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Supported hydrophobic ionic liquid on nano-silica for adsorption of lead

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ABSTRACT

The hydrophobic character incorporated into 1-methyl-3-octylimidazolium bis(trifluoromethylsulfonyl)imide [$OMIM^+Tf_2N^-$] based on both the anion and cation natures was employed to develop a novel solid phase extraction medium based on physical adsorption approach. Two modified nano-silica sorbents were synthesized via direct immobilization of [$OMIM^+Tf_2N^-$] on the surface of active nano-silica [NSi-OH] and amino nano-silica [$NSi-NH_2$] for the formation of [$NSi-OH-OMIM^+Tf_2N^-$] and [$NSi-NH_2-OMIM^+Tf_2N^-$], respectively. Surface characterization was confirmed by TGA, FT-IR and SEM. The surface coverage values were identified in the range of 1.223–1.272 mmol g^{-1}. Modified sorbents were extensively studied and characterized by their high similarity and affinity for lead extraction without the need for chelating intermediate. Excellent sorption capacity values (0.5–0.9 and 0.8–1.3 mmol g^{-1}) of lead were determined in pH 1–7. Other factors such as reaction contact time, sorbent dose, initial metal ion concentration and interfering ions were studied to spot more light on the sorption capability of loaded hydrophobic ionic liquid for application in the solid phase extraction mode. These sorbents were successfully implemented for removal and preconcentration of lead from various water samples via application of a multi-stage micro-column giving rise to percentage recovery values of lead in the range of 98.0–100.0 ± 3.0–4%.

1. Introduction

In recent years, ionic liquids (ILs) have been widely used and extremely found high interests in almost all application fields of chemistry such as organic and inorganic syntheses, catalysis, electrochemistry, chromatography, separation and extraction techniques as well as others owing to their unique and favorable characteristics compared to other conventional organic solvents and compounds. These expanding interests have led to a number of research reports devoted to study and evaluate physico-chemical properties, design of new families of ionic liquids, chemical engineering and wide range of arrangements in which ILs have been utilized in industrial developments [1,2]. Thus, these types of available ILs have been extended to cover some new families and generations with some incorporated and aimed properties. The manipulation of ionic liquids in various fields may be categorized and termed as task-specific compounds such as multifunctional ILs, deep eutectic solvents, protic ILs, polarizable ILs, amphiphil ILs, supported ILs, switchable polarity solvents, metal salts ILs, chiral ILs, and bio ILs [3].

Applications of ILs in analytical chemistry are mainly focused on three major areas including (i) liquid-phase microextraction (LPME) methodologies, (ii) liquid–liquid extraction techniques (LLE) and (iii) modified solid phases in chromatographic applications. Liquid-phase microextraction techniques including single-drop microextraction (SDME) have been recently developed to overcome some of the limitations in manipulation of conventional liquid–liquid extraction techniques. SDME is characterized by several advantages including simplicity, significant reduction in the amount of organic solvent, cost-effectiveness, high sample throughput and combination of the extraction, preconcentration and sample introduction in one step. The applications of ionic liquids in single-drop microextraction techniques for metal ions separation from various systems were numerous as recently reported [4–10]. An improved single-drop microextraction procedure was developed and reported for the preconcentration of lead prior to determination by electrothermal atomic absorption spectrometry by the use of ionic liquid, 1-butyl-3-methylimidazolium hexafluorophosphate [C4MIM][PF6] [4]. An efficient single-drop microextraction procedure using a low-cost room temperature ionic liquid (RTIL), tetradecyl(trihexyl)phosphonium chloride for Pb determination at trace levels in real water samples was studied and discussed [5]. A new liquid-phase microextraction system was developed and described for the pre-concentration of lead via lead transfer into its complex using dithizone as a chelating agent followed by partition into the infinite ionic liquid drops

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at high temperature [6]. A simple and effective hollow fiber-based liquid-phase microextraction (HF–LPME) technique by using ionic liquid, 1-hexyl-3-methylimidazolium hexafluorophosphate, [C6MIM][PF6], coupled with electrothermal atomic absorption spectrometry (ETAAS) was developed for the determination of lead and nickel in environmental and biological samples [7]. Several other methods of single-drop microextraction (SDME) for various metal ions and species were also reported [8–10].

The possible applications of ionic liquids in the processes of liquid–liquid extraction of various metal ions from their matrices is mainly based on combination with some chelating compounds to form metal complexes for the sake of increasing hydrophobicity and the final step is regarded as the transfer and partition of the produced metal complex between the two phases [11,12]. Novel crown ethers (*N*-alkyl aza-18-crown-6 series) and calixarenes crown ethers (calix[4]arene-bis(*tert*-octylbenzocrown-6)) were synthesized and used in RTILs as recyclable extractants for separation of Cs^+ and Sr^{2+} from aqueous solutions [13,14]. Partitioning of sodium ions between aqueous nitrate media and 1-alkyl-3-methylimidazolium bis-[(trifluoromethyl)sulfonyl]imides ($Cnmim^+Tf_2N$) in the presence of dicyclohexano-18-crown-6 was studied and shown to take place via as many as three pathways [15]. A simple and effective method was presented for extractive preconcentration of uranium(VI) from water, in which the ionic liquid, 1-octyl-3-methylimidazolium hexafluorophosphate, abbreviated as $[C_8mim][PF_6]$, was used as a novel medium for liquid–liquid extraction of uranium(VI) and a new reagent, dimethylphenylazosalicylfluorone, abbreviated as DMPASF, was employed to form neutral uranium(VI)-DMPASF complex [16]. Several other related and similar examples were also reported [17–19].

Solid sorbent-immobilized-ionic liquids were recently studied and reported as solid phases in chromatographic applications. A new zwitterionic stationary phase based on silica bonded with 1-alkyl-3-(propyl-3-sulfonate) imidazolium was synthesized, characterized and used as stationary phase for high-performance liquid chromatographic separation of anions [20]. The preparation of a new anion-exchange phase based on immobilization of ionic liquids, *N*-methylimidazolium anion-exchange phase, on silica was reported and used as column packing materials for HPLC separations of some common inorganic anions, including iodate, chloride, bromide, nitrate, iodide, and thiocyanate [21,22]. A new HPLC stationary phase based on *n*-butylimidazolium bromide was studied in binary acetonitrile/water mobile phases for 28 test solutes [23]. Other similar derivatives and phases were recently reported [24,25].

The major disadvantage in applications of ILs for metal extraction from various matrices by using either liquid–liquid extraction technique or single-drop microextraction method is mainly based on finding suitable chelating compounds that are capable of metal binding as well as potential transfer from their matrices to the ionic liquid medium after the complexation step. These limitations have motivated and directed our attention to establish a new solid phase extractor for various metal ions based on combining a hybridization process of the ionic liquid characters with high adsorption efficiency and surface area of nano-silica sorbents for formation of new sorbents of metal ions without the need for partitioning chelating agent as previously reported [11,12].

2. Experimental

2.1. Instrumentation

1-Methyl-3-octyllimidazolium bis(trifluoromethylsulfonyl)imide $[OMIM^+Tf_2N^-]$, the two newly synthesized silica sorbents and active nano-silica sorbent were measured on a Shimadzu Fourier Transform infrared spectrophotometer (FT-IR-8400S) in the range 200–4000 cm^{-1}. The two newly synthesized nano-silica sorbents and active nano-silica sorbent were imaged by a scanning electron microscope (JSM-6360 LA, JEOL Ltd.), (JSM-5300, JEOL Ltd.). An ion sputtering coating device (JEOL-JFC-1100E) was used to coat the SEM specimens with gold to increase the conductivity. A PerkinElmer TGA7 Thermobalance was used to study the thermal gravimetric analysis (TGA) and to collect the thermoanalytical curves. The operating conditions were adjusted to a temperature heating range of 50–700 °C with a heating rate of 10 °C min^{-1}, a flow rate of 20 ml min^{-1} in pure nitrogen atmosphere and sample mass in the range (5.0–7.0 mg). Thermolyne 47900 furnace was used to determine the surface coverage values of modified nano-silica sorbents via thermal desorption analysis. The pH measurements of buffer and metal ion solutions were carried out by using an Orion 420 pH meter calibrated against standard buffer solutions of pH 4.0 and 9.2. Pb(II) concentration in various samples was determined by Shimadzu (AA-6650) atomic absorption spectrophotometer at the specified wavelength.

2.2. Materials and solutions

$LiN(CF_3SO_2)_2$ was purchased from 3 M (Minneapolis, MN) and used as the source of bis(trifluoromethylsulfonyl)imide anion, $F_3C\text{-}SO_2\text{-}N^{(-)}\text{-}SO_2\text{-}CF_3[Tf_2N]^-$. Nano-silica gel with the specifications, SiO_2, particle size 10–20 nm (BET), d 2.6 and 99.5% purity, hydrochloric acid, sodium acetate trihydrate, lead(II) acetate trihydrate and other metal salts are all of analytical grade and purchased from Aldrich Chemical Company and BDH Limited. All chemicals were used without further purification.

The metal ion solutions were prepared from doubly distilled water (DDW). Buffer solutions of pH 1.0, 2.0, 3.0, 4.0, 5.0, 6.0 and 7.0 were prepared from 1.0 M hydrochloric acid solution and 1.0 M sodium acetate trihydrate solution by mixing the appropriate volumes of the two solutions and diluting to 1.0 l. The pH values of resulting solutions were adjusted by a pH meter.

