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Nano-silica sorbents immobilized hydrophobic ionic liquids for enhanced adsorptive extraction of cadmium from acidic aqueous solutions

Mohamed E. Mahmoud[a,*], Hassan M. Albishri[b]

[a]*Chemistry Department, Faculty of Sciences, Alexandria University, P.O. Box 426, Ibrahimia 21321, Alexandria, Egypt*
Tel. +20 140933009; Fax: +20 33911794; email: memahmoud10@sci.alexu.edu.eg
[b]*Department of Chemistry, Faculty of Science, King Abdulaziz University, P.O. Box 80203, Jeddah 21589, Saudi Arabia*

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ABSTRACT

A method is described for adsorptive removal of cadmium from acidic solutions (pH 1.0) via implementation of nano-silica particles physically impregnated hydrophobic ionic liquids (ILs). Two hydrophobic ILs, [$Emim^+Tf_2N^-$] and [$Omim^+Tf_2N^-$], were used to modify the surface of nano-silica amine sorbent [Nano-Si-NH_2] for the formation of [Nano-Si-NH_2-$Emim^+Tf_2N^-$] and [Nano-Si-NH_2-$Omim^+Tf_2N^-$], respectively. The highest cadmium adsorption capacity values (1.100–1.200 mmol g^{-1}) were identified in acidic solutions with pH 1.0, while the lowest mmol g^{-1} values (0.200–0.350) were characterized in solutions with pH 6.0–7.0. Adsorption of cadmium was monitored and optimized under the influence of several operational controlling conditions and factors such as reaction pH, reaction time, sorbent dose, initial cadmium concentration, interfering ions, and hydrophobicity of ILs. [Nano-Si-NH_2-$Omim^+Tf_2N^-$] sorbent was characterized by higher capacity values compared to [Nano-Si-NH_2-$Emim^+Tf_2N^-$] sorbent and this behavior was correlated to the more incorporated hydrophobic character in [$Omim^+Tf_2N^-$] than [$Emim^+Tf_2N^-$]. The two modified nano-silica sorbents were successfully implemented for removal of cadmium from acidic (pH 1.0) drinking tap and industrial wastewater with percentage extraction values of 97.78–99.00 ± 2.65. The determined percentage extraction values (93.44–96.87 ± 2.84) were also identified from water samples adjusted to pH 7.0 after three stages of elution in microcolumn approach.

Keywords: Nano-silica; Hydrophobic ionic liquids; [$Emim^+Tf_2N^-$]; [$Omim^+Tf_2N^-$]; Adsorption; Cadmium

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1. Introduction

Cadmium is a naturally occurring metal and known as an extremely toxic in any of its different chemical forms as chloride, sulfate, sulfide, carbonate, oxide, and others. In recent years, cadmium and its species have become a more prevalent cause for concern because long-term chronic exposure of cadmium can lead to serious health problems [1]. Human toxicity with cadmium is usually related to smoking, refined foods, water pipes, coffee and tea, coal burning, and shellfish [2]. High percentage of accumulated cadmium is deposited and retained in the kidney and liver based on its strong ability to replace the essential mineral zinc in these organs of human body [3]. This

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*Corresponding author.

function has led to serious liver damage, kidney disease, emphysema, bone disorders, and cancer. In addition, binding capability of cadmium to various biological components, such as protein and metallothionein are well documented [4].

Cadmium species are characterized by finding their ways into the aquatic system via different approaches that are mainly related to industrial activities. The various sources of cadmium aquatic ecosystem pollution are mainly due to industrial manufacturing of cadmium-containing alloys, electrical materials, electroplating, colored inks and dyes, plastics, ceramics, dental materials, and in the production of nickel–cadmium (Ni–Cd) batteries [5]. Minimization of the concentration levels of cadmium into the aquatic systems is the primary and essential step to reduce such high toxicity of cadmium via removal from the hydrosphere. Therefore, it is important to develop an accurate, effective, precise, and fast analytical procedure for removal of cadmium from water and wastewater samples [6,7].

In recent years, several methods have been proposed and explored for solid-phase removal and extraction of cadmium from various water samples by using several common binding and uptake mechanisms and processes via natural and waste sorbent materials as well as biosorbents [8–12]. Modified polymers and inorganic sorbents such as silica gel were also identified for their capability of cadmium removal and extraction [13–20].

Ionic liquids (ILs) are representing a certain class of compounds with unique and favorable characteristics compared to other conventional organic solvents and compounds. ILs have been widely used in almost all application fields of chemistry such as organic and inorganic syntheses, catalysis, electrochemistry, chromatography, separation and extraction techniques as well as industrial developments [21]. ILs may be categorized 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 [22]. The applications of ILs in extraction techniques are mainly focused on liquid-phase microextraction (LPME) or single drop microextraction (SDME) [23,24]. Other possible applications of ILs in the field of modified sorbent particles as solid phases in chromatographic applications were recently reported [25,26] as well as in liquid–liquid extraction (L-LE) [27,28]. The possible applications of ILs in the processes of L-LE of various metal ions from their matrices is mainly based on combination with some chelating compounds to form metal complexes in order to increase their hydrophobicity with the final step is regarded as the partition transfer of the produced metal complex between the two phases [29,30].

Immobilization of hydrophobic ILs on the surface of nano-silica particles via physical adsorption approach was recently reported [31,32] for the sake of implementation of these sorbents in the solid-phase extraction of lead from water samples without the need for using an intermediate chelating agent as required by L-LE. The reported sorbents were characterized by high surface coverage of the immobilized ILs as well as high adsorption capacity values compared to other previously published works [33–35]. Such behaviors of immobilized ILs on nano-silica sorbents have directed our interests to implement these sorbents in adsorptive removal of cadmium from various aqueous matrices. All operational and controlling factors in the process of cadmium adsorption and uptake such as reaction pH, reaction time, sorbent dose, initial cadmium concentration, interfering ions, and hydrophobicity of loaded ILs were also explored, studied, optimized, and reported in this study.

