

Impregnation of different ionic liquids onto cationic starch and their comparison in the extraction of Th(IV)

Elif ANT BURSALI, Serap SEYHAN BOZKURT, Mürüvvet YURDAKOÇ*
Department of Chemistry, Faculty of Science, Dokuz Eylül University, İzmir, Turkey

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Abstract: Cationic starch (CS) was prepared by using epichlorohydrin (EPI) and 3-chloro-2-hydroxypropyltrimethylammonium chloride (CHPTMA) and ionic liquids (ILs) having different anionic groups [1-butyl-3-methyl imidazolium tetrafluoroborate ($\text{BMI}^+ \text{BF}_4^-$), 1-butyl-3-methyl imidazolium bromide ($\text{BMI}^+ \text{Br}^-$), 1-butyl-3-methyl imidazolium hexafluorophosphate ($\text{BMI}^+ \text{PF}_6^-$), and 1-butyl-3-methyl imidazolium bis-[(trifluoromethyl)sulfonyl]imide ($\text{BMI}^+ [(\text{TF})_2\text{N}]^-$)] were impregnated onto CS. Thorium(IV) ions were preconcentrated by using IL impregnated CS. The effects of ILs were investigated for extraction of Th(IV) by CS and the results were compared. Th(IV) was preconcentrated with approximately 73% sorption capacity by CS and increased up to 98%–100% for IL impregnated sorbents at pH 7.0. The sorption capacities of Th(IV) were $0.453 \text{ mmol g}^{-1}$, $0.399 \text{ mmol g}^{-1}$, $0.281 \text{ mmol g}^{-1}$, and $0.183 \text{ mmol g}^{-1}$ for CS– $\text{BMI}^+ \text{Br}^-$, CS– $\text{BMI}^+ [(\text{TF})_2\text{N}]^-$, CS– $\text{BMI}^+ \text{PF}_6^-$ and CS– $\text{BMI}^+ \text{BF}_4^-$, respectively. The elution occurred with HCl and NaOH solutions at pH 7.0.

Key words: Thorium extraction, cationic starch, ionic liquids

1. Introduction

Starch has attracted attention in recent years because of its relative low price, renewability, and biodegradability. However, the use of native starch is limited by its physicochemical properties such as water insolubility and swelling power. The performance properties of starches can be altered through such physical or chemical modifications to extend their usefulness in many applications in industrial processes.¹

Cationic starches (CSs) are generally made by treating starch with reagents containing positively charged groups. These starches have physicochemical properties that are significantly different from their raw materials.^{2–4} CSs were frequently used in adsorption and extraction studies of metal ions and due to having a cationic group its mineral binding property has grown in importance.^{5,6}

Ionic liquids (ILs) are inorganic and organic salts with melting points at or below 100°C . Most ILs are composed of organic cations (e.g., imidazolium, pyridinium, pyrrolidinium, ammonium, and phosphonium) and organic (e.g., trifluoromethylsulfonate, trifluoroethanoate) or inorganic (e.g., Cl^- , Br^- , I^- , PF_6^- , and BF_4^-) anions.^{7,8} ILs have attracted interest as green solvents as a result of their exceptional properties. They are nonvolatile and nonflammable, and have negligible vapor pressure, good conductivity, tunable viscosity, an excellent feature of solvation, and high thermal stability. The physical and chemical properties of ILs can be tuned through control of the nature and functionality of the cation or anion.^{9,10}

*Correspondence: m.yurdakoc@deu.edu.tr

ILs have been the focus of many scientific investigations¹⁰ including analytical chemistry,¹¹ synthesis,¹² separation processes,¹³ green chemistry,¹⁴ spectroscopy,¹⁵ and electrochemistry.¹⁶ ILs have been recently used in solid phase extraction studies by being impregnated onto support materials such as silica gel¹⁷ and biopolymers. ILs could adsorb metal ions together with biopolymers or supporting materials having active binding sites by electrostatic attraction.¹⁸

Th(IV) ion, a nonrenewable resource of nuclear energy present in nuclear fuel effluents, mine tailings, seawater, and other sources, is an environmental health threat. Therefore, its preconcentration, extraction, and separation from geological samples and waste sources by biopolymers is important in order to protect the environment from this radioactive element.^{19–21}

In the present study, starch was converted to CS by using epichlorohydrin (EPI) and 3-chloro-2-hydroxypropyltrimethyl-ammonium chloride (CHPTMA). Then ILs containing different anion groups were impregnated onto the CS and obtained sorbents were used for preconcentration of Th(IV) in aqueous solution. The results obtained from the sorbents impregnated with different ILs were compared.

