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RESEARCH PAPER

One-Pot Hydrothermal Synthesis of Functionalized Mesoporous Silica for Effective Removal of Pb(II) Ion

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ABSTRACT

There is a huge scope for the removal of heavy metal ions from aqueous solutions. In this study, mesoporous silica materials, (MSMs), functionalized with (3-Mercaptopropyl) trimethoxysilane, (MPTS/MSMs), were prepared and used for adsorption of Pb(II) ions from aqueous solutions. The synthesis of MPTS/MSMs adsorbent was done using one-pot hydrothermal method by immobilizing 3-Mercaptopropyl trimethoxysilane onto mesoporous silica surface. The structure and properties of the adsorbent were explored using different techniques such as FT-IR, XRD, SEM, TEM, TGA, and N_2 adsorption-desorption isotherms. The adsorption applicability of prepared nanostructure for removal of the Pb(II) ions from the aqueous solution was investigated and the results showed a good selectivity in the absorption of Pb(II) ions over other ions in aqueous solution. The effect of different parameters including the solution pH, Pb(II) concentration, sorbent amount, ion interfering effect, and the contact time onto the removal efficiency of the adsorbent was investigated systematically. The maximum adsorption efficiency (~ 97%) was found for the solutions with pH = 6, the best contact time was seen as 30 min for 50 mg L^{-1} of the analyte under the optimal conditions. The adsorbent was triumphantly used for the removal of Pb (II) ions from the three real water samples, including tap water, well water, and lake water with the removal efficiency of > 95%.

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INTRODUCTION

Metals with the specific gravity of about 5 g cm^{-3} or greater are generally defined as heavy and some of those metal ions such as lead (II), mercury (II), and cadmium (II), often are found in industrial wastewater. Removal of heavy metal ions from the wastewaters has been an extensive industrial research subject and the stricter environmental regulation on the discharge of heavy metals makes it necessary to develop various technologies for their removal. Most of the heavy metals are dangerous to health or to the environment and are not biodegradable and tend to accumulate in living organisms, thus causing different disorders. Therefore, it is necessary to remove them from the polluted streams in order to meet increasingly stringent environmental quality standards [1-3]. These pollutants are found in wastewaters from chemical manufacturing, painting, coating, and greatly threaten the health of human populations and the natural ecosystems. A wide range of techniques to remove heavy metals from water is available, including adsorption, which very popular due to the simplicity and low cost [4].

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Various kinds of adsorption materials have been used for the removal of heavy metals e.g. activated carbon [5-7], and low-cost adsorbents such as agricultural residues and peat [8-10]. However, these materials have many drawbacks as their low loading capacities and their relatively weak interactions with metallic ions. To overcome this disadvantage, many investigators developed functionalized adsorbents such as organoclays and surface modified mesoporous materials [11].

Modified mesoporous silica materials are promising adsorbents with high adsorption capacity for heavy metals [12]. The adsorption mechanism for the removal of toxic heavy metal ions in an aqueous solution is either by electrostatic interaction (ionic interaction between positively charged metal ions and negatively charged matrices) or by chelation (donation of the lone-pair electrons of the matrices to metal ions to form co-ordinate bonds). Although the cost for mesoporous adsorbents per unit is relatively high, some of them can be economically regenerated, while maintaining their great adsorption capacity for heavy metals after multiple reuses [13].

For environmental applications, the development and introduction of new functionalized nanoporous materials are necessary, especially for the preparation of heavy metal adsorbents. Synthesis and characterization of nano hollow structures have been extensively done in recent years. The nano hollow particles often exhibit substantially different properties such as low density, large specific surface area, stability, and surface permeability, from those of common particles [14]. The modification of silica surface through reactions with organosilanes is used in a large variety of technological fields and various industries, from microelectronic to biomedical engineering, polymer and rubber industry, chromatography, and catalysis. Such modifications allow for the improvement of the mechanical performances of these materials [15-19]. This method is especially important in preventing time waste.

As one of these materials, MCM-41, consisting of hexagonal arrays of large and uniform pore size, large surface area, thermal stability, and mild acidic property. Mesoporous silica MCM-41 has been functionalized and employed to eliminate traces of toxic heavy metal from wastewater. For environmental applications, the development of functionalized nanoporous material is necessary [20].

