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

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1   **Synthesis of ion imprinted polymeric nanoparticles for selective pre-**

2   **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 [1]. 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 [2, 3]. Currently, different methods had been reported for metal ion imprinted polymers, such as bulk polymerization [4], suspension polymerization [5] and precipitation polymerization [6]. 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 [7]. Ion imprinted materials have been used in various fields, including chromatography [8], sensors [9] and solid phase extraction [10-13].

Since the first synthesis of crown ether compounds by Pedersen [14] 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 [15, 16] and with neutral molecules [17]. 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 [18]. 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"[19, 20]. 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 [21, 22]. We have previously reported the use of macromolecule crown ether derivatives in the various fields of membrane transport [23], solid-phase [10] and supercritical fluid extraction of metal ions [24] and construction of ion selective membrane potentiometric [25] and optical sensors [26] and spectrophotometric [27] studies.

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

72 Li$^+$-B12C4 template using methacrylic acid (MAA) and ethyleneglycol dimethacrylate

73 (EGDMA) as functional and cross-linking monomers, respectively, in the presence of 2,2′-

74 azobisisobutyronitrile (AIBN) as radical initiator. After removal of lithium ions, the

75 characterization of the synthesized polymer and the adsorption behavior of analytes on the

76 imprinted polymers were investigated in detail. Finally, the ability of polymer to separate and

77 pre-concentrate of Li$^+$ ions from water samples was tested by using flame photometric method.

78

79 2. Experimental

80 2.1. Reagent and materials

81 Methacrylic acid (MAA), ethyleneglycol dimethacrylate (EGDMA) and 2,2′-

82 azobisisobutyronitrile (AIBN) were obtained from Aldrich (St. Louis, MO, USA). Benzo 12-

83 crown-4 was purchased from Fluka (Buchs, Switzerland). All solvents were supplied by Merck

84 (Darmstadt, Germany). Reagent grade LiClO$_4$ and nitrate or chloride salts of other cations were

85 of reagent grade from Merck chemical company (Darmstadt, Germany) and used without any

86 further purification. Solutions of metal ions were prepared in sixth distilled water. Lithium

87 standard solution (Spectro ECON) was purchased from the Chem-Lab NV of Belgium.

88

89 2.2. Apparatus

90 A flame photometer Corning 410 was used for determination of lithium and atomic absorption

91 spectrometer, Shimadzu 680 was applied to the determination of other ions. The IR spectra were

92 measured by Bruker spectrometer (Germany). A model 728 digital pH meter (Metrohm,

93 Germany) was used for the pH value adjustments. The SEM images were taken on a Philips

94 XL30 instrument using a gold film for loading the dried particles on the instrument. The X-ray

95 diffraction (XRD) patterns were obtained using Cu Kα X-ray source and Inel EQUINOX3000

96 diffractometer (France). The surface area analysis was carried out by using Quantachrome

97 autosorbe-1 surface area analyzer (USA).

98

99 2.3. Preparation of lithium-imprinted polymers

100   The Li^+-imprinted polymers were prepared by precipitation polymerization technique according

101   to our previous publications [10]. For this purpose, a mixture of B12C4 (0.2 mmol) and $LiClO_4$ (0.2

102   mmol) were dissolved in 20 mL of acetonitrile at room temperature with continuous stirring for

103   20 min. Then EGDMA (4 mmol) MAA (1 mmol) and 25 mg of AIBN were added to the first

104   step solution and stirred at room temperature. The polymerization mixture was purged with N_2

105   for 5 min, sealed and thermally polymerized in an oil bath at 60 $^\circ$C while stirring for 24 h. After

106   polymerization the polymer was filtered to remove the excess amount of solvent. Then, the

107   resulting powder material was washed with methanol repeatedly, in order to remove the un-

108   reacted materials. The polymer particles were leached with 1 mol L^{-1} HNO_3 until the wash

109   solution was free from Li^+ ions. Finally, the sorbent was washed with six times distilled water

110   until neutral pH is reached. The resulting powder material was dried overnight before sorption

111   studies. The non -imprinted polymer (NIP) materials were prepared in the same way but without

112   the addition of lithium salt. A schematic representation for the synthesis of Li^+- ion imprinted

