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ORIGINAL ARTICLE

Sol–gel processed pyridinium ionic liquid-modified silica as a new sorbent for separation and quantification of iron in water samples

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Abstract 1-Hexylpyridinium hexafluorophosphate [C_6py][PF_6] ionic liquid (IL) was firstly used for chemical modification of silica utilizing the acid-catalyzed sol–gel processing. The obtained pyridinium IL-modified silica was employed as a solid phase extraction (SPE) sorbent for removal of trace levels of Fe(III) ions from aqueous samples. The influence of different variables on the separation efficiency, including the concentration of chelating agent, pH, sample flow rate and volume, eluent type, concentration and volume, and interfering ions was investigated by flame atomic absorption spectrometry (FAAS). In the optimum experimental conditions, the limit of detection (3s), limit of quantification (LOQ) and pre-concentration factor were 0.7 μg L^{-1}, 2.5 μg L^{-1}, and 200, respectively. The relative standard deviation (RSD) for nine replicate determinations of 25 μg L^{-1} Fe was 3.2%. The calibration graph using the pre-concentration system was linear in the range of 2.5–50 μg L^{-1} with a correlation coefficient of 0.9997. The developed method was validated by the analysis of certified reference material and applied successfully to the separation and determination of iron in several water samples.

1. Introduction

d = "p0005" > Iron is an essential and useful element for organism and an important part of tissue and blood in animal and human being (Xiong et al., 2006). Iron deficiency anemia or other hypochromic anemia can affect metabolism in muscles and can as well influence oxygen delivery, which can reduce the activity of iron dependent mitochondrial enzymes. However, if iron concentration exceeds the normal level it may become potential health hazard. For example, high levels of iron are associated with an increased risk for cancer, heart disease, and other illnesses, such as endocrine problems, arthritis,

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diabetes, and liver disease. A sanitary security limit for iron was restricted to 2 mg L^{-1} by World Health Organization (WHO, 2003). Therefore, it is crucial to develop simple, rapid, and efficient methods for monitoring of iron at trace levels in environmental, biological, and food samples.

Direct determination of trace metal ions at low concentrations in complex matrices is often a problem for analytical chemists. In order to overcome this problem, a sample preparation step is often required. The sample preparation in analytical processes typically consists of separation and pre-concentration steps. Up to now, several techniques such as co-precipitation (Tokalıoğlu et al.,2007; Elci et al., 2003), ion exchange (Pehlivan and Altun, 2007; Jiang et al., 2005), liquid–liquid extraction (LLE) (Wanga et al., 2005; Oliva et al., 2002), cloud point extraction (CPE) (Manzoori et al., 2007a, b), solid phase extraction (SPE) (Chang et al., 2007; Divrikli etal., 2007; Ghaedi et al., 2008a, b; Mashhadizadeh et al., 2008; Tu et al., 2009), and etc., have been developed for separation and pre-concentration of metal ions prior to their determination. Among these methods, SPE is one of the most common techniques used for pre-concentration of analytes in water samples because of its advantages of high enrichment factor, high recovery, rapid phase separation, low cost, low consumption of organic solvents, and the ability of combination with different detection techniques in the form of on-line or off-line mode (Zang et al., 2010).

In SPE procedures, the choice of the sorbent is a key point because it can control the analytical parameters such as selectivity, affinity and capacity. Many adsorption materials, such as organic chelate resin, silica, titania, alumina and molecular-imprinted polymers (MIPs), have been used as sorbents for SPE (Zhang et al., 2007). In order to increase the adsorption capacity, to enhance the removal efficiency, and to add selectivity to the solid phase, modification and impregnation techniques of solid phase have been employed (Ghaedi et al., 2009a).

Ionic liquids (ILs) are a class of low melting point ionic compounds containing relatively large asymmetric organic cations and inorganic or organic anions, which have a variety of properties allowing many of them to be sustainable "green solvents" in chemical reactions. Due to their low volatility, high stability, and good solubility for organic and inorganic compounds, ILs have been successfully applied in many fields of analytical chemistry such as sample preparation, organic synthesis, solid-phase micro-extraction, liquid-phase micro-extraction, mobile phase additives or stationary phases in liquid chromatography, electrolyte additives in capillary electrophoresis and stationary phases in gas chromatography and electro-chromatography (Tian et al., 2009; Fang et al., 2010).