Lead is an important compound used as an intermediate in the processing industries such as plating, paint and dyes, and lead batteries. Through the food chain system of soil–plant–animal–human, Pb(II) is transferred into animals and human beings. Therefore, the development of reliable methods for the removal of lead is of particular significance. However, the direct analysis of Pb(II) is often disturbed because of the presence of a complex matrix in the environmental samples. Consequently, the selective separation of Pb(II) from natural samples needs much more attention [21].

In this study, a functionalized mesoporous silica nanostructure, MPTS/MSMs, was prepared by one-pot method and used as an effective adsorbent with a remarkable selectivity for the removal of Pb(II) ions from the aqueous solution. The selectivity of the adsorbent in removal of Pb(II) in the presence of the other ions such as Cu^{2+}, Zn^{2+}, Na^{+}, K^{+}, Ca^{2+}, Mg^{2+}, Cl^{-}, HCO_3^{-} and NO_3^{-} was also investigated. The adsorbent shows a good selectivity in removal of Pb(II) in the presence of other ions. Despite the high stability of presented adsorbent, the loaded Pb(II) ions can be removed without the changes in MPTS/MSMs structure which introduces it as reusable adsorbent for removal of Pb(II) ions. In addition, the superiority of one-pot method over other synthetic nano-silica methods can be considered as the other advantage in the preparation of the adsorbent.

MATERIALS AND METHODS

Chemicals and reagents

Silica (12 nm, 99.99%), ethyl alcohol (99.8%), sodium hydroxide (97 %), hydrochloric acid solution (0.1 N), sodium hydroxide solution (0.1 N) and all organic solvents were purchased from the Merck. Cetyl trimethyl ammonium bromide (CTAB, 99%), 3-Mercaptopropyl trimethoxysilane (MPTS) were purchased from Sigma-Aldrich. The stock solutions of heavy metal ions were prepared from their nitrate salts. The pH of all working solutions was adjusted by adding the appropriate amounts of 0.1 M NaOH and 0.1 M HCl solutions.

Instrumentation

RAYLEIGH FT-IR spectrophotometer (WQF-510A) Fourier transform infrared spectra in the range of 400–4000 cm^{-1} using the KBr pellets. The crystalline structures of the products were evaluated by X-ray diffraction (XRD) analysis on

Table 1. Synthesis details of MPTS/MSMs adsorbent.

Mesoporous Silica	Functionalising agent	Synthesis time (h)	CTAB (mol)
MPTS/MSMs-i	-	24	0
MPTS/MSMs-ii	-	72	0
MPTS/MSMs-iii	MPTS	24	0.5
MPTS/MSMs-iv	MPTS	24	1.0
MPTS/MSMs-v	MPTS	24	2.0
MPTS/MSMs-vi	MPTS	72	0.5
MPTS/MSMs-vii	MPTS	72	1.0
MPTS/MSMs-viii	MPTS	72	2.0

an X'Pert Pro MPD diffractometer with Cu Kα radiation (λ = 1.54060 Å) operated at 40 kV and 40 mA. The SEM images of prepared materials surface for the study of morphology were taken by TESCAN (MIRA3) field-emission scanning electron microscope. The surface area and pore size distribution of the synthesized nano mesoporous structures were characterized by N_2 adsorption–desorption with BET and BJH methods at 77 K using a Micromeritics TriStar II PLUS porosimeter transmission electron microscope. EDAX analysis (Energy-dispersive X-ray) carried out by Philips (Tecnai-20). To determine the residual concentration of Pb(II) ions, an Analytik Jena atomic absorption spectrophotometer model ContrAA-700 was employed. The pH measurements of all solutions were adjusted using a Jenway pH meter (3520) with a combined glass-calomel electrode.

Synthesis of adsorbent

Synthesis of Mesoporous Silica Materials (MSMs)

To perform this synthesis, the exact molar ratio of the consumables is of great importance. A general procedure for the synthesis of mesoporous silica materials is as follows:

2 g sodium hydroxide was added to a suspension of 6 g of silica in 60 mL deionized water and refluxed at 75 ˚C for 24 hours to reach a clear solution. This solution was cooled and used as a source of silica without filtration.

In the next step, as-synthesized silica suspension (60 ml) was added dropwise to a solution of CTAB (0.71 g) in water (100 ml) and stirred for 45 min at ambient temperature. This reaction mixture was kept at 120 °C in a Teflon-lined autoclave for 24 h. Another batch was, however, left in such an autoclave for 72 h.

