

Article

Synthesis of Silica Gel Chelated with Alizarin and 1-Nitroso-2-Naphthol for Solid Phase Extraction of Lead in Ground Water Samples

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Abstract: Silica gel chemically functionalized with alizarin (Si-AZ) and 1-nitroso-2-naphthol (Si-NN) was synthesized and characterized by FT-IR, N₂ adsorption-desorption, SEM, and elemental analysis. The two chelators show adequate sorption properties for Pb (II) and are hence used as SPE sorbents prior to their determination with ICP-MS. Both chelators showed high sorption efficiency for the Pb (II) ion at pH 8. Batch experiments demonstrate that the synthesized resins could remove more than 95% Pb (II) out of solutions containing 100 µg/mL of the ion. At optimum conditions, the maximum adsorption capacities for S-TDI-AZ and S-TDI-NN for Pb (II) were 9.56 and 9.43 mg/g, respectively. Method development was performed to investigate the applicability of the chelating resins as packing materials for SPE using model solutions and real groundwater samples. The method detection limits of SPE were 0.0025 and 0.0026 µg/L with high precision (R.S.D. < 3%). The recoveries of spiked Pb (II) with ground water were 104.70 and 102.62%. The proposed method was successfully applied to the determination of Pb (II) in the groundwater by ICP-MS.

Keywords: trace metals; chelating resin; ICP-MS; modified silica; SPE



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1. Introduction

Over the past several years, much interest has been dedicated to the synthesis of selective solid-phase extraction (SPE) sorbents by immobilizing reactive organic compounds (e.g., chelating moieties) onto porous inorganic supports. Perhaps silica gel is one of the most widely used solid support materials because of its well-defined porosity and large surface area [1–3]. It also resists swelling and straining, has good mechanical strength, and can withstand thermal treatment. Furthermore, the bonding of reactive organic moieties on silica gel is highly stable.

The applications of functionalized silica gel for metal enrichment are still a fertile research area, as can be seen from the number of recent published reports. Silica gels functionalized with various chelating reagents have been reported as efficient chelating collectors for a wide range of metal ions, for example: gallic acid [4,5], sulfasalazine [6], 2,3-dihydroxy benzaldehyde [7], 4-amino-2-mercaptopyrimidine [8,9], Salicylaldehyde [10], 2,6-diamino-4-phenyl-1,3,5-triazine [11], 8-hydroxyquinoline [12], 4-acetyl-3-hydroxyaniline [13], and Benzyl-L-Cysteine [14]. Most of these chelators are immobilized using silane coupling agents as linkage arms to silica surfaces.

Selectivity is difficult to achieve, although structuring ligands with affinities toward certain metals is possible. One of the chelating agents that shows good selectivity is 1-nitroso-2-naphthol [15]. It is an exceptional color-forming chelating agent capable of reacting with Fe (III), Co (II), Ni (II), Cu (II), and other ions to form properly soluble complexes in aqueous solutions [16]. Alizarin, which belongs to the most popular hydroxyanthraquinones, also shows virtuous selectivity toward some ions [17]. Alizarin

encompasses certain donor centers comprised of oxygen atoms from carbonyl (C=O) and hydroxyl (OH) groups. They establish good binding sites for divalent cations.

In the present study, alizarin and 1-nitroso-2-naphthol have been chemically anchored on the surface of silica gel, making use of toluene 2,4-di-iso-cyanate as linkage arms. The new chelating materials were used as a solid-phase extractant for the preconcentration of trace Pb (II) in water samples.

2. Materials and Methods

2.1. Materials

Silica gel [Sigma-Aldrich, Saint-Louis, MO, USA, mesh size 70–230] was used as a silica source. Alizarin (AZ) [C₁₄H₈O₄, Janssen Chimica, Beerse, Belgium] and 1-nitroso-2-naphthol (NN) [C₁₀H₇O₂N, Acros Organics, Geel, Belgium] were the organic modifiers, while toluene 2,4-di-iso-cyanate (TDI) [C₉H₆N₂O₂, Acros Organics] was the organic linker. Triethylamine [C₆H₁₅N, Acros Organics] was used as a catalyst. Di-n-butylamine [C₈H₁₉N, Sigma Aldrich] and hydrochloric acid [HCl, Sigma Aldrich] were used for determining isocyanate groups. Toluene [Fisher Scientific, Loughborough, UK, dried by the use of molecular sieves], acetone [Sigma Aldrich], and dimethyl sulfoxide [Panreac Quimica, Barcelona, Spain] were all used as solvents. The standard solutions of the studied metal were prepared from lead stock solutions [1 mg/mL; Acros Organics] by proper dilution. Nitric acid [Sigma Aldrich] was used as an eluent for trace metal-form resins. Ammonium acetate, aqueous ammonium oxide solution, and acetic acid from Sigma Aldrich were used as pH adjustments for solutions. For purification, the solutions were passed through a column that was packed with Chelex-100 [Bio-Rad, Hercules, CA, USA]. Milli-Q high-purity water has been used throughout all processes.