2.3. Synthesis of modified nano-silica-ILs sorbents

1-Methyl-3-octyllimidazolium bis(trifluoromethylsulfonyl)imide $[OMIM^+Tf_2N^-]$ ionic liquid (FW = 475) was synthesized as previously reported [26,27]. A sample of $LiNTF_2$ “Lithium NT Fluoride” bis(trifluoromethylsulfonyl)imide $F_3C\text{-}SO_2\text{-}N^{(-)}\text{-}SO_2\text{-}CF_3$ $[Tf_2N^-]$ anion (8.6 g and 30 mmol) was weighed and dissolved in 10 ml distilled water and 1-methyl-3-octylimidazolium chloride $[OMIM^+]Cl^-$ (5.7 g and 25 mmol) was also weighed and dissolved in 50 ml distilled water. The two reactants were mixed in a round bottomed flask and stirred for 24 h until two separated layers were formed. The aqueous layer was removed by decantation and the product $[OMIM^+Tf_2N^-]$ ionic liquid was dried under rotavapor at 60 °C and 72 mbar for 4 h.

Active nano-silica-loaded-ionic liquid $[NSi\text{-}OH\text{-}OMIM^+Tf_2N^-]$ was synthesized according to a two-step reaction. The first step was based on an acid activation of silica nano-powder (25.0 g) by refluxing and stirring in concentrated hydrochloric acid (150.0 ml of 1:1 v/v ratio). The activated nano-silica powder was filtered, repeatedly washed with double distilled water until acid free and dried in an oven at 100 °C for 8 h. The second step was based on the physical adsorption of $[OMIM^+Tf_2N^-]$ hydrophobic ionic liquid on the surface of activated nano-silica by suspension of 10.0 g in toluene and 7.2 g of $[OMIM^+Tf_2N^-]$ ionic liquid (∼15 mmol) was then added. The reaction mixture was stirred at room temperature for 6 h then filtered, washed with toluene several times followed by ethanol and diethyl ether, dried in an oven at 60 °C and kept in a desiccator for further use.

Nano-silica amine-loaded-ionic liquid [NSi-NH_2-$OMIM^+Tf_2N^-$] was also synthesized based on a two-step reaction. Active nano-silica particles (10.0 g) were suspended in 150 ml toluene and 20 ml of 3-aminopropyltrimethoxysilane was added. The suspension was heated under reflux for 6 h, filtered washed with toluene, ethanol and diethyl ether and dried in an oven at 80 °C for 8 h to produce nano-silica sorbent chemically immobilized-NH_2, [NSi-NH_2] [28]. The second step was based on a direct reaction of [NSi-NH_2] with [$OMIM^+Tf_2N^-$] ionic liquid according to the following procedure. A mixture of [NSi-NH_2] (10.0 g) and 7.2 g (~15 mmol) of [$OMIM^+Tf_2N^-$] ionic liquid was suspended in toluene and the procedures were completed as above.

2.4. Surface coverage determination

Thermal gravimetric analysis (TGA) as well as thermal desorption method [29] were used to evaluate the surface coverage of nano-silica sorbents with [$OMIM^+Tf_2N^-$] for the formation of modified nano-silica sorbents, [NSi-OH-$OMIM^+Tf_2N^-$] and [NSi-NH_2-$OMIM^+Tf_2N^-$]. In thermal desorption method, 100 ± 1 mg of dry nano-silica sorbents was weighed and ignited at 550 °C in a muffle furnace. The initial temperature was set at 50 °C and gradually increased to 550 °C in about 20 min. The ignited silica was then kept at this temperature for 1 h and left to cool down inside the furnace till 150 °C. The sample was transferred to a desiccator and left to reach the room temperature. The weight loss of hydrophobic ionic liquid was determined by the difference in sample masses before and after the process of thermal desorption. Blank samples of nano-silica were also subjected to the same thermal desorption procedure as described for comparison with the results obtained for modified nano-silica sorbents.

2.5. Sorption of lead by nano-silica-hydrophobic ionic liquid sorbents

2.5.1. Effect of pH

The effect of pH of contact medium on the determined mmol g^{-1} sorption capacity values of Pb(II) was studied and performed by the batch equilibrium technique. In this study, a sample of 10 ± 1 mg of [NSi-OH-$OMIM^+Tf_2N^-$] or [NSi-NH_2-$OMIM^+Tf_2N^-$] was weighed into a 50 ml measuring flask and 1.0 ml of 0.1 molar of Pb(II) was then added followed by 9.0 ml of acetate buffer solution with pH values of 1.0, 2.0, 3.0, 4.0, 5.0, 6.0 and 7.0. The reaction mixture was shaken by an automatic shaker for 30 min at room temperature then filtered and washed with 50 ml of DDW. The filtrate was subjected to further dilution step with double distilled water to reach a concentration range of 1.0–2.0 mg l^{-1} and determined by atomic absorption analysis.

2.5.2. Kinetics of the lead sorption process equilibrium

The batch equilibrium technique was also used at room temperature to perform and study the effect of shaking time (1, 5, 10, 15, 20, 25 and 30 min) on the determined mmol g^{-1} sorption capacity values of Pb(II). A sample of 10 ± 1 mg of [NSi-OH-$OMIM^+Tf_2N^-$] or [NSi-NH_2-$OMIM^+Tf_2N^-$] was weighed into a 50 ml measuring flask. 1.0 ml of 0.1 molar Pb(II) was then added followed by 9.0 ml of acetate buffer solutions with pH values 2.0 and 7.0 to identify the possible kinetics of lead sorption in presence of acidic solutions as well as neutral ones. The reaction mixture was shaken by an automatic shaker for the selected period of shaking time and the unextracted Pb(II) determined as described above.

2.5.3. Effect of sorbent dose

The effect of sorbent dose on the process of Pb(II) extraction by newly modified nano-silica sorbents was studied by using five different mass values of the sorbent in the range of 0.025–0.500 g. A solution of 400 mg l^{-1} of Pb(II) was prepared, buffered to pH 5 and added to the selected sorbent mass dose. This was then automatically shaken for 30 min and the unextracted metal ion was filtered, washed, subjected to further dilution steps to reach a concentration range of 1.0–2.0 mg l^{-1} and determined by atomic absorption analysis.

2.5.4. Effect of interfering anions and cations

A solution of Pb(II) was prepared in various concentration levels (1000–5000 mg l^{-1}) of interfering species including Na^+, K^+, NH_4^+ Ca^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Cd^{2+} and Hg^{2+} as well as Cl^-, F^-, NO_3^- and SO_4^{2-}. A sample of 10 ± 1 mg of either [NSi-OH-$OMIM^+Tf_2N^-$] or [NSi-NH_2-$OMIM^+Tf_2N^-$] was then added to a 50 ml portion of this solution and the reaction mixture was completed via batch equilibrium technique by shaking with an automatic shaker for 30 min. The unextracted Pb(II) was filtered and washed with 50 ml of DDW, subjected to further dilution steps to reach a concentration range of 1.0–2.0 mg l^{-1} and determined by atomic absorption analysis.

2.5.5. Effect of initial metal ion concentration

Six different Pb(II) solutions were prepared with the concentration values of 1.0×10^{-3} up to 5.0×10^{-2} mol l^{-1} at pH 5.0. Samples of 10 ml of these solutions were mixed with 10 ± 1 mg of [NSi-OH-$OMIM^+Tf_2N^-$] or [NSi-NH_2-$OMIM^+Tf_2N^-$]. The reaction mixture was then shaken by an automatic shaker for 30 min, filtered, washed and diluted with DDW and the unextracted metal ion was subjected to further dilution steps to reach a concentration range of 1.0–2.0 mg l^{-1} and determined by atomic absorption analysis.

2.6. Solid phase extraction and preconcentration of lead from real water samples via multi-stage micro-column separation

A multi-stage micro-column system was used and applied to evaluate the efficiency of newly modified nano-silica sorbents, [NSi-OH-$OMIM^+Tf_2N^-$] or [NSi-NH_2-$OMIM^+Tf_2N^-$] for solid phase extraction of Pb(II) from real water matrices. Three identical micro-columns were used in this study and the effluent collected from the first column was allowed to passes to the second column and so on. Each column was packed with 50 ±1 mg of the selected silica sorbent. Two types of water samples were collected from Maryout lake and drinking tap water, Alexandria, Egypt. These were spiked with Pb(II) ~ 1.0 mg l^{-1} and passed over with a flow rate of 20 ml min^{-1}. Samples were collected from the final effluent of the third stage column and subjected to atomic absorption analysis to determine the percentage extraction values at each stage of the extraction process. A preconcentration procedure for Pb(II) (~5.0 μg l^{-1}) from drinking tap water was also performed according to the same experimental conditions. The preconcentrated Pb(II) was eluted by 5.0 ml of concentrated nitric acid followed by direct determination by AAS.

3. Results and discussion

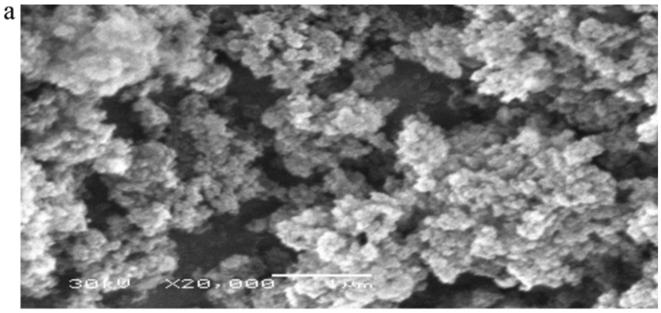
3.1. Surface modification and characterization

1-methyl-3-octylimidazolium bis(trifluoromethylsulfonyl)imide [$OMIM^+Tf_2N^-$] is characterized by excellent hydrophobic characters based on the existence of long chain hydrocarbon represented by the octyl group and the anion moiety, [Tf_2N^-]. The ability of this hydrophobic ionic liquid to adsorb on the surface of active and amino modified silica sorbents was monitored and confirmed by various instrumental techniques including determination of surface coverage via thermal gravimetric analysis (TGA) and thermal desorption method, evaluation of the thermal stability via TGA study, characterization of the loaded surface functional groups via Fourier transform-infrared (FT-IR) analysis as well as surface morphology imaging by using scanning electron microscopic analysis. The newly synthesized nano-silica physically adsorbed-ionic liquid sorbents were repeatedly washed with distilled water to remove any leachable IL molecules before further manipulation for metal extraction. The stability of IL on the surface of silica sorbents was studied and revealed a ≥92.0% stability value of the modified sorbents in water matrices. The following sections represent the confirmation results for surface modification of nano-silica sorbents with 1-methyl-3-octylimidazolium bis(trifluoromethylsulfonyl)-imide [OMIM$^+$Tf$_2$N$^-$].