The final white precipitate was filtered and washed with an excess amounts of ethanol- water. A Soxhlet extraction by 0.1M HCl in ethanol was used to purify the final MSMs product.

Functionalization of Mesoporous Silica Materials (MPTS/MSMs)

For functionalization of *Mesoporous* Silica Materials (MPTS/MSMs), similar synthesis procedure like those for MSMs was applied except the MPTS (0.1 g) as the functionalizing agent was added to the reaction mixture. To follow the effect of CTAB concentration on MPTS/MSMs structure, the different amounts of CTAB (0.5, 1.0 and 2.0 mol) was used (Table 1).

Batch experiments

The batch method was applied to study the adsorption behavior of the prepared MPTS/MSMs in removal of Pb(II) ions [22]. Briefly, known amounts of MPTS/MSMs adsorbent were contacted with 20 ml of the aqueous solution containing the desired concentration of heavy metal ions (a mixture of Pb(II), Cu(II), Co(II), Zn(II), Ni(II) and Ag(I)) at an optimised pH in 50 mL flask and the solution was shaken at 350 rpm in a horizontal shaker for 30 min at ambient temperature. Subsequently, the residual concentrations of Pb(II) ions in the filtrate were analyzed using FAAS. All the tests were repeated three times and the results were used in the calculations.

RESULTS AND DISCUSSIONS

Characterization

FT-IR measurements

Comparison of FT-IR spectra of non-functionlised and functionlised silica adsorbent gives a meaningful information regarding the structure composition of prepared materials. The FT-IR spectra of MPTS/MSMs-i — MPTS/MSMs-viii samples are similar. As shown in Fig. 1, a broad peak at 3500 cm^{-1} a peak at 900 cm^{-1} are attributed to the stretching vibrations of O-H and C–H groups,

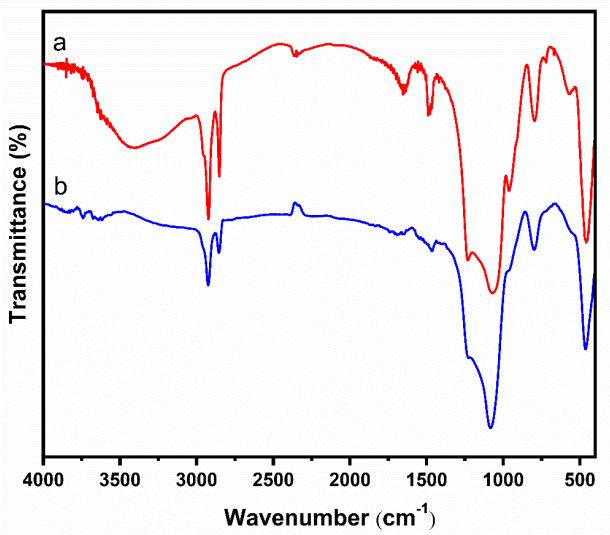

Fig. 1. FT-IR spectra of non-functionalised MSMs, (a), and functionalised MPTS/MSMs-vii, (b).