2.2. Instrumentation

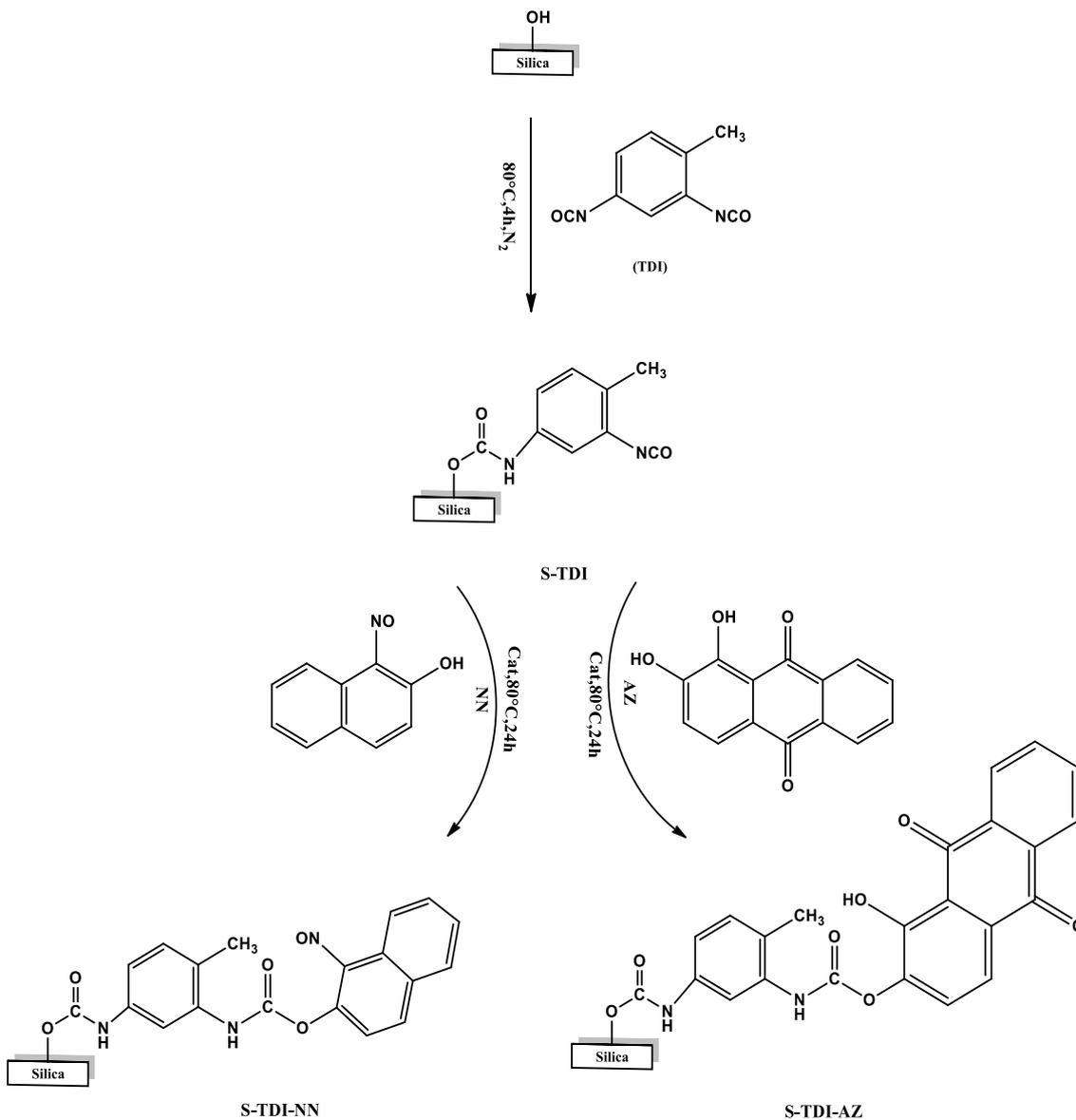
An Agilent Technologies 7500 series inductively coupled plasma mass spectrometry ICP-MS (Santa Clara, CA, USA) was used for the determination of the metal ion. Fourier transform infrared spectroscopy spectra (FT-IR) were recorded on a Perkin Elmer Spectrum 100 (Perkin Elmer, Santa Clara, CA, USA). The spectra were gathered for the samples, which ranged from 400 to 4000 cm⁻¹. Scanning electron microscopy (SEM) analyses were recorded by a JSM-6380 LA instrument. Chemical elemental analysis for C, H, and N was performed using a Perkin Elmer CHN-2400 analyzer. The characterization of porous structure parameters was performed using an automatic physisorption analyzer (micromeritics ASAP 2020) by BET and BJH methods through N₂ adsorption at 77 K. The SPE was performed using a 12-way standard SPE manifold (Ato Science, Shanghai, China) and cartridges (bond straight barrel; Agilent Technologies, Santa Clara, CA, USA) packed with 0.50 g of chelating resin sandwiched between two discs of porous Teflon filters. Operation of the SPE manifold was performed using a vacuum pump (AP-9950; Ato Science, Shanghai, China). Adjustments of pH values were monitored with the HI 2211 digital pH/ORP meter (HANNA Instrument Factory, Vohringen, Germany).

2.3. Preparation of Chelating Resin

The preparation of chelated silica was achieved following the sequences shown in schematic diagram Scheme 1. The attachment of isocyanate groups to the silica surface is accomplished by refluxing the activated silica in excess of TDI [18]. An amount of 200 mL of TDI (dried using a molecular sieve) and 100 g of silica (preheated overnight at 150 °C) were mixed together in a round-bottom flask with a magnetic stirrer. The functionalization was carried out in a dry nitrogen atmosphere for 4 h at 80 °C. After the reaction was complete, the product (labeled S-TDI) was filtered and washed with dry toluene and acetone several times.

For the linkage of organic chelating agents, 20 g of the modified silica S-TDI was stirred with 2.65 mM of the chelators in dry toluene [19]. In the case of alizarin, DMSO was used as solvent. The reaction was catalyzed with a few drops of triethylamine and left

for 24 h in an oil bath at 80 °C under reflux. After that, the product was allowed to cool, separated by filtration, washed with toluene and acetone, and then dried for 24 h under vacuum. The chelating resins were marked as S-TDI-AZ and S-TDI-NN.



Scheme 1. Synthetic rout of the chelating resins.