2. Results and discussion

2.1. FTIR analysis

FTIR spectra of the synthesized ILs were taken. In the spectra, aromatic =C–H and aliphatic –C–H stretching vibrations varied between 3069 and 3167 cm^{-1} and 2860 and 2972 cm^{-1} for four ILs respectively. –C=N stretching vibrations were seen between 1566 and 1573 cm^{-1} . S=O and S–N vibrations were also observed at 1348 cm^{-1} and 1182 cm^{-1} for $\text{BMI}^+[(\text{TF})_2\text{N}]^-$, respectively.

FTIR spectra of CS, CS–ILs and CS–ILs after Th(IV) sorption were so similar that only the spectra of CS, CS– BMI^+Br^- and CS– BMI^+Br^- –Th are given in Figure 1. In Figure 1a, an extremely broad band at 3400 cm^{-1} was due to the hydrogen-bonded hydroxyl groups of CS. Aliphatic C–H stretching vibrations associated with the ring methine hydrogen atoms were observed at around 2928 cm^{-1} . The band at 1653 cm^{-1} , which was due to water adsorbed in the amorphous regions of starch, and the bands located at 1460–1373 cm^{-1} region were probably related to C–H bending vibrations. The bands assigned to C–O and C–C stretching vibrations were observed at around 1018, 1080, and 1158 cm^{-1} .^{1,22} The characteristic C–N bands related to quaternary amine groups (R_4N^+), at around 1460–1373 cm^{-1} and 1158–1018 cm^{-1} regions, probably overlapped with C–H bending, and C–O and C–C stretching vibrations.

The spectra of CS, CS– BMI^+Br^- , and CS– BMI^+Br^- –Th (Figures 1a–1c) were very similar in shape and the frequencies of the characteristic absorption bands did not change very much. Quite small changes were observed in the intensities of the bands of CS and CS– BMI^+Br^- , whereas CS– BMI^+Br^- –Th showed significant differences.

2.2. SEM analysis

SEM analysis was applied to CS–ILs and thorium (IV) treated CS–ILs. Images of the surface of the samples at $250\times$ magnification are shown in Figures 2 and 3.

It was observed that different sized spherical-like particles were present in a sense among the coarse and fine particles in the SEM image of CS (Figure 2a).

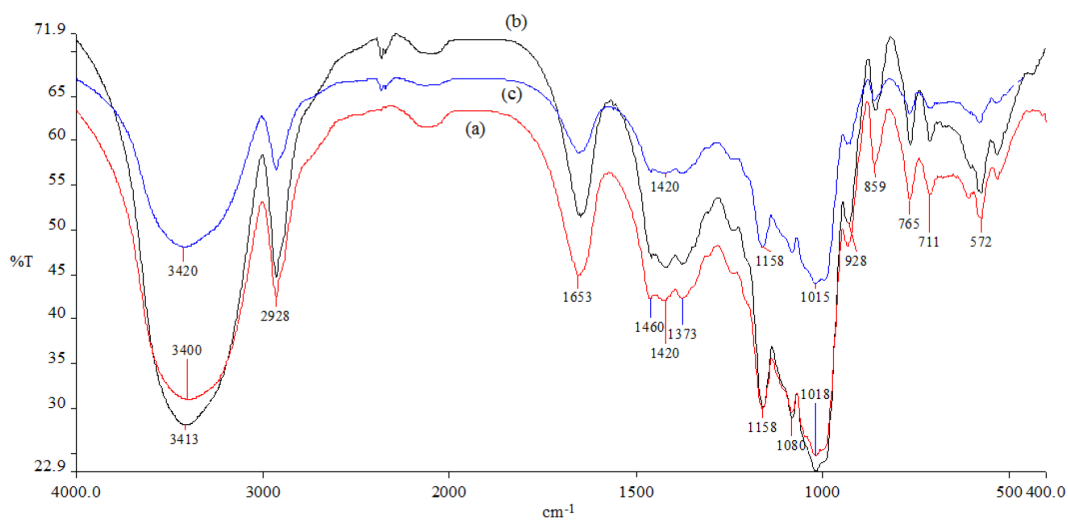


Figure 1. FTIR spectra of CS (a) CS-BMI⁺Br⁻ (b) and CS-BMI⁺Br⁻-Th (c).