The application of immobilized ILs in separation and clean-up procedures has recently aroused much interest. Ionic liquid-modified silica has been successfully used as sorbent for solid phase extraction of some organic compounds (Tian et al., 2009; Fang et al., 2010; Li et al., 2008; Fontanals et al., 2009). In the case of metal ions, one study has been reported about the application of immobilized IL onto silica sorbent for separation and pre-concentration of Cd ions (Liang and Peng, 2010). However, it should be noted that in all procedures modification of silica was performed using imidazolium ILs. The attempt of our research group has currently focused on the application of pyridinium ILs in sample preparation of metal ions (Abdolmohammad-Zadeh and Sadeghi, 2009, 2010; Abdolmohammad-Zadeh and Ebrahimzadeh, 2010). In this work, ionic liquid-modified silica was synthesized employing 1-hexylpyridinium hexafluorophosphate [Hpy][PF_6] ionic liquid by acid-catalyzed sol–gel processing and characterized by FT-IR spectroscopy and scanning electron microscope (SEM). A new method using a column packed with pyridinium ionic liquid-modified silica as a sorbent has been developed for the separation and pre-concentration of a trace amount of Fe(III). The effects of various experimental parameters on the extraction efficiency were investigated and optimized. To evaluate the applicability of the proposed method, it was then applied to determine the amount of iron in real water samples using air–acetylene flame atomic absorption spectrometry.

2. Experimental

2.1. Apparatus and instruments

A Varian model SpectrAA 220 (Mulgrave, Victoria, Australia) flame atomic absorption spectrometer, equipped with a 100 mm burner head, deuterium lamp background correction and an air–acetylene flame, was utilized. An iron hollow cathode lamp (operated at 15 mA) was used as the radiation source at the wavelength of 248.3 nm with 1 nm spectral band pass. The acetylene and air flow rates were 1.5 and 3.5 L min^{-1}, respectively. For the signal readout, time-average integration was used with an integration time of 0.1 s and three replicates. A 2 mL polypropylene cartridge (30 mm × 7 mm i.d.) (Shafa Co., Iran) packed with 0.2 g of pyridinium IL-modified silica and fitted with small cotton beads at both ends to prevent material losses, was used to pre-concentrate the analytes in SPE procedures. The flow rate of solution through the column was controlled with an air-driven fluid pump model P34112 (Taiwan). Infrared spectra (4000–400 cm^{-1}) in KBr were recorded on a FT-IR Vector 22 (Bruker, Germany) spectrometer. A scanning electron microscope (SEM), model P Scan Vega 2 (Czech), was additionally used to examine the morphological characteristics of the sorbent. The pH values were measured with a Metrohm pH-meter (model 827, Switzerland), supplied with a glass-combined electrode. An electronic analytical balance (Mettler Toledo, PB303, Switzerland) was used for weighting the solid materials.

2.2. Standard solutions and reagents

All chemicals used were of analytical-reagent grade and all solutions were prepared with doubly distilled deionized water (Shahid Ghazi Co., Tabriz, Iran). Stock solutions of iron and those used for the interference study (1000 mg L^{-1}) were prepared by dissolving appropriate amounts of their respective pure nitrate salts (Merck, Darmstadt, Germany) in deionized water. Working standard solutions were obtained daily by suitable stepwise dilution of the stock solutions with deionized water and shaking them just prior to use.

The chelating agent, 8-hydroxyquinoline (oxine), acetone, ethanol, acetonitrile, methanol, and all salts used were purchased from Merck. 1-Hexylpyridinium hexafluorophosphate (97%) (Acros organics, Belgium), tetraethylorthosilicate (TEOS, sol–gel precursor) and formic acid (98–100%) were used in synthesis of pridinium IL-modified silica as solid phase extraction sorbent. Suprapur® HNO_3 (65%), and H_2O_2 (30%) were used for sample digestion.

