New results on the extraction of Lithium ions from salt lake brine using ionic liquid tributyl phosphate

Abdloreza Hormati[1], Bahram Rezai[*2], Hadi Hamidian Shoormasti [3], Ghodratollah Rostami Paydar[*4]

[1]Department of Mining Engineering, Science and Research Branch, Islamic Azad University, Tehran, Iran. (hormati_reza@yahoo.com)
[2]Department of Mining Engineering, Amirkabir University of Technology, Tehran, Iran. (rezai@aut.ac.ir)
[3]Department of Mining and Geology, Qaemshahr Branch, Islamic Azad University, Qaemshahr Iran. (hhamidian@Qaemiau.ac.ir)
[4]Department of geology, Ahvaz Branch, Islamic Azad University, Ahvaz, Iran

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ABSTRACT

Lithium is a light metal with outstanding physical and chemical properties with many applications in the modern world. The concentration of lithium in sea water is on average 0.17 ppm and in the effluent of such a unit, it should be increased to 350 ppm on average. In this study, 1-hexyl-3-methylimidazolium [C_6mim^+] as cation and bis (trifluoromethylsulfonyl) imide [NTf_2^-] as anion of ionic liquid (ILS) using the neutral tributyl phosphate (TBP) were developed for efficient extraction of lithium ions (Li^+) from Salt Lake Brine. The effective parameters on lithium ions extraction process were studied including solution pH (~ 7), adsorbent dosage (100 & 300 mg) and extraction time (30 & 120 min). The extraction efficiency of lithium ion was 94 % fir ILS under the optimal conditions. The adsorption rate, adsorption capacity and mechanism are examined with applying the kinetic, isotherm and free energy models on experimental data. The Langmuir isotherm proposed adsorption capacity of 62.5 mg/g for ILs , respectively. This indicated multi-layer pattern for ILs. Free energy model is suggested a physical sorption mechanism for lithium ions. The obtained results are preformed the green ILs can be used as alternative extracting for Li^+ from salt lake brine.

Keywords: Lithium extraction, ionic liquid, tributyl phosphate, salt lake brine

1. Introduction

The lithium as a strategic metal is widely used in various fields such as energy storage, manufacturing heat-stable glass ceramics, pharmaceuticals, nuclear fusion fuel, catalyst production and high strength alloys are used [1-3]. According to the US Geological Survey, the distribution of lithium consumption in 2019 is as follows: batteries (35%); ceramics and glass (32%); lubricating greases (9%); Polymer production (4%); Continuous casting mold powders (4%). air purification (5%), and other things (11%). Lithium resources are usually found in salt lakes, seawater, clay and ore. Natural lithium sources can be divided into mineral and liquid forms. Spodumene, lepidolite and amblygonite and clays such as hectorite can be mentioned among the lithium minerals. The main liquid sources of lithium are seawater and lithium-rich brines [4]. Many salt lakes have high magnesium ions, which makes effective lithium separation very difficult. Today, various separation techniques have been developed to recover lithium from brine salts, which include precipitation, adsorption, ion exchange, liquid extraction with ionic solvent, electrolysis, selective semi-permeable membrane [5-6], evaporative crystallization, electrochemical separation method [7-8]. The organic extractants used in this method must have two important features: 1) have a high extraction efficiency compared to lithium ion. 2) Show a satisfactory separation coefficient for lithium compared to metal ions, especially magnesium. In the process of microextraction by ILs, it is necessary to use dispersing solvents such as acetonitrile, acetone, 2-propanol, n-butanol and methanol and also to separate IL from the water phase without losing IL in the separation step. In order to overcome the mentioned challenges, recently, a dispersive microextraction method based on ionic liquids (IL-DLLME) and magnetic nanoparticles has been developed for the rapid and efficient determination of metal ions, especially lithium ions, followed by extraction with an external magnet. The stability of ILs can be significantly increased by chemical modification by magnetic nanoparticles [9-14]. In this study, a new

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and simple microextraction method based on ionic liquid (IL), by inductively coupled plasma emission spectrometry (ICP-OES) was used to extract lithium from brine. In fact, the innovation of using an ionic liquid consisting of 1-hexyl-3-methylimidazolium (as cation) and bis (trifluoromethylsulfonyl) imide (as anion) ([C6 mim][NTf2-]) along with tributyl phosphate (TBP).