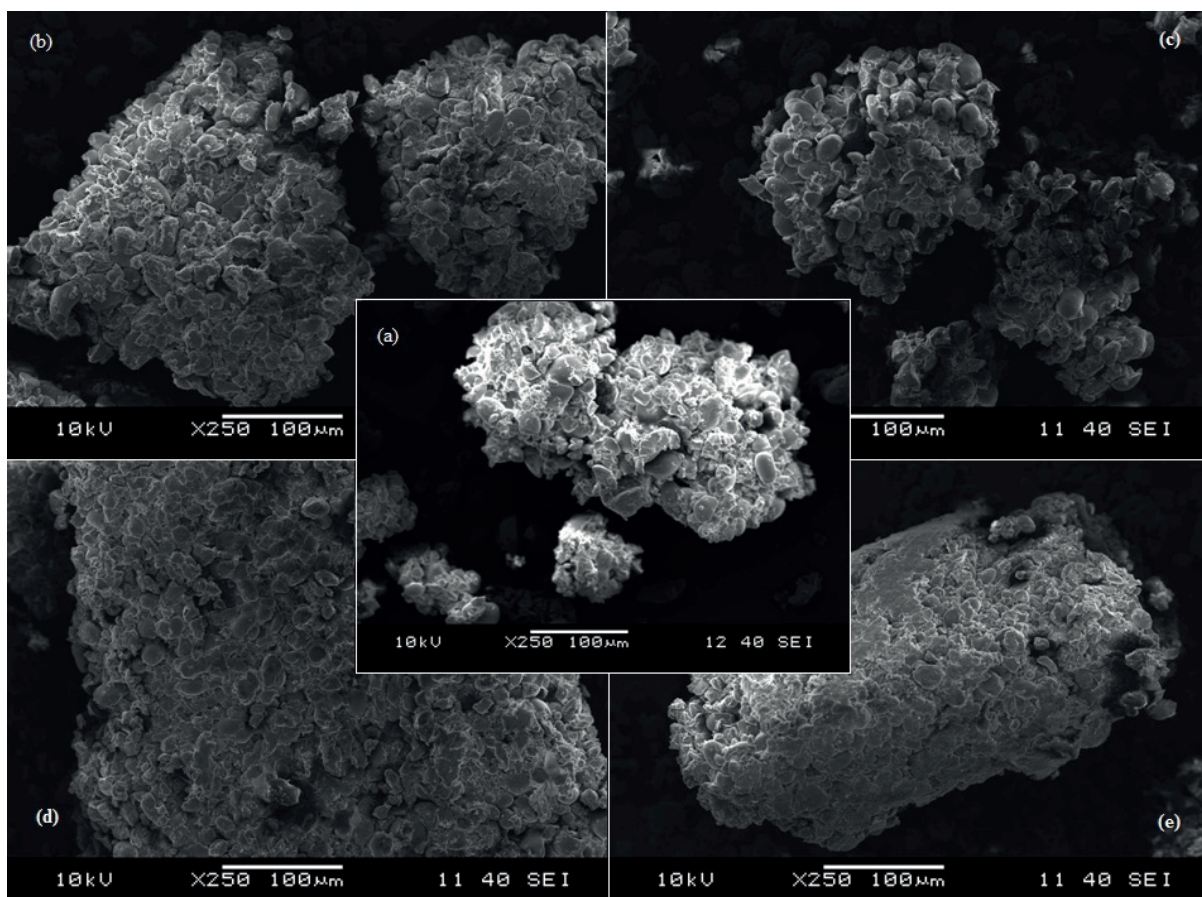


Figure 2. SEM images of the surface of CS and CS-ILs: (a) CS, (b) CS-BMI⁺[(TF)₂N]⁻, (c) CS-BMI⁺Br⁻, (d) CS-BMI⁺BF₄⁻, (e) CS-BMI⁺PF₆⁻.