A stock solution of 5.0×10^{-3} mol L^{-1} oxine was prepared by dissolving appropriate amount of reagent in a 2 mL of

0.1 mol L^{-1} H_2SO_4 and diluting to 100 mL with deionized water after adjusting to pH nearly 4 by adding diluted NaOH solution. A stock buffer solution of (0.5 mol L^{-1}) was prepared by dissolving appropriate amount of sodium acetate in deionized water and adjusting to pH 4 by adding diluted H_2SO_4 solution. A standard reference material, SRM 1566b (Oyster Tissue) (from National Institute of Standards and Technology (NIST), Giathersburg, MD, USA) was used for validation of the proposed method. The pipettes and vessels used for the trace analysis were kept in 15% (v/v) nitric acid at least overnight and subsequently washed three times with deionized water prior to use.

2.3. Preparation of pridinium ionic liquid-modified silica

Acid-catalyzed sol–gel processing was performed for preparation of the solid phase extraction sorbent. For this purpose, tetraethylorthosilicate (TEOS) was selected as the sol–gel precursor. In a typical run, 25 mL of TEOS and 25 mL of formic acid (0.05 mol L^{-1}) were mixed with the deionized water under mild magnetic stirring at room temperature for 6 h. Then, 150 mg of the 1-hexylpyridinium hexafluorophosphate $[C_6py^+][PF_6^-]$ ionic liquid was heated at 40 °C in ethanol until melted and the resultant solution was added to the mixture. The final mixture gelled during 5–10 min and in order to remove the formed ethanol due to the hydrolysis of TEOS, the resultant solid material was dried in vacuum at 40 °C for 24 h. After cooling down to room temperature, the resulting material was washed with deionized water in order to eliminate the remaining acid and it was kept dry in vacuum overnight, leading to a white powder.

2.4. Column preparation

Pridinium IL-modified silica was employed to create the preconcentration column as follows: the column was prepared by introducing 200 mg of IL-modified silica into an empty 2 mL polypropylene cartridge using the dry packing method. Small portion of cotton was placed on both ends of the column. Before loading the sample, 2 mL of 0.8 mol L^{-1} H_2SO_4 solution and 2 mL of deionized water were passed through the column to clean it. Then, the column was conditioned by passing 2 mL of ethanol and 2 mL of the blank solution through the column prior to each use. After the elution, the sorbent in the column was washed with a 2 mL of the eluting solution and 2 mL of deionized water, subsequently.

2.5. Sample preparation

Water samples including tap water, bottled mineral water, and underground water were chosen for the analysis. The bottled mineral water was purchased from local market. Underground water and tap water were collected in PTFE container from local sources. On arrival at laboratory, water samples were stored in a dark place at 4 °C and aliquots of 200.0 mL from each sample solution were analyzed within 24 h of collection without previous treatment or filtration.

An accurately measured amount (25 mg) of standard reference material (NIST SRM 1566b, Oyster Tissue) was heated on a hot plate at a fairly low temperature in the glass beaker containing mixture of concentrated nitric acid 65% (10 mL) and hydrogen peroxide 30% (5 mL) to dryness. After that, the sample was cooled down to room temperature and the residue was dissolved in a 1.0 mL of 0.1 mol L^{-1} HNO_3 (Silva et al., 2008). After dilution with deionized water, the pH was adjusted to nearly 4 by adding diluted NaOH solution. Then, the solution was transferred into a 250.0 mL volumetric flask and after dilution to the mark with the deionized water, the concentration of iron in 200.0 mL of the final sample solution was then determined as described in Section 2.6.

2.6. General procedure

For solid phase extraction and pre-concentration of Fe(III) ions, a 200.0 mL portion of aqueous standard or sample solution containing Fe(III) in the range of 2.5–50 μg L^{-1}, 0.01 mol L^{-1} acetate buffer solution (pH 4) and 5.0×10^{-6} mol L^{-1} oxine solution (chelating agent) was passed through the pyridinium ionic liquid-modified silica adsorbent in a micro-column at a flow rate of 2.0 mL min^{-1}. Afterward, the analyte retained on the micro-column was eluted with 1.0 mL of 0.8 mol L^{-1} H_2SO_4 solution at an elution rate of 1.0 mL min^{-1} and its concentration in the eluted solution was determined by FAAS. A blank solution was run under the same conditions without adding Fe(III). The column could be used repeatedly after regeneration with 0.8 mol L^{-1} H_2SO_4 solution and deionized water, respectively. The optimized conditions are listed in Table 1.

