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# Imprinted Polymer Particles for Aluminum Uptake: Synthesis and Analytical Applications

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This work reports the preparation of molecularly imprinted polymer (MIP) particles for selective extraction and determination of aluminum ion from aqueous media. Polymerization was achieved in a glass tube containing AlCl<sub>3</sub>, morin, 4-vinylpyridine, ethyleneglycoldimethacrylate, 2,2'-azobisisobutyronitrile. The polymer block obtained was ground and sieved (55–75 μm) and the Al (III)-morin complex was removed from polymer particles by leaching with 2 M of HCl, which leaves a cavity in the polymer particles. The polymer particles, both prior to and after leaching, have been characterized by IR and differential scanning calorimetry (DSC) studies. The effect of different parameters, such as pH, adsorption and desorption time, type and least amount of eluent for elution of complex from polymer were evaluated. Extraction efficiencies more than 99% were obtained by elution of the polymers with 15 mL of methanol-acetonitrile mixture (1:2) followed by ICP-OES. The limit of detection of the proposed method was 3.5 μg L<sup>-1</sup>. A dynamic linear range (DLR) in the range of 20 to 200 μg L<sup>-1</sup> was obtained. The relative standard deviation (RSD) was less than 6.5%. The influence of various cationic and anionic interferences on percent recovery of complex was studied. The method was applied to the recovery and determination of aluminum in different real samples.

**Keywords:** Aluminum (III), molecular imprinted polymer, morin, separation, application

## 1 Introduction

Aluminum has long been considered as virtually non-toxic and non-absorbable from the gastrointestinal tract. More recent studies on human, however, expose its acute toxicity (1), including impaired memory, convulsions, characteristic EEG changes, uremia, Shaveró's disease (lung) (2), Alzheimer's disease (brain) (3), and also increased risks of cancer of the lung and pancreas, and leukemia. Al at trace and sub-trace levels in the water used for dialysis can cause brain damage, bone disease and anemia (4). All these findings cause alarming concerns in public health, demanding accurate determination of this metal ion at trace and sub-trace levels.

Molecular imprinting has become a powerful method for the preparation of polymeric materials that have the ability to bind a specific chemical species (5,6). The imprinting process involves polymerizing functionalized monomers in the presence of a template molecule, which is typically the target or a molecule of similar size and chemical functional-

ity. Once the template is removed, a molecular recognition site of appropriate size and chemical functionality is produced to bind the target. Imprinted polymeric materials have been most often used as chromatographic stationary phases (7) or solid-phase extraction (8) materials. But they are finding increasing use as recognition elements in the development of chemical sensors (9).

Historically, there are two major approaches to molecular imprinting. The most widely used strategy, pioneered by Mosbach (10), relies on non-covalent interactions between specific function groups on the polymerizable monomers and spatial orientation prior to polymerization. After polymerization and removal of the template, the functional groups of the polymeric matrix can then bind the target via the same non-covalent interactions. The second imprinting approach developed by Wulff et al. (11), which utilizes reversible covalent bonding between a polymerizable monomer and a template molecule. After polymerization, these bonds are cleaved to liberate the template.

Lemaire and coworkers group (12,13) have developed ion imprinted resins based on EDTA and DTPA derivatives for the selective separation of Gd from La, Nd, Eu and Lu ions. Uezu et al. (14) reported that on post irradiation of imprinted polymer particles by γ-irradiation resulted in better separation of Zn compared with copper.

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Biju et al. (15) reported the effect of  $\gamma$ -irradiation of ion imprinted polymer particles for the preconcentrative separation of dysprosium. Biju et al. (16) reported a preconcentrative separation of dysprosium from Y(III), Nd(III), Lu(III) and La(III) ions by co-polymerizing Dy(III)-5,7-dichloroquinoline-8-ol-4-vinyl pyridine ternary complex, styrene and a crosslinker like divinylbenzene in presence of 2,2'-azobisisobutyronitrile as initiator.

In this study, an ion-imprinting polymer (IIP) was used for selective extraction and preconcentration of aluminum complex from aqueous solution. In synthesis processes, morin, 4-vinylpyridine (VP), ethyleneglycol dimethacrylate (EDMA) and 2,2'-azobisisobutyronitrile (AIBN) were used as Al complexing reagent, monomer, crosslinker and initiator, respectively. The synthesized polymer was applied for the selective extraction of aluminum from aqueous media. The effect of various experimental conditions, e.g. pH, adsorption and desorption time and type and volume of eluent on the extraction efficiency were investigated and optimized. The breakthrough volume, dynamic linear range and limit of detection were evaluated at optimal experimental conditions.