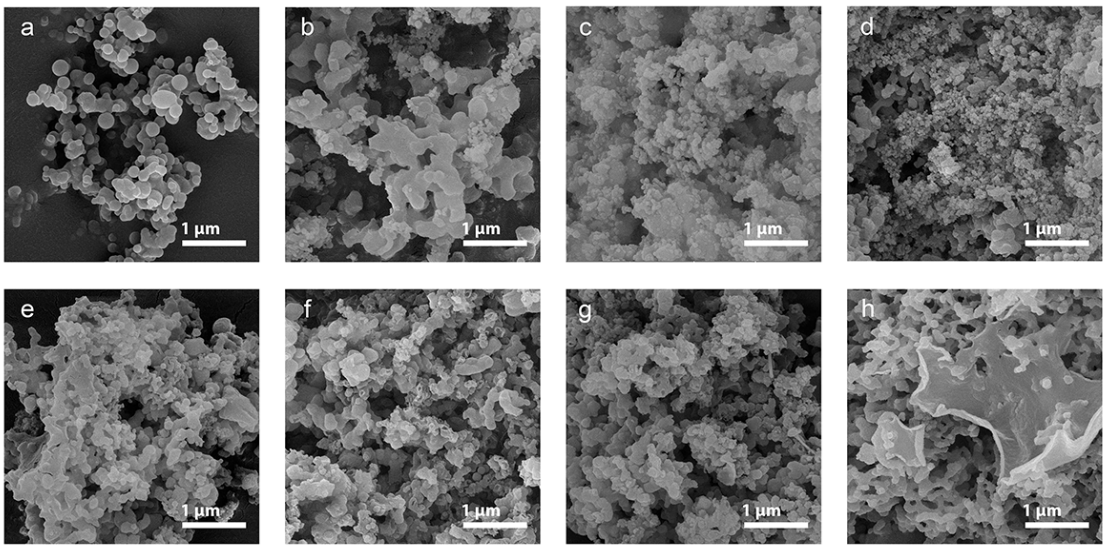

Fig. 2. SEM images of a: MPTS/MSMs-i, b: MPTS/MSMs-ii, c: MPTS/MSMs-iii, d: MPTS/MSMs-iv, e: MPTS/MSMs-v, f: MPTS/MSMs-vi, g: MPTS/MSMs-vii, h: MPTS/MSMs-viii.

respectively. A set of peaks around 800-1000 cm^{-1} was related to the stretching vibrations of Si-O-Si and Si-O groups. The stretching vibration of Si–O–Si bond was observed at approximately 1088 cm^{-1}. The characteristic vibrations at 1635 cm^{-1} are an indicator of H–O–H vibration of water molecules. After removal of the surfactant, the C–H stretching vibrations were observed in the spectrum of MSMs-vii sample.

SEM

More information regarding the morphology of prepared materials was obtained by the scanning electron microscopy (SEM). As shown in Fig. 2 the MPTS/MSMs samples show different morphologies depending to the synthesis procedure from spherical-like to plate-shaped structures. The MPTS/MSMs-i sample with an average sizes less than 200 nm are spherical like, while in MPTS/MSMs-vii sample a mix of spherical and plate shaped structures are observed.

TEM

The TEM image of MPTS/MSMs-vii sample (Fig. 3) revealed that the mesoporous channels of the adsorbent are well ordered and the pores retained

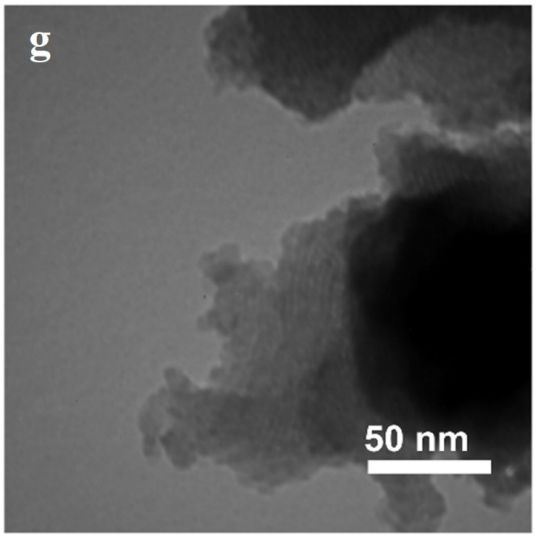

Fig. 3. TEM images of MPTS/MSMs-vii mesoporous material.

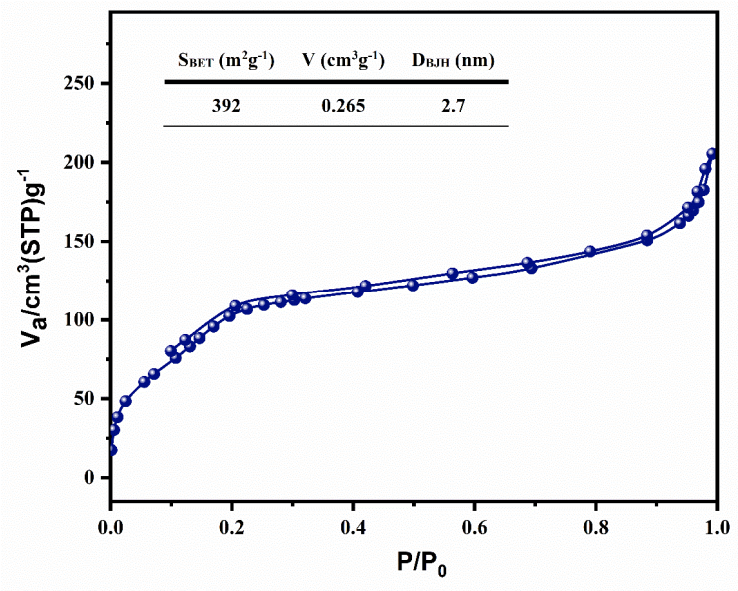

Fig. 4. N_2 adsorption–desorption isotherms of MPTS/MSMs-vii mesoporous material.

open over the functionalisation process.