3. Results and discussion

In order to optimize the sorption conditions for the retention of the iron ions, several experimental variables affecting the preconcentration efficiency such as the pH, concentration of the chelating agent, sample flow rate, and eluent type, concentration and volume, and sample volume were evaluated and optimized. A 25 μg L^{-1} Fe solution was used for all the measurements and in the impact parameters optimization procedure, the limits marked on the figures were obtained from three independent experiments that repeated under the same conditions.

Table 1 Instrumental and experimental conditions for Fe determination.

	Unit	
FAAS conditions		
Wavelength	(nm)	248.3
Lamp current	(mA)	15.0
Spectral bandpass	(nm)	1.0
Acetylene flow rate	(L min^{-1})	1.5
Air flow rate	(L min^{-1})	3.5
Integration time	(s)	0.1
Solid phase extraction conditions		
Working pH	—	4.0
Buffer concentration	(mol L^{-1})	0.01
Fe(III) concentration	(μg L^{-1})	25.0
Oxine concentration	(mol L^{-1})	5.0×10^{-6}
Amount of sorbent	(g)	0.2
Sample volume	(mL)	200.0
Loading flow rate	(mL min^{-1})	2.0

3.1. Acid-catalyzed sol–gel formation mechanism and spectral characteristics

Acid-catalyzed sol–gel processing was used for preparation of the solid phase extraction sorbent. A possible mechanism for the sol–gel formation in the presence of ionic liquid has been reported in the literature (Dai et al., 2000). The sol–gel reaction can be described by Eq. (1):

$$\begin{aligned}&2HC(O)OH + (CH_3CH_2O)_4Si\\&\quad \rightarrow SiO_2 + 2CH_3CH_2OH + 2HC(O)OCH_2CH_3 \qquad (1)\end{aligned}$$

Formic acid initiates the formation of the sol particles, which effectively aggregate in the ionic liquid into a sol–gel network. A long aging time implemented enhances the stability of the sol–gel network and the homogeneity is retained throughout the entire aging process. This indicates that the ionic liquid forms a homogeneous solution with sol–gel precursors. Therefore, this technique allows sol–gel synthesis under mild chemical conditions and eliminates the risky supercritical drying process. A scanning electron micrograph (SEM) of the $[C_6py][PF_6]$ ionic liquid-modified silica sorbent is given in Fig. 1A that shows the good homogeneity of the synthesized sorbent.

Fig. 1B highlights the FT-IR spectrum of $[C_6py][PF_6]$ ionic liquid-modified silica. As can be seen, the absorption peaks at the interval 1404–1652 cm^{-1} could be attributed to the C=C vibration of pyridinium ring. In addition, the bands around 3100 and 2900 cm^{-1} could be assigned to C–H vibration of aromatic cycle and saturated hydrocarbon, respectively. Consequently, the above experimental results suggest that silica is successfully modified by $[C_6py][PF_6]$ ionic liquid.

3.2. Effect of pH

The acidity of a solution has two effects on metal adsorption. First, protons in an acidic solution can protonate the binding sites of the chelating molecules. Secondly, the hydroxide in a basic solution may complex and precipitate many metals (Cui et al., 2007). Therefore, in solid-phase extraction technique, an important parameter for obtaining quantitative adsorption and recovery of trace elements is pH. In this experiment, the effect of pH upon the adsorption of Fe(III) ions was studied within the range of 2–10. The pH was adjusted using either 0.1 mol L^{-1} nitric acid or sodium hydroxide solutions and the recommended procedure was followed. As shown in Fig. 2, quantitative adsorption was found for Fe in the pH range of 3.5–4.5. Therefore, the pH 4 was selected as the working value and in order to maintain a constant working pH that allows complex formation and stability, pH was adjusted at 4 by a 1.0×10^{-2} mol L^{-1} acetate buffer solution in subsequent experiments.