2.4. Determination of Isocyanate Groups in the Reaction System

The content of isocyanate groups in the reaction system was determined by titration [18]. Briefly, 30 mg of S-TDI sample and 3 mL of 0.1 mol/L di-n-butylamine in toluene were placed into a conical flask, and the mixture was stirred for 1 h at room temperature. The unreacted di-n-butylamine was back-titrated with 0.1 mol/L HCl using bromophenol blue as an indicator. The content of isocyanate groups was computed using Equation (1):

$$NCO(\text{mmol/g}) = \frac{(V_0 - V_1) \times f \times 0.1}{W} \tag{1}$$

where V_0 (mL) is the titer of 0.1 mol/L HCl for blank, V_1 (mL) is the titer of 0.1 mol/L HCl for the sample, f is the factor of 0.1 mol/L HCl, and W (g) is the weight of the S-TDI.

2.5. Screening Experiments

The screening experiments were performed according to the batch method. Two chelating resins (S-TDI-NN and S-TDI-AZ) were screened for their ability to remove Pb (II) and Cd (II). The screening experiments were repeated three times, and the average of the resulting removal efficiency was reported.

In this method, 0.05 g of chelating resin were mixed with 10 mL Pb (II) and Cd (II) solutions at 10 µg/mL into 50 mL polyethylene bottles. The mixtures were sealed and shaken at 150 rpm for 24 h. After adsorption, the solid phase was separated by centrifugation at 3500 rpm for five minutes. The concentration of metal ions remaining (C_e) in the aqueous phase after the sorption was then determined by ICP-MS [20]. The removal percentages were calculated using Equation (2) [21]:

$$\%Removal = \frac{(C_o - C_e)}{C_o} \times 100 \quad (2)$$

where C_o is the initial aqueous concentration of metal ions (mg/L) and C_e is the concentration of metal ions after shaking for a certain period of time (mg/L).

2.6. Effect of pH

To examine the pH's effect on the sorption capacity, 0.05 g of the chelating resin was allowed to equilibrate with Pb (II) solution (10 mL of 10 µg/mL in ammonium acetate 0.2 M) over the pH4–9 range. The concentration of Pb (II) left in solution after equilibrium (C_e) with sorbent phase was quantified using ICP-MS [20]. The removal percentages of Pb (II) by chelating resins were calculated using Equation (2).

2.7. Study of Sorption Capacity

For the determination of sorption capacity, 0.05 g of chelating resins were shaken with 10 mL of 50 µg/mL Pb (II) solution at pH 8.0 for 24 h at room temperature, following the batch equilibrium procedure suggested by [20]. The sorption capacities for the two chelators were estimated using Equation (3):

$$q_e(\text{mg/g}) = \frac{C_o - C_e}{W} V \quad (3)$$

where q_e is the sorption capacity (mg/g), C_o is the initial aqueous concentration of metal ions (mg/L), C_e is the concentration of metal ions after equilibrium (mg/L), V (L) is the volume of the solution, and W (g) is the mass of the chelating resins.

2.8. Solid-Phase Extraction Process

To apply the synthesized metal chelators with standard SPE apparatus, 0.1 g of dry resins were packed into the SPE cartridge between 2 Teflon filters. The SPE procedure began with cartridges conditioning with 5 mL of ammonium acetate solution (0.2 M, pH 8) at a flow rate of 1 mL/min. Then 10 mL of sample solutions were loaded at a slow flow rate (0.5 mL/min). The cartridges were then flushed with water to remove any leftover trapped metal and matrices. Finally, the chelated Pb (II) was eluted with 5 mL of 2 M nitric acid at 2 mL/min. The eluted Pb (II) was collected in 10 mL PTFE sample tubes for ICP-MS analysis [20]. The SPE cartridge was regenerated using 5% nitric acid and water to be used in a new SPE cycle. This process was followed for standard and actual samples.

3. Results

3.1. Characterization of Chelating Resins

In this study, two silica modified with different organic chelating have been prepared via modification of activated silica with toluene 2,4-di-iso-cyanate (TDI) as linker, 1-natroso-2-naphthol (NN), and alizarin (AZ) as organic modifier. Toluene 2,4-di-isocyanate was utilized to establish a bridge between the surface of silica and different chelating organics.

TDI has highly unsaturated bonds and two isocyanate groups with different activities towards hydroxyl groups, located at para-position and ortho-position, respectively. It is very active toward hydroxyl.

3.1.1. FT-IR Analysis

Infrared spectroscopy was employed to characterize the functional groups of the products. The vibrational spectra obtained from solid samples confirmed the success of the grafting reactions (Figure 1).