2. Experimental

2.1. Instrumentation

The FT-IR spectra of active nano-silica [Si-OH], nano-silica chemically immobilized amine, [Nano-Si-NH_2], nano-silica amine physically loaded 1-methyl-3-ethylimidazolium bis(trifluorom ethyl-sulfonyl)imide [Nano-Si-NH_2-$Emim^+Tf_2N^-$], and nano-silica amine physically loaded-1-methyl-3-octylimidazolium bis(trifluoromethyl-sulfonyl)imide [Nano-Si-NH_2-$Omim^+Tf_2N^-$] were measured on a BRUKER Tensor 37 FT-IR spectrophotometer in the range 200–4,000 cm^{-1}. Thermal gravimetric analysis (TGA) and thermoanalytical curves were obtained using a Perkin-Elmer TG A7 Thermobalance. The heating temperature range was set at operating condition range of 20–600℃ with heating rate of 10℃ min^{-1}. The flow rate was adjusted to 20 mL min^{-1} in a pure nitrogen atmosphere and a sample mass was selected in the range (5.0–7.0 mg). Scanning electron microscope (SEM) (JSM-6360 LA, JEOL Ltd.), (JSM-5300, JEOL Ltd.) and an ion sputtering coating device (JEOL-JFC-1100E) were used to examine and image the two modified nano-silica sorbents [Nano-Si-NH_2-$Emim^+Tf_2N^-$] and [Nano-Si-NH_2-$Omim^+Tf_2N^-$] as well as [Nano-Si-NH_2]. SEM specimens were coated with gold to increase the conductivity. Cadmium concentrations in all samples were determined by Shimadzu (AA-6650) atomic absorption spectrophotometer at the specified wavelength. A CRISON pH-meter was calibrated against standard buffer solutions of pH 4.01, 7.00, and 9.21 and used to measure the pH values of buffers and metal solutions. Thermolyne 47,900 furnace was used to determine the surface coverage values in mmol g^{-1} of modified nano-silica sorbents via thermal desorption analysis.

2.2. Materials

Silica gel with particle size 10–20 nm (Brauner-Emmet-Teller [BET]), d 2.6 and 99.5% purity was purchased from Aldrich Chemical Company, St Louis, MO, USA. Bis(trifluoromethylsulfonyl)imide anion, [TfN]$^-$, was supplied as LiN(CF$_3$SO$_2$)$_2$ by 3 M (Minneapolis, MN, USA) and used as received. All other chemicals were of reagent grade, obtained from Aldrich (Milwaukee, WI, USA) and BDH limited, Poole, England and used without further purification. Hydrochloric acid, sodium acetate trihydrate, and metal salts were all of analytical grade and purchased from Aldrich Chemical Company, USA and BDH Limited, Poole, England. The metal ion solutions were prepared from doubly distilled water (DDW).

Solutions of 1.0 M-hydrochloric acid 1.0 M-sodium acetate trihydrate were used to prepare the various buffer solutions (pH 1.0, 2.0, 3.0, 4.0, 5.0, 6.0, and 7.0) by mixing the appropriate volumes of the two solutions, adjusting the volume to 1 L by DDW and the pH value of resulting solutions was adjusted by a pH meter.

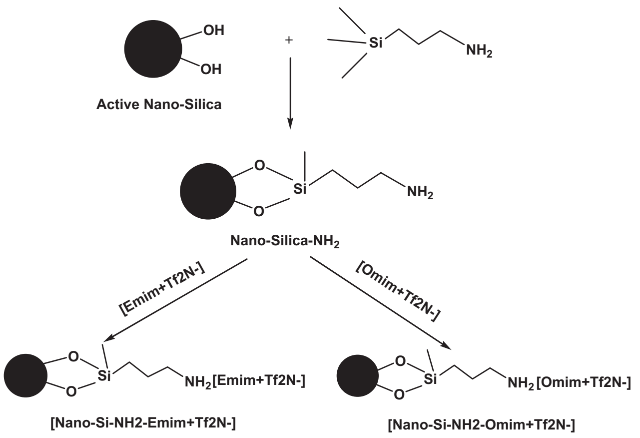
2.3. Synthesis

2.3.1. Synthesis of [Emin$^+$TfN$^-$] and [Omin$^+$TfN$^-$] ILs

[Emin$^+$TfN$^-$] and [Omin$^+$TfN$^-$] ILs were synthesized as previously reported [36,37]. 1-Methyl-3-octyllimidazolium bis(trifluoromethylsulfonyl)imide [Omim$^+$Tf$_2$N$^-$] IL was synthesized according to the following procedures. A sample of LiNTF$_2$ bis(trifluoromethylsulfonyl)imide, [Tf$_2$N$^-$], (8.6 g) was weighed and dissolved in 30 mL distilled water and 1-methyl-3-octyllimidazolium chloride [Omim$^+$Cl$^-$] (5.7 g) was also weighed and dissolved in 30 mL distilled water. 1-Methyl-3-ethyllimidazolium bis(trifluoromethylsulfonyl)-imide [Emim$^+$Tf$_2$N$^-$] IL was synthesized by dissolving 7.9 g-LiNTF$_2$ in 30 mL distilled water and 4.8 g of 1-methyl-3-ethylimidazolium chloride [Emim$^+$Cl$^-$] was also weighed and dissolved in 20 mL distilled water. The two reactants in each case 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$_2$N$^-$] and [Emim$^+$ Tf$_2$N$^-$] ILs were dried under rotavapor at 60˚C and 72 mbar for 4 h.

