged from 0.5 to 300 µg mL$^{-1}$) at pH 9.0. The suspensions were stirred for 15 min using a magnetic stirrer. Then the supernatant solutions were removed using the centrifuge and the final concentrations of lithium ion in solutions were determined by flame photometry.
The resulting plot of $Q$ vs. $C_e$ is shown in Fig. 7. As can be seen, the amount of lithium ions adsorbed per unit mass of the polymer increased linearly with the equilibrium concentration of Li$^+$ ions from 0.03 to 88 µg mL$^{-1}$ and reached a plateau in the adsorption profile at 150 µg mL$^{-1}$ which represents saturation of the active binding cavities on the lithium IIP beads. The maximum sorbent capacity of ion imprinted (IIP) and non-imprinted polymeric (NIP) nanobeads were obtained to be 1019.27 and 625.24 µmol g$^{-1}$, respectively. To the non-imprinted particles, the amount of imprint ions adsorbed per unit mass of the sorbent is obviously lower than that of lithium ion-imprinted particles, due to the fact that there were no active binding cavities on the non-imprinted beads and physical adsorption.

![Fig. 7 The study of adsorption capacity of Li$^+$ on nanoparticles.](image)

### 3.4. Reusability test

To investigate the reusability of the prepared sorbent, the adsorption and desorption cycles were repeatedly performed using the same nanoparticles. The adsorption–elution cycle were performed ten times. Each experiment was performed under optimal conditions. The results indicate that the lithium-imprinted sorbent can be used repeatedly without any significant loss in the initial binding affinity. The relative standard deviation for ten replicates with the same particles was found to be 0.97%.
3.5. Selectivity study

In ion-imprinted polymers, chelating sites possess a uniform distribution and the cavities created after removal of template is complementary to the imprint ion in size and coordination geometries. Furthermore, the complexing agents used in their preparation usually have selective affinities for the imprint ion. Competitive adsorptions of Li$^+$ / Na$^+$, Li$^+$ / K$^+$, Li$^+$ / Rb$^+$ and Li$^+$ / Cs$^+$ from their binary mixtures was investigated in a batch system. The distribution ratio (K$_d$, mL g$^{-1}$) of lithium ion between the IIP particles and aqueous solution was also determined by the following equation:

$$K_d = \frac{(C_i - C_e)V}{C_e m}$$  (3)

Selectivity coefficients for lithium ion relative to foreign ions are defined as:

$$K_{Li^+/M^+}^{Lithium} = \frac{K_{dL}^{Li^+}}{K_{dM}^{M^+}}$$  (4)

where $K_{dL}^{Li^+}$ and $K_{dM}^{M^+}$ are distribution ratios of lithium and foreign ion, respectively. The relative selectivity coefficient, $k'$, is defined as:

$$K' = \frac{K_{imprinted}}{K_{non-imprinted}}$$  (5)

where $k_{imprinted}$ and $k_{non-imprinted}$ are selectivity coefficients of the imprinted and non-imprinted nanoparticles, respectively. In the corresponding mixtures studied, the two metal ions had the same concentration of 1.0 µg mL$^{-1}$ and the sorbent was 15 mg. Table 1 summarizes the distribution ratios (K$_d$), selectivity coefficients (k) and relative selectivity coefficients (k’) calculated using Eqs. (3)–(5), respectively.
Table 1 Distribution ratio ($K_d$), selectivity coefficient ($k$) and relative selectivity coefficient ($k'$) values of ion-imprinted polymer (IIP) and control non-imprinted polymeric (NIP) material for different metal ions.

<table>
<thead>
<tr>
<th>Cation</th>
<th>$K_d^{(IIP)}$ (mL g$^{-1}$)</th>
<th>$K_d^{(NIP)}$ (mL g$^{-1}$)</th>
<th>$K_{Li/M}^{(IIP)}$</th>
<th>$K_{Li/M}^{(NIP)}$</th>
<th>$K'$ $^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li$^+$</td>
<td>16000</td>
<td>883.70</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Na$^+$</td>
<td>662.65</td>
<td>680.13</td>
<td>24.15</td>
<td>1.30</td>
<td>18.58</td>
</tr>
<tr>
<td>K$^+$</td>
<td>307.28</td>
<td>445.37</td>
<td>52.1</td>
<td>1.98</td>
<td>26.24</td>
</tr>
<tr>
<td>Rb$^+$</td>
<td>257.97</td>
<td>419.99</td>
<td>62.02</td>
<td>2.10</td>
<td>29.48</td>
</tr>
<tr>
<td>Cs$^+$</td>
<td>234.23</td>
<td>420.90</td>
<td>69.31</td>
<td>2.10</td>
<td>32.53</td>
</tr>
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</table>