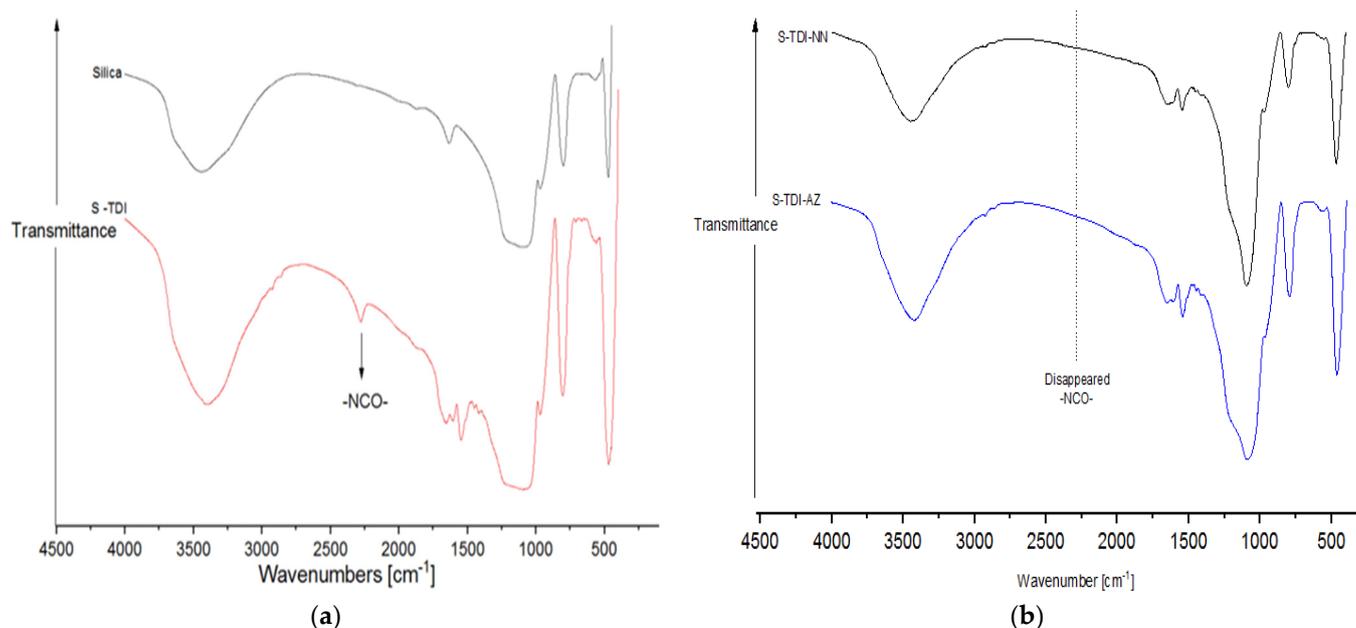


Figure 1. FT-IR spectra of (a) silica and S-TDI; and (b) S-TDI-NN and S-TDI-AZ.

The chelated silica reported in this work has been attained by modification of silica with toluene 2,4-di-iso-cyanate (TDI) as a linker and alizarin (AZ) and 1-natroso-2-naphthol (NN) as organic chelators (Figure 1). The use of toluene 2,4-di-iso-cyanate is essential to creating a bridge linking silica surfaces with organic moieties. TDI contains unsaturated bonds, and it also has two isocyanate groups that tend to react with hydroxyl groups. The modification takes place according to the proposed steps below.

In the first step, isocyanate groups in para-positions react with hydroxyl groups on the silica gel surface, forming S-TDI, while those at the ortho-positions are preserved because of the steric hindrance inside the TDI molecule [22,23]. In the second step, isocyanate groups at ortho-positions in S-TDI interact with OH groups of the organic chelating to form chelated silica with alizarin and 1-natroso-2-naphthol (labeled as S-TDI-AZ and S-TDI-NN, respectively).

3.1.2. SEM Analysis

The SEM images of silica and functionalized silica gel are shown in Figure 2.

3.1.3. Elemental Analysis

Table 1 gives the C, N, and H contents of S-TDI intermediate and silica modified with organic chelating agents.

3.1.4. N₂ Adsorption-Desorption

The nitrogen adsorption–desorption isotherms of plain silica gel and functionalized derivatives are present in Figure 3. The BJH desorption average pore diameter is shown in

Figure 4. Table 2 summarizes the porous structure parameters of the chelating resins on the basis of the nitrogen adsorption data.

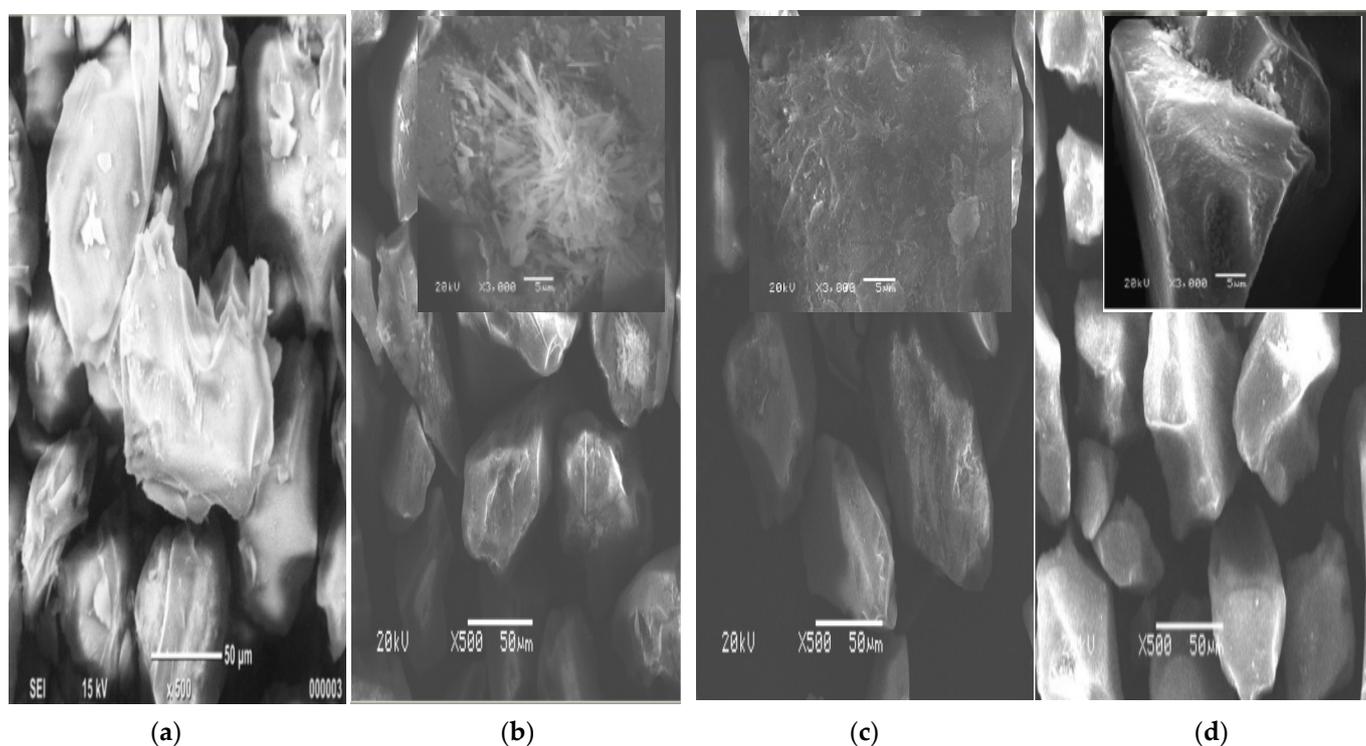


Figure 2. SEM analyses of (a) silica; (b) S-TDI; (c) S-TDI-NN; and (d) S-TDI-AZ.