2.3.2. Synthesis of nano-silica amine-physically adsorbed-ILs

Nano-silica amine physically loaded ILs, [Nano-Si-NH$_2$-Emim$^+$Tf$_2$N$^-$] and [Nano-Si-NH$_2$-Omim$^+$Tf$_2$N$^-$], were synthesized according to the following method. Active nano-silica [Si-OH] (25.0 g) was prepared by refluxing and stirring in concentrated hydrochloric acid (150.0 mL of 1:1 v/v ratio). The activated nano-silica [Si-OH] was filtered, repeatedly washed with double distilled water until acid free and dried in an oven at 100˚C for 8 h. Nano-silica chemically immobilized amine, [Nano-Si-NH$_2$], was synthesized by the reaction of 10.0 g [Si-OH] already suspended in 100 mL toluene with 20 mL of 3-aminopropyltrimethoxysilane. 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 chemically immobilized NH$_2$ [Nano-Si-NH$_2$] [31,32]. [Nano-Si-NH$_2$-Emim$^+$Tf$_2$N$^-$] was synthesized by the direct reaction of [Nano-Si-NH$_2$] with [Emim$^+$TfN$^-$] IL according to the following procedure. [Nano-Si-NH$_2$] (10.0 g) was suspended in toluene and [Emim$^+$TfN$^-$] (5.0 mL) IL was then added. The reaction mixture was stirred at room temperature then filtered, washed with ethanol several times, and dried in an oven at 60˚C. [Nano-Si-NH$_2$-Omim$^+$Tf$_2$N$^-$] was also synthesized by the direct reaction of [Nano-Si-NH$_2$] (10.0 g) with 7.2 g of [Omim$^+$Tf$_2$N$^-$] IL in toluene. The reaction mixture was stirred at room temperature then filtered, washed with ethanol several times, and dried in an oven at 60˚C. Scheme 1 shows the synthetic routes of [Nano-Si-NH$_2$-Emim$^+$Tf$_2$N$^-$] and [Nano-Si-NH$_2$-Omim$^+$Tf$_2$N$^-$].



Scheme 1.

2.4. Surface coverage determination

Thermal desorption method [31,32] was used for determination of the surface coverage values of [Nano-Si-NH_2-$Emim^+Tf_2N^-$] and [Nano-Si-NH_2-$Omim^+Tf_2N^-$] according to the following procedures. A sample of 100 ± 1 mg of the dry nano-silica was weighed and ignited in a muffle furnace at 550 °C. 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, left to cool down inside the furnace till 150 °C and transferred to a desiccator to reach to the room temperature. The weight losses of adsorbed [$Emim^+Tf_2N^-$] and [$Omim^+Tf_2N^-$] ILs from the surface of nano-silica were determined by weight differences 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.

2.5. Adsorption of Cd(II) by nano-silica-physically adsorbed-ILs

2.5.1. Effect of pH

A batch equilibrium technique was used to perform this study. A sample of 10 ± 1 mg of [Nano-Si-NH_2-$Emim^+Tf_2N^-$] or [Nano-Si-NH_2-$Omim^+Tf_2N^-$] was weighed into a 50 mL measuring flask. A 1.0 mL of 0.1 M of Cd(II) was then added followed by 9.0 mL of acetate buffer solution (pH 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, filtered through filter paper, and washed with 50 mL of DDW. The unextracted Cd(II) in the filtrate was subjected to complexometric titration for determination of the metal capacity value (mmol g^{-1}) under each buffering condition.

2.5.2. Effect of shaking time

The effect of shaking time was studied by the selection of time interval values 1, 5, 10, 15, 20, 25, and 30 min and by using the batch equilibrium technique at room temperature. A sample of 10 ± 1 mg of either [Nano-Si-NH_2-$Emim^+Tf_2N^-$] or [Nano-Si-NH_2-$Omim^+Tf_2N^-$] was weighed into a 50 mL measuring flask. A 1.0 mL of 0.1 M Cd(II) was then added that followed by 9.0 mL of the selected acetate buffer solutions either pH 1.0 or 7.0 to cover acidic and neutral ranges. The reaction mixture was shaken by an automatic shaker for the selected shaking time period at room temperature and the unextracted Cd(II) was filtered and washed with 50 mL of DDW. The filtrate was subjected to complexometric titration for determination of the metal capacity value (mmol g^{-1}) under each shaking time condition.

2.5.3. Effect of initial cadmium concentration

Six different solutions of Cd(II) were prepared with the concentration values of 1.0×10^{-3}, 2.5×10^{-3}, 5.0×10^{-3}, 1.0×10^{-2}, 2.5×10^{-2}, and 5.0×10^{-2} mol L^{-1}. These metal ion solutions were buffered to a pH 1.0. A 10.0 mL portion of these solutions was mixed with 10.0 mg of either [Nano-Si-NH_2-$Emim^+Tf_2N^-$] or [Nano-Si-NH_2-$Omim^+Tf_2N^-$]. The reaction mixture was shaken by automatic shaker for 30 min, filtered, washed with 50 mL DDW, and the unextracted metal ion was subjected to further dilution to reach a concentration range of 1.0–2.0 mg L^{-1} and determined by atomic absorption analysis.

2.5.4. Effect of sorbent dose

The effect of sorbent dose was studied by using five different doses (0.025–0.500 g) of the sorbents. A 1.0 mL of 0.1 M Cd(II) was then added to the selected nano-silica sorbent and 9.0 mL of buffer pH 1.0 was then added and the mixture was automatically shaken for 30 min. The unbound metal ion was filtered, washed with 50 mL DDW to reach a concentration range of 1.0–2.0 mg L^{-1}, and subjected to determination by atomic absorption analysis.

2.5.5. Effect of coexisting ions

A solution of Cd(II), 0.1 mol L^{-1}, was prepared and buffered to a pH 1. Na(I), K(I), NH_4^+, Co(II), Ni(II), and Cu(II) were used as the selected cations and added to cadmium solution in order to obtain a final concentration of these cations as 1,000–2,000 mg L^{-1} each. The above Cd(II)-cation binary mixture solutions were also associated by the presence of some selected anions (1,000–2,000 mg L^{-1} each) such as Cl^-, NO_3^-, SO_4^{2-}, and acetate. A 10.0 mg of either [Nano-Si-NH_2-$Emim^+Tf_2N^-$] or [Nano-Si-NH_2-$Omim^+Tf_2N^-$] was added to 50 mL of the above Cd(II)-cation binary mixture solution and the reaction was completed by the batch equilibrium technique via shaking by an automatic shaker for 30 min. Free Cd(II) was filtered, 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.