113   polymer is shown in Fig. 1.
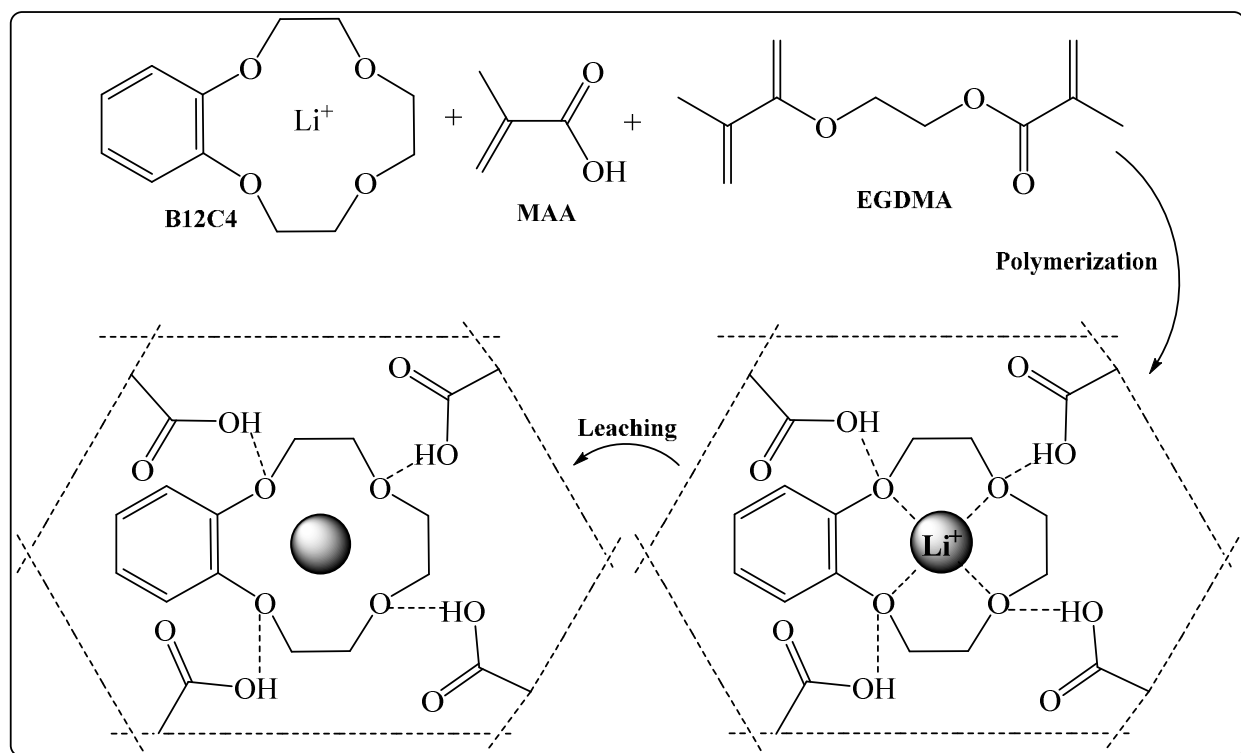
114

115   **Fig. 1** Schematic representation of the synthesis of the ion-imprinted polymer.

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2.4.   Sorption and desorption procedure

119   The sorption studies of the Li^+ ions by the ion- imprinted and non-imprinted polymer particles
120   were carried out in the batch procedures as follows. In the batch experiment, 15 mg of sorbent
121   was added to a 10 mL solution of 1 μg mL^{-1} lithium ion. The pH of the solution was maintained
122   to 9.0 by adding Tris buffer solution. After centrifugation (5 min, 5000 rpm) the supernatant
123   solution was removed and the Li^+ ions pre-concentrated onto sorbent were then eluted by using 4
124   mL of 0.5 mol L^{-1} HNO_3, while stirring for 15 min. Finally, the resulted solution was used for
125   determining its lithium content by flame photometer. The percentage of metal ion adsorbed on
126   the sorbent was determined by comparing its initial, C_i (μg mL^{-1}), and equilibrium
127   concentrations, C_e (μg mL^{-1}), as [28]

128

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

129

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

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

132

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

135

3. Results and discussion

3.1.   Sorbent characterization

138   In this study the new sorbent based on the [Li-B12C4] was characterized by IR spectroscopy and
139   scanning electron microscopy (SEM). In the IR spectra (Fig. 2), the absorptions due to C=O
140   stretch (1735 cm^{-1}), C-O stretch (1161 cm^{-1}), C-O bend (1263 cm^{-1}), C-H stretch (2993 cm^{-1}),
141   CH_3 and CH_2 bends (1390 and 1459 cm^{-1}, respectively) were observed. Similarities between the