2. Experimental

2.1 Materials and chemicals

The ionic liquid of 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl) imide ([C_6mim^+][TF_2N^-]) is purchased from Atlas-Shimi (Zanjan, Iran). Tributyl phosphate, tetraethoxysilane (TEOS), $FeCl_2.4H_2O$, $FeCl_3.H_2O$, ammonia and hydrochloric acid (HCl 36%) were obtained from Merck chemicals (Darmstadt, Germany). Salt Lake Brine was obtained from sarbandar of the Khouzestan, South West of Iran with pH 6.7 and density 1.25[7].

2.2 Instruments

IR spectra were recorded in the range of 400-4000 cm^{-1} using Bruker IR spectrometer (Bern, Germany). Morphology IL was analyzed with Zeiss (Bremen, Germany) field emission scanning electron microscopy equipped with energy dispersive accessory (EDX). So the Inductively coupled plasma mass spectrometry (ICP-OES) was from Varian (CA, USA) was used for analysis of lithium ions and other metal cations in solution.

2.3 Microexterction method based on ionic liquid

The precursor of ionic liquid is 1-hexyl-3-methylimidazolium chloride. The reaction mechanism of the formation of this precursor is shown in Figure 1. The ion exchange reaction of NTF2⁻ is performed instead of Cl⁻ during the mechanism of Figure 2

because the chloride anion is a good leaving group and can be easily removed and replaced. Finally, the hydrophobic ionic liquid [C6mim+][TF2N-] is formed and it is separated from the aqueous phase first with the help of a decanter, and then with the help of distilled water, the impurities and unreacted raw materials are separated and after removing it, at a temperature of 100 degrees is heated, until the distilled water is completely removed.
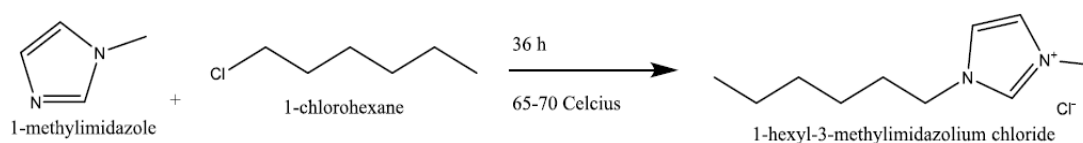
Fig. 1. Mechanism of ionic liquid formation 1-methylimidazolium and 1-chlorohexane
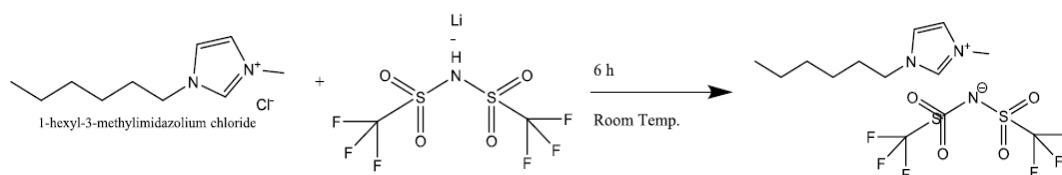

Fig. 2. Mechanism of ionic liquid formation   1-hexyl-3-methylimidazolium $[C_6mim^+][TF_2N^-]$

The synthesis of magnetic ionic liquids can be divided into three steps: 1) synthesis of Fe_3O_4 magnetic nanoparticles 2) functionalization of Fe_3O_4 nanoparticles with silica (Fe_3O_4@SiO_2) 3) coating of Fe_3O_4@SiO_2 nanoparticles with ionic liquid (MNPs@ILs).