$^a K' = K_{Li/M}^{(IIP)} / K_{Li/M}^{(NIP)}$

3.6. Analytical performance

The characteristics of the analytical pre-concentration procedure were obtained under the optimized conditions. The resulting calibration curve was linear within the concentration range of 10-300 µg L$^{-1}$. The relative standard deviation (RSD.) for 5 replicate measurements of 50 µg L$^{-1}$ Li$^+$ was 2.1%. The limit of detection (LOD) corresponding to three times of the standard deviation of blank was found to be 3.29 µg L$^{-1}$. The pre-concentration factor evaluated from the ratio of the sample volume (400 mL) to the leachant volume (4 mL), is 100.

3.7. Analysis of real samples

To test the reliability of the prepared polymer particles, the proposed method was applied to the extraction and recovery of lithium ion in tap and well water samples. The corresponding relative recoveries are summarized in Table 2 indicate the high potential of the prepared polymer for pre-concentration and recognition of lithium ions from different water samples. Moreover, the accuracy of the proposed method was checked by analyzing of lithium standard solution (Spectro ECON) with the lithium concentration of 1000 ± 2 µg mL$^{-1}$. The lithium content obtained (mean ± S.D., n=3) was 992.2 ± 2.1 µg mL$^{-1}$, which is in satisfactory agreement with reported value, thus confirming the validity of the analytical procedure.
Table 2 Analytical results for the determination of lithium ion in water samples.

<table>
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<tr>
<th>Sample</th>
<th>Added (µg L&lt;sup&gt;-1&lt;/sup&gt;)</th>
<th>Found (µg L&lt;sup&gt;-1&lt;/sup&gt;)</th>
<th>Recovery (%)</th>
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<td>Tap water</td>
<td>00</td>
<td>10.50</td>
<td>---</td>
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<tr>
<td></td>
<td>30</td>
<td>40.17</td>
<td>98.9 ± 2.55</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>60.33</td>
<td>99.7 ± 2.08</td>
</tr>
<tr>
<td>Well water</td>
<td>0</td>
<td>11.33</td>
<td>---</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>40.67</td>
<td>97.8 ± 1.92</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>60.83</td>
<td>99.0 ± 1.73</td>
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</tbody>
</table>

4. Conclusions

In this study we have reported the synthesis of Li<sup>+</sup>- ion imprinted polymer which has efficient analytical performance in pre-concentration of lithium. The proposed sorbent permits fast recognition of analyte in aqueous sample. The selectivity factor of polymer particles relative to Na<sup>+</sup>, K<sup>+</sup>, Rb<sup>+</sup> and Cs<sup>+</sup> was determined. The established extraction procedure can be applied to the determination of lithium in real water samples. The sorbent characteristics, including adsorption/desorption time, relative selectively coefficient, maximum sorbent capacity, polymer size and reusability of the proposed Li<sup>+</sup>–IIP system were compared with those of the previously reported one (Table 3).
Table 3 Comparison of the proposed method with previous extraction method for determination of lithium.

<table>
<thead>
<tr>
<th>Ligand</th>
<th>Ads./Des. time (min)</th>
<th>Particle size (nm)</th>
<th>Maximum sorbent capacity (µmol g⁻¹)</th>
<th>Reuse number</th>
<th>Relative selectively coefficient</th>
<th>Ref.</th>
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<tr>
<td>2M12C4a</td>
<td>10/--</td>
<td>300</td>
<td>586</td>
<td>5</td>
<td>Na (4.92)</td>
<td>35</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>K (4.10)</td>
<td></td>
</tr>
<tr>
<td>12C4</td>
<td>15/15</td>
<td>50-60</td>
<td>1019.27</td>
<td>10</td>
<td>Na (18.58)</td>
<td>This work</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>K (26.24)</td>
<td></td>
</tr>
</tbody>
</table>

a 2-methylol-12-crown-4
References


A new Li⁺-IIP has been prepared for the fast determination and selective separation of lithium ions in aqueous sample.