142   IR spectra of un-leached and leached ion-imprinted materials suggested that the leaching process

143   does not affect on given different groups in the polymeric network.
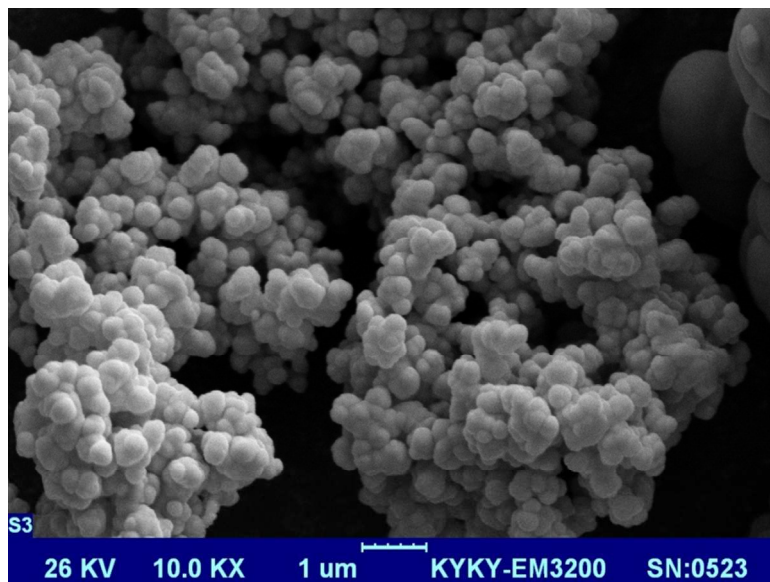
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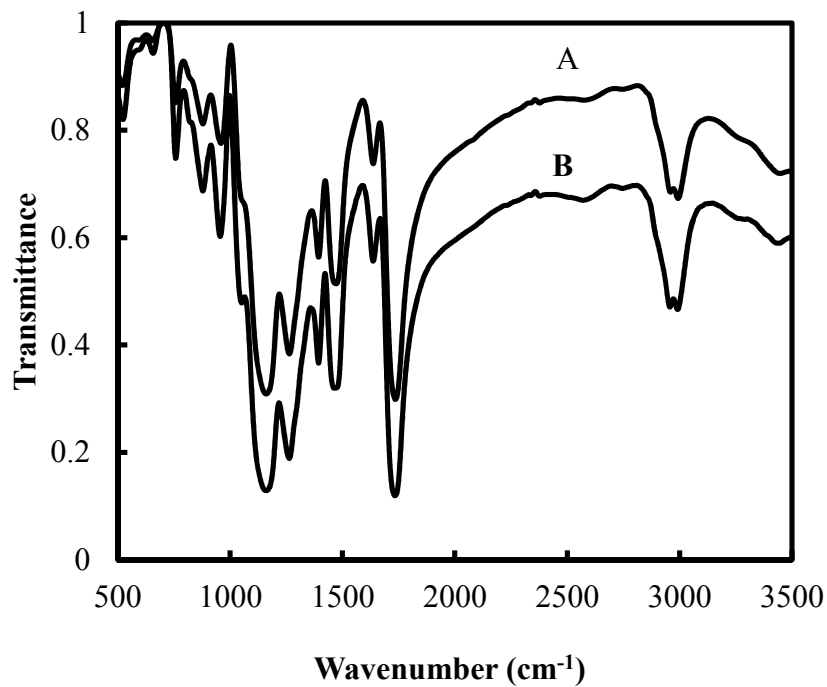
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146   **Fig. 2** FT-IR spectra of leached (A) and un-leached (B) polymers.

147

148   The morphology of the polymers, produced by the precipitation method, was assessed by

149   SEM (Fig. 3). It was observed that the size of particles of polymer was in the range of 50-60 nm

150   which are slightly irregular in shape.