The extraction method of lithium ions was carried out under two different methods. Magnetic solid phase extraction method (Figure 3B): Briefly, the magnetic adsorption process continued with the dispersion of 100 mg of MNPs@IL in 20 mL of aqueous solution. Then the effect of pH on the removal process was investigated in the range of 2 to 9, adsorbent dose from 10 to 300 mg and extraction time from 10 to 120 minutes. The adsorbent was collected with the help of an external magnet, and the aqueous solution was filtered with a syringe filter (PTFE, 0.2 μm) before injection into ICP-OES for residual lithium ion analysis

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(dispersive liquid-liquid microextraction by ionic liquids (ILs-DLLME) with tributyl phosphate (TBP) extractant shown in Figure 3C. Briefly, the ILs-DLLME method for the extraction of lithium ions was carried out using [C6mim+][TF2N-] and TBP as extractants in a ratio of 1:10. For this purpose, 300 mg of [C6mim+][TF2N-] was stirred in 20 ml of water for 5 minutes, then 3 ml of TBP was added and it was examined in different time intervals in the range of 10-120 minutes and different pH. After the extraction process, the mixture was centrifuged for 5 min (500 rpm) and the aqueous phase (lower phase) was analyzed by ICP-OES to identify the remaining lithium ions.
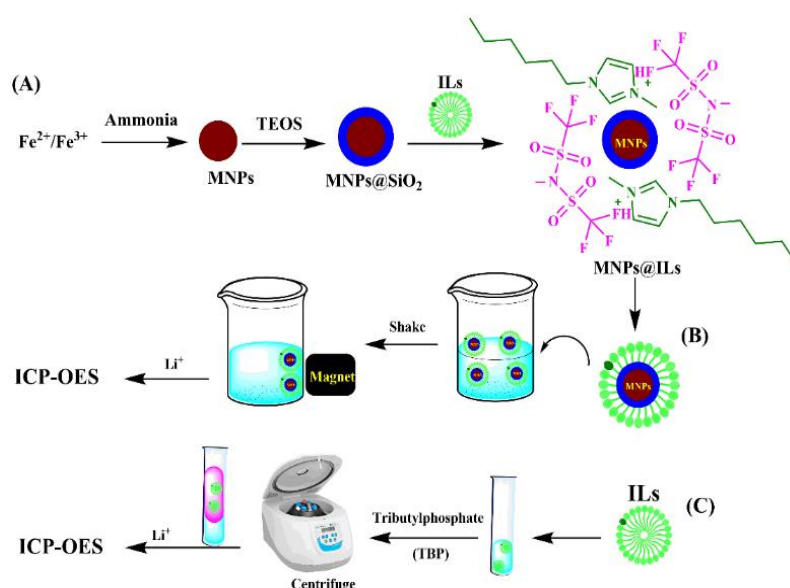
Fig. 3. Schematic procedure for preparation of MNPs@ILs nanocomposite.