2.6. Adsorptive removal of Cd(II) from real water samples by micro-column separation

Two types of water samples were used to study the potential applications of [Nano-Si-NH_2-$Emim^+Tf_2N^-$] and [Nano-Si-NH_2-$Omim^+Tf_2N^-$] for removal and extraction of Cd(II) from real aqueous samples. The first water sample was collected from industrial wastewater, while the second was collected from drinking tap water. One liter sample of each was spiked with Cd(II) ~ 1.0–2.0 $mg\,L^{-1}$, adjusted to pH 1.0 and passed over a multistage microcolumns with a flow rate of 20 $mL\,min^{-1}$. Two additional water samples were spiked each with Cd(II) ~ 1.0–2.0 $mg\,L^{-1}$, adjusted to pH 7.0, and passed over a multistage microcolumns. Each column was packed with 50 ± 1 mg of the selected [Nano-Si-NH_2-$Emim^+Tf_2N^-$] or [Nano-Si-NH_2-$Omim^+Tf_2N^-$] sorbent. The collected water samples from the effluents were subjected to atomic absorption analysis to determine the percentage extraction values at each stage of extraction.

3. Results and discussion

3.1. Adsorption of Cd(II) in various controlling factors

The synthetic routes for the preparation of modified nano-silica sorbents, [Nano-Si-NH_2-$Emim^+Tf_2N^-$] and [Nano-Si-NH_2-$Omim^+Tf_2N^-$], are given in Scheme 1. Structural identification and characterization were confirmed by using FT-IR analysis, TGA, and surface imaging with SEM as recently reported [31,32]. Physical adsorption of [$Emim^+Tf_2N^-$], as the selected IL, to the surface of [Nano-Si-NH_2] may be in the form of hydrogen bonding or ion-pair interaction. The surface coverage values for immobilization of the hydrophobic ILs—[$Emim^+Tf_2N^-$] and [$Omim^+$ Tf_2N^-]—on nano-silica amine [Nano-Si-NH_2] for the formation of [Nano-Si-NH_2-$Emim^+Tf_2N^-$] and [Nano-Si-NH_2-$Omim^+Tf_2N^-$] were found 1.310–1.320 and 1.220–1.230 $mmol\,g^{-1}$, respectively as identified from the TGA as well as thermal desorption method.

Adsorption and interaction processes of Cd(II) with the two modified nano-silica sorbents were studied, monitored, and evaluated under the influence of several operational and controlling factors such as reaction pH (1.0–7.0), contact time (1.0–30.0 min), sorbent dose (10.0–500 mg), initial cadmium concentration (1.0×10^{-3}–5.0×10^{-2} $mol\,L^{-1}$), and interfering anions and cations. The following sections present the data and interpretation of these operational conditions.

3.1.1. Effect of reaction pH

It is well known that the reaction pH value is strongly influencing the adsorption process between the metal ion and solid surface. The contact reaction pH affects not only the surface active centers and charge of sorbent, but also the degree of ionization, solubilization, and speciation of adsorbate in aqueous solutions. Identification of the optimum pH for adsorption of Cd(II) on [Nano-Si-NH_2-$Emim^+Tf_2N^-$] and [Nano-Si-NH_2-$Omim^+Tf_2N^-$] sorbents is very important for further implementation of these two sorbents in various applications. In order to find the optimum pH value(s) for maximum metal uptake and extraction efficiency, experiments were carried out in the pH range 1.0–7.0 only owing to the possible precipitation of the metal hydroxide in higher pH values. Fig. 1 shows cadmium adsorption capacity values at different buffer solutions, pH 1.0–7.0. Several points can be outlined form this study. [Nano-Si-NH_2-$Emim^+Tf_2N^-$] and [Nano-Si-NH_2-$Omim^+Tf_2N^-$] sorbents were found to exhibit high cadmium adsorption capacity values especially in low pH value of contact solutions. Initially, it is important to list out the adsorption capacity values of Cd(II) by [Nano-Si-NH_2] sorbent in an attempt to evaluate the contribution of this sorbent in the adsorption process of Cd(II). The lowest metal capacity value, 0.065 $mmol\,g^{-1}$, was identified in pH 1.0, while the highest one was characterized as 0.495 $mmol\,g^{-1}$ in pH 7.0 solution. It is evident from the listed data in Fig. 1 that as the pH value increases, the metal capacity values of the newly synthesized sorbents [Nano-Si-NH_2-$Emim^+Tf_2N^-$] and [Nano-Si-NH_2-$Omim^+Tf_2N^-$], increase on going from pH 1.0 to 7.0. The highest metal capacity values, in this study, were characterized and identified in buffer solution with pH 1.0 as 1.20 and 1.10 $mmol\,g^{-1}$ for [Nano-Si-NH_2-$Omim^+Tf_2N^-$] and [Nano-Si-NH_2-$Emim^+Tf_2N^-$], respectively. Several reasons can be used to account for such high metal adsorption capacity values under lower pH values. To account for such abnormal behavior of the tested sorbents for binding with Cd(II), one must consider the presence of anion exchange character of [Tf_2N^-] moiety in the structure of [Nano-Si-NH_2-$Omim^+Tf_2N^-$] and [Nano-Si-NH_2-$Emim^+Tf_2N^-$]. The proposed adsorption mechanism is typically based on anion exchange phenomenon and can be used to account for the high and strong affinity of Cd(II) toward nano-silica loaded ILs sorbents in lower pH buffer solutions (1.0–2.0). These buffer solutions are very rich in [Cl^-] ion based on the method of buffer preparation from 1.0 M hydrochloric acid. This chloride rich medium favors the formation of Cd

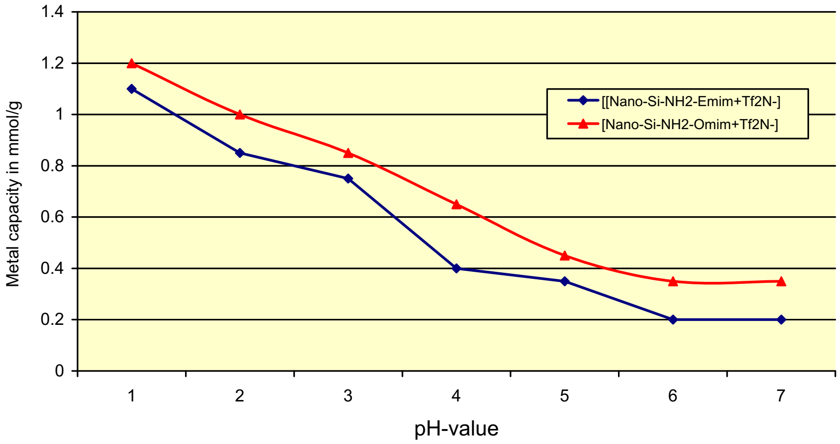


Fig. 1. Effect of pH on the Cd(II)-mmol g^{-1} capacity values.