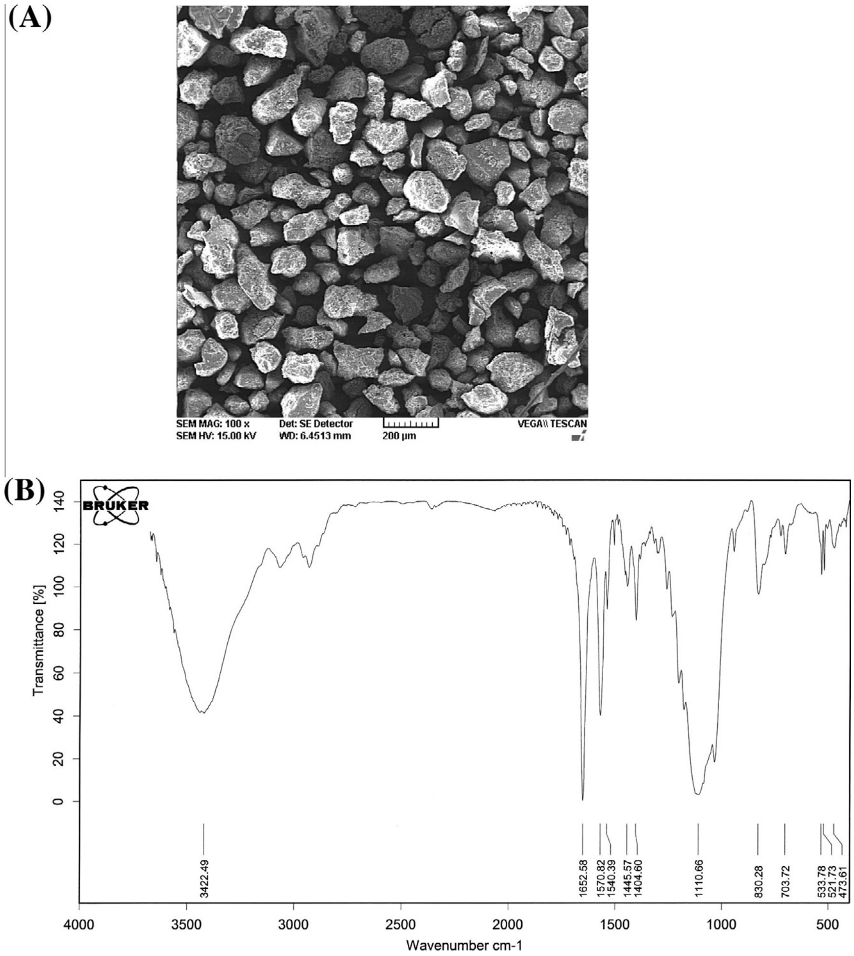

Figure 1 (A) SEM image, (B) FT-IR spectrum of $[C_6py][PF_6]$ ionic liquid-modified silica.

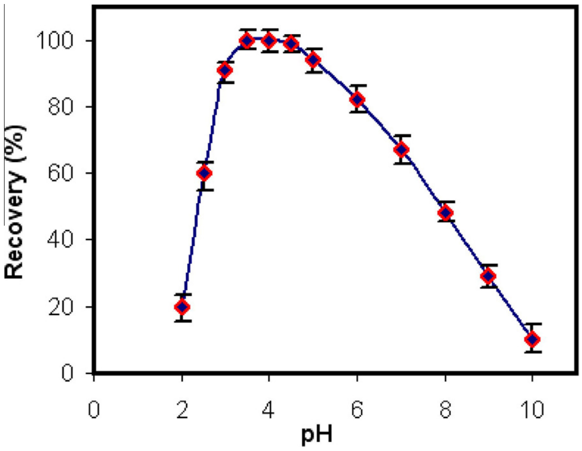

Figure 2 Effect of pH upon the adsorption of Fe on [C_6py][PF_6] IL-modified silica. Fe concentration: 25 μg L^{-1}; oxine concentration 5.0×10^{-5} mol L^{-1}; sample volume: 50 mL; flow rate: 2.0 mL min^{-1}.

