

ORIGINAL RESEARCH PAPER

Highly Selective Removal of Pb(II) Ions Using One-Pot Thiol-Functionalized Nanoporous Silica with a Low Amount of Directing Agent

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ABSTRACT

In this study, thiol-functionalized nanostructure silica type MCM-41 was successfully prepared via the facile one-pot hydrothermal method with a low amount of directing agent. The mesoporous silica indicated a remarkable adsorption behavior toward Pb(II) ions without any interference of the competing ions. The main experimental parameters affecting removal efficiency of the adsorbent were examined, and the optimized conditions were achieved to be 6, 50 mg, and 30 min for solution pH, the adsorbent dosage, and contact time, respectively. The adsorbent was triumphantly used for the removal of Pb(II) ions from real water samples with a notable removal efficiency of 95%. The concentrations of the competitive ions in the solution were about 10 to 100 times more than Pb(II) ions. The results show that other ions had no interfering effect on the removal efficiency of Pb(II) ions. It means that SH-SiO₂ has excellent selectivity for Pb(II) ions and is an appropriate candidate for removing Pb(II) ions from the real samples.

Keywords: Adsorbent, Thiol- mesoporous silica, Pb(II) ions

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INTRODUCTION

In general, pollutants are introduced into the environment through natural phenomena and human activities. Environmental pollution such as heavy metal ions has been caused serious concern because of their toxicities and no degradable behavior. Lead ion uses greatly in many industries while it is one of the most toxic heavy metal ions and can be caused by many different crucial diseases even at low concentrations due to accumulation in living organisms [1]. To date, the removal of them is important to achieve environmental quality standards [2–4]. There is a wide range of techniques for removing heavy metal ions from

water, including precipitation, ion exchange, and adsorption. Among them, adsorption is very popular due to its simplicity and low cost [5].

Recently, various kinds of adsorption materials like activated carbon, peat, and zeolite have been used to remove heavy metal ions [6–11]. However, these components have low loading capacities and weak interactions with metallic ions. To overcome these drawbacks, the use of mesoporous silica, such as MCM-41, SBA-15, and SBA-16 has been developed due to their high surface area, hydrothermal stability, and appropriate pore size [6,12]. The pure silica materials have poor selectivity and sensitivity; therefore, it is necessary to create particular binding sites through the functionalization of the adsorbent with functional

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groups, such as -SH, -COOH, and -NH₂ [7,8]. The functionalized surface has been generally obtained by direct co-condensation and post-synthesis grafting methods with organo-alkoxysilanes [9].

One of the best ways is direct synthesis. Given the superiority of the one-pot method over other synthetic nano-silica methods, it has the following advantages: regular and uniform distribution of organic groups on the surface of synthesized nano-silica, the unavailability of cavities in the prepared materials, the possibility of including two or more functional groups in the surface, shorter preparation time, simplicity of the method and higher organic loading rate [13–15].

The most well-known mesoporous silica materials include MCM-41 (hexagonal), MCM-48 (cubic), and MCM-50 (lamellar) [16].

Vartuli and coworkers found that the ratio of the surfactant to silica can influence the mesopore structure [10]. Many researchers have been synthesized layered nanocrystal particles, while these materials had low thermal stability. Patents have been registered that are not thermally stable [17,18]. Pannavaia and his group provided a highly stable compound with poor resistance to the factorization process [19].

Since most of the mesoporous materials have been synthesized at high surfactant levels, have not had good thermal stability, and have not been resistant to direct and indirect causation, In this study, mesoporous silica was successfully directly functionalized with (3-mercaptopropyl) trimethoxysilane (MPTMS) and finally removed the surfactant. In this method, due to the environmental effects of surfactants, the lowest amount of surfactant was used. Further studies revealed that the mesoporous silica acts as a suitable adsorbent for Pb(II) ions in the real samples.

EXPERIMENTAL

Chemicals and reagents

Silica (12nm, 99.99%), ethanol, sodium hydroxide, hydrochloric acid, cetyl trimethyl ammonium bromide (CTAB), (3-mercaptopropyl) trimethoxysilane (MPTMS), and all organic solvents were purchased from Merck and Sigma-Aldrich. The nitrate salts of ions were used for stock solutions. The pH was adjusted using the addition of NaOH and HCl solution (0.1 M).