Table 1. Results of element analysis for modified silica.

Chelating Resins	%C	%N	%H
S-TDI	8.85	1.94	1.21
S-TDI-NN	10.62	2.44	1.29
S-TDI-AZ	10.94	1.40	2.51

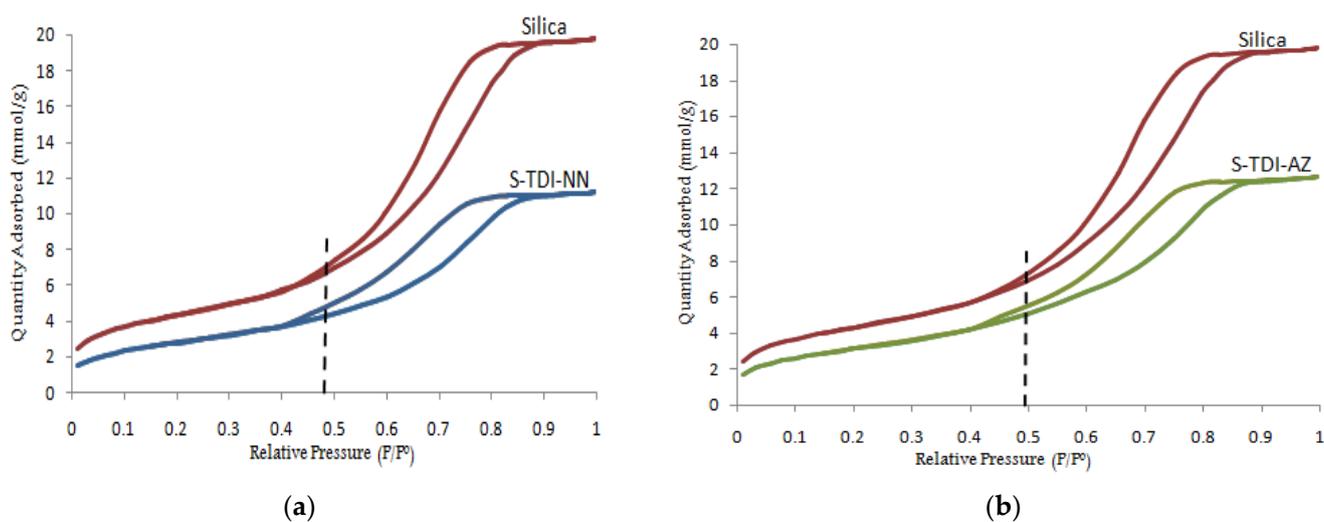


Figure 3. Nitrogen adsorption-desorption isotherms of (a) silica and S-TDI-NN; and (b) silica and S-TDI-AZ.

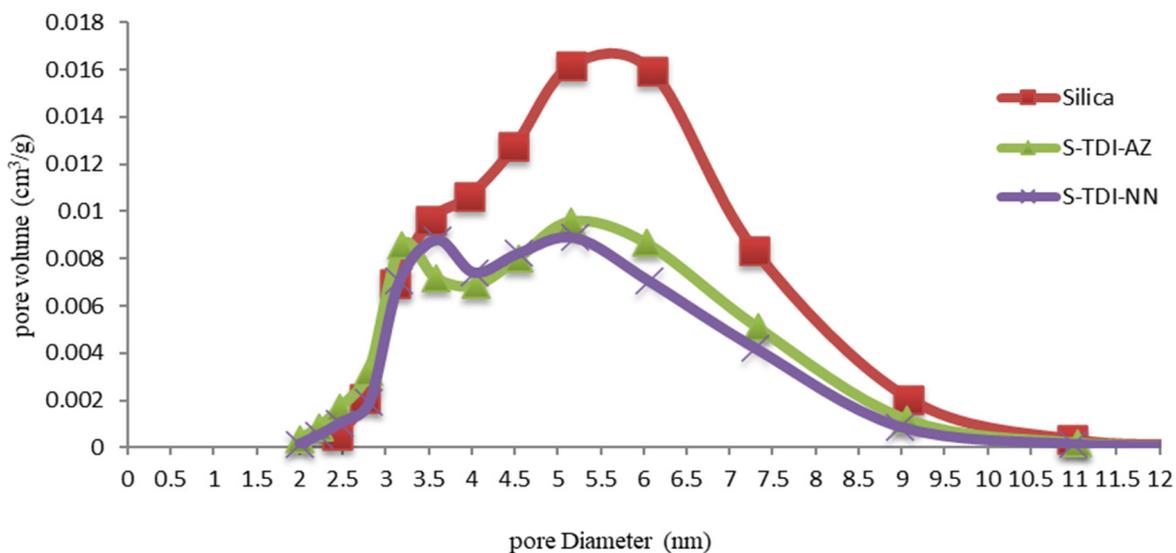


Figure 4. BJH pore size distribution patterns of silica and modified silica.

Table 2. Parameters of porous structure of silica and modified silica.

Sample	BET Surface Area (m ² /g)	BJH Desorption Cumulative Volume of Pores (cm ³ /g)	BJH Desorption Average Pore Diameter (nm)
Silica	520	0.69	5.34
S-TDI-AZ	353	0.44	5.06
S-TDI-NN	319	0.39	4.95

3.2. Screening Result

To identify an efficient chelating resin, two chelating resins were screened for Pb (II) and Cd (II) removal. The removal percentages of the two modified silicas were calculated and presented in Figure 5.