(II)-chloroanionic species in the form of [$CdCl_3^-$] and [$CdCl_4^{2-}$] which are then subjected to exchange by the negatively charged [Tf_2N^-] anion as a part of the surface-loaded ILs. The formation of [$CdCl_3^-$] or [$CdCl_4^{2-}$] species are in favor of anion exchange mechanism according to the following Eqs. (1)–(3).

$$Cd^{2+} + 3Cl^- \rightarrow [CdCl_3]^- \quad (1)$$

$$\begin{aligned}&[\text{Nano-Si-NH}_2\text{-Emim}^+\text{Tf}_2\text{N} + [\text{CdCl}_3]^- \\ &\quad \rightarrow [\text{Nano-Si-NH}_2\text{-Emim}^+\text{CdCl}_3^-] + [\text{Tf}_2\text{N}^-]\end{aligned} \quad (2)$$

$$\begin{aligned}&[\text{Nano-Si-NH}_2\text{-Omim}^+\text{Tf}_2\text{N} + [\text{CdCl}_3]^- \\ &\quad \rightarrow [\text{Nano-Si-NH}_2\text{-Omim}^+\text{CdCl}_3^-] + [\text{Tf}_2\text{N}^-]\end{aligned} \quad (3)$$

It is evident from the data shown in Fig. 1 that the loaded hydrophobic ILs, [$Emim^+Tf_2N^-$] and [$Omim^+Tf_2N^-$], were found to be efficient in reacting as direct extraction media of the metal ion. Moreover, the determined metal adsorption capacity values by [Nano-Si-NH_2-$Omim^+Tf_2N^-$] are higher than those identified by [Nano-Si-NH_2-$Emim^+Tf_2N^-$] under any buffering condition. The simple comparison between the adsorption metal capacity values denotes to the superior behavior of [Nano-Si-NH_2-$Omim^+Tf_2N^-$] compared to [Nano-Si-NH_2-$Emim^+Tf_2N^-$]. This trend can be interpreted by the more incorporated hydrophobic character of octyl group in [Nano-Si-NH_2-$Omim^+Tf_2N^-$] than that of ethyl group in [Nano-Si-NH_2-$Emim^+Tf_2N^-$]. More evidence for the superiority of [Nano-Si-NH_2-$Omim^+Tf_2N^-$] compared to [Nano-Si-NH_2-$Emim^+Tf_2N^-$] may be concluded by considering the surface coverage values listed above and the highest metal adsorption capacity values listed shown in Fig. 1 as 1.20 and 1.10 mmol g^{-1}, respectively. The adsorption reactions of Cd(II) to the surface of [Nano-Si-NH_2-$Emim^+Tf_2N^-$] and [Nano-Si-NH_2-$Omim^+Tf_2N^-$] can be identified to proceed with ~83.0 and 97.0%, respectively, by assuming that the molar stoichiometric ratios in both cases were followed as 1:1.

3.1.2. *Effect of reaction contact time*

The relationship between contact time and cadmium sorption onto newly modified nano-silica sorbents [Nano-Si-NH_2-$Emim^+Tf_2N^-$] and [Nano-Si-NH_2-$Omim^+Tf_2N^-$] under two different buffer solutions (pH 1.0 and 7.0) was examined by the batch equilibrium technique and the results of this study are listed in Table 1. The two buffer solutions were selected to give a good idea about the rapidness of Cd(II) binding to the sorbent surface in two different ranges, acidic and neutral ones. The adsorption process of cadmium by [Nano-Si-NH_2-$Emim^+Tf_2N^-$] in presence of buffer solution, pH 1, was found to be rapidly completed than [Nano-Si-NH_2-$Omim^+Tf_2N^-$]. A required reaction time of 10 min was needed to reach a 100% extraction of the cadmium ion in solution by [Nano-Si-NH_2-$Emim^+Tf_2N^-$], while 25 min was needed in the case [Nano-Si-NH_2-$Omim^+Tf_2N^-$] to obtain a 100% extraction of cadmium. Moreover, both nano-silica sorbents were found to exhibit two steps of cadmium adsorption. The first step was found to follow a gradual increase in the percentage extraction and this required about 5 and 20 min for [Nano-Si-NH_2-$Emim^+Tf_2N^-$] and [Nano-Si-NH_2-$Omim^+Tf_2N^-$], respectively, by reaching <100% extraction of the specified mmol g^{-1} values. The second adsorption step is mainly based on

Table 1
Cadmium adsorption capacity in various contact time values[a]

Time (min)	pH	[Nano-Si-NH_2-$Emim^+Tf_2N^-$] (mmol g^{-1})	[Nano-Si-NH_2-$Omim^+Tf_2N^-$] (mmol g^{-1})
1	1.0	1.00	0.90
5		1.05	0.95
10		1.10 (100%)	0.95
15		1.10 (100%)	1.00
20		1.10 (100%)	1.10
25		1.10 (100%)	1.20 (100%)
30		1.10 (100%)	1.20 (100%)
1	7.0	0.10	0.10
5		0.10	0.15
10		0.10	0.25
15		0.20 (100%)	0.35 (100%)
20		0.20 (100%)	0.35 (100%)
25		0.20 (100%)	0.35 (100%)
30		0.20 (100%)	0.35 (100%)

[a] mmol g^{-1} values are based on triplicate analysis with ± 0.050.

the complete saturation (100%) of the surface with the target adsorbed cadmium ion.

The sorption processes of Cd(II) by [Nano-Si-NH_2-$Emim^+Tf_2N^-$] and [Nano-Si-NH_2-$Omim^+Tf_2N^-$] in neutral contact solution (pH 7) were also found to proceed similarly by following two adsorption steps as described above. Both nano-silica sorbents were found to exhibit a gradual increase in the metal capacity values of Cd(II) up to 15 min of contact time followed by a complete extraction and surface saturation >15 min.