Instrument

Fourier transform infrared spectra were

obtained by using a RAYLEIGH WQF-510 A in the range of 400–4000 cm⁻¹ using KBr pellets. The crystal structures of the products were evaluated by X-ray diffraction (XRD) on X'Pert Pro MPD diffractometer by Cu K α radiation ($\lambda = 1.54060$ Å). The morphology and the surface area of samples were studied by MIRA3 TESCAN field emission-scanning electron microscope (FE-SEM) and N₂ adsorption-desorption isotherms on a Micromeritics TriStar II Plus, respectively. Energy-dispersive X-ray (EDX) microanalysis carried out by Philips (Tecnai-20). Atomic absorption spectrophotometer (Analytik Jena model ContrAA-300) was used to determine the residual concentration of Pb (II) ions.

Synthesis and functionalization of adsorbent

To synthesis, the mesoporous, 6 g of silica was dissolved in 60 mL of deionized water containing 2 g of sodium hydroxide in a glass beaker and stirred for 24 h at 75 °C. Then, the solution of 0.71 g CTAB and 1.42 g MPTMS (in 30 mL water) were slowly added dropwise to the above solution and stirred for 45 min at room temperature. The resulting suspension was autoclaved at 120 °C for 72 h. Afterward, the white precipitate was filtered and washed with an excess amount of ethanol and distilled water (so-called SH-SiO₂-CTAB). Finally, the surfactant was removed by 0.1M HCl in ethanol for 2 h (so-called SH-SiO₂).

Batch adsorption experiments

The adsorption experiments were performed according to the approach described in the previous literature [20]. Briefly, known amounts of the mesoporous silica as an adsorbent were poured into the solution ions (20 mL) with the desired concentration of Pb(II), Cu(II), Co(II), Zn(II), Ni(II) and Ag(I) with optimum pH and shook at room temperature. Subsequently, to remove the adsorbent, the mixture was centrifuged for 5 min, and the residual solution was taken out to measure the concentration of residual ions using flame atomic absorption spectrometry (FAAS). All tests were repeated three times, and the average of the results was used in the calculations.

RESULTS AND DISCUSSION

Characterization

The hexagonal structure of SH-SiO₂-CTAB with surfactant and without surfactant is proved by the XRD pattern, which is shown in Fig. 1.