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Fig. 3 Scanning electron micrograph of the Li$^+$-imprinted polymeric nanoparticles obtained via precipitation polymerization method.
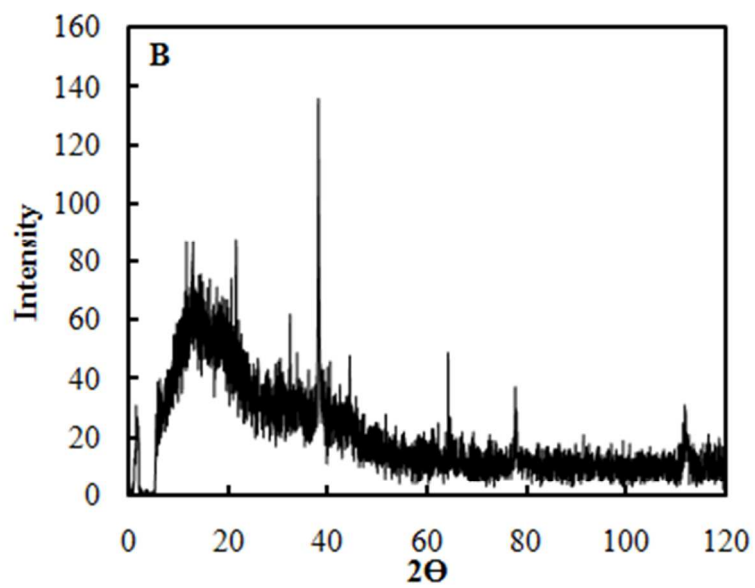
The XRD patterns of leached and un-leached ion-imprinted polymers are presented in Fig. 4. As can be seen, the XRD of leached IIP is similar to corresponding XRD patterns of un-leached ion -imprinted polymer, except for the peak corresponding to lithium ion. This behavior confirms complete removal of 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.
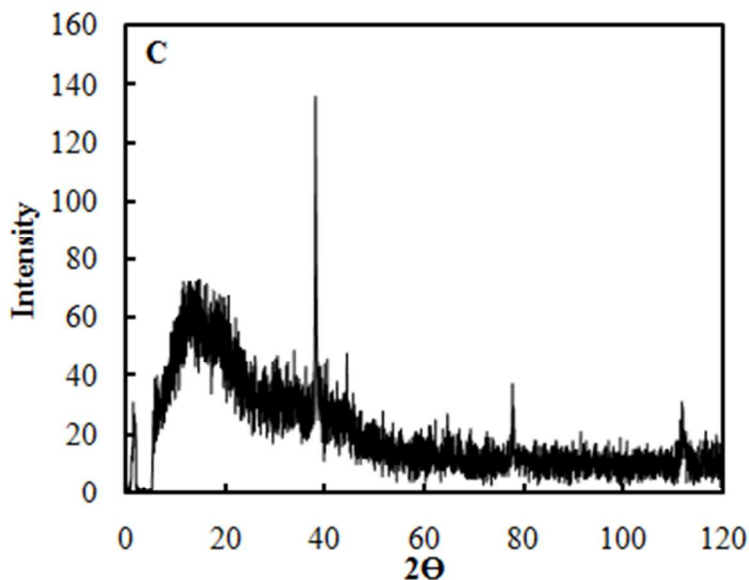
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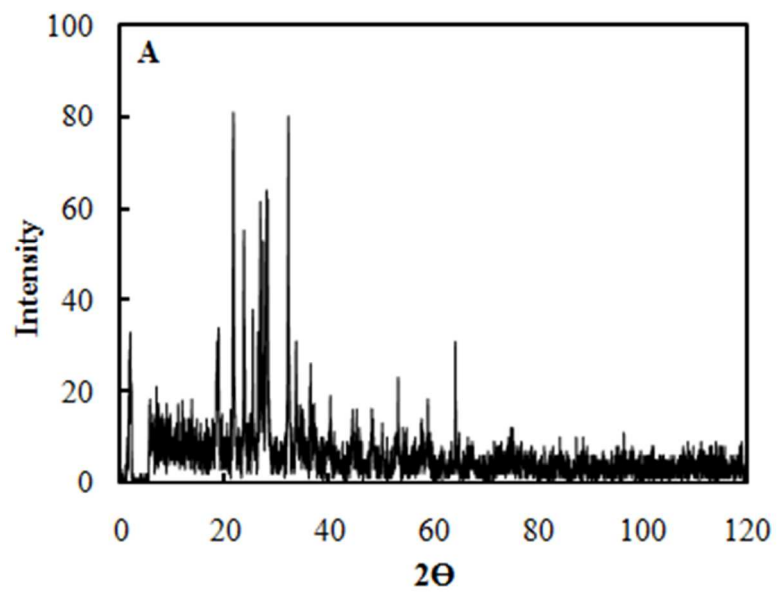
Fig. 4 XRD patterns of (A) pure lithium perchlorate, (B) un-leached and (C) leached nano particles.

167

168   The specific area of the sorbent was determined using Brunauer–Emmett–Teller (BET)
169   theory whereas the pore volume and average pore diameter were derived by the Barrett–Joyner–
170   Halenda (BJH) theory (Fig. 5). BET theory aims to explain the physical adsorption of gas
171   molecules on a solid surface and serves as the basis for an important analysis technique for the
172   measurement of the specific surface area of a material. The surface area, BJH adsorption
173   cumulative pore volume and BJH adsorption average pore diameter of the prepared lithium
174   imprinted polymer were found to be 98.03 m^2g^{-1}, 0.336 cm^3g^{-1} and 2.317 nm, respectively. These
175   data indicate that polymer materials with nano- pore and excessive surface area have been
176   prepared.