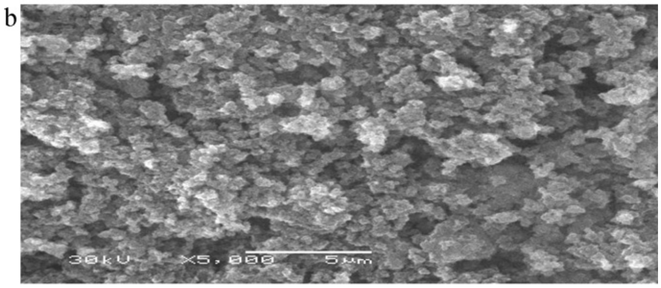
3.1.1. *Surface coverage and thermal analysis*

Determination of the surface coverage values (mmol g^{-1}) of newly synthesized nano-silica sorbents [NSi-OH-OMIM$^+$Tf$_2$N$^-$] and [NSi-NH$_2$-OMIM$^+$Tf$_2$N$^-$] as well as evaluation of their thermal stability trends were studied and evaluated on the basis of thermal gravimetric analysis (TGA) and thermal desorption method. TGA was found to confirm the high thermal stability of [NSi-OH-OMIM$^+$Tf$_2$N$^-$] without any noticeable degradation up to 310 °C. However, at 450 °C, the surface loaded hydrophobic ionic liquid [OMIM$^+$Tf$_2$N$^-$] was found to completely decompose and desorb from the surface yielding only the residual silica gel matrix. This conclusion was supported by the capability of bis(trifluoromethylsufonyl)amide anion [Tf$_2$N$^-$] to exhibit high thermally stable characters (up to 400 °C) [30] with further and successive thermal degradation steps at temperature >400 °C. [NSi-OH-OMIM$^+$Tf$_2$N$^-$] was characterized by a 58.079% loss owing to the complete thermal decomposition of the loaded hydrophobic ionic liquid [OMIM$^+$Tf$_2$N]. The translation of this percentage loss into surface coverage expression was found to yield a value of 1.223 mmol g^{-1} based on the direct calculation of the mass loss from the TGA. The high surface area of nano-silica particles allowed excellent surface coverage value by the target hydrophobic ionic liquid. The thermal desorption analysis of [NSi-OH-OMIM$^+$Tf$_2$N$^-$] was found to prove a surface coverage value of 1.272 mmol g^{-1} which is considered in agreement with that determined by the TGA studies.

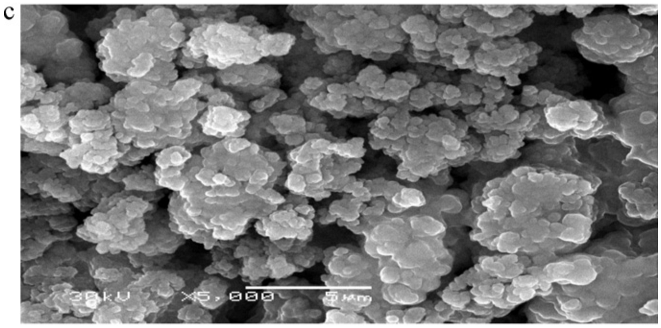
On the other hand, chemical modification of active nano-silica particles with aminopropylsilane derivative has resulted in the formation of surface immobilized amino group. The thermal stability of [NSi-NH$_2$-OMIM$^+$Tf$_2$N] can be discussed on the basis of TGA and referred to the high stability up to 350 °C. A one step of thermal decomposition was identified and characterized as a 69.408% loss in the temperature range of 350–480 °C in this thermogram. This thermal decomposition step is mainly due to the complete degradation process of the loaded hydrophobic ionic liquid [OMIM$^+$Tf$_2$N] as well as the organic aminopropylsilane moiety. The surface coverage of loaded amino silane derivative on nano-silica particles was determined from the thermal gravimetric analysis of [NSi-NH$_2$] and found to give a 1.534 mmol g^{-1} value. However, the estimated surface coverage value of [NSi-NH$_2$-OMIM$^+$Tf$_2$N$^-$] was characterized as 1.231 mmol g^{-1} on the basis of thermal gravimetric analysis. In addition, determination of the surface coverage value of [NSi-NH$_2$-OMIM$^+$Tf$_2$N$^-$] by thermal desorption method was found to produce 1.255 mmol g^{-1}. These two values may be used to account for ~80.25–82.81% surface coverage of [NSi-NH$_2$] with [OMIM$^+$Tf$_2$N$^-$]. The high surface area of nano-sized silica particles has favored such high surface coverage values.



SEM-image of active silica



SEM-image of **[NSi-OH-OMIM$^+$Tf$_2$N$^-$]**



SEM-image of **[NSi-NH$_2$-OMIM$^+$Tf$_2$N$^-$]**

Fig. 1. SEM images of modified nano-silica hydrophobic ionic liquids sorbents.

3.1.2. *Scanning electron microscope*

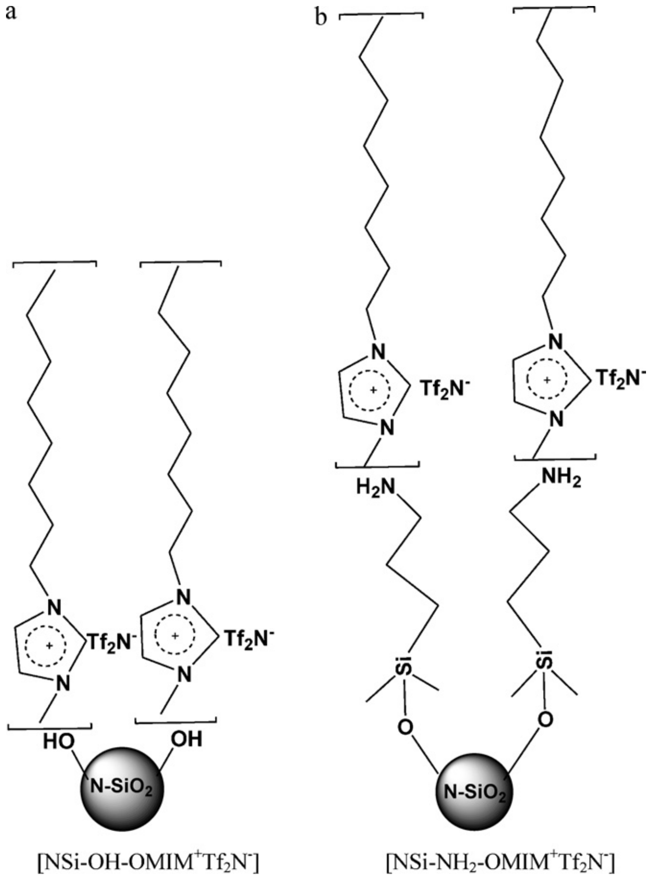
Various RTILs and eutectic ionic liquids were found to exhibit strong affinity for solubilization and solvation of a number of inorganic metal oxides including zironia, magnesia, titania and others [31]. Therefore, it is important to study and confirm that modified nano-silica sorbents have retained their solid states without the possibility of dissolution in the selected hydrophobic ionic liquids. Scanning electron microscope (SEM) via surface imaging of newly synthesized nano-silica sorbents can be directly implemented to prove and provide a direct evidence for such existence of solid particles. The results of SEM-analysis are clearly denoting to the capability of [OMIM$^+$Tf$_2$N$^-$] hydrophobic ionic liquid to react and adsorb on the surface of both active silica gel [Si-OH] as well as amino-modified-nano-silica [NSi-NH$_2$] and maintaining the solid characters of silica sorbents without solubilization as shown in Fig. 1. In addition, scanning electron microscope was used to compare the surface morphology as well as surface modification of newly synthesized nano-silica ionic liquid sorbents with active nano-silica particles. Fig. 1(a) shows the SEM image of active nano-silica particles magnified to 20,000 times. The image is clearly showing the particles as individually distributed in a uniform and homogeneous arrangement. The morphology of newly modified nano-silica sorbents-immobilized-hydrophobic ionic liquid, [NSi-OH-OMIM$^+$Tf$_2$N$^-$] and [NSi-NH$_2$-OMIM$^+$Tf$_2$N$^-$] were characterized via SEM imaging of these two sorbents as shown in Fig. 1(b) and 1(c) under the same magnification order (5000×). It is evident from these two images that physical adsorption of [OMIM$^+$Tf$_2$N$^-$] to the surface of [Si-OH] and [NSi-NH$_2$] led to a pronounced and characterized change in the surface morphology of these two newly synthesized sorbents. It is also evident from Fig. 1(b) and 1(c) that some nano-silica particles are partially existing in aggregate forms that are completely covered with the hydrophobic ionic liquid [$OMIM^+Tf_2N^-$].