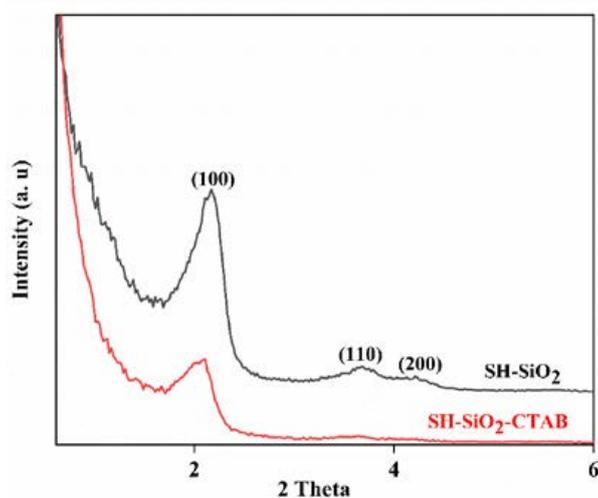


Fig. 1. XRD patterns of SH-SiO₂ and SH-SiO₂-CTAB

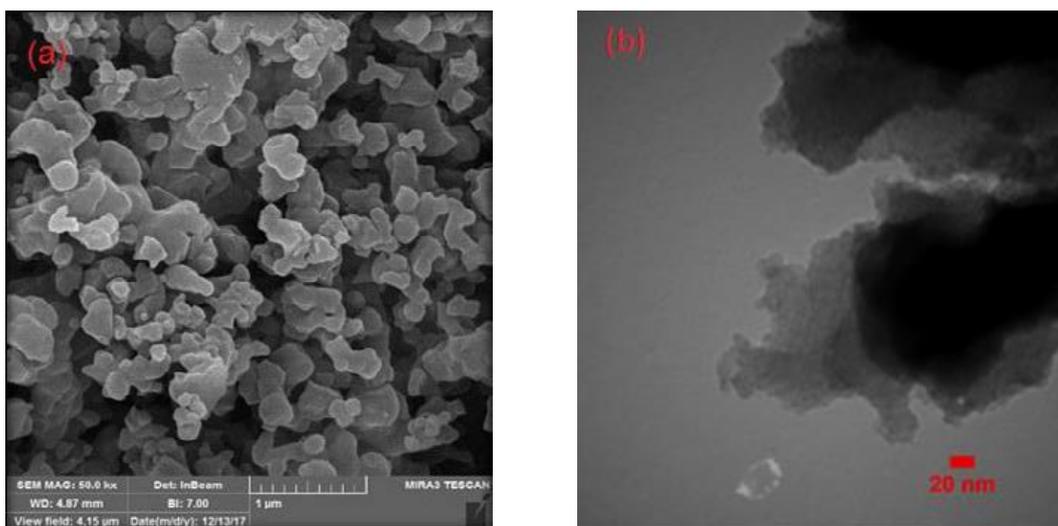


Fig. 2. (a) SEM and (b) TEM image of SH-NPSiO₂.

In the sample containing surfactant (a), the modified mesoporous silica indicates three reflections. All samples show a distinct reflection at around 2° and two weak reflections at 3.7° and 4° which are assigned to (100), (110), and (200) lattice planes.

The intensity of these peaks is low due to the presence of surfactants. These peaks are characteristic of the hexagonal phase.

In the sample without surfactant (b), the first strong reflection in $2\theta \approx 2$ is related to (100) plane and two weak reflections in $2\theta \approx 3.7$ and 4 are related to (110) and (200) planes, respectively that

are characteristic reflections of a hexagonal lattice with symmetry $p6mm$ [21].

Examination of these two spectra also reveals that after the surfactant is removed, the structure is preserved.

FE-SEM image exhibits that the morphology of the mesoporous silica is hexagonal, which confirms with XRD patterns (Fig. 2 (a)). TEM images were revealed the porous structure of products (Fig.2b).

As shown in Fig. 3, the SH-SiO₂ indicates type IV isotherm, which is related to the mesoporous structure. Besides, the surface area and pore volume were increased due to the removal of the surfactant

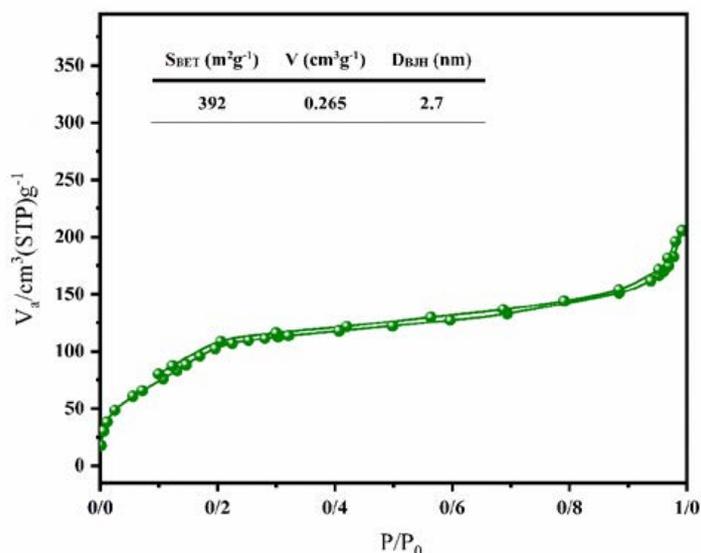


Fig. 3. The N₂ adsorption-desorption isotherm of SH-SiO₂

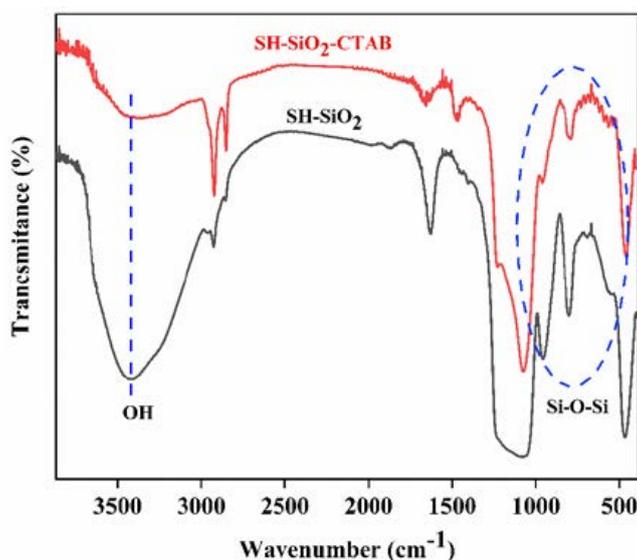


Fig. 4. FTIR spectrum of SH-SiO₂ and SH-SiO₂-CTAB

(Inset of Fig. 3).