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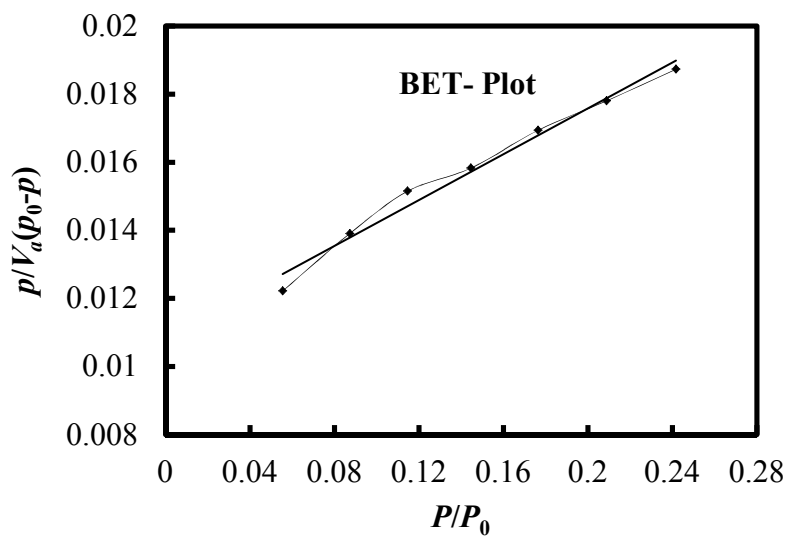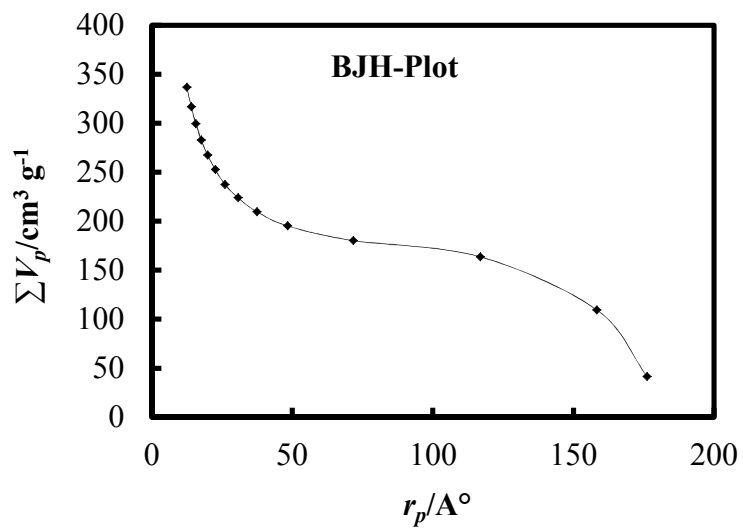
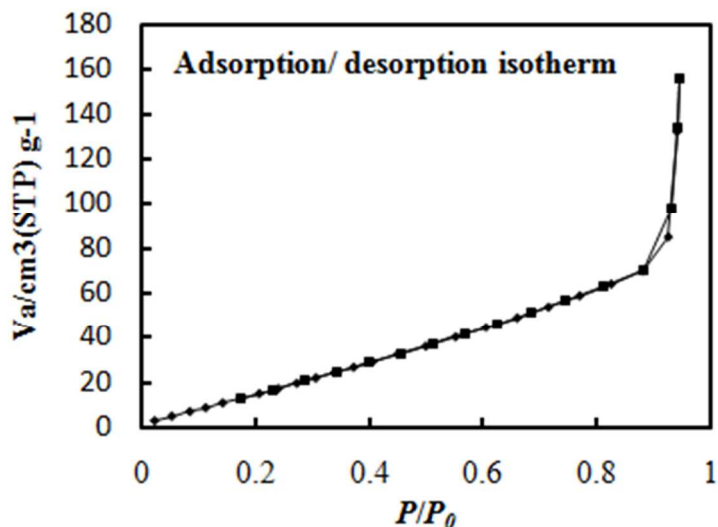**Fig. 5** BET, BJH and adsorption/desorption isotherms plots of the prepared lithium imprinted sorbent.

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

201 results indicated that more than 98% lithium uptake was achieved within 15 min (Fig. 6B). This

202 rapid adsorption equilibrium time is most probably due to high affinity between Li^+ ion and the

203 cavities in the polymer network structure.