3.1.3. FT-IR analysis

Surface modification of nano-silica sorbents can be also tested and evaluated by using Fourier Transform infrared spectroscopic analysis [32–35]. Comparison of the various functional groups present in active nano-silica, hydrophobic ionic liquid [$OMIM^+Tf_2N$], [NSi-OH-$OMIM^+Tf_2N^-$] and [NSi-NH_2-$OMIM^+Tf_2N^-$] is an important step in the evaluation process of physical adsorption and surface loading of a hydrophobic ionic liquid. The study of FT-IR spectra of newly synthesized sorbents were found to produce several characteristic functional peaks that are related to both IL and silica matrix as represented by Fig. 2 of [NSi-NH_2-$OMIM^+Tf_2N^-$]. The possible assigned chemical structures of nano-sized silica sorbents-immobilized-hydrophobic ionic liquids, [NSi-OH-$OMIM^+Tf_2N^-$] and [NSi-NH_2-$OMIM^+Tf_2N^-$] are shown in Scheme 1.

3.2. Sorption properties of Pb(II) in various controlling factors

The distribution of an analyte between sorbent and solvent phases is a result of its relative affinity for each phase. This behavior is mainly attributed to the interacting forces between analyte molecules and those of the solvent and sorbent phases. Such interaction is highly dependent on the physico-chemical features of the hydrophobic or polar sorbate characters as well as sorbent [36]. The types of analyte–sorbent interactions between solute and sorbent may be classified into three major well-defined sorption categories including physical, chemical, and electrostatic interactions. The physical interaction processes involve interactions between dipole, either permanent or induced moments, of sorbate and sorbent molecules. On the other hand, chemical interactions involve covalent bond formation between the two interacting species. Finally, electrostatic interactions are identified by the involvement of ion–ion and ion–dipole forces [37]. Moreover, several other mechanisms can also be postulated for sorption of metal species by various sorbents such as physical adsorption, hydrogen bonding, coordination complexes, association or bridged complexes and chemical adsorption. Some of these mechanisms are normally taking place simultaneously and depending on the nature of the functional groups of the surface loaded molecules as well as other several important contributing factors. The major important factors that contribute and influences the metal sorption processes to the surface of functionalized solid sorbents such as modified silica are mainly based on the effect of pH, reaction contact time, sorbent dose, initial metal ion concentration and interfering ions. There-



Scheme 1. Possible structure of modified nano-silica hydrophobic ionic liquids sorbents.

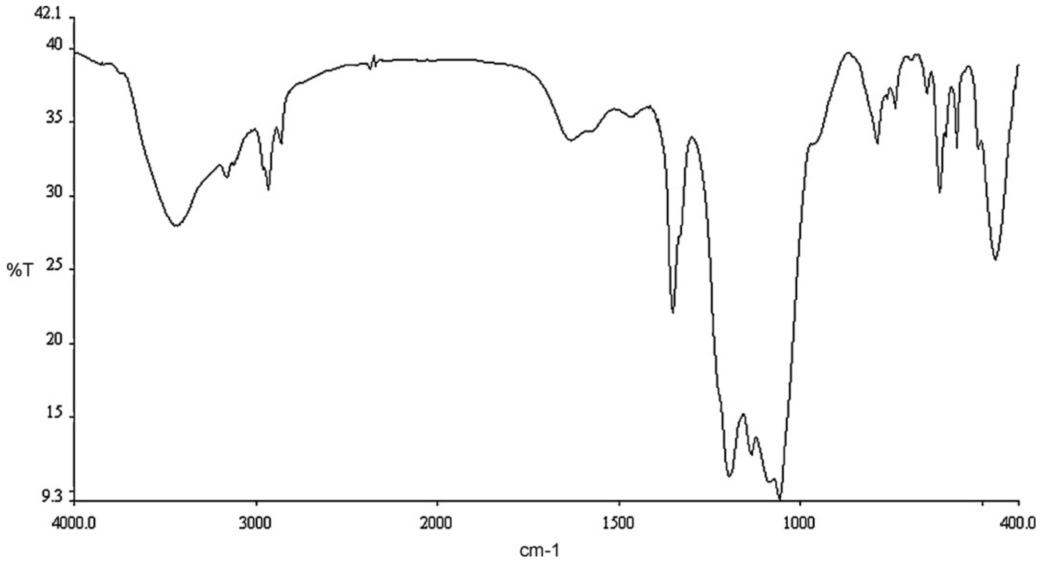


Fig. 2. FT-IR spectrum of [NSi-NH_2-$OMIM^+Tf_2N^-$].

Table 1
Effect of pH on the mmol g^{-1} sorption capacity values.

pH	Metal capacity in mmol g^{-1}	
	[NSi-OH-OMIM$^+$Tf$_2$N$^-$]	[NSi-NH$_2$-OMIM$^+$Tf$_2$N$^-$]
1	0.8	0.5
2	0.9	0.6
3	1.1	0.7
4	1.2	0.8
5	1.3	0.9
6	0.9	0.8
7	0.9	0.8

Values are based on triplicate analysis.

fore, these factors are extensively studied, explored and evaluated in the following sections.

3.2.1. *Effect of pH*

Identification and characterization of the optimum pH is very important owing to the influence of medium pH not only on the surface active centers and charge of sorbent but also on the degree of ionization, solubilization and speciation of sorbate in aqueous solutions. Therefore, monitoring the pH effect of contact solution between sorbate such as Pb(II) and sorbents such as nano-sized silica-loaded-hydrophobic ionic liquids, [NSi-OH-OMIM$^+$Tf$_2$N$^-$] and [NSi-NH$_2$-OMIM$^+$Tf$_2$N$^-$], is considered of great importance. Owing to the possible precipitation of Pb(II) hydroxide in higher pH values, experiments were carried out in the pH range 1–7 in order to find out the optimum pH for maximum metal uptake and extraction efficiency. Table 1 compiles the collected results from determination of the mmol g^{-1} sorption capacity values by newly synthesized nano-sized silica-loaded-hydrophobic ionic liquids. The results of metal sorption capacity values revealed that [NSi-OH-OMIM$^+$Tf$_2$N$^-$] sorbent was characterized by its superiority toward uptake of Pb(II) at all the studied buffer solutions compared to [NSi-NH$_2$-OMIM$^+$Tf$_2$N$^-$]. In addition, the adsorption capacity values of the presented sorbents are much higher than those previously reported phases [38–40]. Based on the determined lead sorption capacity values (0.8–1.3 mmol g^{-1}), one can easily identify the capability of surface loaded hydrophobic ionic liquid to react as a direct extraction medium for Pb(II). The determined 1.223 mmol g^{-1} surface coverage value of [NSi-OH] by [OMIM$^+$Tf$_2$N$^-$] hydrophobic ionic liquid for the formation of [NSi-OH-OMIM$^+$Tf$_2$N$^-$] can be used to account for such superior behavior and incorporated metal binding properties of this sorbent with Pb(II) under all buffering conditions. Thus, one can easily determine and conclude that a molar stoichiometric ratio of 1:1 under reaction conditions of pH 5 as the optimum value.

The effect of reaction pH on the sorption process of Pb(II) by newly modified nano-silica sorbent [NSi-NH$_2$-OMIM$^+$Tf$_2$N$^-$] was also studied under the same buffering conditions (pH 1–7). The same behavior and trend were also evident in the sorption process such as the gradual increase in the mmol g^{-1} sorption capacity values to the optimum pH 5 as listed in Table 1. In addition, the relative closeness in sorption capacity values (0.8–0.9 mmol g^{-1}) in presence of buffer solutions (pH 4.0–7.0) is suggesting a plateau of Pb(II) extraction under these buffering conditions. However, the outlined results in Table 1 indicate that the metal capacity values of Pb(II) determined by [NSi-OH-OMIM$^+$Tf$_2$N$^-$] under any studied buffering medium are higher than those identified by [NSi-NH$_2$-EMIM$^+$Tf$_2$N$^-$] at the same buffer solutions. This may be attributed to the presence of available and exchangeable free silanol groups especially in acidic buffer solutions with a pH range 1–5.

The direct contact and binding of lead sorbate with the newly modified nano-sized silica-physically adsorbed-hydrophobic ionic liquid are suggested to proceed via various possible modes. First, is the possible binding interaction with the surface loaded hydrophobic ionic liquid. Second, is the possible coordination via complex formation with the active donor atoms such as oxygen and nitrogen in both silica sorbents. Third, is the potentiality of cation exchange mechanism between active surface silanol groups and Pb(II), especially in the case of [NSi-OH-OMIM$^+$Tf$_2$N$^-$]. Fourth, is the direct ion-pair formation with surface charged species.