## 2 Experimental

### 2.1 Materials

VP, EDMA and AIBN were obtained from Aldrich (Milwaukee, WI). All acids used were of the highest purity available from Merck (Darmstadt, Germany) and used as received. Reagent grade  $\text{AlCl}_3$  and nitrate or chloride salts of other cations (all from Merck) were of the highest purity available and were used without any further purification. Reagent grade morin (Merck) was used as received. A stock solution of Al (1000 ppm) was prepared by dissolving the proper amount of  $\text{AlCl}_3$  in doubly distilled water in a 50-mL flask and diluting to the mark with water. Dilute solutions were prepared by appropriate dilution of the stock solution in doubly distilled water.

### 2.2 Apparatus

The measurements were performed with a simultaneous inductively coupled plasma optical emission spectrometry (ICP-OES, Varian Vista-Pro, Australia) coupled to a V-groove nebulizer and equipped with a charge coupled device (CCD). The ICP conditions are shown in Table 1. The pH was determined with a model 630 Metrohm pH meter with combined glass-calomel electrode.

### 2.3 Preparation of Polymer

The following procedure was used for synthesizing the polymer: 1.33 g of  $\text{AlCl}_3$  and 0.91 g of morin were weighed in a glass tube and dissolved in 15 mL of methanol. Four

**Table 1.** ICP-OES instrumental conditions

Plasma	Argon
RF generator power (kW)	1.5
Plasma gas flow rate ( $\text{L min}^{-1}$ )	15.0
Auxiliary gas flow rate ( $\text{L min}^{-1}$ )	1.5
Frequency of RF generator (MHz)	40.0
Observation high (mm)	8.0
Nebulizer pressure (KPa)	240

mmol of VP, 20 mmol of EDMA and 50 mg of AIBN were added into the solution. The oxygen of the solution was removed by bubbling of nitrogen through it for 10 min, then it was frozen with liquid nitrogen and sealed under vacuum. The polymerization reaction was performed in a water bath at  $60^\circ\text{C}$  for 10 h. After completion of polymerization, the solid polymer was crushed, ground and sieved to obtain particles with diameters in the range of 55–75  $\mu\text{m}$ . Fine particles were removed by suspending polymer beads in methanol and decantation of methanol three times. To remove templates, the remaining particles were treated with 2 M of HCl for 72 h, and the excess amount of HCl was washed by methanol. The complete removal of template was followed by ICP-OES. Finally, the particles were dried at  $80^\circ\text{C}$ . Figure 1 schematically shows the synthesis of ion imprinted polymer.

### 2.4 Complex Adsorption-Desorption Studies

Adsorption of complex from aqueous solutions was investigated in batch experiments. The polymer beads were suspended in aqueous solutions and the pH was adjusted at 5.2 by dropwise addition 1 M of sodium hydroxide or hydrochloric acid solutions. In the adsorption step, 0.2 g of imprinted polymer particles was added into a 25 mL aqueous solution containing 25  $\mu\text{g}$  of aluminum. The concentrations of aluminum ion in aqueous phases after desired treatment periods were measured by ICP-OES. The instrument response was periodically checked with known aluminum standard solutions. Three replicate extractions and measurements were performed for each aqueous solution. Percent extraction Al of was calculated from the following equation:

$$\% \text{ Extraction} = (C_A - C_B/C_A) \times 100$$

Where  $C_A$  and  $C_B$  are the concentrations of Al ion before and after extraction in the solution.

The adsorbed aluminum complex was desorbed from the IIP by treatment with 15 mL of methanol- acetonitrile (1:2 v/v). The imprinted polymer containing Al were placed in the desorption medium and stirred continuously at 600 rpm and room temperature for 8 h. The unbound aluminum amount to the polymer was obtained by subtracting the aluminum bound amount to the polymer from that of the initial aluminum loaded to the polymer.

