New thiamine functionalized silica microparticles as a sorbent for the removal of lead, mercury and cadmium ions from aqueous media

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Abstract: The existence of heavy metal ions in aqueous media is one of the biggest environmental pollution problems and thus the removal of heavy metals is a very important procedure. In this work, a new adsorbent was synthesized by modifying 3-aminopropyl-functionalized silica gel with thiamine (vitamin B1) and characterized. The influence of the uptake conditions, such as pH, contact time, initial feed concentration and foreign metal ions, on the binding capacity of thiamine-functionalized silica gel sorbent (M3APS) were investigated. Maximum obtained adsorption capacities for Pb(II), Hg(II) and Cd(II) were 39.4±0.2, 30.9±0.5 and 9.54±0.4 mg g^{-1} M3APS, respectively, at pH 5.0. The observed selectivity of M3APS for these metal ions was the following: Pb(II) > Hg(II) > Cd(II). Adsorption isotherm models were also applied to the adsorption process. As a result, the Langmuir isotherm model gave the best fit for the adsorption of metal ions on M3APS. The Gibbs energy change (ΔG) for the adsorption of Pb(II), Hg(II) and Cd(II) were calculated to predict the nature of adsorption process. Having such satisfactory adsorption results, M3APS is a potential candidate adsorbent for Pb(II) and Hg(II) removal from aqueous media.

Keywords: heavy metal ions; adsorption; AAS; environmental remediation.

INTRODUCTION

Due to the rapid industrialization, dangerous wastewater has become a worldwide environmental problem. The disposal of heavy metals has caused much concern for the environment. Commonly used industrial processes, such as metal plating, smelting, battery manufactures, mining activities, dyeing, *etc*., are environmentally problematic. Many industries discharge toxic aqueous effluents containing highly toxic metals ions, such as lead, mercury, cadmium, copper,

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zinc and nickel, to natural resources They are highly toxic and non-degradable even at low concentrations for living organisms.[1–4] Moreover, they have negative environmental and economic impact.[5] Therefore, the removal of heavy metals from the environment is a very important.

Many methods have been employed for the removal of toxic and polluting heavy metal ions from industrial effluents, biological materials and wastewater, such as solvent extraction, ion exchange, liquid–liquid extraction, co-precipit-ation, reverse osmosis and adsorption.[6–9] Adsorption is the most effective and widely used method for the removal of heavy metal ions among the other pro-cesses.[6] Different types of adsorbents are used for the adsorption of heavy metals from aqueous media, such as minerals,[3,7] biomass,[8,9] plants[10–14] and synthetic materials containing chelating groups.[15–18]

Presently, there is growing interest in the use of modified silica gel that has great importance as a solid support. Silica gel is chosen for the preparation of modified products because of its high surface area, high mechanical endurance and thermal stability.[19–21] Silica-modified adsorbents can be prepared easily for the adsorption of the desired heavy metal(s). Different kinds of modified silica gels have been used for adsorption studies in aqueous media.[22–27]

In this study, 3-aminopropyl silica gel was modified with thiamine hydro-chloride (vitamin B1) to prepare a thiamine functional silica gel sorbent (M3APS). Then the sorbent was characterized and used to remove Pb(II), Hg(II) and Cd(II) from aqueous solution. The adsorption isotherms were examined and then com-pared to the data obtained from the Langmuir and Freundlich equations. Accord-ingly, the adsorption capacities were determined and the Gibbs energy change of the adsorption was calculated.