3. Results and discussion

The surface morphology of the ionic liquid supported magnetic MNPs@ILs nanoparticles was investigated with FESEM microscopy. Elemental composition of the MNPs@ILs nanocomposite is performed with EDX spectroscopy as reported as EDX spectra (Fig. 4C) and EDX mapping (Fig. 4D). The EDX spectra of MNPs@ILs nanocomposite is provided the expected elements properly, which are including C, P, N, S, F, Si and Fe with weight percentage of 21, 11, 11, 2, 0.3 and 0.2 w/w%, respectively.
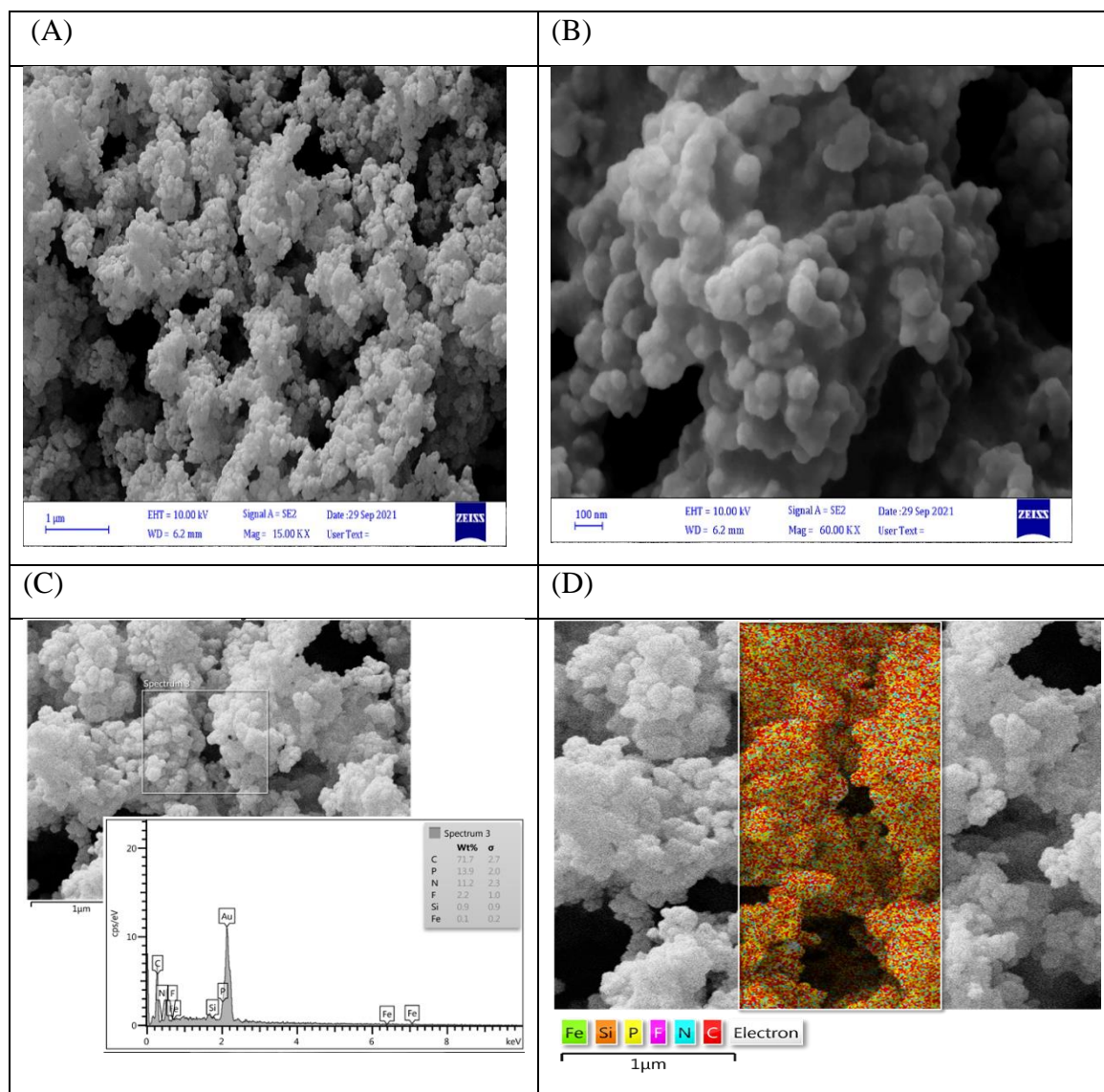
Fig. 4. SEM micrograph of MNPs@ILs (A) magnification 1500 kx and (B) magnification 6000kx. EDX spectra (C) and mapping (D) of MNPs@ILs.

The functional groups of magnetic nanoparticles and magnetic ILs (MNPS@ILs) were studied by FT-IR spectroscopy. In figure 5, the infrared spectrum was recorded in the wave number range of 400-4000 cm for MNPs@SiO$_2$ and MNPs@IL. As shown in spectrum A, the distinct peaks at 1040 and 570/cm are related to Si-O and Fe-O functional groups of MNPs@SiO$_2$ nanoparticles, respectively. The immobilization of ILs on MNPs shows new peaks in the spectrum (B) that include 3208, 2985, 1305, 1065, 1020 and 800/cm, which are respectively related to the functional groups N-H, C-H (-CH$_3$ bonds), SO$_2$, CF3, S-N and C-N