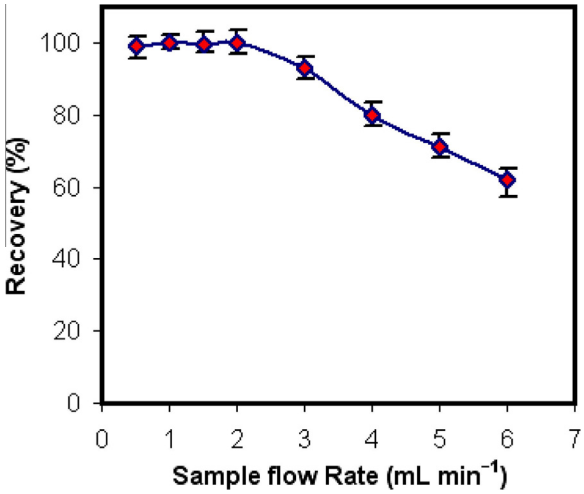

Figure 3 Effect of sample flow rate upon the adsorption of Fe on [C_6py][PF_6] IL-modified silica. Fe concentration: 25 μg L^{-1}; pH 4.0; oxine concentration 5.0×10^{-6} mol L^{-1}; sample volume: 50 mL.

3.3. Effect of chelating agent concentration

The influence of the concentration of oxine, as chelating agent, on the adsorption process was investigated in the range from 2.5×10^{-8} to 2.5×10^{-5} mol L^{-1}. Based on the obtained results, the adsorption percentage increases by increasing the oxine concentration from 2.5×10^{-8} to 2.5×10^{-6} mol L^{-1}, and then remains constant up to an oxine concentration of 2.5×10^{-5} mol L^{-1}. Therefore, an oxine concentration of 5.0×10^{-6} mol L^{-1} was employed as the optimum.

3.4. Effect of flow rate

The sample flow rate through the packed column is a very important parameter, since the retention of analyte on the adsorbent depends on the flow rate of sample solution. In fact, the sample flow rate not only affects the adsorption percentage of analyte but also is one of the variables that controls the analysis time. The influence of the sample loading rate on the adsorption percentage was investigated between 0.5 and 6.0 mL min^{-1}. Fig. 3 shows that the sample solution flow rate in the interval 0.5–2 mL min^{-1} had no significant influence on the adsorption of Fe. However, at flow rates higher than 2 mL min^{-1} the recovery of Fe(III) ions reduced. Thus, all subsequent experiments were performed at a sample flow rate of 2.0 mL min^{-1}.

3.5. Effect of elution parameters

In order to obtain the best analyte recovery, an eluent should effectively elute the retained metal ions on the solid phase. The type and concentration of eluting agents have a significant effect on the elution process. As could be seen from Fig. 2, the adsorption of Fe ions is negligible at low pH; therefore, the acidic eluents are the best solutions for extraction of adsorbed Fe ions. For this reason, various mineral acids such as hydrochloric acid, sulfuric acid, and nitric acid were tested at different concentration levels and volume at a flow rate of 1.0 mL min^{-1}. Based on the obtained results, the quantitative recovery could be achieved when sulfuric acid was used as eluent, and 0.8 mol L^{-1} H_2SO_4 was sufficient for complete elution of the retained Fe ions from the column.

The effect of eluent volume on the recovery of Fe was also studied by keeping the H_2SO_4 concentration of 0.8 mol L^{-1}. It was found that quantitative recovery could be obtained with 1.0 mL of 0.80 mol L^{-1} H_2SO_4. Therefore, optimum volume of the eluent was chosen as 1.0 mL. The flow rate of eluent was 1.0 mL min^{-1}.

3.6. Sample volume and pre-concentration factor

When real samples are analyzed by pre-concentration techniques, sample volume is one of the most important parameters to be studied. In order to obtain a higher enrichment factor, a large amount of volume of sample solution is required. Thus, the effect of sample solution volume on the iron adsorption was investigated by passing 10–250 mL sample solutions containing 5 μg of Fe at a flow rate of 2.0 mL min^{-1} according to the recommended procedure. It was found that the maximum sample volume of 200 mL could be passed through the column with quantitative recovery. Above 200 mL, the percent of adsorption decreased for the analyte. So, an enrichment factor of 200 was achieved by this method using 1.0 mL of 0.80 mol L^{-1} H_2SO_4 as eluent at the flow rate of 1.0 mL min^{-1}.