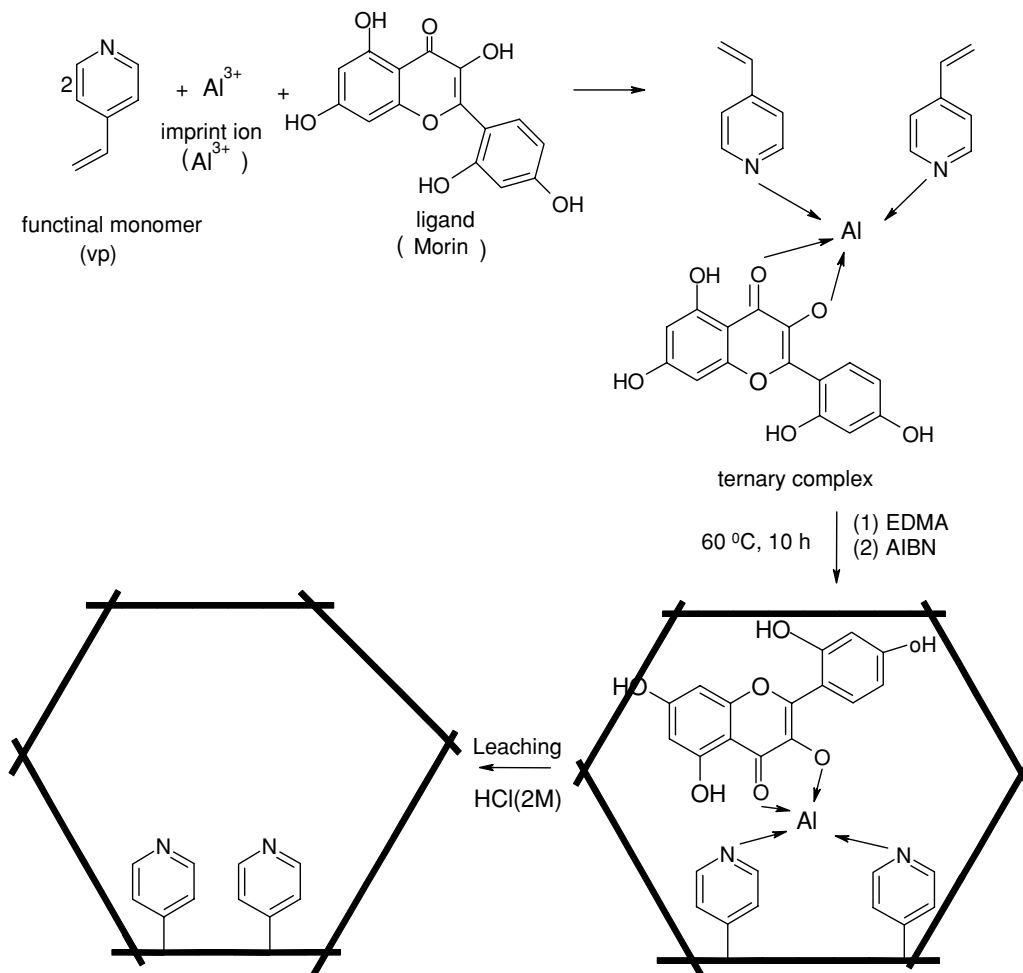


Fig. 1. Preparation of ion imprinted polymer material.

### 3 Results and Discussion

#### 3.1 Characterization of Polymer

##### 3.1.1. IR spectra

The IR spectra of unleached and leached aluminum imprinted polymer materials were recorded by using a KBr pellet method (Fig. 2). As is obvious, no band is present in the region of  $1648\text{--}1638\text{ cm}^{-1}$  indicating the absence of vinyl groups in polymer materials. This confirms the complete polymerization of vinyl pyridine. Meanwhile, there are other distinct differences between the IR spectra of the leached and unleached polymer. In the leached polymer, there is a band around  $2990\text{ cm}^{-1}$ . This band is lost in the unleached polymer's spectrum.

##### 3.1.2. Differential Scanning Calorimetry

DSC curves may also be used to evaluate polymer purities. This is possible because the temperature range over which a mixture of compounds melts is dependent on their relative amounts. Figure 3 shows the DSC plots of unleached and

leached aluminum imprinted polymer particles. In the case of unleached aluminum imprinted polymer particles, the change in DSC plots at  $280^\circ\text{C}$  is due to the aluminum-morin complex.