After being impregnated with BMI⁺Br⁻, the size of both particles and the holes inside the particles were not changed so much when compared with surface morphology of CS. However, the sizes of these holes

were greatly diminished due to aggregation in $\text{BMI}^+[(\text{TF})_2\text{N}]^-$, $\text{BMI}^+\text{BF}_4^-$, and $\text{BMI}^+\text{PF}_6^-$ impregnated CSs (Figures 2b–2e). Especially in $\text{BMI}^+\text{BF}_4^-$ and $\text{BMI}^+\text{PF}_6^-$ impregnated CSs, huge clusters were observed similar to each other.

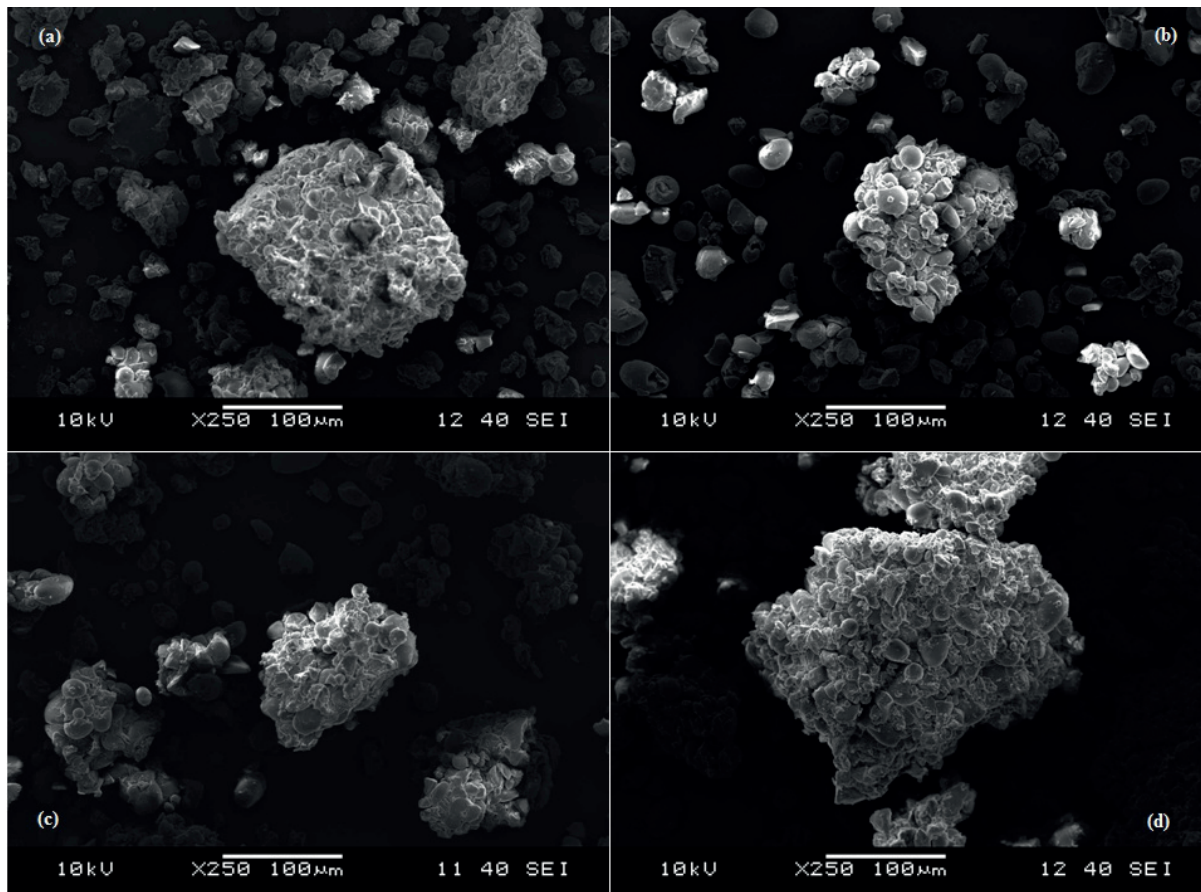


Figure 3. SEM images of the surface of CS-ILs treated with Th(IV): (a) CS-BMI⁺[(TF)₂N]⁻-Th, (b) CS-BMI⁺Br⁻-Th, (c) CS-BMI⁺BF₄⁻-Th, (d) CS-BMI⁺PF₆⁻-Th.