EXPERIMENTAL

Materials and reagents

3-Aminopropyl silica gel (40–63 μm, containing ≈1 mmol g^{-1} NH$_2$, 3APS), thiamine hydrochloride (vitamin B1) and sodium acetate trihydrate were purchased from Sigma–Ald-rich, glutaraldehyde 25 % aqueous solution, ethanol, lead(II) nitrate, mercury(II) nitrate monohydrate were purchased from Merck, cadmium nitrate tetrahydrate was purchased from Alfa Aesar and atomic absorption spectrophotometry standard solutions of 1000 mg L^{-1} Pb(II), Hg(II) and Cd(II) were purchased from Merck. A certified reference material (SPS WW1 Batch 109) was purchased from Spectrapura Standards AS (Oslo, Norway). All the other chemicals were of analytical grade and used without further purification. All water used in the metal chelation experiments was purified by a Milli Q-water purification system (Milli-pore). The resulting purified water had a specific conductivity of 18.2 MΩ cm.

Characterization

FTIR spectra of modified thiamine-functionalized silica gel were taken on a Perkin––Elmer ATR-FTIR spectrophotometer in the wavenumber range 4000–400 cm^{-1}. SEM imag-ing of the adsorbent was performed on a Philips XL30 ESEM-FEG/EDAX. The adsorbent was prepared for SEM by freeze fracturing in liquid nitrogen and applying a gold coating of

approximate thickness 300 Å. An Analytikjena Zeenit 700 flame atomic absorption spectro-photometer equipped with deuterium lamp for continuous background correction was employed.

Modification of silica microparticles

First, 3-aminopropyl-functional silica gel (3APS, 1 g) was gradually added into 30 mL of glutaraldehyde and the mixture was stirred 2 h at room temperature. After centrifugation, a brown solid was obtained, which was washed three times with ethanol and then carefully filtered. Thiamine hydrochloride (0.35 g) was dissolved in 50 mL 30 % ethanol and the brown solid was added to the thiamine hydrochloride solution and stirred overnight. The obtained thiamine functional silica gel (M3APS) was washed three times with 30 % ethanol and filtered. Finally, the M3APS was dried in a vacuum oven at 30 °C for 4 h.

Single-component heavy metal adsorption studies

The absorption capacity of M3APS was investigated in the batch mode at room tempe-rature. To find optimum conditions for maximum absorption of Pb(II), the effects of the initial heavy-metal ion concentration and the pH of the medium on the equilibrium adsorption time were studied. To determine the optimum pH for the absorption, 0.1 g of M3APS was added into a number of beakers containing 20 mL of a metal ion solution. These solutions contained the same initial concentration (100 mg L^{-1}) in NaAc–AcOH buffers of different pH values (in the range of 2–6). The contents of the flasks were stirred at 200 rpm for up to 2 h. After the adsorption equilibrium time and optimum pH were determined, the samples were contacted with different concentration of metal ion solutions (0.5–500 mg L^{-1}) at the optimum pH and contact time. All the adsorption experiments were repeated three times and average values are reported. After the adsorption study, the adsorbent was separated by centrifugation in 5,000 rpm for 5 min and supernatant liquor was analyzed. The concentrations of heavy metal ions were determined, before and after the adsorption experiments, by flame atomic absorption spectrophotometry (FAAS) with a deuterium background correction. The instrument was checked with the quality control (QC) solutions in all batches. The adsorbed amount of metal ions per unit mass of M3APS (mg metal ion g^{-1} M3APS) were calculated using the following expression:

$$q_e = \frac{(c_0 - c)V}{1000m}$$

where q_e is the amount of adsorbed metal ion (mg g^{-1}), c_0 is the initial concentration of metal ion (mg L^{-1}); c is metal ion concentration remaining in solution after the adsorption period (mg L^{-1}); V is the volume of metal ion solution (mL) and m is the amount of M3APS (g).