are compatible. It is clear that the new peaks on Si-O and Fe-O bands are related to ILs, and it confirms the successful immobilization of ILs on MNPs. In figure 5(C), the magnetic properties of the MNPs@ILs nanocomposite have been investigated, which includes the s-shaped symmetrical curve, which shows that the nanomagnetic particles are surrounded by the ionic liquid, and the direction of the extraction process with the help of the supercenter magnetic field of the ionic liquid with the nanomagnetic particles.
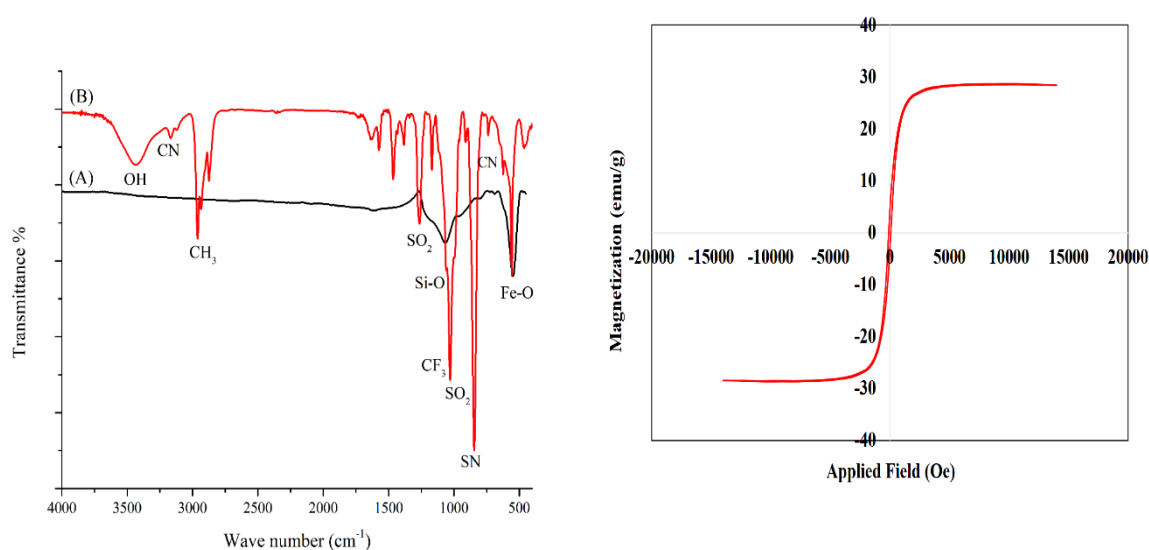
Fig. 5. FTIR spectra of (A) silica MNPs and (B) MNPs@ILs. (C) VSM analysis of MNPs@ILs nanocomposite.