The surface morphology of CS-ILs treated with Th(IV) ions (Figures 3a–3d) showed that aggregates were dissociated into extremely small particles in all IL impregnated CSs.

2.3. Thermal stability

Thermogravimetric analysis (TGA) was used to determine the thermal decomposition behavior of CS, CS-ILs, and CS-ILs-Th. The thermal behaviors of the CS-ILs and CS-ILs-Th(IV) showed similar results. The mass losses temperatures of the CS-ILs and CS-ILs-Th were between 296 and 298 °C and 304 and 307 °C, respectively. Thermal decomposition temperature of all the Cs-ILs after Th(IV) extraction increased about 8–9 °C. TGA curves of CS, CS-BMI⁺PF₆⁻, and CS-BMI⁺PF₆⁻-Th are given in Figure 4.

2.4. Interaction between cationic starch and ionic liquids

The schematic illustration of the interaction between CS and ILs is given in Figure 5.

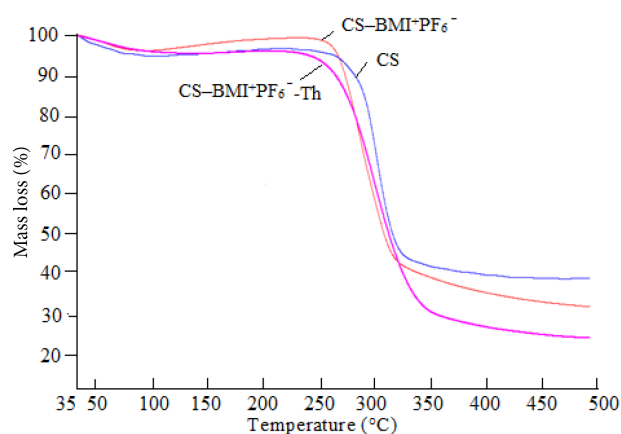


Figure 4. TGA curves for CS, CS-BMI⁺PF₆⁻, and CS-BMI⁺PF₆⁻-Th.

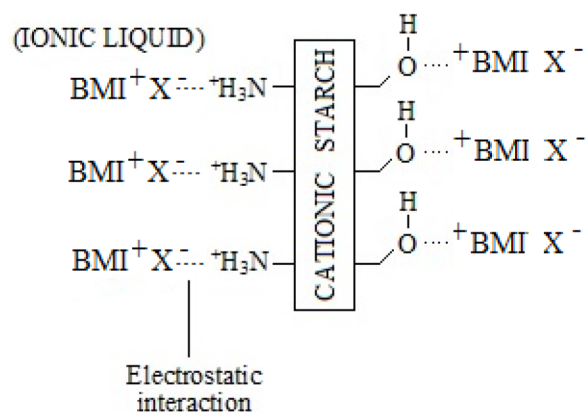


Figure 5. Hypothetically proposed interaction between CS and ILs.

The anionic parts of the ILs interacted with positively charged groups of CS by the electrostatic interaction. Moreover, the imidazolium groups of ILs interacted with the lone pair of electrons of oxygen atoms in the hydroxyl groups of CS.

2.5. Effect of pH on the sorption of thorium ion

The effect of pH on the preconcentration of thorium(IV) ion by CS was investigated and the results are given in Figure 6. As seen from the figure, in the range of pH 6.0–8.0, thorium (IV) was preconcentrated with approximately 73% sorption capacity by CS. The experiments were repeated for different IL impregnated CSs. The results showed that sorption values were increased up to 98%–100% for all ILs. However, the IL difference did not affect the pH of metal ion preconcentration. Therefore, the optimum pH value was accepted as pH 7.0 for all other experiments.