204   The effect of desorption time was also investigated in batch experiments. The results

205 showed that the template ions could be quantitatively desorbed from the sorbent with 4 mL of

206 0.5 mol L^{-1} HNO_3 during 15 min. Therefore, 15 min was selected as desorption time for

207 subsequent experiments. (Fig. 6C)

208   In order to choose a proper eluent for leaching the adsorbed Li^+ ion, after its uptake from

209 aqueous media, lithium ion was eluted by different acidic solutions such as HNO_3, HCl, H_3PO_4

210 and H_2SO_4. After leaching of adsorbed lithium using 4 mL of 0.5 mol L^{-1} of each acid, the

211 effluent lithium was determined by flame photometer. It was found that the template ions could

212 be quantitatively (> 99%) desorbed from the particles with nitric acid. After selecting of HNO_3

213 as a proper leachant, in order to study its optimum concentration, several 4 mL portions of nitric

214 acid solutions with different concentrations (i.e., 0.001, 0.01, 0.1, 1.0 and 2.0 mol L^{-1}) were used

215 for leaching of Li^+ ions from the imprinted sites in the polymer network. It was found that a

216 concentration of 0.5 mol L^{-1} HNO_3 was required to remove the bound Li^+ ion (Fig. 6D). Thus, 4

217 mL of 0.5 mol L^{-1} HNO_3 was selected as optimal leachant solution. It is most possibly due to

218 complete protonation of donating hetero-atoms of binding sites in the cavities of sorbent, when

219 0.5 mol L^{-1} HNO_3 penetrate into polymeric network.

220   In the analysis of real samples, the sample volume is one of the important parameters

221 influencing the pre-concentration factor. Therefore, maximum sample volume up to which

222 quantitative Li^+ sorption occurred was determined by varying the sample volume (from 10 to 600

223 mL) each containing a constant amount of lithium ion. The results indicated that, the maximum

224 sample volume can be up to 400 mL with the recovery >97%. Thus, 400 mL was selected as the

225 maximum sample volume and a pre-concentration factor of 100 can be obtained.

226   The effect of the polymer particles weight on the quantitative adsorption of Li^+ ion onto

227 the prepared sorbent was studied. The results indicate no difference between 15 and 50 mg of IIP

228 particles in pre-concentration of lithium ions onto active sites of IIP. Thus, 15 mg of particles

229 were used for sorption- desorption studies.

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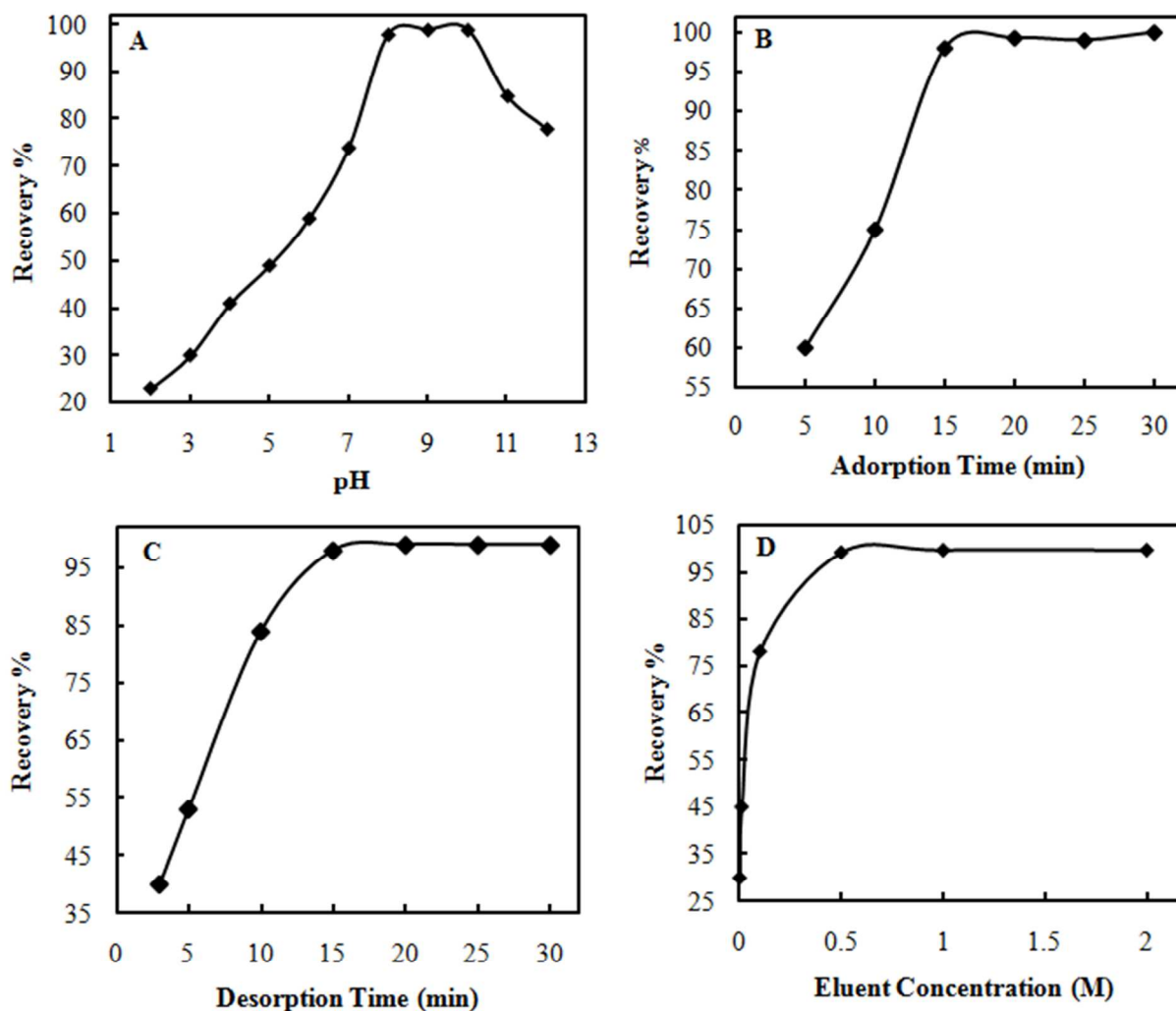
Fig. 6 Effect of different parameters on sorption of lithium ions on nano beads: (A) pH of solution, (B) adsorption time, (C) desorption time, (D) eluent concentration.