N_2 adsorption-desorption isotherms

Nitrogen adsorption–desorption isotherms were recorded to study the surface properties and the pore size distribution of mesoporous MPTS/MSMs-vii sample (Fig. 4). The BET surface area and total pore volume were calculated as 392 m^2/g and 0.265 cm^3/g, respectively. N_2 adsorption-desorption analysis of MPTS/MSMs-vii demonstrate a type IV isotherm with H2 hysteresis, confirms the spherical-plate mixture structure of the adsorbent [23].

Low angle XRD analysis

The crystalline structures of the synthesized mesoporous materials were analyzed by the low angle PXRD (Fig. 5). In one sample the strong reflection in 2θ = 2 is related to (100) plane and two weak reflections in 2θ = 3 and 4 are related to (110) and (200) planes. In the two cases of the synthesized products (MPTS/MSMs-ii, MPTS/

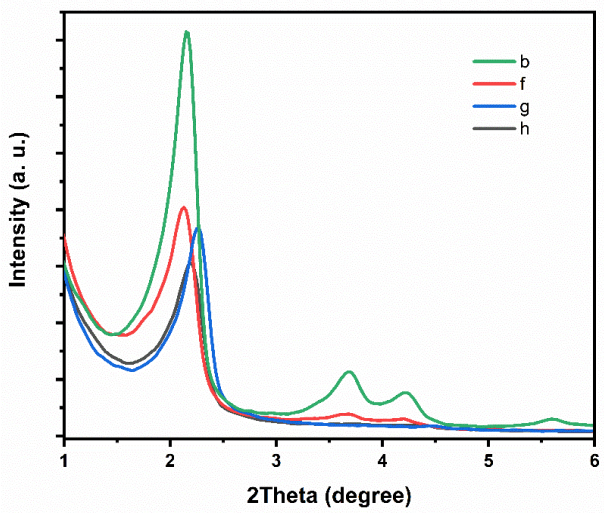

Fig. 5. XRD patterns of prepared b: MPTS/MSMs-ii, f: MPTS/MSMs-vi, g: MPTS/MSMs-vii h: MPTS/MSMs-viii mesoporous materials.

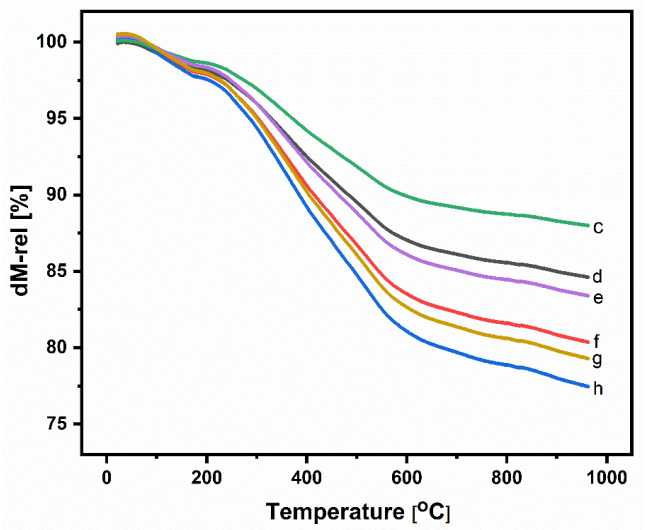

Fig. 6. TGA curves of c: MPTS/MSMs-iii, d: MPTS/MSMs-iv, e: MPTS/MSMs-v, f: MPTS/MSMs-vi, g: MPTS/MSMs-vii and h: MPTS/MSMs-viii mesoporous materials.