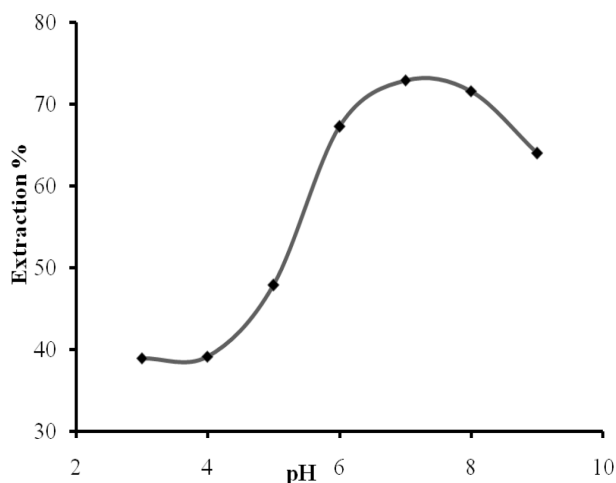


Figure 6. Effect of pH on Th (IV) ion preconcentration.

2.6. Sorption capacity

To determine the sorption capacity of the sorbents, different volumes of 5 $\mu\text{g mL}^{-1}$ Th(IV) were passed through the column. The loaded Th(IV) ions were eluted with stripping solutions from each sorbent and

measured spectrophotometrically. The sorption capacities of Th(IV) were $0.453 \text{ mmol g}^{-1}$, $0.399 \text{ mmol g}^{-1}$, $0.281 \text{ mmol g}^{-1}$, and $0.183 \text{ mmol g}^{-1}$ for CS-BMI⁺Br⁻, CS-BMI⁺[(TF)₂N], CS-BMI⁺PF₆⁻, and CS-BMI⁺BF₄⁻, respectively.

On the other hand, the sorption of Th(IV) reached $0.040 \text{ mmol g}^{-1}$ for PAN/zeolite,²³ $0.082 \text{ mmol g}^{-1}$ for diatomite,²⁴ $0.215 \text{ mmol g}^{-1}$ for $\gamma\text{-Al}_2\text{O}_3$,²⁵ $0.001 \text{ mmol g}^{-1}$ for SiO₂,²⁶ $0.006 \text{ mmol g}^{-1}$ for Zr₂O(PO₄)₂,²⁷ $0.057 \text{ mmol g}^{-1}$ for oxidized multiwall carbon nanotubes,²⁸ and 0.58 mmol g^{-1} for graphene oxide,²⁹ respectively.

2.7. Stripping of thorium from CS-ILs

In order to determine the stripping of Th(IV) from sorbents, hydrochloric acid and sodium hydroxide with concentrations of 0.1, 0.5, 1, and 2 mol L⁻¹ were used. For quantitative recovery of Th(IV), 1.0 mol L⁻¹ HCl for CS-BMI⁺Br⁻ and CS-BMI⁺[(TF)₂N]⁻, and 1.0 mol L⁻¹ and 0.1 mol L⁻¹ NaOH for CS-BMI⁺BF₄⁻ and CS-BMI⁺PF₆⁻, respectively, were found sufficient.

To optimize the stripping volume, different volumes of stripping solutions were tested for each sorbent. It was observed that the stripping volume was 8 mL for CS-BMI⁺Br⁻, 3 mL for CS-BMI⁺[(TF)₂N]⁻, 5 mL for BMI⁺BF₄⁻, and 7 mL for CS-BMI⁺PF₆⁻.

3. Conclusion

In this work, CS-based solid phase extraction sorbents having different ILs were used to separate Th(IV) ions from aqueous solutions and for preconcentration of this ion.

The optimum pH value for preconcentration of Th(IV) ions was pH 7.0. Th(IV) was preconcentrated with approximately 73% sorption capacity by CS but this value increased up to 98%–100% for IL impregnated sorbents. The IL difference did not affect the pH.

Sorption capacities for Th(IV) ions were $0.453 \text{ mmol g}^{-1}$ and $0.399 \text{ mmol g}^{-1}$ for CS-BMI⁺Br⁻ and CS-BMI⁺[(TF)₂N]⁻ sorbents, respectively, with the highest sorption values. It could be concluded that, due to the excess of cavities in the sorbent impregnated with IL including Br⁻ as anionic group, the sorption capacity was higher than that of the other ILs. Furthermore, in CS-BMI⁺[(TF)₂N]⁻ sorbent not only the cavities but also the structure of the anionic group acting as a ligand by itself affect the increase in sorption capacity of Th(IV) ion.