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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.

242   The resulting plot of Q vs. C_e is shown in Fig. 7. As can be seen, the amount of lithium

243   ions adsorbed per unit mass of the polymer increased linearly with the equilibrium concentration

244   of Li^+ ions from 0.03 to 88 µg mL^{-1} and reached a plateau in the adsorption profile at 150 µg mL^{-1}

245   which represents saturation of the active binding cavities on the lithium IIP beads. The

246   maximum sorbent capacity of ion imprinted (IIP) and non-imprinted polymeric (NIP) nanobeads

247   were obtained to be 1019.27 and 625.24 µmol g^{-1}, respectively. To the non-imprinted particles,

248   the amount of imprint ions adsorbed per unit mass of the sorbent is obviously lower than that of

249   lithium ion-imprinted particles, due to the fact that there were no active binding cavities on the

250   non-imprinted beads and physical adsorption.

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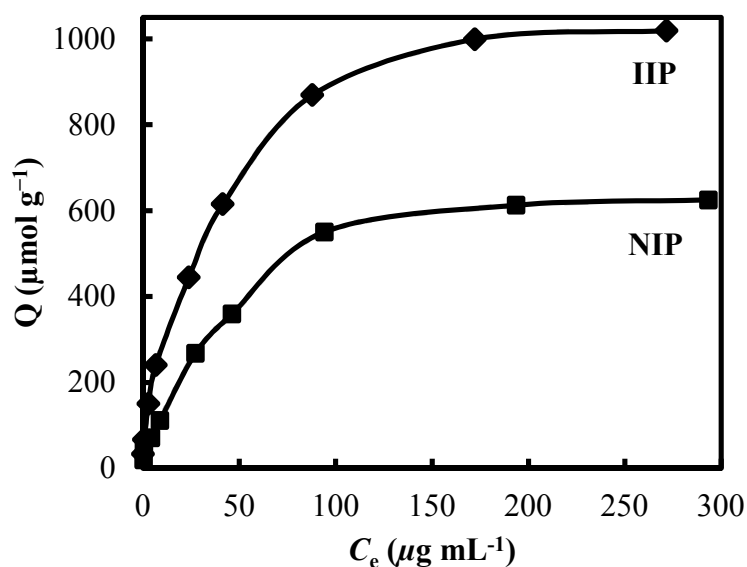
252

253   **Fig. 7** The study of adsorption capacity of Li^+ on nanoparticles.

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255   **3.4.   Reusability test**

256   To investigate the reusability of the prepared sorbent, the adsorption and desorption cycles were

257   repeatedly performed using the same nanoparticles. The adsorption–elution cycle were

258   performed ten times. Each experiment was performed under optimal conditions. The results

259   indicate that the lithium-imprinted sorbent can be used repeatedly without any significant loss in

260   the initial binding affinity. The relative standard deviation for ten replicates with the same

261   particles was found to be 0.97%.