3.1 Effect of parameters on extraction

Firstly the amount of IL and MNPs@ILs synthesized on the extraction efficiency was tested in the mass range of 10 to 300 mg, and the corresponding graph is shown in Figure 6. Therefore, 300 mg and 100 mg were selected for ILs and MNPs@ILs, respectively. Secondly, the pH of the solution directly affects the charge distribution of the adsorbent and thus its interaction with the analytes. Therefore, the pH of the solution was checked in the range of 2-10. As shown in Figure 7, the extraction efficiency with ILs is not significantly affected by pH from 2 to 10. In fact, at the proposed pHs, the change in efficiency is less than 5%, which can be attributed to the stability of ILs at different pHs.
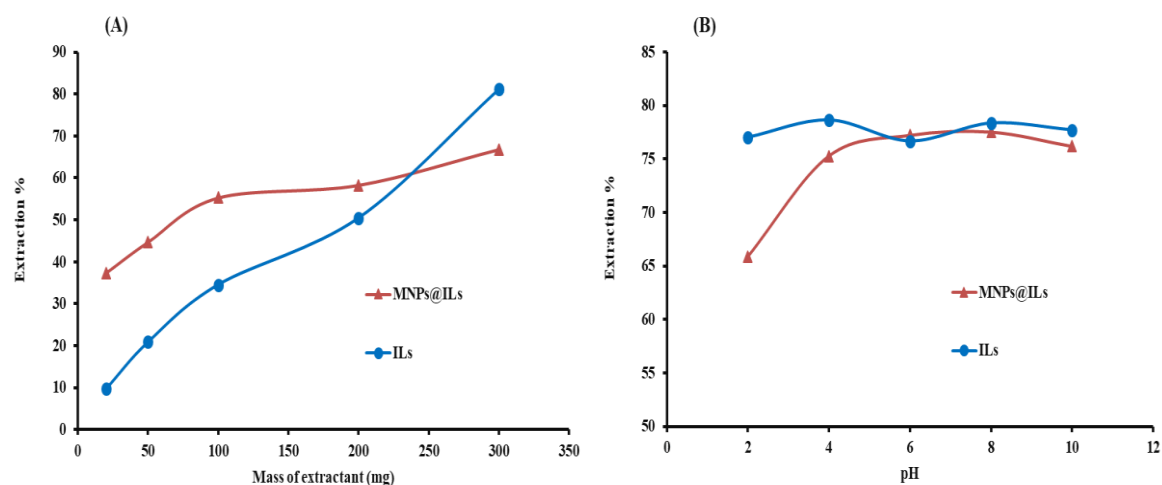
Fig. 6. (A) Effect of amount of ILs and MNPs@ILs dosage on extraction efficiency
(B) Effect of solution pH on extraction efficiency

The experiments show that the back extraction (striping) of lithium ion with pure water is done with low efficiency, while the extraction efficiency is 45.5% and 3.92% for ([C6mim+][TF2N-]) IL and MNPs. @ILs were obtained using pure water and 71.78% and 98.64% of lithium ions were separated from the ILs phase with 0.5 M and 2 M HCl solutions, respectively, which shows that Li+ is easily separated from the ionic liquid phase loaded with HCl. will be This is due to the presence of massive chloride ions that interact with Li+. In addition, 91.78% of lithium ion was separated from MNPs@ILs with 2 M HCl solution. The contact time between lithium ion and ILs or MNPs@ILs is an important parameter in the extraction process, which directly affects the extraction efficiency. The contact time is to increase the mass transfer between the solution containing lithium ions and IL or MNPs@IL until reaching the equilibrium and obtaining the highest extraction efficiency. Therefore, the extraction efficiency was investigated in the range of 5 to 120 minutes for ILs (300 mg) and MNPs@ILs (100 mg). As shown in Figure 7, the extraction efficiency increased continuously from 60 min for IL and MNPs@IL. Thus, 60 min was selected for ILs and for MNPs@ILs for further extraction process. The adsorption rate, adsorption capacity and mechanism are

examined with applying the kinetic, isotherm and free energy models on experimental data, respectively [7]. The Langmuir isotherm proposed adsorption capacity of 62.5 mg/g and 20.8 mg/g for ILs and MNPs@ILs, respectively[15].
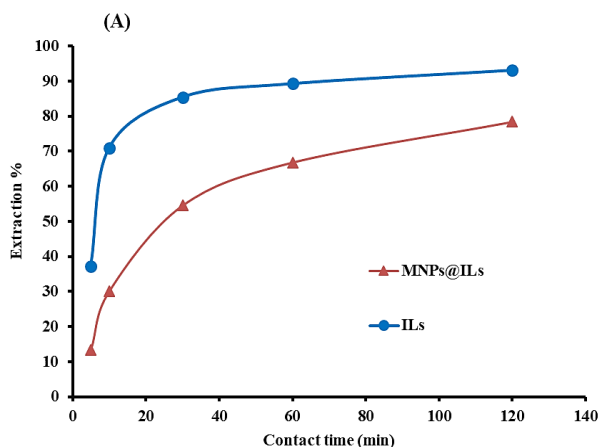