In the case of stripping of Th(IV) ion from the sorbents, NaOH solutions were used for CS-BMI⁺BF₄⁻-Th and CS-BMI⁺PF₆⁻-Th due to the fact that the ILs have low electron density on the central atom, X⁻. On the other hand, HCl solutions were used for CS-BMI⁺[(TF)₂N]⁻-Th and CS-BMI⁺Br⁻-Th because the ILs have high electron density on the central atom, X⁻.

4. Experimental

4.1. Materials, reagents, solvents, and measurements

Thorium concentrations were determined spectrophotometrically by arsenazo-III method with a Shimadzu 1601 UV-Vis spectrophotometer.^{30–32}

FTIR spectra of the obtained sorbents and ILs were recorded with a PerkinElmer Spectrum BX-II Model

Fourier Transform IR spectrometer using KBr pellets in the range of 4000 and 400 cm^{-1} , at a resolution of 4 cm^{-1} , and with an average of 50 scans.

Morphological analyses of samples were performed with an emission scanning electronic microscope (SEM), JEOL JSM 6300F, operated at an acceleration voltage of 10 kV.

Thermal analyses of the samples were carried out using a PerkinElmer Diamond TG/DTA instrument. The analysis was performed under nitrogen flow from 30 °C to 600 °C at a heating rate of 10 °C/min.

A Denver 215 model pH meter for adjustment of pH and a Heidolph MR standard magnetic stirrer were used for the preparation of the sorbents. The solvents during synthesis of ILs were evaporated by a Buchi Rotary evaporator. Millipore Milli-Q system ultrapure water equipment was used during the study. A Watson Marlow 323i model peristaltic pump was used in the preconcentration process. For solid phase experiments a Varian cartridge (plastic container, 1.0 cm \times 10.0 cm) equipped with 20-mm polypropylene frits was used. PTFE tubing with i.d. of 0.5 mm was used for all connections.

N-methyl imidazole (Aldrich), butyl bromide (Aldrich), ammonium hexafluorophosphate (Aldrich), ammonium tetrafluoroborate (Aldrich), lithium bis(trifluoromethanesulfonyl)imide (Merck), potato starch (Fluka), epichlorohydrin (Aldrich), 3-chloro-2-hydroxypropyl-trimethyl-ammonium chloride (Fluka), ammonium hydroxide solution (Fluka), sodium hydroxide (Fluka), hydrochloric acid (Riedel-de Haën), and all other reagents used were of analytical reagent grade and were used without any further purification. Potato starch was dried in an oven for 2 h at 105 °C before use. The water used throughout the study was deionized.

The stock thorium solutions were prepared by dissolving analytical reagent grade nitrate salt of thorium(IV) (Merck) in ultrapure water. Working solutions were prepared by appropriate dilution of the stock solutions. For pH adjustments, NaOH and HCl solutions were used.

4.2. Preparation of cationic starch

In order to prepare CS, 1.62 g (10 mmol) of potato starch was mixed with EPI as cross-linking agent and also with CHPTMA in alkali medium of NH_4OH (25% solution) and NaOH. The molar ratios used were 0.030 (EPI):0.010 (NH_4OH):0.050 (NaOH):0.372 (H_2O):0.030 (CHPTMA). The mixture was stirred for 24 h at room temperature at 500 rpm. The product was filtered and washed with deionized water up to neutral pH. Then the product was washed further with ethanol and acetone. Finally it was dried at 45 °C for 3 h.⁵

4.3. Preparation of ionic liquids

ILs having different anionic groups (Figure 7) were synthesized and impregnated onto CS. ILs were mainly synthesized according to Özdemir et al.³³ and Ceyhan et al.³⁴ Therefore, the preparation procedures given here were shortly and modified in the following parts.