3.1.3. Effect of sorbent dose

The determined mmol g^{-1} values of Cd(II) sorption under various sorbent doses of the two nano-silica hydrophobic ILs, [Nano-Si-NH_2-$Emim^+Tf_2N^-$] and [Nano-Si-NH_2-$Omim^+Tf_2N^-$] were also studied and evaluated. The results of this sorption study are compiled in Table 2. The interacting initial concentration of Cd(II) was adjusted in all measurements to pH 1.0 as the optimum one. It is evident from the listed data that as the mass of sorbents increases, the mmol g^{-1} values decrease. Such high metal capacity values in lower sorbent doses (10 and 25 mg) are mainly due to the presence of available high concentration of Cd(II) ion compared to the exposed surface area. In the case of high sorbent dose (500 mg), the opposite behavior was characterized due to the high availability of active surface centers compared to the present cadmium ion in solution. The contribution of hydrophobic character of physically adsorbed [$Omim^+Tf_2N^-$] on [Nano-Si-NH_2-$Omim^+Tf_2N^-$] was also observed by providing higher determined mmol g^{-1} adsorption capacity values than those found in the case of surface loaded [$Emim^+Tf_2N^-$] on [Nano-Si-NH_2-$Omim^+Tf_2N^-$].

Table 2
Effect of sorbent dose[a]

Mass (mg)	[Nano-Si-NH_2-$Emim^+Tf_2N^-$] (mmol g^{-1})	[Nano-Si-NH_2-$Omim^+Tf_2N^-$] (mmol g^{-1})
10.0	1.100	1.200
25.0	0.490	0.540
50.0	0.230	0.250
100.0	0.110	0.115
250.0	0.052	0.054
500.0	0.028	0.030

[a] mmol g^{-1} values are based on triplicate analysis with ± 0.050.

3.1.4. Effect of metal concentration

Adsorption of metal ions by sorbents or biosorbents is heavily dependent on the initial concentration of the examined metal ion. Various adsorption isotherms are well known and used to provide important and valuable information about the adsorption mechanisms and processes. In addition, adsorption isotherms are commonly applied to obtain the optimized conditions of sorbent applications. The three most commonly employed models are the Langmuir, Freundlich, and BET isotherms, which have shown to be suitable for describing short-term and monocomponent adsorption of metal ions by different sorbents and biosorbents [38,39]. Under these models, an equilibrium condition must be established and a relationship exists between the concentration of the solution interacting species and the sorbed molecules. Langmuir adsorption model is a measure of sorption process on a homogeneous surface by monolayer without interaction between various species and also assumes the adsorptive forces are similar to the forces in chemical interaction. The Langmuir equation in the linearized form is given by Eq. (4).

$$1/q_e = 1/q_{max} + 1/(q_{max}K_L)C_e \tag{4}$$

where q_e (mg/g) is the surface sorbed Cd(II) in equilibrium condition, while, C_e (mg/L) is the solution equilibrium concentration of Cd(II), q_{max} (mg/g) is the maximum amount of Cd(II) ion which can be taken

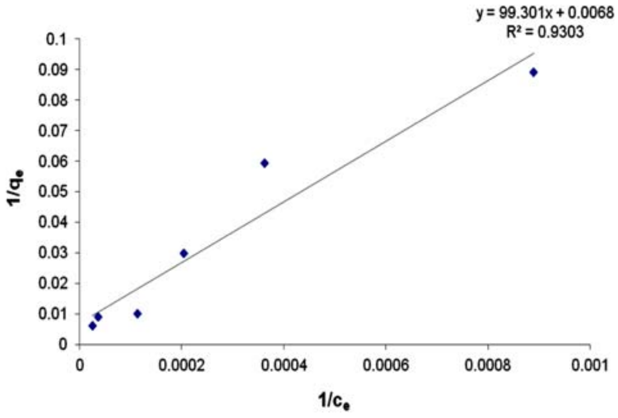


Fig. 2a. Langmuir adsorption model by [Nano-Si-NH_2-$Emim^+Tf_2N^-$].

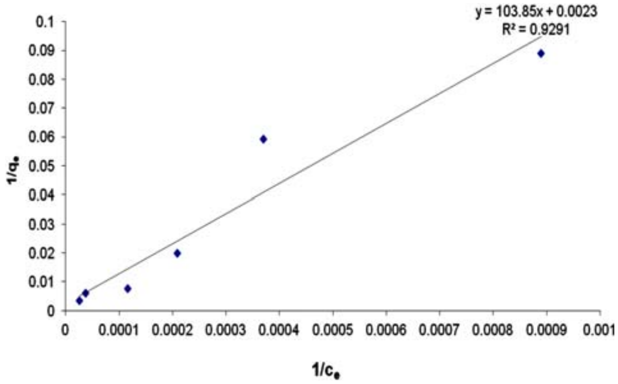


Fig. 2b. Langmuir adsorption model by [Nano-Si-NH_2-$Omim^+Tf_2N^-$].

up by the sorbent, and K_L (Lmg^{-1}) is the Langmuir constant. The application of Langmuir adsorption model for the interaction process of Cd(II) with the two nano-silica hydrophobic ILs, [Nano-Si-NH_2-$Emim^+Tf_2N^-$] and [Nano-Si-NH_2-$Omim^+Tf_2N^-$] were found to follow this model by producing straight lines as shown in Figs. 2(a) and 2(b). The identified q_{max} values from Figs. 2(a) and 2(b) by [Nano-Si-NH_2-$Emim^+Tf_2N^-$] and [Nano-Si-NH_2-$Omim^+Tf_2N^-$] were found as 166.7 and 500.0 mg/g, respectively. The highest characterized q_{max} value can be also interpreted on the basis of more hydrophobic character incorporated into [$Omim^+Tf_2N^-$] than [$Emim^+Tf_2N^-$]. In addition, the characterized K_L values by [Nano-Si-NH_2-$Emim^+Tf_2N^-$] and [Nano-Si-NH_2-$Omim^+Tf_2N^-$] were found as 6.04 E-05 and 1.93 E-05, respectively.