Fig. 7. Effect of contact time on extraction efficiency

3.2 Lithium extraction mechanism

As shown in Figure 8(A) and survey literature, cation exchange mechanism is highly recommended for extraction of lithium ions using ILs, As discussed in previous studies, the extraction of lithium using ([C4mim][NTF$_2$]) and TBP are following the cation exchange mechanism (Shi, Jing and Jia, 2016), which is close to current study for Li$^+$ extraction with ([C6mim][NTF$_2$]) and TBP. The cation exchange mechanism between Li$^+$ and ILs is demonstrated by assistance of UV absorbance principal [16-18] While, magnetic extraction of Li$^+$ over MNPs@ILs nanocomposite is provided different mechanism (Fig. 8 B), which is including π-cation and electrostatic interaction. Due to the negative nature of Fluorine (F) it can be interact with Li$^+$ via electrostatic interaction.
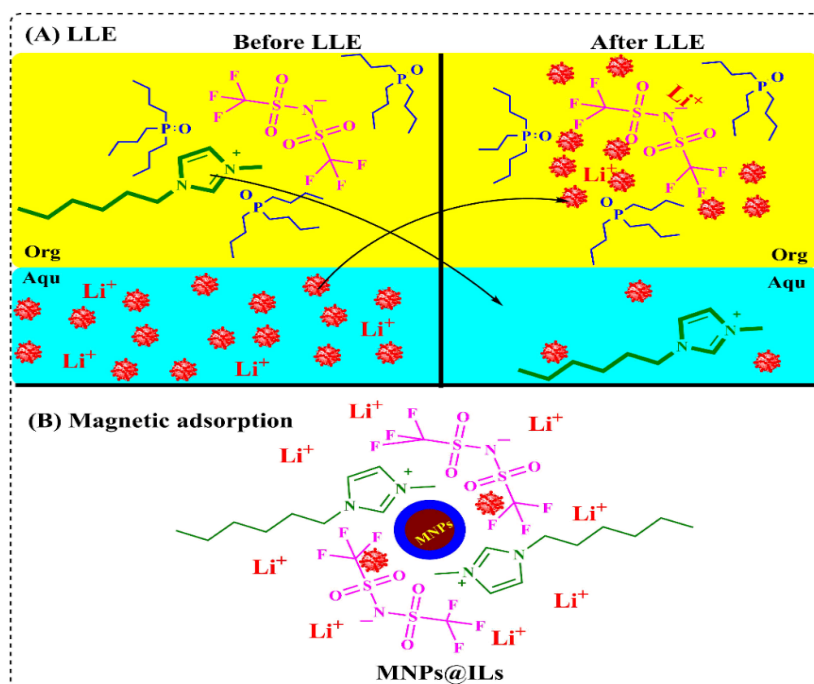
Fig. 8. Proposed mechanism for extraction of lithium using **(A)** ILs and **(B)** MNPS@Ils

4. Conclusion

Dispersive liquid microextraction method has advantages such as high concentration factors, simplicity of work, cheapness and consumption of small amount of organic solvent. In this work, ionic liquids that have characteristics such as being liquid in a wide range of temperatures, low vapor pressure, and non-volatility were used, and minimal organic solvent was used in this work. Finally, it is worth noting that using the test design method in the micro-extraction of the dispersive liquid is very useful due to reducing the number of tests and considering the effect of different factors at the same time. The use of ionic liquid (ILs) and magnetic ionic liquid (MNPs@ILs) as a green extractant for the absorption of lithium ions from the sludge has been investigated. 1) Examining the peaks obtained from FTIR confirmed the synthesis of ILs, the doping of ILs on the surface of MNPs. 2) Using electron microscope in different magnifications and FE-SEM examination of the morphology (morphology) of the surface of nanoparticles showed that the synthesis of MNPs@ILs has been done successfully. 3) The effect of different parameters on lithium absorption by

MNPs@ILs adsorbent shows that the extraction efficiency of Li+ reached the maximum at pH=4-8 for MNPs@IL adsorbent. The highest extraction efficiency of 90% and 83% of lithium ion was obtained with IL and MNPS@IL, respectively. Compared with other adsorbents, ILs and MNPs@ILs are an inexpensive material with high extraction efficiency, high adsorption capacity and lithium cation exchange potential.

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