As shown in Fig. 4, a broad peak of the hydroxyl group in all samples and the vibration of the C-H were observed at around 3500 cm⁻¹ and 2925 cm⁻¹, respectively. A set of peaks at 800-1000 cm⁻¹ was related to the stretching Si-O-Si and Si-O groups. The stretch vibration of the Si-O-Si bond is at approximately 1088 cm⁻¹. After removal of surfactant, the CH stretching remained. It can be assigned a propyl group of the organo-thiol group on the surface.

The TGA curve depicts in Fig. 5. There are two weight loss steps for SH-SiO₂; the observed first weight loss before 200 °C can be related to the absorbed water on the surface [22]. The significant weight loss occurred between 200-600 °C, which was attributed to the decomposition of the MPTMS chain and other organic compounds. The above 600 °C, the inorganic compounds decomposed. The number of organic moieties on the surface mesoporous was calculated as 0.13 mmol. Besides, the buoyancy effects were observed as an exceeding

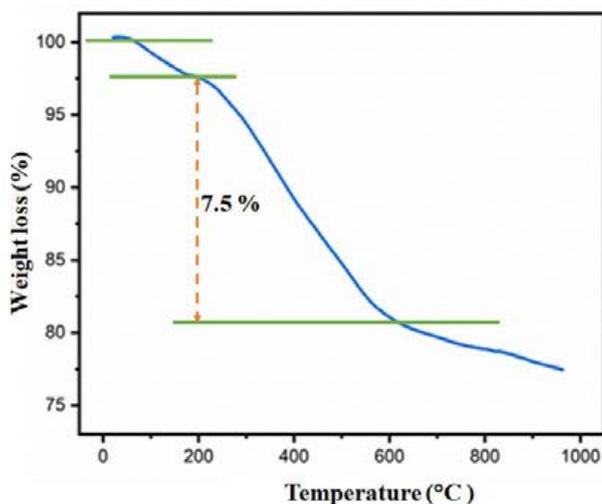


Fig. 5. TGA curve of SH-SiO₂.

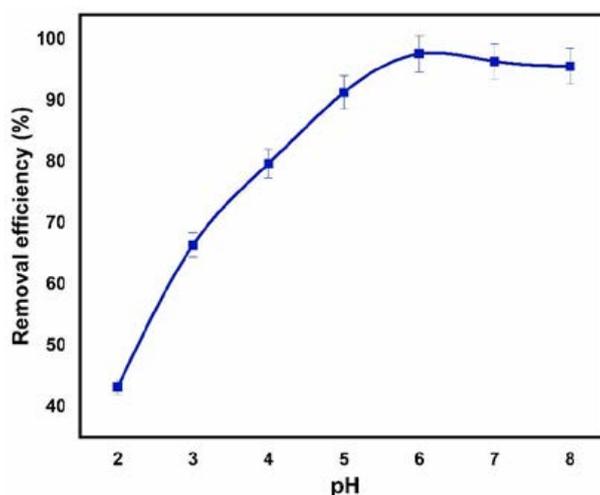


Fig. 6. The effect of solution pH on the adsorption process by mesoporous adsorbent. (aqueous solution volume: 20 ml, stirring rate: 350 rpm, initial concentration: 50 mg. L⁻¹, sorbent dosage: 50 mg, contact time: 30 min)

initial weight in the curve [23].