Multi-component heavy metal adsorption studies

One metal ion could be selectively adsorbed in the presence of other metal ions. Select-ivity of an adsorbent towards different metal ions is an important factor in competitive ads-orption. The competitive adsorption of Pb(II), Cd(II), and Hg(II) ions was examined using the M3APS adsorbent in aqueous solutions. The concentration of each metal ion in the mixture was 1 mmol L^{-1}. The pH of the solution was adjusted to 5.0 and in order to adjust salinity, 700 mg L^{-1} NaCl was added to the synthetic wastewater.[30] Competitive adsorption of metal ions by M3APS was also performed in SPS-WW1 Batch 109 wastewater and tap water by spiking a certain amount of metal ions. In the selectivity studies, a fixed amount of M3APS was equi-librated with solutions of mixed metal ions for 2 h at room temperature. The concentrations of the metal ions were determined by FAAS as described above.

Adsorption isotherms of heavy metals

The studies of the adsorption isotherms of heavy metals on M3APS were performed at room temperature with 0.1 g of M3APS and initial concentrations heavy metal ion in the range 10–500 mg L^{-1} at a pH value of 5.0.

<div align="center">RESULTS AND DISCUSSION</div>

In this study, a new adsorbent for heavy metals was prepared through modification of 3-aminopropyl-functionalized silica gel using glutaraldehyde and thiamine hydrochloride (vitamin B1). The adsorption capacity and selectivity were investigated for the new thiamine-functionalized silica gel (M3APS) adsorbent.

Characterization

The presence of functional groups in the modified thiamine functionalized silica gel (M3APS) was confirmed by FTIR spectroscopy. The FTIR spectra of the starting material (3APS) and the new adsorbent (M3APS) are shown in Fig. 1. The sharp peak at 1046 cm^{-1} indicated Si–O–Si stretching vibrations. A new characteristic bond appeared around 1654 cm^{-1} from C=N vibrations.[27] Bands at 3044 cm^{-1}, stretching of the –CH$_2$ bond, 1613 cm^{-1}, stretching of pyrimidine ring, and 691 cm^{-1}, –CS stretching in thiazole ring,[28] could be seen, through which thiamine (vitamin B1) was covalently attached to surface of the 3-aminopropyl silica. The structure of M3APS is given Fig. 2.
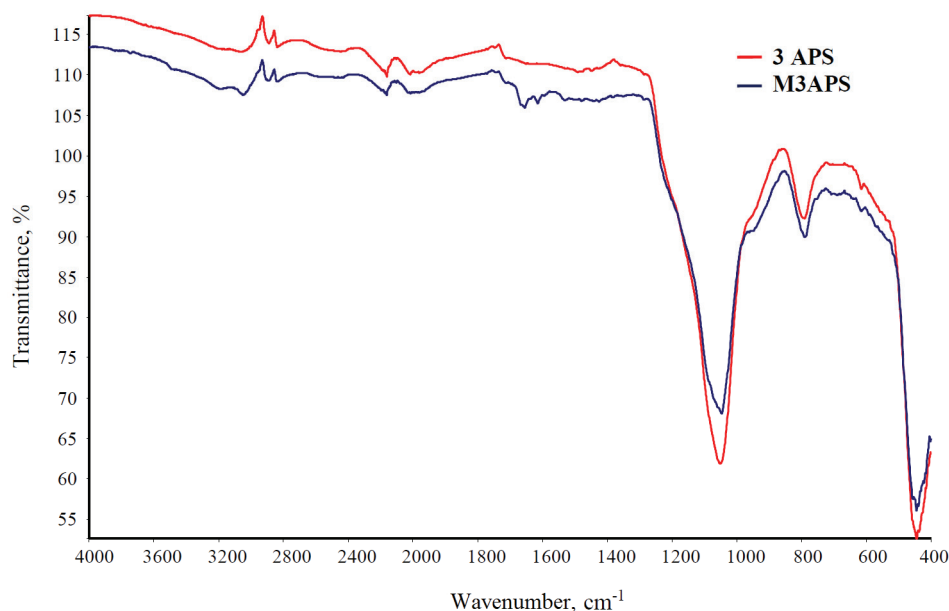
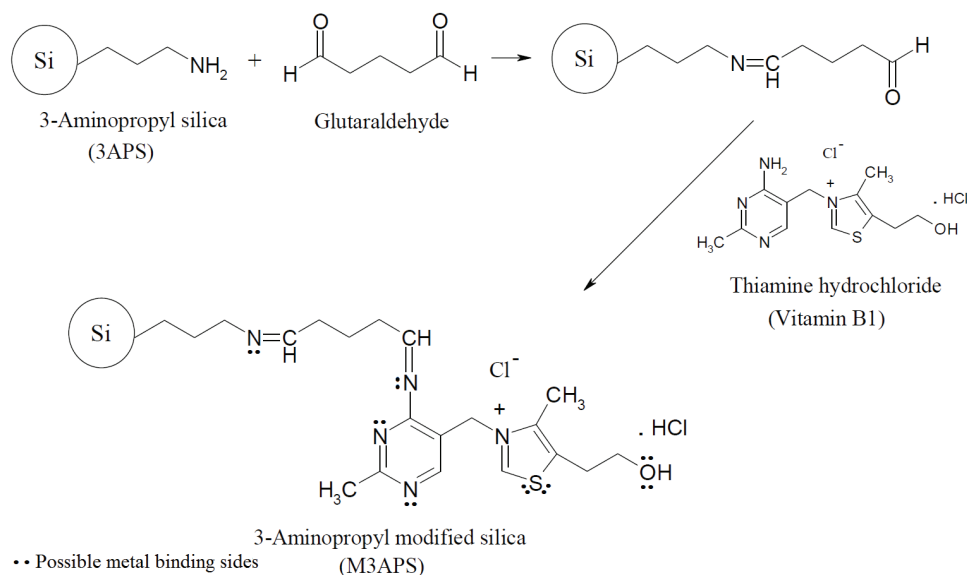