#### 3.2 Optimization of Adsorption and Elution of Aluminum Ion Using IIP in the Batch Method

In order to optimize conditions for obtaining high efficiency in a preconcentration of aluminum ions by IIP, it is necessary to adjust several factors including pH, adsorption and desorption time, type and the least amount of eluent.

##### 3.2.1. Effect of pH

The effect of pH value on adsorption of aluminum ion from water samples was investigated in the pH range of 1.5–5.5. A set of solutions containing  $25\text{ }\mu\text{g}$  of aluminum and  $75\text{ }\mu\text{g}$  of morin in 25 mL were taken. The pH of the solution was adjusted to the required value by the addition of 1 M sodium hydroxide and 1 M hydrochloric acid.

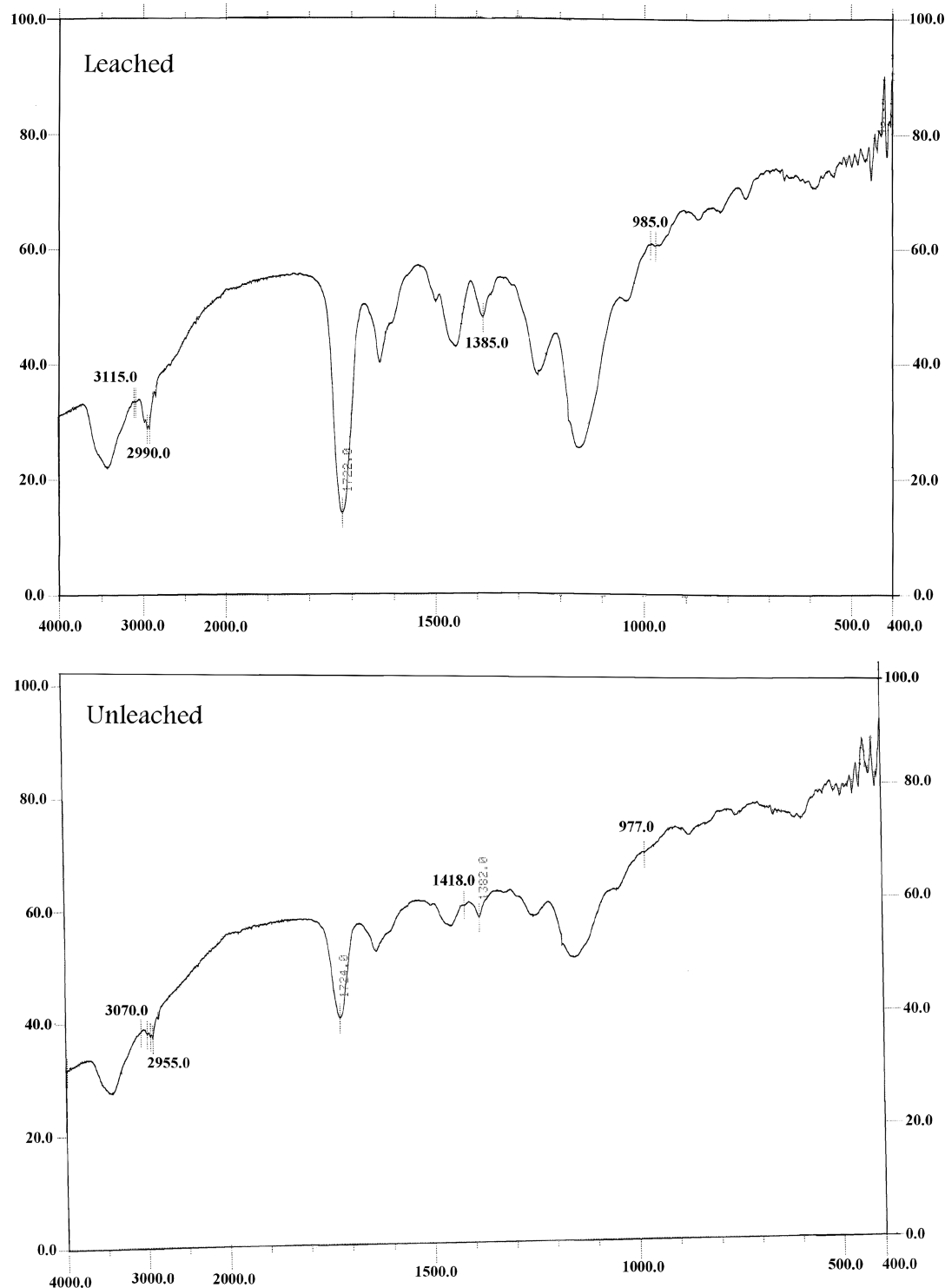


Fig. 2. IR spectra of unleached and leached aluminum imprinted polymer.