3.2.2. *Kinetics of the sorption system*

The effect of shaking time represents one of the major contributing factors to the sorption process when the batch equilibrium technique is utilized [41–43]. The importance of shaking time factor comes from the need for identification of the possible rapidness of binding and extraction processes of the tested metal ions by the newly modified nano-silica sorbents. In addition, certifying the optimum time for complete extraction of the target metal ion is usually aimed for many reasons, such as the comparison with other

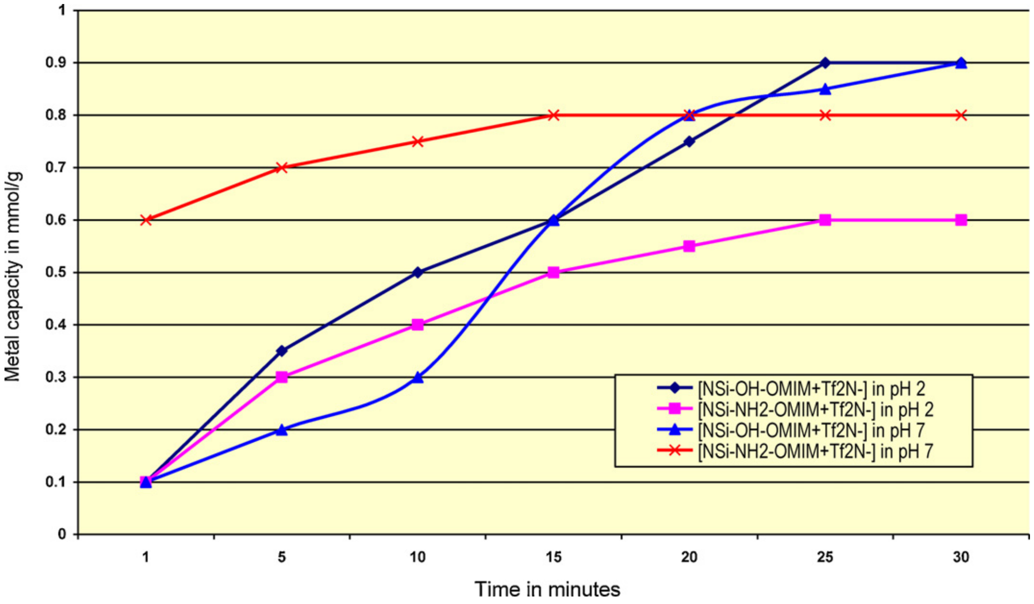


Fig. 3. Effect of shaking time on the Pb(II) sorption by modified nano-silica sorbents.

Table 2
Effect of sorbent dose on Pb(II) sorption by [NSi-OH-OMIM$^+$Tf$_2$N$^-$] and [NSi-NH$_2$-OMIM$^+$Tf$_2$N$^-$] in buffer solution with pH 5.

Adsorbent mass (mg)	[NSi-OH-OMIM$^+$Tf$_2$N$^-$]		[NSi-NH$_2$-OMIM$^+$Tf$_2$N$^-$]	
	%-Extraction	mmol g^{-1}	%-Extraction	mmol g^{-1}
25.0	15.79%	0.120	15.79%	0.120
50.0	31.58%	0.120	31.58%	0.120
100.0	44.74%	0.085	44.11%	0.084
250.0	68.42%	0.052	63.32%	0.048
500.0	100.00%	0.038	93.00%	0.032

% extraction values are based on triplicate analysis with highest standard deviation values of 2.84%.

well-known modified sorbents. Moreover, the optimum time is usually useful when separation of the target analyte from other interfering species is aimed. Fig. 3 shows a direct representation for the relationship between the contact time and lead sorption by newly modified nano-silica sorbents [NSi-OH-OMIM$^+$Tf$_2$N$^-$] and [NSi-NH$_2$-OMIM$^+$Tf$_2$N$^-$] at two different buffer solutions (pH 2 and 7) as examined by the batch equilibrium technique. The two buffer solutions were selected to give some idea about the rapidness of Pb(II) binding to the sorbent surfaces in acidic and neutral solutions. As shown in Fig. 3, the adsorption processes in both buffer solutions were found to follow two stages. The first is the gradual increase in the metal sorption capacity as well as percentage extraction and this stage required 15–25 min for reaching a 100% extraction of the specified mmol g^{-1} values. [NSi-NH$_2$-OMIM$^+$Tf$_2$N$^-$] was found to exhibit the highest percentage extraction values when examined in buffer solution (pH 7) compared to other tested buffer solution (pH 2) as well as the other examined nano-silica sorbent [NSi-OH-OMIM$^+$Tf$_2$N$^-$]. In addition a 15 min contact time was identified as the maximum period to establish a 100%-extraction of Pb(II) by this sorbent. This high equilibration time periods in the case of [NSi-NH$_2$-OMIM$^+$Tf$_2$N$^-$] in buffer solution (pH 2) and [NSi-OH-OMIM$^+$Tf$_2$N$^-$] in both examined buffer solutions (pH 2 and 7) is mainly due to the initial accumulation of metal ion on the surface, assuming large surface area of nano-sorbents were available. With the gradual occupation of surface binding sites, the sorption process was slowed down giving rise to the second stage of complete surface interaction and coverage of the sorbate on sorbents.

3.2.3. *Effect of sorbent dose*

The determined percentage extraction and mmol g^{-1} values of Pb(II) sorption under various sorbent doses of the two newly synthesized nano-silica hydrophobic ionic liquid, [NSi-OH-OMIM$^+$Tf$_2$N$^-$] and [NSi-NH$_2$-OMIM$^+$Tf$_2$N$^-$] were also studied and evaluated. The results of this sorption study are compiled in Table 2. The interacting initial concentration of Pb(II) was adjusted in all measurements to 400 ppm in buffer solution with pH 5 as the optimum one. It is evident from the listed data that as the mass of sorbents increases, the percentage extraction values of Pb(II) also increase owing to the possible high surface area and more exposure of active loaded hydrophobic ionic liquid moiety. In presence of 500 mg of [NSi-OH-OMIM$^+$Tf$_2$N$^-$] sorbent, a 100.00%-extraction of the interacting metal ion was achieved. On the other hand, [NSi-NH$_2$-OMIM$^+$Tf$_2$N$^-$] was found to establish a 93.00%-extraction value under the same experimental conditions. In addition, the two studied sorbents were found similarly behaving in their sorption interaction properties with Pb(II) under the examined sorbent doses of 25, 50 and 100 mg. The determined percentage extraction values by [NSi-OH-OMIM$^+$Tf$_2$N$^-$] and [NSi-NH$_2$-OMIM$^+$Tf$_2$N$^-$] were found in the range of 15.79–44.74 ± 2.38% and 15.79–44.11 ± 2.51%, respectively. However, at higher mass doses of the sorbents (250–500 mg), [NSi-OH-OMIM$^+$Tf$_2$N$^-$] was found to be more superior in the process of Pb(II) sorption than [NSi-NH$_2$-OMIM$^+$Tf$_2$N$^-$] as listed in Table 2. This observation is again in good agreement with the surface coverage values of the two newly synthesized silica sorbents as well as the results collected and described in Section 3.2.1. On the other hand, the determined mmol g^{-1} sorption capacity values were found to exhibit a peak at both 25 and 50 mg-sorbent dose for both [NSi-OH-OMIM$^+$Tf$_2$N$^-$] and [NSi-NH$_2$-OMIM$^+$Tf$_2$N$^-$] sorbents. In addition, the decrease in mmol g^{-1} with high sorbent doses are not surprising, as in all the sorbents and biosorbents dosage experiments, percent metal adsorption is inversely related to the metal uptake capacity of sorbents. The reason for this may be attributed to the high electrostatic repulsion caused by the presence of excessive surface binding sites [44].

Table 3
Effect of interfering ions on metal sorption capacity of Pb(II).

Sorbent mass (mg)	pH	Nano-silica sorbent	Interfering ion	Mass (mg)	mmol g^{-1}
100	5.0	[NSi-NH$_2$-OMIM$^+$Tf$_2$N$^-$]	Na^+	1000	0.900
			K^+	1000	0.870
			Ca^{2+}	1000	0.865
			Co^{2+}	1000	0.335
			Ni^{2+}	1000	0.350
			Cu^{2+}	1000	0.305
			Cd^{2+}	1000	0.325
			Hg^{2+}	1000	0.355
			Cl^-	5000	0.900
			$NO_3{}^-$	2000	0.890
			$SO_4{}^{2-}$	1000	0.875
			CH_3COO^-	2000	0.900
100	5.0	[NSi-OH-OMIM$^+$Tf$_2$N$^-$]	Na^+	1000	1.300
			K^+	1000	1.290
			Ca^{2+}	1000	1.260
			Co^{2+}	1000	0.270
			Ni^{2+}	1000	0.315
			Cd^{2+}	1000	0.335
			Hg^{2+}	1000	0.350
			Cu^{2+}	1000	0.285
			Cl^-	5000	1.300
			$NO_3{}^-$	2000	1.295
			$SO_4{}^{2-}$	1000	1.280
			CH_3COO^-	2000	1.270

Values of mmol g^{-1} are based on triplicate analysis with highest standard deviation values of 0.035.

3.2.4. *Effect of interfering ions*

A series of selected cations and anions was used to study and evaluate their interfering effects on the sorption processes of Pb(II) by [NSi-OH-OMIM$^+$Tf$_2$N$^-$] and [NSi-NH$_2$-OMIM$^+$Tf$_2$N$^-$]. The selected anions were Cl^-, $NO_3{}^-$, $SO_4{}^{2-}$ and CH_3COO^- and the selected cations were Na^+, K^+, Ca^{2+}, Co^{2+}, Ni^{2+} and Cu^{2+}, Cd^{2+} and Hg^{2+}. The results of this study are compiled in Table 3. The data listed are clearly showing that some of the selected cations such as (Na^+, K^+ and Ca^{2+}) and the studied anions (Cl^-, $NO_3{}^-$, $SO_4{}^{2-}$ and CH_3COO^-) were characterized by their no or minimum interference in the process of solid phase extraction of Pb(II) by the two newly modified nano-silica sorbents [NSi-OH-OMIM$^+$Tf$_2$N$^-$] and [NSi-NH$_2$-OMIM$^+$Tf$_2$N$^-$]. The metal sorption capacity values of Pb(II) in presence of these interfering anions were identified in the range of 0.865–0.900 and 1.270–1.300 mmol g^{-1} as determined by [NSi-NH$_2$-OMIM$^+$Tf$_2$N$^-$] and [NSi-OH-OMIM$^+$Tf$_2$N$^-$], respectively. However, Co^{2+}, Ni^{2+}, Cu^{2+} Cd^{2+} and Hg^{2+} were found to exhibit high interference in Pb(II) extraction by the two newly synthesized nano-silica sorbents owing to the possible competition for active donor centers incorporated onto the surface of modified sorbents. The determined metal sorption capacity values of Pb(II) by [NSi-OH-OMIM$^+$Tf$_2$N$^-$] in the presence of interfering Co^{2+}, Ni^{2+} and Cu^{2+}, Cd^{2+} and Hg^{2+} were found as 0.335, 0.350, 0.305, 0.335 and 0.350 mmol g^{-1}, respectively. The same interference trends and behavior of Co^{2+}, Ni^{2+} and Cu^{2+} Cd^{2+} and Hg^{2+} cations were also evident in the solid phase extraction of Pb(II) by [NSi-NH_2-BMIM+Tf_2N^-] giving rise to sorption capacity values of 0.270, 0.315, 0.285, 0.325 and 0.355 mmol g^{-1}, respectively as listed and compiled in Table 3.