Fig. 1. FTIR spectra of 3APS and M3APS.

Fig. 2. Possible structure of M3APS.

The elemental composition of the surface of M3APS was determined by ESEM-FEG/EDAX. The analysis revealed that the surface of M3APS was composed of 15.45 % C, 23.20 % O, 55.01 % Si, 3.06 % N and 0.35 % S. These results demonstrated that the surface modification was successful. The morphology of M3APS was analyzed by scanning electron microscopy (SEM). The SEM images are presented in Fig. 3. SEM images show that the particles of M3APS had an irregular and inflexed surface morphology with <50 μm particle size.
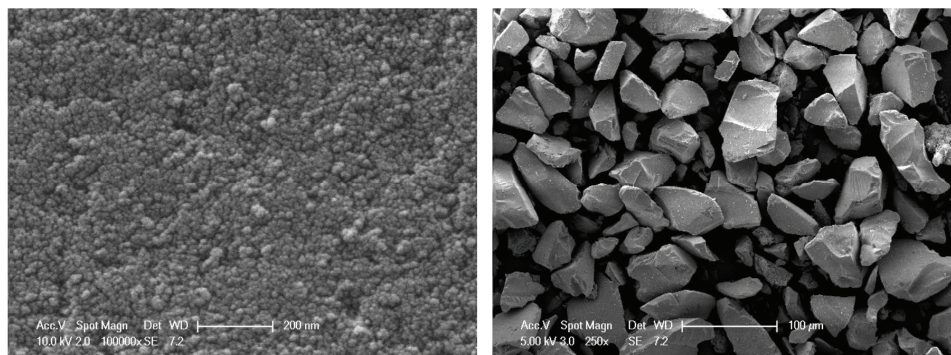

Fig. 3. SEM images of M3APS.