The effect of adsorption pH on the percent extraction of aluminum is shown in Figure 4. The results showed the optimum pH for adsorption of aluminum ions is pH of 5.2. Hence, the pH was adjusted to 5.2 in all subsequent studies.

### 3.2.2. Effect of amount of ligand

In order to investigate the optimum amount of morin on the quantitative extraction of aluminum by the IIP, ion extraction was conducted by varying the  $(\text{ligand})/(\text{Al})$  mole ratio from 1 to 10 and the results are shown in Figure 5. The

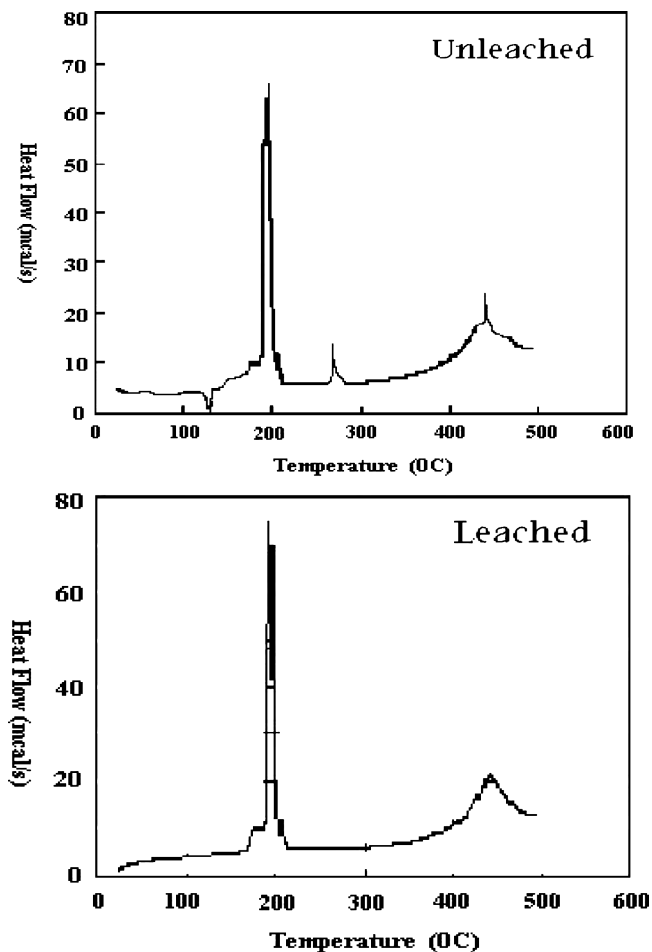


Fig. 3. DSC plots of unleached and leached aluminum imprinted polymer materials.

extraction of aluminum was found to be quantitative using (ligand)/(Al) mole ratios greater than 2. Hence, subsequent extraction experiments were carried out with (ligand)/(Al) ratio of 3.

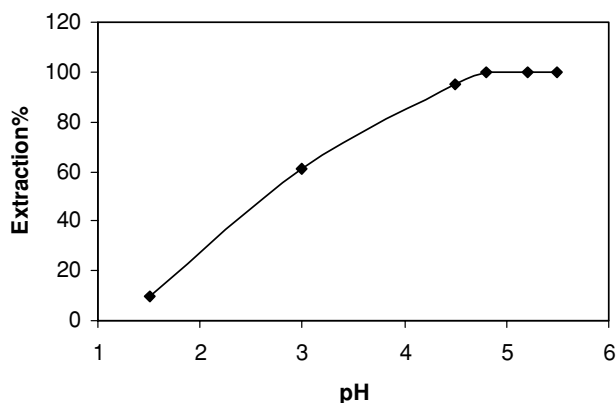


Fig. 4. Effect of pH on extraction efficiency of aluminum ions.