The effect of ionic strength on sorption properties of Pb(II) by [NSi-OH-$OMIM^+Tf_2N^-$] and [NSi-NH_2-$OMIM^+Tf_2N^-$] was also and evaluated. Various ionic strength values (0.01-–0.1) of NaCl were used and the results were found to show negligible influence on the metal sorption capacity of Pb(II) by the two sorbents. The identified capacity values were in the range of 0.8–0.9 and 1.2–1.3 mmol g^{-1} for [NSi-OH-$OMIM^+Tf_2N^-$] and [NSi-NH_2-$OMIM^+Tf_2N^-$], respectively.

3.2.5. *Effect of initial lead (II) concentration*

Adsorption and metal uptake processes by various sorbents are heavily dependent on the initial metal ion concentration. Generally, a number of well-known adsorption isotherms are basically used to provide important and valuable information for optimizing the conditions of sorbent applications. The potential affinity between sorbate and adsorbent, bond energy and sorption capacity can be determined and evaluated from the various isotherm equilibrium models. The two most commonly employed models are the Langmuir and Freundlich isotherms and shown suitable for describing short-term and mono-component adsorption of metal ions by different materials [45]. According to Langmuir, the sorption process is normally taking place on the sorbent surface in a homogeneous way and the sorbate species is expected to form a monolayer, without mutual interactions. This adsorption model was found to provide no information about the sorption mechanism and still used to obtain the uptake capacities as well as other sorption characteristics of the sorbents. The expression of Langmuir adsorption model is given in equation (1):

$$q_e = \frac{q_{\max} b C_e}{1 + b C_e}, \tag{1}$$

where 'q_e' is the amount of metal sorbed at equilibrium (mg/g), '$q_{\max}$' is the monolayer sorption capacity (mg/g), 'b' is the Langmuir constant, 'C_e' is concentration of metal ions in solution at equilibrium. The linear form of Langmuir adsorption model is given by equation (2):

$$\frac{C_e}{q_e} = \frac{C_e}{q_{\max}} + \frac{1}{b q_{\max}}. \tag{2}$$

If Langmuir adsorption model is obeyed, a straight line is obtained with slope of $(1/q_{\max})$ and an intercept of $(1/b\, q_{\max})$ when a plot of (C_e/q_e) versus C_e is drawn.

The Freundlich adsorption isotherm gives an expression of the surface heterogeneity and exponential distribution of the active sites and their energies as well as non-ideal sorption on heterogeneous surfaces in a multilayer way. The Freundlich adsorption model is generally described by equation (3):

$$q_e = K_f C_e^{1/n}, \tag{3}$$

where K_f and $1/n$ are the Freundlich constants. The linearized form of the Freundlich adsorption isotherm is given in equation (4):

$$\ln q_e = \ln K_f + \frac{1}{n} \ln C_e. \tag{4}$$

A plot of '$\ln q_e$' or '$\log q_e$' versus '$\ln C_e$' or '$\log C_e$' would produce a straight line with '$1/n$' as the slope and '$\ln K_f$' or '$\log K_f$' as an intercept.

In this study, both Langmuir and Freundlich isotherm models have been implemented to identify the possible type(s) of Pb(II)/sorbents interaction processes. The results of this evaluation study revealed the suitability of Langmuir model to fit better with the experimental data compared to the Freundlich model. The illustrations of (C_e/q_e) versus C_e for the two newly synthesized nano-silica sorbents [NSi-OH-$OMIM^+Tf_2N^-$] and [NSi-NH_2-$OMIM^+Tf_2N^-$], respectively, were found to produce straight lines suggesting that the sorption of Pb(II) obeys Langmuir isotherm over the entire range of studied sorption concentrations as represented by Fig. 4. The $q_{\max}$ values of the two sorbents were calculated and identified as 2300 and 2500 (mg/g) for [NSi-NH_2-$OMIM^+Tf_2N^-$] and [NSi-OH-$OMIM^+Tf_2N^-$], respectively. The calculated Langmuir constant (b) were found as 5.0X10^{-6} and 6.0X10^{-6} for the two sorbents [NSi-NH_2-$OMIM^+Tf_2N^-$] and [NSi-OH-$OMIM^+Tf_2N^-$], respectively. The closeness in the determined $q_{\max}$ and b values is clearly referring to the similarity in lead sorption mechanisms by the two newly synthesized nano-silica sorbents. In addition, the initial concentration of metal ion in solution has remarkably influenced the equilibrium uptake of lead(II) by [NSi-OH-$OMIM^+Tf_2N^-$] and [NSi-NH_2-$OMIM^+Tf_2N^-$] due to higher availability of metal ion for the sorption. Moreover, higher initial concentration provides increased driving force to overcome all mass transfer resistance of metal ion between the aqueous and solid phase resulting in higher probability of collision between metal ion and sorbent. This trend is commonly in favor of and results in higher metal uptake.

3.3. *Implementation of supported hydrophobic ionic liquid as solid phase extraction medium for lead from real water samples via multi-stage micro-column separation*

The potential applications of newly synthesized nano-silica sorbents-physically adsorbed-hydrophobic ionic liquid as packing materials in micro-column separation of lead from real matrices were studied and explored. A multi-stage micro-column based on three successive passages of water sample was used in this procedure. A sample of 50 ± 1 mg of the selected silica sorbent was used as the packing materials in each column. Two types of water samples were collected from Maryout lake and drinking tap water, Alexandria, Egypt. Water samples were then spiked with Pb(II) ~ 1.0 mg l^{-1} and passed over each column stage with a flow rate of 20 ml min^{-1}. The collected samples from effluents were subjected to atomic absorption analysis to determine

Table 4
Percentage extraction of Pb(II) from real water sample by multi-stage micro-column separation.

Sample	Phase	Mass (mg)	Spiked Pb(II) (ppm)	First stage %-extraction	Second stage %-extraction	Third stage %-extraction
1.0 l Maryout lake water	[NSi-OH-$OMIM^+Tf_2N^-$]	50 ± 1 each stage	0.985	67.0 ± 4.0%	97.0 ± 2.0%	100.0 ± 3.0%
1.0 l drinking tap water		50 ± 1 each stage	0.979	65.0 ± 4.0%	92.0 ± 3.0%	100.0 ± 4.0%
1.0 l Maryout lake water	[NSi-NH_2-$OMIM^+Tf_2N^-$]	50 ± 1 each stage	0.998	32.0 ± 5.0%	89.0 ± 3.0%	100.0 ± 3.0%
1.0 l drinking tap water		50 ± 1 each stage	0.980	28.0 ± 5.0%	77.0 ± 4.0%	99.0 ± 4.0%

% extraction values are based on triplicate analysis.

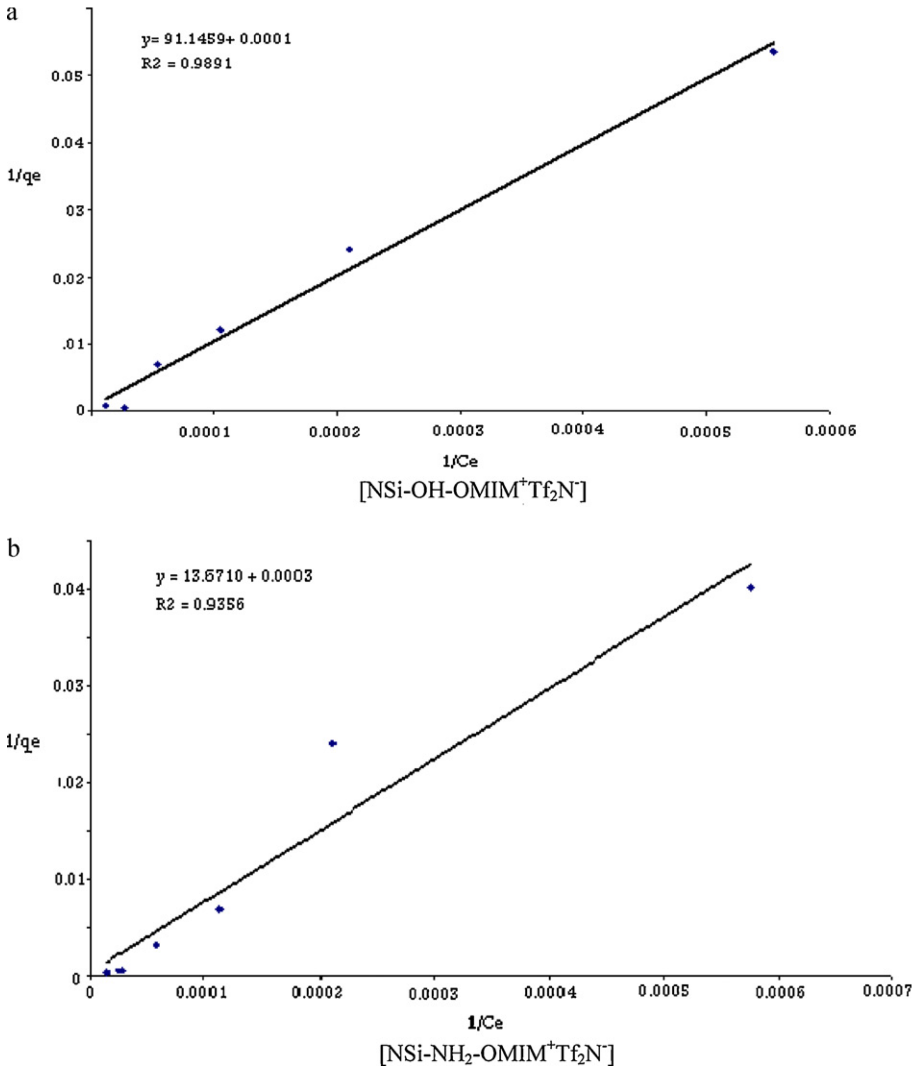


Fig. 4. Langmuir isotherm models of lead sorption.