262   **3.5.   Selectivity study**

263   In ion-imprinted polymers, chelating sites possess a uniform distribution [31] and the cavities

264   created after removal of template is complementary to the imprint ion in size and coordination

265   geometries [32]. Furthermore, the complexing agents used in their preparation usually have

266   selective affinities for the imprint ion. Competitive adsorptions of Li^+ / Na^+, Li^+ / K^+, Li^+ / Rb^+

267   and Li^+ / Cs^+ from their binary mixtures was investigated in a batch system. The distribution ratio

268   (K_d, mL g^{-1}) of lithium ion between the IIP particles and aqueous solution was also determined

269   by the following equation:

270

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

271

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

273

$$K_{Li^+/M^+} = \frac{K_d^{Li^+}}{K_d^{M^+}} \qquad (4)$$

274

275   where $K_d^{Li^+}$ and $K_d^{M^+}$ are distribution ratios of lithium and foreign ion, respectively. The relative

276   selectively coefficient, k′, is defined as:

277

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

278

279   where $k_{imprinted}$ and $k_{non-imprinted}$ are selectivity coefficients of the imprinted and non-imprinted

280   nanoparticles, respectively. In the corresponding mixtures studied, the two metal ions had the

281   same concentration of 1.0 μg mL^{-1} and the sorbent was 15 mg. Table 1 summarizes the

282   distribution ratios (K_d), selectivity coefficients (k) and relative selectively coefficients (k′)

283   calculated using Eqs. (3)–(5), respectively.

284 **Table 1** Distribution ratio (K_d), selectivity coefficient (k) and relative selectively coefficient (k´)

285 values of ion-imprinted polymer (IIP) and control non-imprinted polymeric (NIP) material for

286 different metal ions.

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

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

288

289 ### 3.6. Analytical performance

290 The characteristics of the analytical pre-concentration procedure were obtained under the

291 optimized conditions. The resulting calibration curve was linear within the concentration range

292 of 10-300 µg L^{-1}. The relative standard deviation (RSD.) for 5 replicate measurements of 50 µg

293 L^{-1} Li$^+$ was 2.1%. The limit of detection (LOD) corresponding to three times of the standard

294 deviation of blank was found to be 3.29 µg L^{-1}. The pre-concentration factor evaluated from the

295 ratio of the sample volume (400 mL) to the leachant volume (4 mL), is 100.

296

297 ### 3.7. Analysis of real samples

298 To test the reliability of the prepared polymer particles, the proposed method was applied to the

299 extraction and recovery of lithium ion in tap and well water samples. The corresponding relative

300 recoveries are summarized in Table 2 indicate the high potential of the prepared polymer for pre-

301 concentration and recognition of lithium ions from different water samples. Moreover, the

302 accuracy of the proposed method was checked by analyzing of lithium standard solution (Spectro

303 ECON) with the lithium concentration of 1000 ± 2 µg mL^{-1}. The lithium content obtained (mean

304 ± S.D., n=3) was 992.2 ± 2.1 µg mL^{-1}, which is in satisfactory agreement with reported value,

305 thus confirming the validity of the analytical procedure.

306   **Table 2** Analytical results for the determination of lithium ion in water samples.

Sample	Added ($\mu g\ L^{-1}$)	Found ($\mu g\ L^{-1}$)	Recovery (%)
Tap water	00	10.50	---
	30	40.17	98.9 ± 2.55
	50	60.33	99.7 ± 2.08
Well water	0	11.33	---
	30	40.67	97.8 ± 1.92
	50	60.83	99.0 ± 1.73

307

308

4. Conclusions

310   In this study we have reported the synthesis of Li^+- ion imprinted polymer which has efficient

311   analytical performance in pre-concentration of lithium. The proposed sorbent permits fast

312   recognition of analyte in aqueous sample. The selectivity factor of polymer particles relative to

313   Na^+, K^+, Rb^+ and Cs^+ was determined. The established extraction procedure can be applied to the

314   determination of lithium in real water samples. The sorbent characteristics, including

315   adsorption/desorption time, relative selectively coefficient, maximum sorbent capacity, polymer

316   size and reusability of the proposed Li^+–IIP system were compared with those of the previously

317   reported one (Table 3).

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325 **Table 3** Comparison of the proposed method with previous extraction method for determination

326 of lithium.

Ligand	Ads./Des. time (min)	Particle size (nm)	Maximum sorbent capacity (μmol g^{-1})	Reuse number	Relative selectively coefficient	Ref.
2M12C4[a]	10/--	300	586	5	Na (4.92) K (4.10)	[33]
12C4	15/15	50-60	1019.27	10	Na (18.58) K (26.24)	This work

327 [a] 2-methylol-12-crown-4

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Table of Content

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