3.7. Adsorption capacity

The adsorption capacity is one of the important factors, because it determines how much sorbent is required to quantitatively concentrate the analytes from a solution and given by milligram of metal per gram solid phase. The adsorption capacities of various metal ions probably differ due to their size, degree of hydration and the value of their binding constant with the ligand immobilized onto matrix (Zhu et al., 2007). The adsorption capacity was tested following the batch procedure; 100 mg of the [C_6py][PF_6] IL-modified silica was added to 25.0 mL of solution containing 5.0 mg of Fe(III) ions

Table 2 Tolerance limits of interfering ions in the adsorption of 25 μg L^{-1} Fe.

Ions	Foreign ion to analyte ratio	Change in signal (%)
Li^+, Na^+, K^+, Ca^{2+}, Ba^{2+}, NH_4^+	1000	−3.3, −2.4, −2.1, −3.5, −3.5, −2.7
Cl^-, Br^-, NO_3^-, CH_3COO^-, SO_4^{2-}, CO_3^{2-}	1000	−3.3, −1.2, −2.4, −3.1, −1.0, −3.9
Pb^{2+}, Ag^+, Sr^{2+}	800	−3.2, −3.4, 1.1
Mg^{2+}	700	−3.1
Al^{3+}	600	−3.7
I^-	500	−3.2
Cd^{2+}, Co^{2+}	300	−2.1, −1.9
Bi^{3+}	50	−3.3
V(V)	5	−2.8
Mo(VI)	1	−4.9

Table 3 Comparison of the some recent published solid phase extraction methods for the pre-concentration of Fe with the proposed method.

Adsorbent	Pre-concentration factor	Adsorption capacity (mg g^{-1})	Extraction time (min)	Sample volume (mL)	LOD (μg L^{-1})	Reference
Functionalized silica	75	25.21	150	150	0.34	Chang et al., 2007
Triton X-100-coated PVC	90	2.7	80	450	0.95	Ghaedi et al., 2008a
Modified silica gel	75	0.46[a]	150	150	0.15	Zhu et al., 2007
Modified alumina	292	6.3	437.5	1750	0.68	Ghaedi et al., 2008b
Functionalized activated carbon	100	77.8	100	200	0.27	Tu et al., 2009
SDS-coated alumina	63	15.7	90	500	2.6	Ghaedi et al., 2009b
Pyridinium IL-modified silica	200	11.8	100	200	0.7	This work

PVC: Polyvinyl chloride.
SDS: Sodium dodecyl sulfate.
[a] mmol g^{-1}.

and stirred for 60 min under optimized conditions. After filtration of the mixture, the iron ions were eluted from the adsorbent by 0.8 mol L^{-1} of H_2SO_4 and the amounts of the Fe(III) ions adsorbed to the IL-modified silica were determined by FAAS after dilution. The capacity of IL-modified silica for Fe(III) ions was found to be 11.8 mg g^{-1}.

3.8. Column reuse

The potential regeneration and stability of the column were also investigated. The column could be reused after regenerating with 2.0 mL 0.8 mol L^{-1} H_2SO_4 and 2.0 mL deionized water, respectively. Moreover, it was observed that sorbent understudy stable up to at least 250 adsorption–elution cycles could be repeatedly used without significant loss of uptake capacity. In fact, this is one of the advantages of the $[C_6py][PF_6]$ IL-modified silica as a solid phase extraction sorbent.

3.9. Study of interferences

For demonstrating the selectivity of the developed pre-concentration system, the solid phase extraction of iron ion was examined in the presence of spiked known amounts of interfering ions. In these experiments, different amounts of ions were added to the test solutions containing 25 μg L^{-1} of iron and then followed according to the general procedure. The tolerance limits of the coexisting ions, defined as the maximum concentration of the foreign ion causing a change in the analytical signal no higher than ±5%, when compared with the signal of 25 μg L^{-1} iron alone, are given in Table 2. As can be seen, those commonly encountered concomitant ions such as alkali and alkaline earth elements do not interfere at high concentrations. Whereas, some of species tried such as Bi^{3+}, V(V) and Mo(VI) probably interfered with the determination of Fe(III). However, the concentrations of these ions in water and biological samples are commonly lower than iron. Therefore, the proposed method is relatively selective for the determination of iron.