the percentage extraction values. The results of this study are compiled in Table 4. The percentage extraction and recovery values of Pb(II) were found to increase by going from the first stage micro-column to the third one. In the case of [NSi-OH-OMIM$^+$Tf$_2$N$^-$] sorbent, the average percentage extraction and recovery values were found as 66.0, 94.5 and 100.0 ± 4.0%, while in the case of [NSi-NH$_2$-OMIM$^+$Tf$_2$N$^-$] these were found as 30.0, 83.0 and 99.5 ± 5.0% based on first, second and third stage column passages, respectively. In addition, column packed with [NSi-OH-OMIM$^+$Tf$_2$N$^-$] were found to exhibit a higher percentage recovery values of Pb(II) from the two studied water samples under all micro-column stages as listed in Table 4. This trend can also be used to account for the superiority of [NSi-OH-OMIM$^+$Tf$_2$N$^-$] compared to [NSi-NH$_2$-OMIM$^+$Tf$_2$N$^-$] as mentioned in previous sections. However, the collected data from this application study for lead extraction by the two newly synthesized nano-silica sorbents are clearly denoting to the excellent percentage extraction and recovery values after three stages of micro-column extraction. It is important to report here that the percentage recovery values of Pb(II) from real water matrices via applications of multi-stage micro-column extraction procedures were found to be more superior than those concluded by single stage micro-column separation.

A preconcentration procedure was also performed in order to generalize the potential application and implementation of newly synthesized sorbents for Pb(II) from drinking tap water. The results of this study proved a 98.5 ± 2.0% recovery value of the spiked concentration of Pb(II) ($\sim$5.0 μg l^{-1}) from tap water with a preconcentration factor of 200.

3.3.1. *Comparison with other methods*

The suggested method in this work is directly compared with other previously reported methods of implementing ionic liquids in liquid–liquid extraction and single-drop microextraction techniques as summarized and compiled in Table 5. The advantages of the present work are mainly focused on the following points. First is the potential application of newly reported sorbents for metal extraction without the need for partitioning chelating agent. Second is the capability of both sorbents to favor solid phase extraction of lead from acidic and neutral aqueous solutions. Other important features are mainly focused on factors optimization and surface characterization. In addition, the efficiency of the two newly synthesized sorbents as solid phase extractors revealed their superiority compared to other C18-SPE [46].

Table 5
Comparison with other previously reported methods.

Ionic liquid	Extraction technique	Chelating intermediate	Analyte	Optimum pH range	Matrix	Percent recovery	Reference
[bmim][PF6]	Liquid–liquid extraction	8-Sulfonamido-quinoline	Co, Cu, Zn and Cd	–	Aqueous solutions	–	[11]
($C_n$mim+)(NTf2$^-$)	Liquid–liquid extraction	Crown ethers	Na, Cs and Sr	–	Aqueous solutions	–	[13,14]
[C_8mim][PF_6],	Liquid–liquid extraction	Dimethylphenylazosalicylfluorone	Uranium(VI)	–	Aqueous solutions	97.2–104.2%	[16]
[BMIM][PF6]	Liquid–liquid extraction	2-Aminothiophenol	Ni, Cu and Pb	≥4.0–6.0	Water samples	20.0–76.0%	[17]
(C_4mim$^+$$Tf_2N^-$)	Liquid–liquid extraction	2-Thenoyltrifluoro acetone	Lanthanide (III) (Ln)	–	Aqueous solutions	–	[19]
[C4MIM][PF6]	Single-drop microextraction	Ammonium pyrroldinedithio-carbamate	Pb	3.0	Water and food samples	94.7–105.3%	[4]
Tetradecyl(trihexy) phosphonium chloride	Single-drop microextraction	2-(5-Bromo-2-pyridylazo)-5-diethylaminophenol	Pb	9.0	Real water samples	95.0%	[5]
[C6MIM][PF6]	Liquid-phase microextraction	Dithizone	Pb	8.0	Environmental samples	94.8–104.1%.	[6]
[C6MIM][PF6]	Hollow fiber-based liquid-phase microextraction	Ammonium pyrroldine dithiocarbamate	Pb and Ni	3.0	Real samples	96.1–103.2%	[7]
[BMIM+Tf_2N^-]	Solid phase extraction	–	Pb	1.0–7.0	Lake and drinking water	99.0–100.0%	This work

4. Conclusion

Several important points can be concluded and summarized as follows:

- The ability of hydrophobic ionic liquid to bind and adsorb on the surface of nano-sized silica sorbents either in the form of active surface loaded silanol or amino groups with almost the same surface coverage values.
- The suitability of newly synthesized nano-silica sorbents-immobilized-ionic liquid for applications in the solid phase extraction technique of Pb(II) from various water matrices without the need for using a chelating intermediate as described in the case of L–L extraction by using ionic liquids.
- Excellent metal capacity values of [NSi-OH-OMIM$^+$$Tf_2N^-$] and [NSi-$NH_2$-OMIM$^+$$Tf_2N^-$] toward Pb(II) sorption, extraction and removal of Pb(II) from strongly acidic as well as other aqueous solutions (pH 1–7).
- The fast equilibration kinetics of sorbent/sorbate interaction processes as concluded by the time range of 15–25 min.
- The increase in the percentage extraction of Pb(II) with the increase of the sorbent mass owing to the increase in the surface area of sorbent, which provided more binding sites for the sorption.
- The sorption models of Pb(II) by both sorbents were found to be similarly with respect to Langmuir isotherms over the entire range of studied sorption metal concentrations.
- The superiority of sorption and uptake characteristics of [NSi-OH-OMIM$^+$$Tf_2N^-$] toward Pb(II) under all the studied and evaluated factors when compared to [NSi-NH_2-OMIM$^+$$Tf_2N^-$].
- The excellent percentage recovery values of Pb(II) from water matrices upon the use of multi-stage micro-column separation techniques as compared to single-stage micro-column approach.

References

[1] L.A. Blanchard, D. Hancu, E.J. Beckman, J.F. Brennecke, Green processing using ionic liquids and CO_2, Nature 399 (1999) 28–29.
[2] C.P. Mehnert, R.A. Cook, N.C. Dispenziere, M. Afeworki, Supported ionic liquid catalysis—a new concept for homogeneous hydroformylation catalysis, J. Am. Chem. Soc. 124 (2002) 12932–12933.
[3] H. Olivier-Bourbigou, L. Magna, D. Morvan, Ionic liquids and catalysis: recent progress from knowledge to applications, Applied Catalysis A: General 373 (2010) 1–56.
[4] J.L. Manzoori, M. Amjadi, J. Abulhassani, Ultra-trace determination of lead in water and food samples by using ionic liquid-based single drop microextraction-electrothermal atomic absorption spectrometry, Anal. Chim. Acta 644 (2009) 48–52.
[5] E.M. Martinis, P. Bert́n, J.C. Altamirano, U. Hakala, R.G. Wuilloud, Tetradecyl(trihexyl)phosphonium chloride ionic liquid single-drop microextraction for electrothermal atomic absorption spectrometric determination of lead in water samples, Talanta 80 (2010) 2034–2040.
[6] H. Bai, G. Qingxiang Zhou, J. Xie, Xiao, Temperature-controlled ionic liquid–liquid-phase microextraction for the pre-concentration of lead from environmental samples prior to flame atomic absorption spectrometry, Talanta 80 (2010) 1638–1642.
[7] J. Abulhassani, J.L. Manzoori, M. Amjadi, Hollow fiber based-liquid phase microextraction using ionic liquid solvent for preconcentration of lead and nickel from environmental and biological samples prior to determination by electrothermal atomic absorption spectrometry, J. Hazard. Mater. 176 (2010) 481–486.
[8] L. Li, B. Hu, L. Xia, Z. Jiang, Determination of trace Cd and Pb in environmental and biological samples by ETV-ICP-MS after single-drop microextraction, Talanta 70 (2006) 468–473.
[9] F. Pena-Pereira, I. Lavilla, C. Bendicho, L. Vidal, A. Canals, Speciation of mercury by ionic liquid-based single-drop microextraction combined with high-performance liquid chromatography-photodiode array detection, Talanta 78 (2009) 537–541.
[10] M. Gharehbaghi, F. Shemirani, M.D. Farahani, Cold-induced aggregation microextraction based on ionic liquids and fiber optic-linear array detection spectrophotometry of cobalt in water samples, J. Hazard. Mater. 165 (2009) 1049–1055.
[11] Taku Ajioka, Syunichi Oshima, Naoki Hirayama, Use of 8-sulfonamidoquinoline derivatives as chelate extraction reagents in ionic liquid extraction system, Talanta 74 (2008) 903–908.