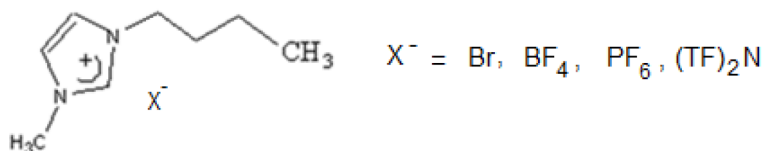


Figure 7. The ILs used in the study.

4.3.1. 1-Butyl-3-methyl imidazolium bromide ($\text{BMI}^+ \text{Br}^-$)

A mixture of 0.04 mol N-methyl imidazole, 0.04 mol butyl bromide, and 25 mL of toluene was refluxed at 60–70 °C for 2 h. After cooling to room temperature, the lower phase, which contained the product, was separated from the upper phase. The product was washed a few more times with toluene and yellowish viscous liquid was obtained in 95% yield.

4.3.2. 1-Butyl-3-methyl imidazolium tetrafluoroborate ($\text{BMI}^+ \text{BF}_4^-$)

First 0.02 mol imidazolium bromide salt, 0.02 mol NH_4BF_4 , and 50 mL of dichloromethane solvent were mixed at room temperature for 24 h. Then ammonium bromide was filtered and the solvent was evaporated using a rotary evaporator. The yield was calculated as 75%.

4.3.3. 1-Butyl-3-methyl imidazolium hexafluorophosphate ($\text{BMI}^+ \text{PF}_6^-$)

First 0.02 mol imidazolium bromide salt and 0.02 mol NH_4PF_6 were added to 50 mL of dichloromethane. The mixture was then stirred at room temperature for 24 h. At end of the reaction, ammonium bromide was filtered and dichloromethane was evaporated using a rotary evaporator. The yield was calculated as 75%.

4.3.4. 1-Butyl-3-methyl imidazoliumbis-[(trifluoromethyl)sulfonyl]imide $\text{BMI}^+ [(\text{TF})_2\text{N}]^-$

First 0.02 mol imidazolium bromide salt was added to 50 mL of dichloromethane and mixed. Then 0.02 mol bis(trifluoromethanesulfonyl)imide salt of lithium was added to the stirring solution of imidazolium bromide salt. The mixture was left stirring for about 24 h at room temperature. Then the lithium bromide salt was filtered and the concentrated AgNO_3 solution was added to the solution. The resulting solution was washed with pure water so that AgBr was allowed to pass into the water phase. Then dichloromethane was evaporated with a rotary evaporator. The yield was calculated as 60%.

4.4. Preparation of ionic liquid impregnated cationic starch

First 0.5 g of CS was added to a solution of 0.5 g of ILs ($\text{BMI}^+ \text{Br}^-$, $\text{BMI}^+ \text{BF}_4^-$, $\text{BMI}^+ \text{PF}_6^-$, and $\text{BMI}^+ [(\text{TF})_2\text{N}]^-$) in acetone. The mixture was then stirred for 24 h at room temperature, filtered, and washed with deionized water. The resulting material was dried at 45 °C for 3 h.

4.5. Preconcentration method

First, 0.1 g of CS–IL sorbent was wetted in 5 mL of methanol and 5 mL of ultrapure water was added. The mixture was transferred to the solid phase extraction column. Later, 10 mL of methanol:water (10:90) was passed through the column. In the preconcentration experiments 50 mL of 5 ppm Th(IV) solution was used. The pH of the solution was adjusted to 7.0 and then passed through the column at a flow rate of 1.0 mL min^{-1} . Th(IV) ions were eluted from the column by 8 mL of 1.0 mol L^{-1} HCl for CS– $\text{BMI}^+ \text{Br}^-$, 3 mL of 1.0 mol L^{-1} HCl for CS– $\text{BMI}^+ [(\text{TF})_2\text{N}]^-$, 5 mL of 1.0 mol L^{-1} NaOH for CS– $\text{BMI}^+ \text{BF}_4^-$, and 7 mL of 0.1 mol L^{-1} NaOH for CS– $\text{BMI}^+ \text{PF}_6^-$ sorbents. Eluted ions were determined spectrophotometrically at 667.5 nm after the addition of 1 mL of KCl/HCl buffer and 0.2 mL of arsenazo III in a total volume of 5 mL.

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