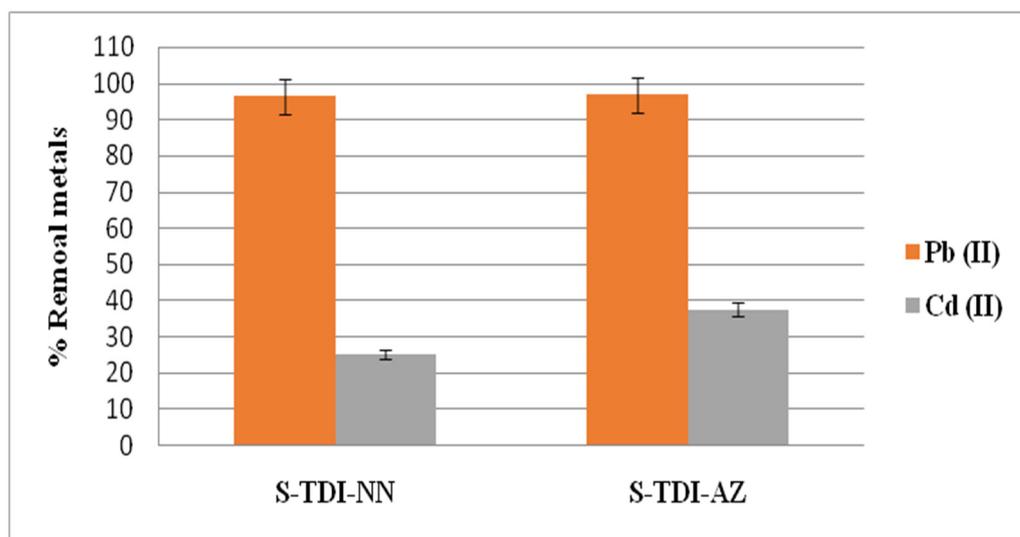


Figure 5. Removal percentages of metal ions by chelating resins.

3.3. Efficiency of the Chelating Resins

To confirm the efficiency of the synthesized chelating resins for metal removal (Figure 1), a standard solution (100 µg/mL) of Pb (II) ions has been used. The removal percentages of the two metal chelators are calculated and demonstrated in Figure 6.

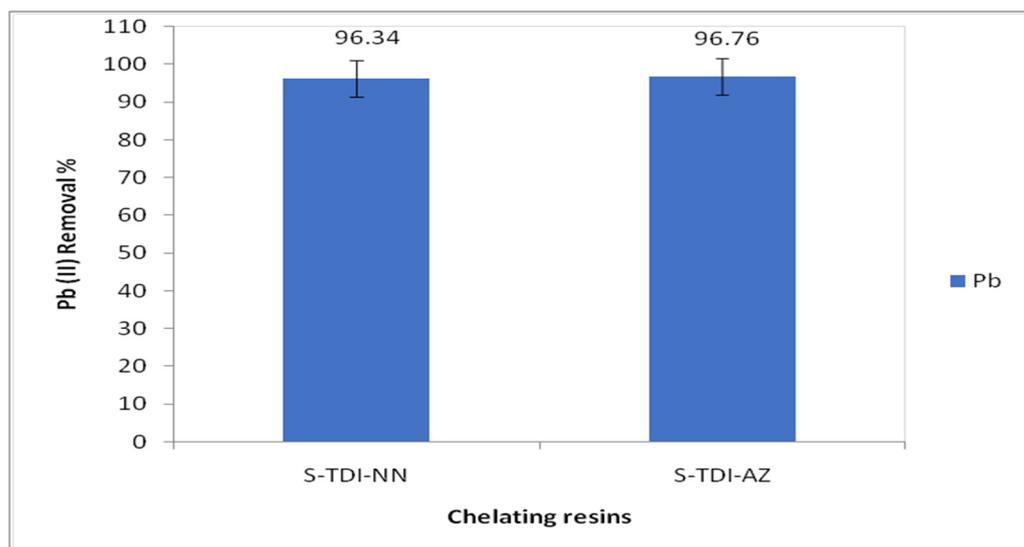


Figure 6. Removal percentage of Pb (II) by chelating resins.

3.4. Influence of pH on Pb (II) Uptake

The pH of the sample solution influences the resin’s capability to remove metal ions. Thus, the pH’s effect on the removal percentage of Pb (II) was studied, and the results are displayed in Figure 7.

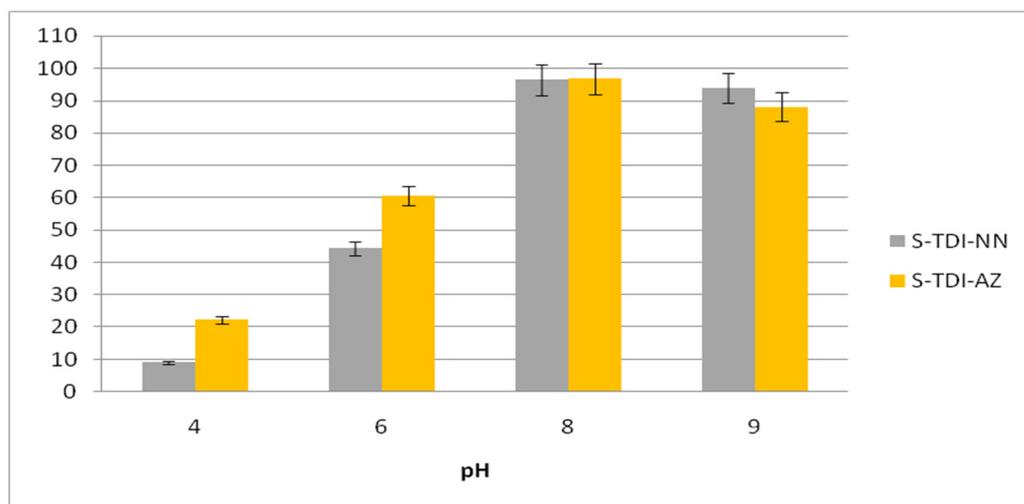


Figure 7. Effect of pH on sorption of 10.0 µg/mL Pb (II).