MSMs-vi), the intensity of these two reflections decreases with increasing sulfide functions, and new reflection appears in 2θ = 5 that the mentioned reflection is characteristics of plate-like phase. Anyway, the final sample shows a mixture of spherical-plate morphologies together. Higher concentrations of surfactant, the expected structure of the X-ray diffraction pattern, is obtained with the P2-spatial symmetry. Also, after 2θ = 1, two distinct reflections are observed in regions 2.5 and 5. At the critical concentration of the micelles for surfactant (CTAB = 0.9), the cubic, hexagonal phase is formed in among the laminar phase. So, this point means that after this concentration, the surface layer can be reached with surfactant and it is shown in two cases of products (MPTS/MSMs-vii, MPTS/MSMs-viii).

TGA analysis

Thermogravimetric analysis (TGA) of MPTS/MSMs samples are shown in Fig. 6. In all samples, a lost observed in the region 25-200 °C is attributed to the desorption water from the samples. The weight loss observed in the range of 200–700 °C is assigned to the combustion and removing of organic moieties in the structures of prepared

Table 2. The amount of factor groups deployed on the sample surface.

Mesoporous Silica Materials	Functional group ($mmolg^{-1}$)
MPTS/MSMs-iii	1.16
MPTS/MSMs-iv	1.66
MPTS/MSMs-v	2.16
MPTS/MSMs-vi	1.5
MPTS/MSMs-vii	2
MPTS/MSMs-viii	2.5

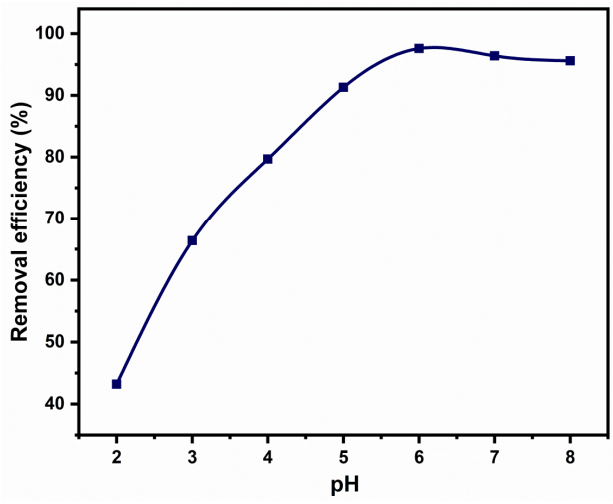

Fig. 7. The effect of pH on Pb(II) adsorption.

samples. The approximate amounts of organic groups in functionalised MPTS/MSMs samples are listed in Table 2. The TGA results illustrate that the maximum level of surface modification occurs at the highest CTAB concentrations and longer heating times.

Optimization of adsorption process

There are several variables affecting the efficiency of heavy metal ions adsorption with prepared mesoporous silica materials, including sample solution pH, initial metal ion concentration, sorbent amount, and contact time. The influence of these parameters was examined and then the optimized conditions were selected.

Adsorbent choice

The choice of a suitable absorbent depends on our knowledge of the mechanisms of interaction between the adsorbent and the target ions, which in turn, depends on understanding the hydrophobic, polar, and inorganic properties of both the solute and the adsorbent [24]. The hydrogen bonding, polar interactions, non-polar interactions, and ionic interactions are the most common mechanisms in the adsorption process. In this study, mesoporous silica adsorbent was successfully synthesized under several conditions and functionalized by MPTS. Based on the results, it was concluded that by using a 1 mole of CTAB amount and 3 days as a pause time, the best mesoporous material with high efficiency (MPTS/MSMs-vii) was obtained. Therefore, MPTS/MSMs-vii adsorbent was selected as a suitable adsorbent for Pb(II) adsorption process.

Effect of sample solution pH

The pH of the sample solution is a dominant factor in the removal of heavy metal ions by mesoporous silica materials and suitable pH value can improve the removal efficiency and adsorption percentage [25]. 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 on the synthesized mesoporous silica materials. In order to optimize the pH of the sample solution, a set of experiments at fixed values of all variables was done at different pH value in the range of 2-8 and the results are given in Fig. 7. As can be

seen, the adsorption efficiency of Pb(II) increased from pH 2 to 6, and the maximum adsorption (~ 97%) occurred in the pH = 6. This result can be attributed to the competition between Pb(II) ions and protons at lower pH values, 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 to achieve 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 surface sites, thereby increasing the adsorption of Pb(II) [26]. In addition, with increasing pH, precipitation of Pb(II) cations in 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.