Adsorption study

The pH of the sample solution is a dominant factor in the removal of heavy metal ions by mesoporous silica materials, and a suitable pH value can improve the removal efficiency and adsorption percentage [22]. The pH values alter not only the existent metal ion forms in aqueous sample solution but also the protonation degree of the functional groups in the surface of the synthesized mesoporous silica materials. To optimize the pH of the sample solution, a set of experiments at fixed values of all variables was done at different pH

values in the range of 2-8, and the results are given in Fig. 6. As can be seen, the adsorption efficiency of Pb(II) increased from pH 2 to 8, and the maximum adsorption occurred in the pH = 6. This result can be attributed to the competition between Pb(II) ions and protons at a lower pH value, which results in poor absorption of lead ions. Additionally, due to the protonation of the adsorbent surface active sites, strong electrostatic repulsion forces prevent the Pb(II) ions from achieving the adsorbent active sites. On the other hand, as the pH increases, decreasing the concentration of H⁺ ions in the sample solution lead to reduce the competition between Pb(II) ions and H⁺ ions at the adsorbent

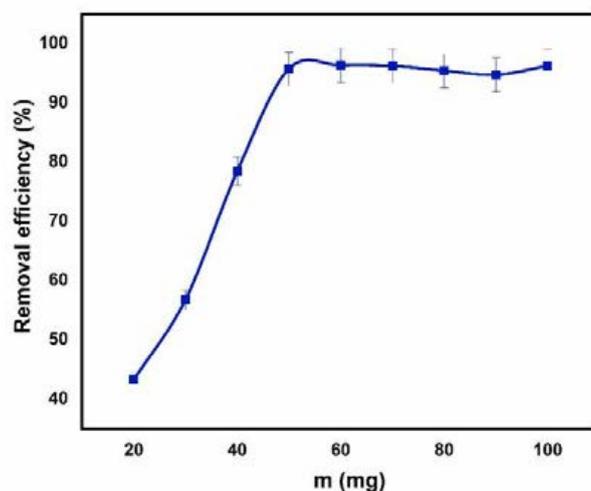


Fig. 7. The effect of adsorbent dose on the adsorption of Pb (II) ions by mesoporous adsorbent (aqueous solution volume:20 ml, stirring rate: 350 rpm, initial concentration: 50 mg . L⁻¹, contact time: 30 min, pH= 6)

surface sites, thereby increasing the adsorption of Pb(II) [24]. Also, with increasing pH, precipitation of Pb(II) cations in the basic medium occurs due to the formation of lead hydroxide in the solution, which can be reduced the reproducibility and adsorption efficiency of the method. Therefore, pH 6 was selected as the optimum pH for subsequent experiments. The efficiency of adsorption of ions depends on different parameters such as solution pH, the initial concentration of the target analyte, sorbent amount, and contact time. The influence of these parameters was investigated to optimize the conditions.

To optimize the solution pH, a set of experiments was performed at a range of pH 2-8, and the results are given in Fig. 6. As can be seen, the maximum adsorption occurred in pH 6. At lower pH than 6, the competition between Pb(II) ions and protons was observed, which caused the reduction of the absorption of ions. The protonation of the active sites of adsorbent prevented the uptake of Pb(II) ions into those sites. At higher pH than 6, the efficiency of adsorption decreased due to the increasing OH⁻ ions and the formation of lead hydroxide precipitation in the solution. Therefore, pH 6 was selected as the optimal pH for subsequent experiments.

The adsorption efficiency can be influenced by the concentration of Pb(II) and it is highly important to optimize the initial concentration of the sample solution [10]. The influence of the different concentrations of Pb(II) ions (10-100 mg

L⁻¹) was investigated and the residual concentrations of Pb(II) ions in sample solutions were measured by atomic absorption spectrometry (AAS). The adsorption efficiency increased by rising the initial concentration from 10 to 50 mg L⁻¹, while the adsorption rate decreased after 50 mg L⁻¹. It is probably due to the decreasing the available adsorption active sites that occupied rapidly at a known concentration of Pb(II) ions and reduced the removal efficiency of the analyte at the higher concentration. Therefore, the optimum initial concentration of the solution was chosen 50 mg L⁻¹.

Another important factor is the adsorption dosage. It should be noted that increasing the amount of adsorbent leads to be accessible more active sites and increase the adsorption efficiency of the adsorbent [23,25].