3.5. Adsorption Capacity

The calculation of adsorption capacity for sorbent medium is essential to approximate the amount of resins needed to quantitatively extract Pb (II) from solution [24]. The adsorption capacities of the two chelators, S-TDI-AZ and S-TDI-NN for Pb (II), were found to be 9.56 and 9.43 mg/g, respectively (Table 3). It is clear that there is no significant variation in adsorption capacity values.

Table 3. Comparison of adsorption capacities (mg/g).

Chelating Resins	Adsorption Capacity (mg/g)	Ref.
Amberlite XAD-2000-diethyldithio carbamate	6.42	[25]
Silica gel modified by allyl 6-methyl-4-phenyl-2-thioxo-1,2,3,4-tetra hydroypyrimidine-5-carboxylate	5.0	[1]
Amberlite XAD-2-o-aminophenol	3.32	[26]
Amberlite XAD-2000-HQ	7.20	[27]
S-TDI-AZ	9.56	Current study
S-TDI-NN	9.43	Current study

3.6. Analytical Features

The calibration curve for the determination of Pb (II) was computed under the optimum extraction parameters as described in the experimental Section 2.8. Table 4 gives a summary of the analytical features of the method.

Table 4. Analytical features of the chelating resins for Pb (II).

Calibration Parameters	Pb (II) (µg/L)	
	S-TDI-AZ	S-TDI-NN
Concentration range (µg/L) (n = 5)	0.1–18	0.1–18
% RSD at 18 µg/L (n = 4)	1.742	2.018
Correlation coefficient, R ²	0.997	0.996
Sensitivity, CPS ratio/(µg/L)	98,900	98,679
LOD (µg/L)	0.0025	0.0026

3.7. Analytical Application

The synthesized resins have been used as sorbents for the extraction/preconcentration of Pb (II) ions in groundwater samples prior to their determination by ICP-MS. The sample was collected from north Al Medianh Al Munawarah (Saudi Arabia), Taited district. The sample was spiked with 5 µg/L of Pb (II) for verification. The results are represented in Table 5.

Table 5. Analysis of groundwater sample using different chelating resins.

Chelating Resins	Pb (II) Spiked (µg/L)	(Found ± RSD) ^a	Recovery (n = 4) (%)
S-TDI-AZ	0	2.315 ± 0.061	-
	5	7.550 ± 0.023	104.70
S-TDI-NN	0	2.729 ± 0.053	-
	5	7.860 ± 0.013	102.62

^a Mean ± RSD (µg/L) of four determinations.

4. Discussion

The success of silica functionalization with AZ and NN can be evidenced from the FT-IR spectrum (Figure 1). The spectrum of the unmodified silica as well as the S-TDI materials (Figure 1a) was influenced by strong bands distinctive of the support matrix, which indicates that the support framework stayed unaffected. Meanwhile, bands shown at 3397 cm⁻¹ and 1632 cm⁻¹ represent hydroxyl groups on the silica surface. The distinguished band related to Si–O–Si stretching vibration can be seen at 1078–1243 cm⁻¹,

whereas the peaks appear around 800 cm^{-1} and 469 cm^{-1} assigned to the Si–O–Si symmetric stretching and bending vibrations. Furthermore, a characteristic stretching band of the free silanol group Si–OH is centered at 970 cm^{-1} [28].

The incorporation of isocyanate functionalities on the surface has been accomplished by adding excess TDI to the silica. This was indicated by a distinctly discernible band appearing at 2280 cm^{-1} which corresponds to the asymmetric stretching of the appended terminal isocyanate groups; this was further indicated by the appearance of benzene rings at 1453 , 1602 , and 2969 cm^{-1} in the FTIR spectrum. The signals that correspond to the C=O and C–N stretches of the established carbamate linkages connecting the silica and the isocyanate functionality in the compound S-TDI appeared at 1654 cm^{-1} and 1545 cm^{-1} [29]. The results clearly confirmed that the toluene 2,4-di-iso-cyanate molecule was covalently linked to the silica gel surface.

The leftover isocyanate groups at ortho-positions in the (S-TDI) chelator were reacted with the hydroxyl groups of the chelating agents AZ and NN. This can be evidenced by the disappearance of some peaks (Figure 1b). The FTIR spectra of AZ and NN show the absence of the –NCO distinctive band at about 2280 cm^{-1} , indicating the reaction of both functional groups of toluene-2,4-di-iso-cyanate [18]. The spectra of S-TDI-AZ (Figure 1b) present a strong band at 3421 cm^{-1} , corresponding to the aromatic OH and the –OH group of the silica surface. A band at 1635 – 1654 cm^{-1} allocated to C=O stretching vibrations of conjugate carbonyl groups ($\nu\text{C=O}$) in AZ and urethane groups, at 1460 cm^{-1} and 1240 cm^{-1} corresponded to rocking vibrations of the hydroxyl bonds ($\delta\text{O-H}$) [30]. In the case of S-TDI-NN (Figure 1b), the N=C peak at 1632 cm^{-1} could be fused with the C=O stretches of the formed urethane groups. The band appeared at 1078 – 1238 cm^{-1} , was referred to as Si–O–Si, and $\nu(\text{NO})$, respectively [31].

From SEM images (Figure 2), it can be seen that the overall size of S-TDI, S-TDI-AZ, and S-TDI-NN was similar to that of bare silica gel. This demonstrates that silica gel has exceptional mechanical stability and that the irregular structure has not been destroyed throughout the modification process [20,32].

The micrographs (Figure 2) also reveal that the plain silica gel had a smooth and even surface, whereas the modified silica with TDI shows a remarkable fibrous surface. Compared with S-TDI, the surface of silica modified with chelating agents exhibited dense microstructures and a coarse surface. Analogous results have been previously reported for other modified silica [33,34].