Effect of pH

It is well known that metal ion adsorption on adsorbents depends on the pH of the medium. Cations can be readily adsorbed on negatively charged surface

sites of functional groups. At low pH values, the high concentration of H^+ can react with hydroxyl group, and nitrogen and sulfur atoms on adsorbent and hence compete with metal ions for the adsorption sites, which decreases the adsorption capacity for cations. The electron pair on the N, S and O atoms of vitamin B1 lead to an enhanced electrostatic interaction between metal ions and corresponding interaction sites. On the other hand, most metal ions are prone to precipitation at higher pH values.[29] In this study, to investigate the effect of pH on adsorption capacity, the adsorption experiments were performed in the pH range 2–6 and the results were given in Fig. 4. The maximum metal ion adsorption was achieved at pH 5.0.
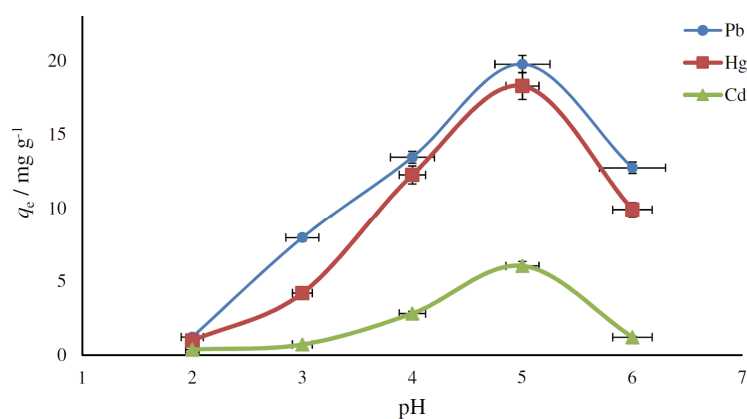

Fig. 4. Effect of pH on the adsorption of Pb(II), Hg(II) and Cd(II) by M3APS; $c = 100$ mg L^{-1}, $t = 60$ min.

Effect of initial metal ion concentration

To investigate the effect of initial metal ion concentration on the adsorption capacity, M3APS was equilibrated with metal ion solutions of increasing concentration. Adsorption capability of M3APS for different initial concentrations of Pb(II), Hg(II) and Cd(II) ions between 0.5 and 500 mg L^{-1} at pH 5.0 is shown in Fig. 5. It could be seen that the metal ion adsorption increased rapidly with increasing initial metal ion concentration, and then reached a maximum adsorption at 250, 100 and 100 mg L^{-1} for Pb(II), Hg(II) and Cd(II), respectively. From these plateau values, the maximum load capacities (q_e) were estimated as 39.4±0.2 mg g^{-1} for Pb(II), 30.9±0.5 mg g^{-1} for Hg(II) and 9.54±0.4 mg g^{-1} for Cd(II) ions.

Effect of contact time

In adsorption studies, the equilibrium time is another important parameter for feasible processes. Removal of the metal ions from different sources is a time-consuming process and it should be a fast method for industrial applications.
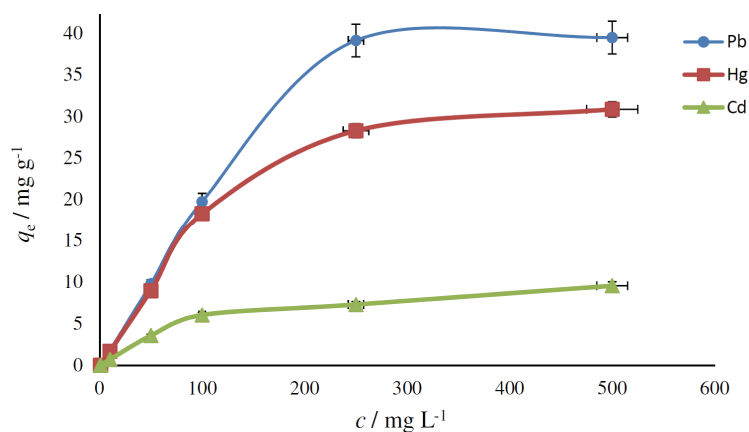
Fig. 5. Effect of initial metal ion concentration on the adsorption capacity of M3APS; pH 5.0, t = 60 min.