3.10. Analytical figures of merit

The calibration graph was obtained by applying the general procedure for different concentration of iron under the optimum conditions. A linear calibration graph was obtained in the range of between 2.5 and 50 μg L^{-1} of iron in the initial

Table 4 Determination of iron in water samples (results of recoveries of spiked samples and certified reference material analysis).

Samples	Added Fe (μg L^{-1})	Found Fe[a] (μg L)	Recovery (%)[b]
Tap water[c]	—	18.57 ± 0.45	—
	10.0	29.11 ± 0.37	105.4
	20.0	38.37 ± 0.51	99.0
Mineral water[d]	—	5.83 ± 0.39	—
	10.0	16.27 ± 0.56	104.4
	20.0	25.40 ± 0.57	97.8
Underground water[e]	—	48.57 ± 0.52	—
NIST SRM 1566b	Certified values (μg g^{-1})	Assayed values (μg g^{-1})	Relative error (%)
	205.6 ± 6.8	202.8 ± 6.3	−1.4

[a] Mean of three experiments ± standard deviation.
[b] Recovery (%) = [(found−base)/added] × 100.
[c] From drinking water system of Tabriz, Iran.
[d] From Zam Zam Co. Tabriz, Iran.
[e] Collected from underground water of Azarshahr, Iran.

solution, with a correlation coefficient of 0.9997. The linear regression equation was $A = 0.0139\ C_{(\mathrm{Fe})} + 0.0231$, where A is the absorbance and $C_{(\mathrm{Fe})}$ is iron concentration in μg L^{-1}, respectively. The limit of detection (LOD) of this method, evaluated as the concentration corresponding to three times the standard deviation of nine replicate measurements of blank solution using the pre-concentration method, was found to be 0.7 μg L^{-1} for the pre-concentration of 200 mL of sample solution. The relative standard deviation (R.S.D.) resulting from the analysis of nine replicates of 200 mL solution containing 25 μg L^{-1} Fe was 3.2%. Comparative information from some recent studies on solid-phase extraction of Fe(III) by various adsorbents for the figure of merits is given in Table 3. In comparison with other reported methods, the proposed method has good LOD, adsorption capacity and pre-concentration factor. The method developed in this work is proposed as a suitable alternative to more expensive instruments for Fe determination at trace levels.

3.11. Analysis of real samples

To test the reliability of the proposed procedure, the method was employed to determine the trace amounts of Fe in different water samples i.e., bottled mineral water, tap water and underground water. In order to verify the accuracy of the established procedure, recovery experiments were also carried out by spiking the samples with different amounts of iron before any pretreatment. Table 4 shows the obtained results. As can be seen, recoveries between 97.8% and 105.4% were obtained, which confirm the accuracy of the proposed method. Additionally, the accuracy of the proposed methodology was evaluated by analyzing a standard reference material, NIST SRM 1566b Oyster Tissue. The analytical value (202.8 ± 6.3 μg g^{-1}) was in good agreement with the certified value (205.6 ± 6.8 μg g^{-1}). It can be concluded that the proposed method is accurate and free from systematic errors.

4. Conclusions

This paper describes a pioneering study of the synthesis and application of pyridinium IL-modified silica as SPE sorbent, which effectively extracts Fe(III) ions from aqueous samples. The preparation of the sorbent using the acid-catalyzed sol–gel processing is simple and its reusability is as high as greater than 250 cycles without any loss in its sorption behavior. As far as we know, this is the first time that the pyridinium IL-modified silica have been used as packing material for the selective solid-phase extraction of Fe(III) ions from aqueous solutions. Based on the obtained results, the new sorbent has high analytical potential for pre-concentration of trace Fe(III) ions from water samples. The presented procedure shows good LOD, adsorption capacity, pre-concentration factor and precision with reasonable eluent volume and sample loading flow rate over other SPE off-line pre-concentration methods. Moreover, this methodology is a reproducible, simple and low cost technique and does not require further instrumentation and it can be used with regular FAAS equipment.

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