Another important factor affecting the removal efficiency of the heavy metal ions is the adsorption dosage material. It should be noted that as the adsorbent amount increases, more active adsorption sites are accessible to Pb(II) ions, which leads to increasing adsorption efficiency of the prepared adsorbent through the metal ions complex mechanism [16,25]. To optimize this factor, the effect of various amounts of the adsorbent dose on the removal percentage of Pb (II) ions was evaluated in the range of 20-100 mg. As shown in Fig. 7, the removal adsorption increased until 50 mg and then remained constant due to interacting with all adsorption sites with the target ions. According to the obtained results, it can be concluded that the

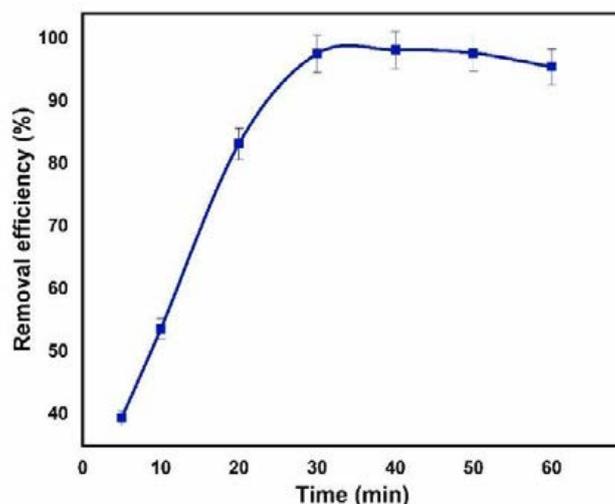


Fig. 8. The influence of contact time on the adsorption of Pb (II) ions by mesoporous adsorbent (aqueous solution volume:20 ml, stirring rate: 350 rpm, initial concentration: 50 mg L⁻¹, sorbent dosage: 50 mg, pH= 6)

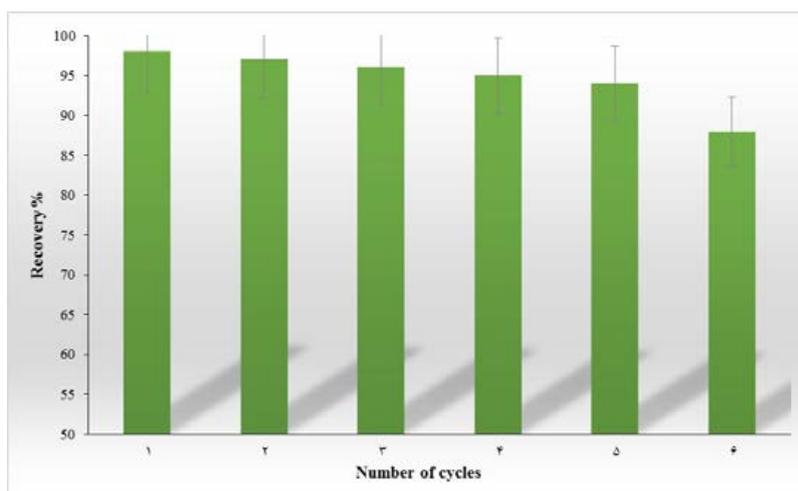


Fig. 9. Reusability and stability of the adsorbent in several successive separation processes.

optimal amount of the adsorbent was 50 mg.

To achieve the maximum adsorption efficiency, the contact time was optimized. Fig. 8 demonstrates the influence of contact time on the removal of Pb(II) ions. The removal efficiency of the Pb(II) ions increased with increasing contact time, and after 30 min, it became constant. This means that Pb(II) ions have quickly filled the adsorbent surface, and 30 min was selected as an optimal time.

The interference of common coexisting ions such as Na⁺, K⁺, Ca²⁺, Mg²⁺, Cu²⁺, Zn²⁺, Cl⁻, HCO₃⁻, NO₃⁻, and SO₄²⁻ on the removal efficiency of the adsorbent was investigated and the results are given in Table

1. The concentrations of the competitive ions in the solution were about 10 to 100 times more than Pb(II) ions. The results show that other ions had no interfering effect on the removal efficiency of Pb(II) ions. It means that SH-SiO₂ has excellent selectivity for Pb(II) ions and is an appropriate candidate for removing Pb(II) ions from the real samples.