[12] A.E. Visser, R.P. Swatloski, W.M. Reichert, S.T. Griffin, R.D. Rogers, Traditional extractants in nontraditional solvents: groups 1 and 2 extraction by crown ethers in room-temperature ionic liquids, Ind. Eng. Chem. Res. 39 (2000) 3596–3604.

[13] H. Luo, S. Dai, P.V. Bonnesen, A.C. Buchanan III, J.D. Holbrey, N.J. Bridges, R.D. Rogers, Extraction of cesium ions from aqueous solutions using calix[4]arene-bis(*tert*-octylbenzo-crown-6) in ionic liquids, Anal. Chem. 76 (2004) 3078–3083.

[14] H. Luo, S. Dai, P.V. Bonnesen, Solvent extraction of Sr^{2+} and Cs^{+} based on room-temperature ionic liquids containing monoaza-substituted crown ethers, Anal. Chem. 76 (2004) 2773–2779.

[15] M.L. Dietz, D.C. Stepinski, A ternary mechanism for the facilitated transfer of metal ions into room-temperature ionic liquids (RTILs): implications for the "greenness" of RTILs as extraction solvents, Green Chem. 7 (2005) 747–750.

[16] C. Jie, L. Zaijun, L. Ming, Spectrophotometric determination of ultra trace uranium(VI) in seawater after extractive preconcentration with ionic liquid and dimethylphenylazosalicylfluorone, Intern. J. Environ. Anal. Chem. 88 (2008) 580–583.

[17] R. Lertlapwasin, N. Bhawawet, A. Imyim, S. Fuangswasdi, Ionic liquid extraction of heavy metal ions by 2-aminothiophenol in 1-butyl-3-methylimidazolium hexafluorophosphate and their association constants, Sep. Purif. Technol. 72 (2010) 70–76.

[18] S. Pandey, Analytical applications of room-temperature ionic liquids: a review of recent efforts, Anal. Chim. Acta 556 (2006) 38–45.

[19] M.P. Jensen, J. Neuefeind, J.V. Beitz, S. Skanthakumar, L. Soderholm, Mechanisms of metal ion transfer into room-temperature ionic liquids: the role of anion exchange, J. Am. Chem. Soc. 125 (2003) 15466–15473.

[20] H. Qiu, Q. Jiang, Z. Wei, X. Wang, X. Liu, S. Jiang, Preparation and evaluation of a silica-based 1-alkyl-3-(propyl-3-sulfonate) imidazolium zwitterionic stationary phase for high-performance liquid chromatography, J. Chromatogr. A 1163 (2006) 63–69.

[21] H. Qiu, S. Jiang, X. Liu, *N*-Methylimidazolium anion-exchange stationary phase for high-performance liquid chromatography J, J. Chromatogr. A 1103 (2006) 265–270.

[22] H. Qiu, S. Jiang, X. Liu, L. Zhao, Novel imidazolium stationary phase for high-performance liquid chromatography, J. Chromatogr. A 1116 (2006) 46–50.

[23] Y. Sun, A.M. Stalcup, Mobile phase effects on retention on a new butylimidazolium-based high-performance liquid chromatographic stationary phaseJ, J. Chromatogr. A 1126 (2006) 276–282.

[24] Q. Wang, G.A. Baker, S.N. Baker, L.A. Colón, Surface confined ionic liquid as a stationary phase for HPLC, Analyst 131 (2006) 1000–1005.

[25] M. Tian, H. Yan, K.H. Row, Solid-phase extraction of tanshinones from *Salvia Miltiorrhiza* Bunge using ionic liquid-modified silica sorbents, J. Chromatogr. B 877 (2009) 738–742.

[26] P. Bonhote, A. Dias, N. Papageorgiou, K. Kalyanasundaram, M. Gratzel, Hydrophobic, highly conductive ambient-temperature molten salts, Inorg. Chem. 35 (1996) 1168–1178.

[27] J.G. Huddleston, A.E. Visser, W.M. Reichert, H.D. Willauer, G.A. Broker, R.D. Rogers, Characterization and comparison of hydrophilic and hydrophobic room temperature ionic liquids incorporating the imidazolium cation, Green Chem. 3 (2001) 156–164.

[28] M.E. Mahmoud, M.M. El-Essawi, S.A. Kholeif, E.I. Fathallah, Aspects of surface modification, structure characterization, thermal stability and metal selectivity properties of silica gel phases-immobilized-amine derivatives, Anal. Chim. Acta 525 (2004) 123–132.

[29] D.R. Mac Farlane, J. Sun, J. Golding, P. Meakin, M. Forsyth, High conductivity molten salts based on the imide ion, Electrochim. Acta 45 (2000) 1271–1278.

[30] H. Matsumoto, H. Kageyama, Y. Miyazaki, Room temperature molten salts based on tetraalkylammonium cations and bis(trifluoromethylsulfonyl)imide, Chem. Lett. (2001) 182–185.

[31] A.P. Abbott, D. Boothby, G. Capper, D.L. Davies, R.K. Rasheed, Deep eutectic solvents formed between choline chloride and carboxylic acids: versatile alternatives to ionic liquids, J. Am. Chem. Soc. 126 (2004) 9142–9147.

[32] A. Yokozeki, D.J. Kasprzak, M.B. Shiflett, Thermal effect on C–H stretching vibrations of the imidazolium ring in ionic liquids, Phys. Chem. Chem. Phys. 9 (2007) 5018–5026.

[33] O. Höfft, S. Bahr, V. Kempter, Investigations with infrared spectroscopy on films of the ionic liquid [EMIM]Tf$_2$N, Langmuir 24 (2008) 11562–11566.

[34] M.L. Bruening, D.M. Mitchell, J.S. Bradshaw, R.M. Izatt, R.L. Bruening, Effect of organic solvent and anion type on cation binding constants with silica gel bound macrocycles and their use in designing selective concentrator columns, Anal. Chem. 63 (1991) 21–24.

[35] E.M. Soliman, M.E. Mahmoud, S.A. Ahmed, Synthesis, characterization and structure effects on selectivity properties of silica gel covalently bonded diethylenetriamine mono- and bis-salicyaldehyde and naphthaldehyde Schiff·s bases towards some heavy metal ions, Talanta 54 (2001) 243–253.

[36] J.W. Hamaker, J.M. Thompson, in: C.M. Goring, J.W. Hamaker (Eds.), Organic Chemicals in the Soil Environment, vol. 1, Marcel Dekker, New York, 1972, pp. 49–143.

[37] Z-W.J. Weber, P.M. Mc Ginley, L.E. Katz, Sorption phenomena in subsurface systems: concepts, models and effects on contaminant fate and transport, Water Res. 25 (1991) 499–528.

[38] M.E Mahmoud, O.F. Hafez, M.M. Osman, E. Elmelegy, Implementation of hybrid inorganic/organic adsorbents for removal and preconcentration of heavy metals from industrial waste and drinking waters, Sep. Sci.Technol. 45 (2010) 1302–1312.

[39] M.E. Mahmoud, O.F. Hafez, M.M. Osman, A.A. Yakout, A. Alrefaay, Hybrid inorganic/organic alumina adsorbents-functionalized-purpurogallin for removal and preconcentration of Cr(III), Fe(III), Cu(II), Cd(II) and Pb(II) from underground water, J. Hazard. Mater. 176 (2010) 906–912.

[40] M.E. Mahmoud, Study of the selectivity characteristics incorporated into physically adsorbed alumina phases 2-mercaptonicotinic acid and potential applications as selective stationary phases for separation, extraction, and preconcentration of lead (II) and copper (II), J. Liq. Chromatogr. Rel. Technol. 25 (2002) 1187–1199.

[41] M.E. Mahmoud, A.A. Soayed, O.F. Hafez, Selective solid phase extraction and pre-concentration of heavy metals from sea water by silica gel phases-physically and chemically immobilized-4-amino-3-hydroxy-2(2-chloro-benzene)-azo-1-naphthalene sulfonic acid, Microchimica Acta 143 (2003) 65–70.

[42] M.M. Osman, S.A. Kholeif, N.A. Abou Al-Maaty, M.E. Mahmoud, Metal sorption, solid phase extraction and pre-concentration properties of two silica gel phases-chemically immobilized-2-hydroxynaphthaldehyde, Microchimica Acta 143 (2003) 25–31.

[43] M.M Osman, S.A. Kholeif, N.A. Abou Al-Maaty, M.E. Mahmoud, Synthesis, characterization of silica gel phases-chemically immobilized-4-aminoantipyrene and application in the solid phase extraction, pre-concentration and potentiometric studies, Anal. Sci. 20 (2004) 847–852.

[44] B. Benguella, H. Benaissa, Cadmium removal from aqueous solutions by chitin: kinetic and equilibrium studies, Water Res. 36 (2002) 2463–2474.

[45] R. Han, W. Zou, Y. Wang, L. Zhu, Removal of uranium(VI) from aqueous solutions by manganese oxide coated zeolite: discussion of adsorption isotherms and pH effect, J. Environ. Radioact. 93 (2007) 127–143.

[46] M. Shamsipur, F. Raoufi, H. Sharghi, Solid phase extraction and determination of lead in soil and water samples using octadecyl silica membrane disks modified by bis[1-hydroxy-9,10 anthraquinone-2-methyl]sulfide and flame atomic absorption spectrometry, Talanta 52 (2000) 637–643.