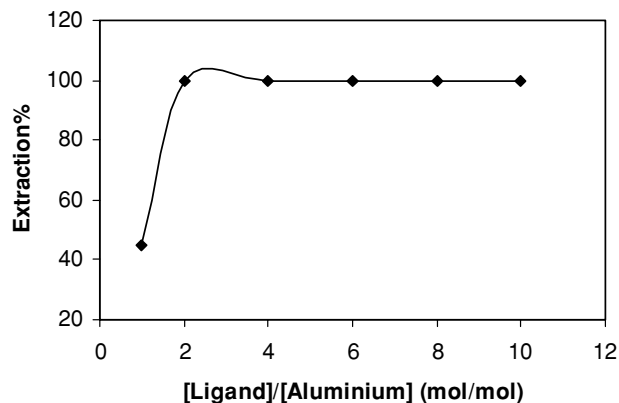


Fig. 5. Effect of the amount of ligand on the extraction efficiency.

### 3.2.3. Choice of eluent

In order to choose a proper eluent for the retained aluminum complex, after its extraction from water, the complex was stripped with different acidic solutions and organic solvents. From the data given in Table 2, it is obvious that 15 mL of a 1:2 (v/v) mixture of methanol-acetonitrile can accomplish the quantitative elution of complex from the imprinted polymer.

### 3.2.4. Effect of adsorption and desorption time

Figure 6 shows that the percent extraction of aluminum, increased by increasing adsorption time and reached to maximum at 90 min. Therefore, the optimum adsorption time of 120 min was selected and used in all subsequent studies.

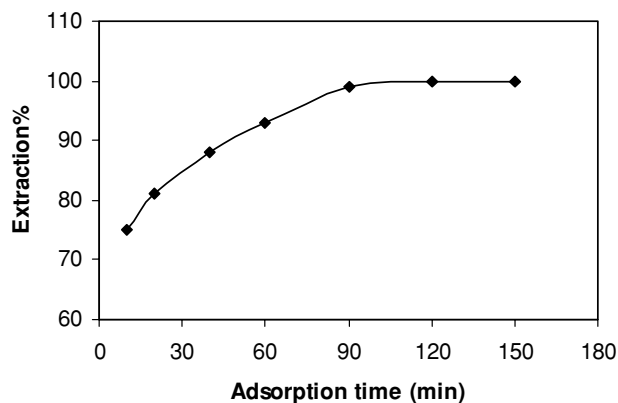
As shown in Figure 7, for quantitative recovery of pre-concentrated aluminum ions from dilute solutions, 8 h of elution with 15 mL of a 1:2 (v/v) mixture of methanol-acetonitrile is required.

## 3.3 Analytical Performance

The breakthrough volume of sample solution was tested by dissolving 25  $\mu\text{g}$  of aluminum and 75  $\mu\text{g}$  of ligand in 25, 50, 100, 250 and 500 mL solutions and the recommended procedure was followed. The aluminum ion recoveries for

Table 2. Effect of type and amount of eluent on extraction efficiency

Eluent	Volume (mL)	Recovery%
HCl 0.5 M	10.0	8.5
HCl 2 M	10.0	15.8
HNO <sub>3</sub> 2 M	10.0	14.2
CH <sub>3</sub> OH	10.0	10.0
CH <sub>3</sub> OH-CH <sub>3</sub> COOH (1:2)	15.0	60.5
CH <sub>3</sub> OH-CH <sub>3</sub> CN (1:2)	15.0	100.0



**Fig. 6.** Effect of adsorption time on extraction efficiency of aluminum ions.

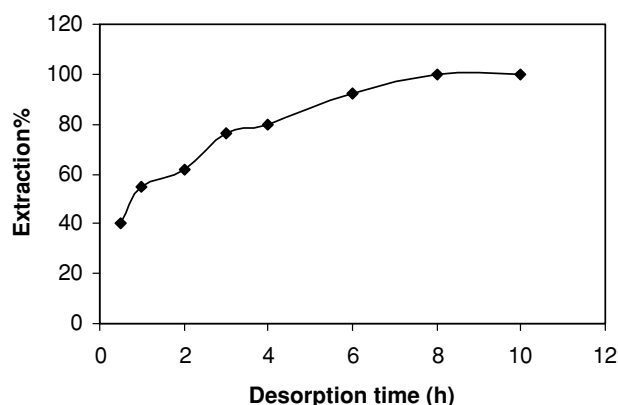
the above volumes were 100, 100, 100, 96 and 87%, respectively. Thus, 250 mL was the maximum sample volume in which quantitative extraction of Al is possible. At higher sample volumes, the recovery decreased.