Effect of initial Pb(II) concentration

The adsorption efficiency can be influenced by the concentration of Pb(II) and it is very important to optimize the initial concentration of the sample solution [27]. To evaluate the initial concentration of heavy metal ion on the removal efficiency of the prepared adsorbent, different concentrations of Pb(II) ions ranging from 10 to 100 mg L^{-1} were examined and residual concentrations of Pb(II) in sample solutions were measured by atomic absorption spectrometry. The obtained results indicated that the adsorption efficiency, increased as the initial concentration increased from 10 to 50 mg L^{-1}, but the amount of adsorption after 50 mg L^{-1} decreased. Following the formation of a mono ionic layer on the surface of modified mesoporous silica adsorbent at the lower concentrations of Pb(II), the interaction of lead ions in the solution and on the adsorbent surface, prevents the formation of a more adsorption layer at higher concentration of the Pb(II). Also, at low concentration of the heavy metal ion, because of the high mole ratio of target ion to the adsorbent active site, a part of the adsorption behavior of the functionalized mesoporous silica adsorbent becomes independent of the initial ion concentration, but at the higher concentration of Pb(II), decreasing the available adsorption sites for Pb(II), reduces the removal efficiency of this ion. Therefore, the optimum initial concentration of the solution was determined as 50 mg L^{-1}.

Effect of sorbent dosage

Another important factor affecting the removal efficiency of the heavy metal ions, is the adsorption dosage material. It should be noted that as adsorbent amount increases, more active adsorption sites be accessible to Pb(II) ions, which leads to increasing adsorption efficiency of the prepared adsorbent through the metal ions complex mechanism [28, 29]. In the present study, the effect of the adsorbent dosage on the removal percentage of Pb(II) was evaluated experimentally at ambient temperature by varied amounts of the mesoporous silica adsorbent in the rang of the 20-100 mg under previously determined optimized experimental conditions. The results are presented in the Fig. 8. According to the obtained results, it was concluded that the optimum amount of the adsorbent was 50 mg in this study.

Effect of contact time

To achieve the maximum adsorption efficiency at the minimum adsorption time, the effect of contact time on adsorption processes must be examined. Fig. 9 demonstrates the influence of contact time on Pb(II)removal. As can be seen, the removal efficiency of the Pb(II) increases with increasing contact time in the kinetic range, while in the equilibrium range, it becomes independent of the removal time. This result is due to the fact that all active sites initially available for adsorption of Pb(II) were filled or occupied at the 30 min, meaning that the Pb(II) saturation occurred on the adsorbent surface. As a result, the equilibrium time was obtained about 30 min for prepared silica adsorbent.

Effect of other ions on the removal of Pb(II) ions

The interference of the common coexisting ions including Na^+, K^+, Ca^{2+}, Mg^{2+}, Cu^{2+}, Zn^{2+}, Cl^-, HCO_3^-, NO_3^-, and SO_4^{2-} found in real samples on Pb(II) removal efficiency using MPTS/MSMs adsorbent was also investigated. The results are given in Table 3. The concentrations of the interfering ions in the test solution were about 10 to 100 times more than the Pb(II) ions. This results indicated that all of the examined ions had not interfering effect on the removal efficiency of Pb(II) ions. It means that the prepared adsorbent has a good selectivity for Pb (II) ion and is appropriate to the removal of Pb(II) ion from the real samples with complicated matrix.

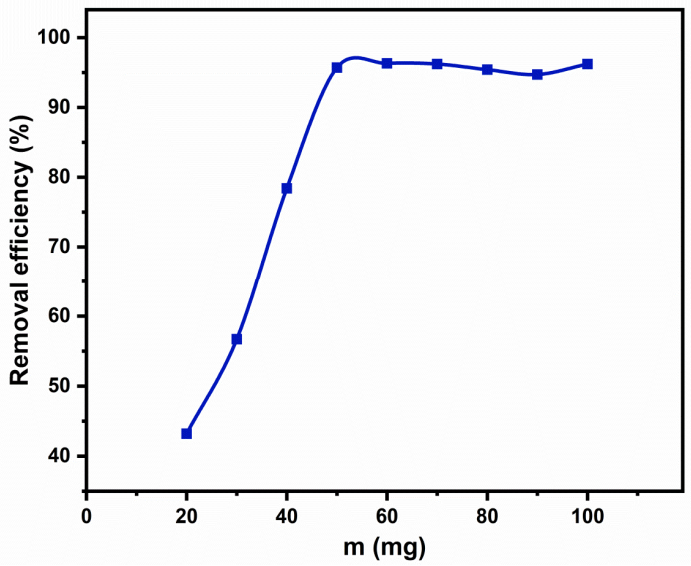

Fig. 8. Effect of adsorbent dose on the adsorption of Pb(II).