The adsorption kinetics of the metal ions were investigated at 250 mg L^{-1} for Pb(II), and 100 mg L^{-1} for Hg(II) and Cd(II) ions at pH 5.0. The results of the investigation are presented in Fig. 6. The data showed that the maximum adsorption of Pb(II), Hg(II) and Cd(II) ions onto M3APS occurred in 60 min and remained constant up to 120 min. Thus, the adsorption process could be described as very fast and adsorption capacities of 72.8, 66.7 and 61.1 % of the maximum adsorption capacities of Pb(II), Hg(II) and Cd(II) ions, respectively, were reached in 15 min.
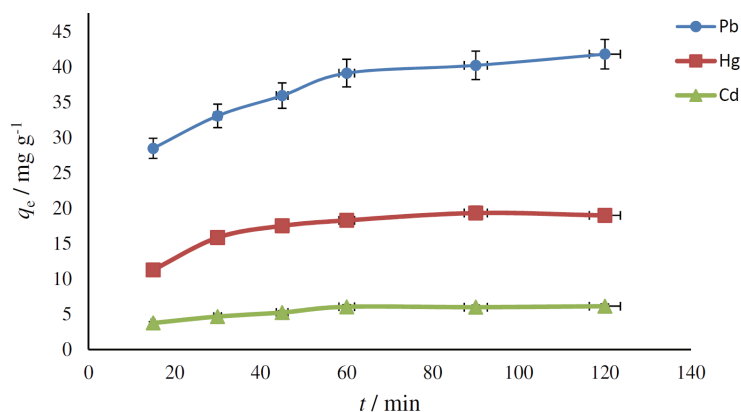

Fig. 6. Effect of contact time on the adsorption of Pb(II), c = 250 mg L^{-1}, and Hg(II) and Cd(II), c = 100 mg L^{-1}, at pH 5.0.

Multi-component heavy metal chelation

Adsorption studies were performed in the batch system to investigate the adsorption selectivity of M3APS for Pb(II), Hg(II) and Cd(II) ions from spiked

tap water, synthetic wastewater and SPS-WW1 Batch 109 wastewater,. The synthetic wastewater contained Ni(II), Zn(II), Fe(II), Co(II), Sn(II) and Ag(I). Concentration of each metal ion in synthetic wastewater was 0.1 mmol L^{-1}. In order to adjust the salinity, 700 ppm NaCl was added to the synthetic wastewater.[30] The contents of the elements in SPS-WW1 Batch 109 wastewater are given in Table I.

TABLE I. Content of the elements in SPS-WW1 Batch 109 wastewater

Element	Concentration ng mL^{-1} (20 °C)	Element	Concentration ng mL^{-1} (20 °C)	Element	Concentration ng mL^{-1} (20 °C)
Al	2000±10	Cu	400±2	Pb	100.0±0.5
As	100.0±0.5	Fe	1000±5	V	100.0±0.5
Cd	20.0±0.1	Mn	400±2	Zn	600±6
Co	60±0.3	Ni	1000±5		
Cr	200±1	P	1000±5		

The results of the adsorption study are given in Table II. The results showed that the adsorption capacities (q_e) of Pb(II), Hg(II) and Cd(II) were decreased under competitive conditions and adsorption capacities can be ordered as Pb(II) > > Hg(II) > Cd(II).

TABLE II. Adsorption amounts of metal ions under competitive conditions

Metal ion	Non-competitive		Competitive with synthetic wastewater		Competitive with SPS-WW1 batch 109 wastewater		Competitive with tap water	
	mg g^{-1}	mmol g^{-1}	mg g^{-1}	mmol g^{-1}	mg g^{-1}	mmol g^{-1}	mg g^{-1}	mmol g^{-1}
Pb(II)	39.40	0.19	28.04	0.14	36.17	0.17	37.08	0.18
Hg(II)	30.90	0.15	15.21	0.08	25.53	0.13	26.72	0.13
Cd(II)	9.54	0.08	2.23	0.02	1.86	0.02	2.31	0.02