Reusability of the mesoporous silica adsorbent

In practical applications, the reusability of the adsorbent is the most major parameter for adsorption evaluation. In practical applications, the stability and reusability of the prepared adsorbent is

Table 1. The tolerance of coexisting ions.

| Interfering ion | Fold ratio | Removal efficiency (%) |
|-------------------------------|------------|------------------------|
| Cu ²⁺ | 10 | 95.6 |
| Zn ²⁺ | | 98.1 |
| Cl ⁻ | 50 | 95.2 |
| SO ₄ ²⁻ | | 97.1 |
| Na ⁺ | | 98.2 |
| K ⁺ | | 99.3 |
| Ca ²⁺ | 100 | 96.7 |
| Mg ²⁺ | | 95.9 |
| HCO ₃ ⁻ | | 96.4 |
| NO ₃ ⁻ | | 95.5 |

Table 2. Application of the cited adsorbent in the real samples.

| sample | Removal efficiency (%) |
|------------|------------------------|
| Tap water | 95±3 |
| Well water | 98±2 |
| Lake water | 97±5 |

Table 3. Comparison of maximum adsorption capacities sorbents for the lead.

| Adsorbents | Sorption capacity (mg/g) | Ref |
|---|--------------------------|------|
| Carbon aerogel | 34.72 | [28] |
| Modified silica- Thiol modified silica | 9.41 | [2] |
| Biosorbents-Penicillium purpurogenum | 41.8 | [29] |
| Biosorbents-Poly(vinyl alcohol)/teaaste (PVA/TW) | 81.56 | [30] |
| Sorbents containing sulphur ligands- MPTS-CNTs/Fe ₃ O ₄ | 65.40 | [31] |
| Sorbents containing sulphur ligands- PMO-II-SII | 11.4 | [32] |

the main parameter to evaluate the adsorbent [26]. In the recycling experiment, HCl 0.1 M solution was used to the regeneration of the Pb-loaded mesoporous silica adsorbent after the adsorption equilibrium. Adsorption-desorption tests were done under optimum conditions for six consecutive cycles. Based on the results, the adsorption capacity was reduced with just a little change during the five continuous cycles, showing that mesoporous silica material could retain its adsorption capacity to be 95% [27].

Application of adsorbent for environmental water sample

The adsorbent was used to treatment of Pb(II)

ions in three real water samples, including tap, well, and lake waters. To check the application of the adsorbent in real samples, water samples were spiked with 20 mg L⁻¹ of Pb(II) ions, and the removal efficiency of the adsorbent was examined under optimal conditions. The results are presented in Table 2. It is clear that Pb(II) ions have been successfully removed from the real samples using the cited adsorbent.

Comparison with other adsorbents

Table 3 shows a comparison of the maximum adsorbent capacities of this sorbent with several other prepared materials reported in the literature for the removal of Pb(II) ions. According to Table



3, the adsorbent adsorption capacity in this study is higher than, those of almost all of the other reported adsorbents.

CONCLUSION

Since the higher the porosity and size of the adsorbent, the higher the adsorption efficiency was. Finally, precision was used in the synthesis of this microzone, and factors such as temperature and contact time of the adsorbent with heavy metal and pH also affected the adsorption. All of these factors were optimized, and each of these can change the adsorption efficiency during the adsorption process.

Regarding our experiments, functionalized mesoporous silica adsorbent materials were prepared under several experimental conditions by using functionalized nanoporous silica as a template and fumed silica as the silica source utilizing a one-pot hydrothermal method for the removal of Pb(II) ions from aqueous solution. Fourier transform infrared spectrometer (FT-IR), scanning electron microscopy (SEM), transmission electron microscopy (TEM), Brunauer-Emmett-Teller (BET), and low angle X-ray analysis (XRD) were used to the characterization of the prepared mesoporous adsorbent. Batch adsorption experiments were applied to define the adsorption behavior of Pb(II) ions upon the prepared mesoporous silica materials. It was estimated that with an initial concentration of 50 mg L⁻¹, 95% of Pb(II) ions were removed at an equilibrium time of 30 min, solution pH 6, the adsorbent dosage of 50 mg, and an initial concentration of 50 mg L⁻¹ as the optimized condition. The proposed adsorbent was used for the removal of Pb (II) ions from real samples with reliable removal efficiency.

Functionalized mesoporous silica adsorbent materials were directly prepared. The characterization results were proved the structure of the mesoporous silica. Adsorption behavior of SH-SiO₂ exhibited its high affinity to Pb(II) ions with any interference. The maximum removal efficiency was achieved at 95% under contact time of 30 min, solution pH 6, the adsorbent dosage of 50 mg, and an initial concentration of 50 mg L⁻¹ as the optimized condition. The proposed adsorbent was used for the removal of Pb(II) ions from real samples with reliable removal efficiency.

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CONFLICT OF INTEREST

The authors declare that they have no conflict of interest.

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