Elemental analysis (Table 1) evidences the accomplishment of ligand immobilization on silica surfaces. The percentage of C in silica modified with organic chelators has been enhanced by about 2% in comparison with the C percentage of S-TDI, indicating that the ligand was successfully grafted on the surface of S-TDI.

The nitrogen adsorption–desorption isotherms of prepared materials (Figure 3) are all known as type IV based on the IUPAC classification that is identified by the hysteresis loops [35]. The hysteresis loops of silica gel and its functionalized form are relatively similar. This suggests that the pore shape of the synthesized chelating resins is also similar, and the pore structure stays unaffected throughout the functionalization process. There was a sharp increase at a relative pressure (P/P^0) of about 0.5 in the volume adsorbed for all isotherms, which represents capillary condensation of nitrogen inside the consistent mesoporous structure [34]. The inflection point slightly shifted to less relative pressure while the adsorbed nitrogen's volume decreased with the occurrence of functionalization, which resembled other functionalized silica gels [34,36].

The average pore diameter of BJH desorption depicted in Figure 4 shows that the dominant pore size for all chelating resins ranged from 2 to 11 nm. The pore size distribution is shifted toward a smaller diameter due to functionalization. Table 2 summarizes the porous structure parameters of the chelating resins from the nitrogen adsorption data. For bare silica gel, the surface area is $520\text{ m}^2/\text{g}$, and the desorption volume of pores is around $0.69\text{ cm}^3/\text{g}$. However, the surface area, the pore diameter, and the pore volume decreased upon the attachment of chelating agents. The reduction in pore size can be attributed to the

development of an organic layer inside the pores, which blocks the adsorption of nitrogen molecules [36].

As can be seen from Figure 5, the removal percentages followed the order of S-TDI-AZ > S-TDI-NN, and the removal percentages followed the order of Pb (II) > Cd (II). This can be attributed to the nature of the organic chelating and could be explained by the theory of hard and soft acids and bases [3,28,37,38]. The chelating resins had higher affinity for the hard acid of the Pb (II) ion versus lower removal toward the soft acid of the Cd (II) ion, which was mainly dominated by the donor atoms of O and N. Since the modified silica gel with organic chelating gave the highest removal percentage for Pb (II), these ions were selected for subsequent experiments.

Both chelating resins displayed efficient adsorption of Pb (II); the removal percentages reached more than 95%. As can be seen from Figure 6, the removal percentages of S-TDI-AZ were higher than those of S-TDI-NN. This slight difference in removal percentages might be attributed to the increasing number of functional groups and binding sites [39].

The results in Figure 7 indicate that the removal of Pb (II) is correlated with pH changes. This could be explained by the fact that at low pH, a large number of protons are available in solution and can compete with metal cations for the adsorption sites on the sorbent. Also, the surface of the adsorbent will be associated with a hydronium ion (H_3O^+). As a result, the surface will maintain a net positive charge, preventing the access of positively charged metal ions. As the pH increases, the positive charge on the sorbent surface will gradually decrease. Thus, it reduces the repulsion between the sorbent surface and the cation [40]. Meanwhile, the removal percentage reaches maximum values (up to 96–100%) at pH 8, but reduces significantly at $pH \leq 6$. This could be attributed to the fact that chelating resins are protonated at $pH \leq 6$. Thus, low metal adsorption occurs in highly acidic solutions. On the other hand, at higher pH values ($pH > 8$), the adsorption efficiency decreases. This is most likely caused by the formation of Pb (II) hydroxides [41]. Therefore, the working pH was chosen as 8 for the following experiments. These results are in agreement with the results expressed in previous work [7,42].

Comparative data from several papers on the removal of Pb (II) using different adsorbents is summarized in Table 3. The synthesized resins reported in this work show higher or comparable adsorption capacity values and good affinity for adsorption of Pb (II) from aqueous solutions.

Table 4 illustrates a summary of the analytical features of the method. The analytical calibration curve for Pb (II) generated using chelating resins was linear in the range of 0.1–18 $\mu\text{g/L}$, with a correlation coefficient value exceeding 0.99 for Pb (II) with two chelating resins. The detection limits were between 0.0025 and 0.0026 $\mu\text{g/L}$ for the investigated ion. The low relative standard deviation (RSD) of the four replicate determinations was <3.0% for Pb (II) at 18 $\mu\text{g/L}$. This indicates that the method has great precision for the analysis of trace Pb (II) in 10 mL solution samples.

The recovery values from the spiked sample were 104.70 and 102.62% for S-TDI-AZ and S-TDI-NN resin, respectively (Table 5). The results confirm the reliability of the synthesized chelating resins as selective solid-phase extractions for the extraction/preconcentration of trace Pb (II) in groundwater samples.

5. Conclusions

This work reports a straightforward synthesis for efficient chelating resins by immobilizing alizarin and 1-natroso-2-naphthol onto silica surfaces, utilizing toluene 2, 4-di-isocyanate as a coupling agent (linker). Characterization using FT-IR, SEM, N_2 adsorption-desorption, and elemental analysis confirmed the success of the proposed functionalization. The preparation of the chelating resins is relatively simple, rapid, and low-cost because it uses affordable on-the-shelf chemicals.

The synthesized chelating resins presented an efficient adsorption capability for Pb (II) from an aqueous solution at pH 8. The sorption capacities of the two resins, S-TDI-AZ and S-TDI-NN, were 9.56 and 9.43 mg/g, respectively. At optimum parameters, the removal

percentages exceeded 95%. When used as SPE sorbents to extract/preconcentrate Pb (II) ions from groundwater samples, both resins show adequate performance, as indicated by the recovery values of Pb (II) from spiked samples: 104.70 and 102.62% for S-TDI-AZ and S-TDI-NN in the same order. This finding suggests that both resins are suitable for sample preparation by SPE in trace analysis of metals.

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