Adsorption isotherms

General information about adsorption isotherms are given in Supplementary material to this paper. In order to investigate the effect of the initial metal ion concentration on the adsorption capacity of M3APS, experiments were performed with initial metal concentrations between 10 and 500 mg L^{-1} at room temperature for 24 h. The adsorption isotherm plots of the metal ions are presented in Figs. 7 and 8 for the Freundlich and Langmuir models, respectively, and the constants of the adsorptions isotherms are summarized in Table III. It could be seen that the Langmuir equation fitted well for metal ion adsorption on M3APS.

The recovery and reuse data for M3APS, the Gibbs energy change of the adsorption process and comparison of M3APS with some other adsorbents are presented in the Supplementary material.
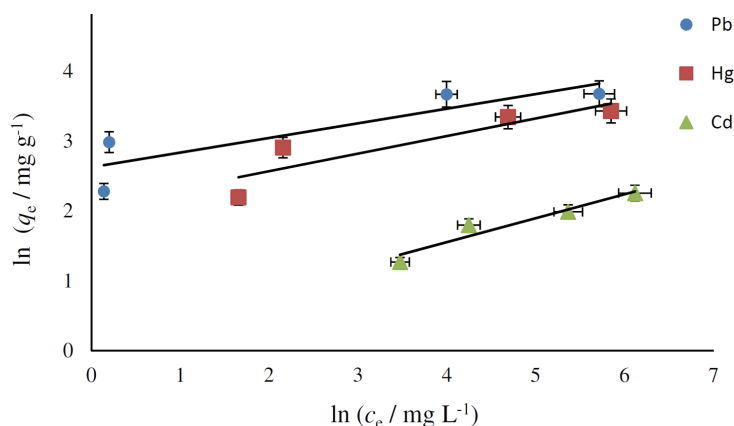
Fig. 7. Freundlich isotherm plots for the adsorption of Pb(II), Hg(II) and Cd(II) ions on M3APS.
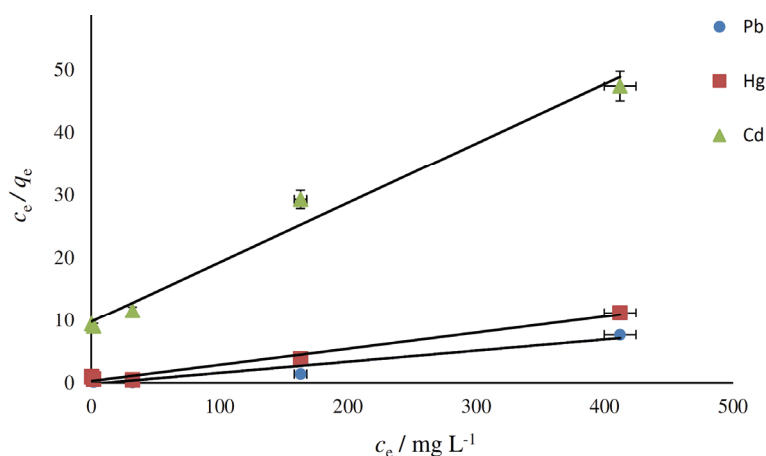

Fig. 8. Langmuir isotherm plots for the adsorption of Pb(II), Hg(II) and Cd(II) ions on M3APS.