The BET isotherm *model* proposes that the initial sorbed layer can act as a substrate for further sorption, then the isotherm, instead of leveling off to some saturated value at high concentrations it will be able to increase indefinitely. The simplified nonlinear form of BET is generally expressed by the following Eq. (5).

$$q = \frac{q_{\max} K_B}{(C_s - C)[1 + (K_B - 1)C/C_s]} C \qquad (5)$$

where q is the amount of sorbed Cd(II) per unit weight of sorbent, C is the equilibrium concentration of Cd(II) in solution (mg/L or mol/L), C_s is the saturation concentration of the Cd(II), and K_B is a constant (function of energy of adsorption and temperature). The application of BET isotherm model to the process of cadmium sorption *by* [Nano-Si-NH_2-$Emim^+Tf_2N^-$] and [Nano-Si-NH_2-$Omim^+Tf_2N^-$] was also studied. The results collected from applications of this model are represented by Figs. 3(a) and 3(b) and clearly denote to the possible sorption of cadmium on the surface of these sorbents according to the BET postulates of adsorption models [40].

On the other hand, the third evaluated adsorption model is the Freundlich adsorption isotherm which is commonly used to describe expression of the surface

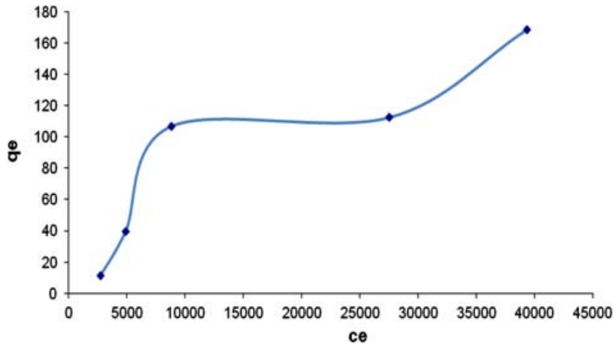


Fig. 3a. BET isotherm model by [Nano-Si-NH_2-$Emim^+Tf_2N^-$].

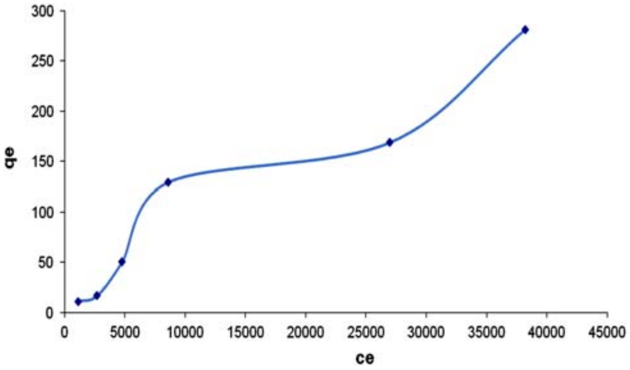


Fig. 3b. BET isotherm model by [Nano-Si-NH_2-$Omim^+Tf_2N^-$].

heterogeneity and exponential distribution of the active sites and their energies. The linearized Freundlich expression is given by Eq. (6).

$$\log \cdot q_e = \log \cdot K_F + 1/n \cdot \log \cdot C_e \tag{6}$$

where K_F and $1/n$ are the Freundlich constants. The application of linearized form of Freundlich isotherm model to the process of cadmium sorption by [Nano-Si-NH_2-$Emim^+Tf_2N^-$] and [Nano-Si-NH_2-$Omim^+Tf_2N^-$] sorbents were found to produce nonstraight lines indicating that such adsorption model is not applicable in this case of cadmium adsorption by the two nano-silica sorbents.

3.1.5. Effect of interfering ions

A series of selected cations, Na(I), K(I), NH_4^+, Co (II), Ni(II), and Cu(II) as well as anions, Cl^-, NO_3^-, SO_4^{2-}, and acetate were used to study and evaluate the possible interference in the sorption processes of Cd(II) by [Nano-Si-NH_2-$Emim^+Tf_2N^-$] and [Nano-Si-NH_2-$Omim^+Tf_2N^-$]. This study was performed and implemented in buffer solution with pH 1.0 as the optimum solution for cadmium uptake by the two sorbents. Cadmium adsorption capacity values were determined in each case and compiled in Table 3. It is evident from the listed data that some of the selected cations such as Na(I), K(I), and NH_4^+ were identified and characterized by their no or minimum interference in the adsorption process of Cd(II) by the two nano-silica sorbents, [Nano-Si-NH_2-$Emim^+Tf_2N^-$] and [Nano-Si-NH_2-$Omim^+Tf_2N^-$]. These cations were found to exhibit ~7.3–7.7% interference in the process of Cd(II) uptake. The determined metal capacity values of Cd(II) in presence of NaCl, $NaNO_3$, Na_2SO_4, and CH_3COONa are giving a good evidence for the insignificant contribution of these anions (Cl^-, NO_3^-, SO_4^{2-}, and CH_3COO^-) in the adsorption process of Cd(II) by [Nano-Si-NH_2-$Emim^+Tf_2N^-$] and [Nano-Si-NH_2-$Omim^+Tf_2N^-$]. On the other hand, Ni(II) was found to exhibit some low interference of 12.09 and 16.92% in the case of [Nano-Si-NH_2-$Emim^+Tf_2N^-$] and [Nano-Si-NH_2-$Omim^+Tf_2N^-$], respectively. The same trend was also observed when Co(II) was used as a coexisting cation with Cd(II) and was found to exhibit 11.91 and 18.08% in the process of Cd(II) extraction by the two nano-silica sorbents. This behavior may be interpreted on the possible competition for active centers incorporated onto the surface of modified sorbents. Finally, The determined metal adsorption capacity values of Cd(II) by [Nano-Si-NH_2-$Emim^+Tf_2N^-$] and [Nano-Si-NH_2-$Omim^+Tf_2N^-$] in the presence of interfering Cu(II) were found 0.880 and 0.936 mmol g^{-1}, respectively. These two values are the lowest ones among all determined metal capacity values of Cd(II) by the two nano-sorbents and giving rise to 20.00 and 22.00% interference, respectively. Such interference behavior of Cu(II) may be due to the possible formation of [$CuCl_3^-$] anionic species that is capable of direct competition with the surface active anion [Tf_2N^-] as described by Eqs. (2) and (3).