Under the optimum conditions described, the calibration curve was linear over a concentration range of 20–200  $\mu\text{g L}^{-1}$ . The least square equation at above dynamic linear range was as follows:

$$A = 0.0049 \times C (\mu\text{g L}^{-1}) - 0.00764 \quad (r^2 = 0.998)$$

The limit of detection (LOD) of the proposed method for the determination of aluminum was studied under the optimal experimental conditions. The LOD obtained from  $C_{\text{LOD}} = 3(S_d)_{\text{blank}} \text{ m}^{-1}$  was  $3.5 \mu\text{g L}^{-1}$ .

All the statistical calculations are based on the average of triplicate extraction and measurement of each standard solution in the given range.



**Fig. 7.** Effect of desorption time on extraction efficiency of aluminum ions.

**Table 3.** Extraction of aluminum from binary mixtures<sup>a</sup>

Foreign ion	Amount taken (mg)	Recovery%
Li <sup>+</sup>	12.5 <sup>b</sup>	100.0
Na <sup>+</sup>	12.5	100.0
K <sup>+</sup>	12.5	100.0
Mg <sup>2+</sup>	12.5	100.0
Ca <sup>2+</sup>	12.5	100.0
Sr <sup>2+</sup>	12.5	100.0
Ba <sup>2+</sup>	12.5	100.0
Cu <sup>2+</sup>	2.0	90.0
Zn <sup>2+</sup>	2.0	92.0
Pb <sup>2+</sup>	2.0	96.0

<sup>a</sup>Amount of aluminum taken is 50  $\mu\text{g}$ .

<sup>b</sup>12.5 mg is the maximum of cation that was tested.

In order to investigate the selective separation and determination of aluminum ion from its binary mixtures with diverse metal ions, an aliquot of aqueous solution (25 mL) containing 50  $\mu\text{g}$  aluminum and milligram amounts of other cations was taken and the recommended procedure was followed. The results were summarized in Table 3. The results clearly revealed that the Al content was retained almost completely by the IIP, even in the presence of up to 12.5 mg of the diverse ions. Since the chloride, nitrate and sulphate salts were employed in this study without any interference, their respective anions pose no possibility of interference.

In order to assess the applicability of the method to real samples with different matrices, it was applied to the extraction and separation of aluminum ions from 50 mL of four different samples. Table 4 shows the extraction of 2.5  $\mu\text{g}$  of added aluminum ions from different samples. Results of four replicate analysis of each sample show that the aluminum recovery was almost quantitative.

**Table 4.** Recovery of 2.5  $\mu\text{g}$  aluminum added to 50 mL of samples.

Sample	Spiked amount ( $\mu\text{g L}^{-1}$ )	aluminum found ( $\mu\text{g L}^{-1}$ )	Recovery%	RSD%
Tap water	—	6.5	—	1.6
Tap water	50.0	56.8	101.4	1.8
Chahnemeh Water	—	6.9	—	2.1
Chahnemeh Water	50.0	56.7	99.7	2.2
Waste water	—	8.3	—	2.5
Waste water	50.0	58.6	100.5	2.8
Urine	—	—	—	—
Urine	50	50.5	101.0	6.5

#### 4 Conclusion

Molecular imprinting is a technique used for preparing polymers with synthetic recognition sites having predetermined selectivity for analyte of interest. The imprint is obtained by arranging polymerizable functional monomers around a template (the analyte). Complexes are then formed through molecular interactions between the analyte and the monomer precursors. The complexes are assembled in the liquid phase and fixed by crosslinking polymerization. Removal of the template from the resulting polymer matrix creates vacant recognition sites that exhibit affinity for the analyte. The potential of MIPs is high, since they show physical robustness, high mechanical strength, resistance to elevated temperature and pressures, and stability in the presence of extremes of acids, bases, metal ions and organic solvents, features that are favorable for routine analysis (10,11).

In the present work, a molecular imprinted polymer was prepared using the combination of VP as functional monomers, EDMA as crosslinker and Al-morin complex as template. The crosslinked imprinted adsorbents have good chemical and physical stability. The prepared MIP revealed high affinity and selectivity toward its template. The Al-imprinted adsorbent, which was highly selective toward Al ions, is expected to be a useful material for the interference-free extraction and preconcentration of Al ions.

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