TABLE III. Equations of adsorption isotherms of M3APS

Adsorbed metal ion	Freundlich Model		Langmuir Model			
	Equation	R^2	Equation	R^2	Q_m	k_L
Pb(II)	$\ln q_e = 0.209\ln c_e + 2.63$	0.771	$c_e/q_e = 0.018c_e + 0.19$	0.982	55.56	0.094
Hg(II)	$\ln q_e = 0.252\ln c_e + 2.07$	0.798	$c_e/q_e = 0.026c_e + 0.28$	0.982	38.46	0.095
Cd(II)	$\ln q_e = 0.342\ln c_e + 0.927$	0.927	$c_e/q_e = 0.095c_e + 9.8$	0.981	10.53	0.009

CONCLUSIONS

In this study, a silica-based, environmental friendly and tough adsorbent was prepared *via* modifying 3-aminopropyl silica gel with thiamine hydrochloride (vitamin B1). Its toxic metal adsorption capacity was investigated. The adsorp-

tion studies showed that pH, contact time and initial metal ion concentration were important parameters affecting the maximum adsorption capacity of the new thiamine-functionalized silica gel (M3APS) adsorbent. The effects of these parameters were investigated and the optimum conditions determined were pH value 5.0, contact time 60 min and initial concentration 250 mg L^{-1} for Pb(II), and 100 mg L^{-1} for Hg(II) and Cd(II). The results indicated that the Langmuir equation fitted well the sorption of metal ions onto M3APS. The experimental and calculated adsorption capacity (Q_m) data did not agree, especially for Pb(II) and Hg(II). The Q_m was attained at different contact times for the different metal ions. Obtaining higher adsorption capacities is a time consuming process. In this study, 60 min. was determined as the optimum contact time. The adsorption of the heavy metal ions on the M3APS was in the order of Pb(II) > Hg(II) > Cd(II), indicating selective adsorption.

The Gibbs energy change of the adsorption showed that adsorption process was thermodynamically spontaneous under the optimum conditions.

Comparative data showed that the proposed method using M3APS has relatively high adsorption capacities and high pH values in comparison with other methods in which modified silica gels were used as the adsorbent.

Reuse studies showed that M3APS could be used five times without loss of the adsorption capacity. Desorption ratios of over 90 % were achieved for all the tested toxic metals ions.

These results suggest that M3APS has great potential for the removal of Pb(II) and Hg(II) ions from wastewater.

SUPPLEMENTARY MATERIAL

General information about adsorption isotherms, recovery and reuse data of M3APS, Gibbs energy change of adsorption process and comparison M3APS with some other adsorbents are available electronically at the pages of journal website: http://www.shd.org.rs/ /JSCS/, or from the corresponding author on request.

ИЗВОД
НОВИ ТИАМИНСКИ ФУНКЦИОНАЛИЗОВАНИ МИКРОЧЕСТИЧНИ СИЛИЦИЈУМ-
-ДИОКСИД КАО СОРБЕНТ ЗА УКЛАЊАЊЕ ЈОНА ОЛОВА, ЖИВЕ И КАДМИЈУМА ИЗ
ВОДЕНИХ СРЕДИНА

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Јони тешких метала у воденој средини су један од највећих проблема загађења животне средине. Због тога је уклањање тешких метала врло значајан поступак. У овом раду је синтетисан и карактерисан нови адсорбенс модификовањем 3-аминопропил си-

лика гела функционализованог тиамином (витамин Б1). Испитани су утицаји услова сорпције као што су pH, време контакта, почетна концентрација на улазу и присуство страних металних јона на капацитет везивања силика гела функционализованог тиамином (MZAPS). Одређени су максимални капацитети сорпције за Pb(II), Hg(II) и Cd(II), који износе 39,4±0,2; 30,9±0,5, односно 9,54±0.4 mg g^{-1} MZAPS при pH 5,0. Селективност MZAPS за ове јоне метала била је редом: Pb(II)>Hg(II)>Cd(II). Примењени су и модели адсорпционих изотерми. Најбоље слагање добијено је моделом Лангмирове изотерме а адсорпцију ових јона на MZAPS. Да би се предвидела природа адсорпционог процеса израчуната је промена Гибсове енергије (ΔG) адсорпције Pb(II), Hg(II) и Cd(II). Уз тако задовољавајуће резултате адсорпције, MZAPS је постао кандидат за сорпцију Pb(II) и Hg(II) из водених средина.

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