Table 3
Cadmium adsorption capacity in presence of coexisting ions[a]

Analyte	Coexistingion	[Nano-Si-NH_2-$Emim^+Tf_2N^-$] (mmol g^{-1})	[Nano-Si-NH_2-$Omim^+Tf_2N^-$] (mmol g^{-1})
Cd(II)	–	1.100	1.200
	NH_4Cl	1.050	1.200
	KCl	1.084	1.174
	NaCl	1.090	1.200
	$NaNO_3$	1.020	1.107
	CH_3COONa	1.056	1.144
	Na_2SO_4	1.077	1.169
	Ni(II)	0.967	0.997
	Co(II)	0.969	0.983
	Cu(II)	0.880	0.936

[a] mmol g^{-1} values are based on triplicate analysis with ± 0.050.

3.2. Adsorptive removal of cadmium from real aqueous matrices

The potential applications of nano-silica physically loaded hydrophobic ILs, [Nano-Si-NH_2-$Emim^+Tf_2N^-$] and [Nano-Si-NH_2-$Omim^+Tf_2N^-$], for adsorptive removal of Cd(II) from real water matrices were studied and evaluated in this section. Two drinking tap water samples and two industrial wastewater samples were spiked with 1.000–2.000 mg L^{-1} and adjusted to either pH 1.0 or 7.0. One liter of these water samples was passed over a multistage microcolumn packed with 50 ± 1 mg of the selected sorbent with a flow rate of 20 mL min^{-1}. The percentage extraction of Cd(II) from the examined water samples in this study are listed in Table 4. It is event from the data listed that adjusting the pH value of water sample to 1.0 was found to produce excellent recovery of Cd(II) from water sample after only one passage over the microcolumn. The percentage extraction values of Cd(II) from drinking tap water were found 98.93 and 99.00% for [Nano-Si-NH_2-$Emim^+Tf_2N^-$] and [Nano-Si-NH_2-$Omim^+Tf_2N^-$], respectively. The same behavior was

Table 4
Adsorptive removal of cadmium from real aqueous samples

Sorbent	Water sample	Adjusted pH	mg L^{-1} Cd(II)	Percentage extraction[a]		
				First run	Second run	Third run
[Nano-Si-NH_2-$Emim^+Tf_2N^-$]	Drinking tap water	1.0	1.129	98.93	–	–
[Nano-Si-NH_2-$Emim^+Tf_2N^-$]	Drinking tap water	7.0	1.129	60.97	77.30	93.56
[Nano-Si-NH_2-$Omim^+Tf_2N^-$]	Drinking tap water	1.0	1.129	99.00	–	–
[Nano-Si-NH_2-$Omim^+Tf_2N^-$]	Drinking tap water	7.0	1.129	60.26	71.94	96.87
[Nano-Si-NH_2-$Emim^+Tf_2N^-$]	Industrial wastewater	10	1.950	97.75	–	–
[Nano-Si-NH_2-$Emim^+Tf_2N^-$]	Industrial wastewater	7.0	1.950	54.91	77.12	95.51
[Nano-Si-NH_2-$Omim^+Tf_2N^-$]	Industrial wastewater	1.0	1.950	98.78	–	–
[Nano-Si-NH_2-$Omim^+Tf_2N^-$]	Industrial wastewater	7.0	1.950	56.04	70.35	93.44

[a]Percentage extraction values are based on triplicate analysis with ± 2.00–3.00%.

also observed for the two examined industrial wastewater samples by the same two sorbents. The identified percentage extraction values of Cd(II) as detected by [Nano-Si-NH_2-$Emim^+Tf_2N^-$] and [Nano-Si-NH_2-$Omim^+Tf_2N^-$] from the two studied industrial water samples were found as 97.75 and 98.78%, respectively. On the other hand, the two [Nano-Si-NH_2-$Emim^+Tf_2N^-$] and [Nano-Si-NH_2-$Omim^+Tf_2N^-$] sorbents were also used to study the adsorptive removal of Cd(II) from adjusted water samples to pH 7.0. The first stage was found to give a percentage extraction range of 54.91–60.97%, while the second passage on a microcolumn was found to produce a percentage extraction range of 70.35–77.30% by the two sorbents. The third step of multistage microcolumn extraction of cadmium from the same water matrices was found to exhibit near completion of the adsorptive removal with a percentage range of 93.44–96.87%.

The results of adsorptive removal of cadmium from real aqueous samples matrices reveals the same conclusion outlined and described above for the two sorbents, [Nano-Si-NH_2-$Emim^+Tf_2N^-$] and [Nano-Si-NH_2-$Omim^+Tf_2N^-$] as highly efficient for Cd(II) removal from acidic solution (pH 1.0).

4. Conclusion

The outlined data in this study are clearly demonstrating that the two evaluated nano-silica physically loaded hydrophobic ILs can be used as strong anion exchangers and implemented as efficient sorbents for adsorptive removal and extraction of cadmium from acidic solutions (pH 1.0). Under all studied and evaluated experimental conditions, the hydrophobic character incorporated into [$Omim^+Tf_2N^-$] was found to enhance the cadmium adsorption capacity process compared to the less hydrophobic IL [$Emim^+Tf_2N^-$]. The overall sorption processes of cadmium were investigated and found to be governed by different operational parameters such as reaction pH, contact time, initial cadmium concentration, sorbent mass, and interfering ions. The sorption data of cadmium were fitted well to the Langmuir as well as Brauner-Emmet-Teller (BET) isotherms and not to Freundlich isotherm model. A higher $q_{\max}$ value (500.0 mg/g) was identified from the Langmuir isotherm of [Nano-Si-NH_2-$Omim^+Tf_2N^-$] sorbent compared to that calculated by [Nano-Si-NH_2-$Emim^+Tf_2N^-$] as (166.7 mg/g). The two modified nano-silica sorbents were successfully utilized and implemented for removal and extraction of cadmium from real acidic water samples adjusted to pH 1.0 via a single step microcolumn technique.

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