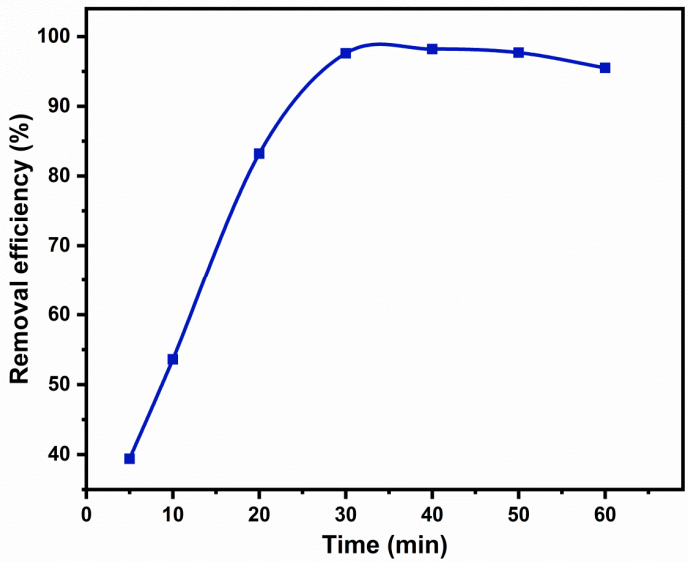

Fig. 9. Effect of contact time on the adsorption of Pb(II).

Stability and reusability of the mesoporous silica adsorbent

In practical applications, the stability and reusability of the prepared adsorbent are the main parameter to evaluate the adsorbent [30]. In the recycling experiment, HCl 0.1 M solution was used for the regeneration of the Pb-loaded mesoporous silica adsorbent after the adsorption equilibrium. Adsorption-desorption tests were done under optimum conditions for five 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%.

Application of mesoporous silica adsorbent for environmental water sample

The mesoporous silica adsorbent was used to remove Pb(II) ions in three real water samples,

Table 3. The effect of interfering ions on Pb (II) adsorption.

Interfering ion	Fold ratio	Removal efficiency (%)
Cu^{2+}	10	95.6
Zn^{2+}	50	98.1
Cl^{-}		95.2
SO_4^{2-}		97.1
Na^{+}	100	98.2
K^{+}		99.3
Ca^{2+}		96.7
Mg^{2+}		95.9
HCO_3^{-}		96.4
NO_3^{-}		95.5

Table 4. Pb(II) removal efficiency of MPTS/MSMs adsorbent in an environmental water sample.

Water sample	Removal efficiency (%)
Tap water	95.1±3.1
Well water	98.4±1.7
Lake water	96.9±4.6

including tap water, well water, and lake water. As no lead contamination was found in any of the selected samples, the 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 described above. The results are presented in Table 4. It is clear that Pb(II) ions were successfully removed from the environmental real samples using this adsorbent.

CONCLUSION

Functionalized mesoporous silica adsorbent materials (MPTS/MSMs) were prepared by one-pot hydrothermal method and using MPTS precursor as the functionalising agent onto the mesoporous Silica as the template. The analysis of the absorbent confirms the successful functionalisation of the mesoporous silica. The MPTS/MSMs adsorbent was applied for the removal of Pb(II) ions from aqueous solution. The sorption of Pb(II) strongly depends on the adsorbent dose, solution pH, flow-rate and contact time. It was estimated that with an initial concentration of 50 mg L^{-1}, 95% of Pb(II) ions were removed in 30 min at the pH of 6 and adsorbent dosage of 20 mg L^{-1}. The usefulness of the MPTS/MSMs adsorbent was demonstrated by the example of removal of lead in real samples of tap water, well water, and lake water. The removal efficiency of MPTS/MSMs adsorbent in of 20 mg L^{-1} Pb(II) ions from these three samples was found ~ 95.1%. The proposed MPTS/MSMs adsorbent shows a good selectivity and suitable reusability in removal of Pb(II) ions in aqueous solution and real samples.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this manuscript.

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