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Cysteine modified silica submicrospheres as a new sorbent for preconcentration of Cd (II) and Pb (II)

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In this research, submicronsized silica (SiO_2) spheres with uniform spherical morphology are grown using the Stöber sol-gel process and subsequently, functionalized with (3-aminopropyl)-trimethoxysilane (APS). These spheres are further modified by chemical binding with L-cysteine (SiO_2-CYS). The composition, structure, morphology and surface properties of the particles obtained are characterized by using elemental analysis, SEM, XRD, Zeta potential and N_2 adsorption measurements. Experiments performed showed that SiO_2-CYS particles permit fast and quantitative sorption of Cd (II) and Pb (II) in the pH range 7-8 and could be used for the separation and preconcentration of Cd (II) and Pb (II) in water samples. Sorption procedure developed is characterized with high concentration factors and ensures quantification of 0.01 µg/L Cd and 0.1 µg/L Pb in various types of water samples. Relative standard deviation for the concentration range 0.01–1 µg/L Cd and 0.1–10 µg/L Pb varied between 4 and 11% for both elements. Analytical method is applied for the determination of Cd and Pb in river, lake and sea water and verified by parallel analysis using ICP-MS

Key words: amine functionalized silica submicrospheres, L-cysteine modification, solid-phase extraction, trace lead and cadmium, surface waters.

INTRODUCTION

High concentration of minerals (approximately 3%) and very low content of metal ions in highly salted sea lakes and sea waters are the two major problems that preclude the application of simple, direct instrumental approach for their analysis [1]. Therefore, the isolation and enrichment of analytes is a key stage of each analytical procedure for the determination of ultra trace concentrations. Methods based on solid phase extraction (SPE) are widely used for this purpose. The efficiency of SPE procedure depends mainly on the nature and properties of the sorbent material [2]. Among the many types of solid phases used in SPE, silica is the most common due to its advantageous characteristics of thermal and mechanical stability, no swelling and hydroxyl reactive groups [3]. Effectiveness and selectivity of the adsorbent may be improved by introducing suitable functional agents capable to react with the silanol groups on the silica surface [4]. Functionalization of silica particle surfaces is commonly achieved using layer-by-layer assembly [5], physical adsorption [6] and silane coupling agents [7,8]. In recent years, silica particles chemically modified with various ligands like 3-aminopropyltriethoxysilane [9], 8-hydroxyquinoline [10], thiourea [11], glycerol [12], thioacetamide [13], alizarin violet [14]. 2-aminothiazole [15] and etc. have been proposed in various SPE procedures. (3-aminopropyl)-trimethoxysilane (APS) functionalization is the most preferred method for obtaining exposed amine groups on silica surface. Cysteine (CYS) can be easily immobilized onto silica surface, previously functionalized with amine groups and in the same time it is a suitable ligand for metal ions sorption due to the presence of three functional groups ($HSCH_2CH(NH_2)COOH$) in the molecule. CYS has been already used to modify surface of the controlled pore glass [16], porous carbon [17], poly(hydroxyethylmethacrylate) microbeads [18] and silica gel [19]. However, the use of submicronsized silica spheres modified by cysteine for separation and preconcentration of trace metal ions has not been reported in the literature.

In the present work, we focus our attention on the synthesis and characterization of L-cysteine

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modified silica submicrospheres and their application for separation and preconcentration of trace analytes. Submicronsized SiO_2 spheres with uniform spherical morphology are prepared using a variation of the method developed by Stöber et al. [20]. Subsequently, the surface of these spheres is functionalized with (3-aminopropyl)-trimethoxysilane and further modified by chemical binding of L-cysteine to the functionalized surface using the bifunctional reagent (glutaraldehyde) (SiO_2-CYS particles). The characterization studies showed that SiO_2-CYS possess high affinity toward Cd (II) and Pb (II), ensuring very fast process of quantitative sorption. This new sorbent was successfully applied for SPE and determination of Cd and Pb in surface waters.

EXPERIMENTAL

Reagents

Tetraethylorthosilicate (TEOS, 99%, Fluka, Germany), ammonia (25 wt. % NH_3 in water), absolute ethanol (EtOH, 99.6%), doubly distilled water (DDW) and 3-aminopropyltrimethoxysilane, (APS Fluka, Germany) were used to prepare the bare silica (SiO_2) and amine-functionalized (SiO_2-NH_2) spheres.

The stock standard solutions of Cd (II), and Pb (II) (1000 μg/mL) were Titrisol, Merck (Darmstadt, Germany) in 2% HNO_3. All reagents used were of analytical reagent grade. Working standard solutions were daily prepared by appropriate dilution with DDW. L-cysteine, hydrochloric acid, nitric acid and glutaraldehyde (GLA, 25 wt.%) were provided from Sigma–Aldrich, Germany and used to prepare the cysteine-modified silica sorbent (SiO_2-CYS). The following buffer solutions were used for pH adjustment: CH_3COONa/CH_3COOH for pH 5–6 and KH_2PO_4 /NaOH for pH 7 and 8. All solutions used in the experiments were prepared using DDW.

Apparatus and characterization

Flame atomic absorption spectrometry (FAAS) measurements were carried out on a Perkin Elmer Zeeman 1100 B spectrometer (Überlingen, Germany) with an air/acetylene flame. The instrumental parameters were optimized in order to obtain maximum signal-to-noise ratio. Electrothermal AAS (ETAAS) measurements were carried out on a Perkin-Elmer (Norwalk, CT, USA) Zeeman 3030 spectrometer with an HGA-600 graphite furnace. The light sources used were hollow cathode lamps for Pb and electrodeless discharge lamps for Cd. Optimal instrumental parameters as recommended by the manufacturer are used. Elemental analysis was carried out with an universal CHNOS elemental analyzer Vario EL III (Elementar Analysensysteme GmbH, Germany). The centrifuge K-1000 (KUBOTA Corporation, Osaka, Japan) was used to separate silica microspheres and extracted metal solution in batch experiments. A microprocessor pH-meter (Hanna Instruments, Portugal) was used for pH measurements. X-ray diffraction (XRD) patterns were measured using Siemens D500 instrument with the CuKα radiation (λ = 1.54Å) in 2θ ranging from 15° to 85°. Scanning Electron Microscopy (SEM) of the silica particles was carried out using a JEOL JSM 5510 instrument operating at 10kV. A Nano ZS Zetasizer (Malvern Instruments Ltd.) was used to determine zeta (ζ) potential of the particles. The specific surface areas were determined by the BET method through N_2 adsorption at 77K.

Synthesis methods

Figure 1 presents the scheme of preparation of SiO_2-CYS particles by chemical binding of L-cysteine to amine-functionalized surface of SiO_2 submicrospheres.

Sol-gel synthesis of silica submicrospheres and surface functionalization. Silica submicron-sized particles were synthesized by the modified Stöber

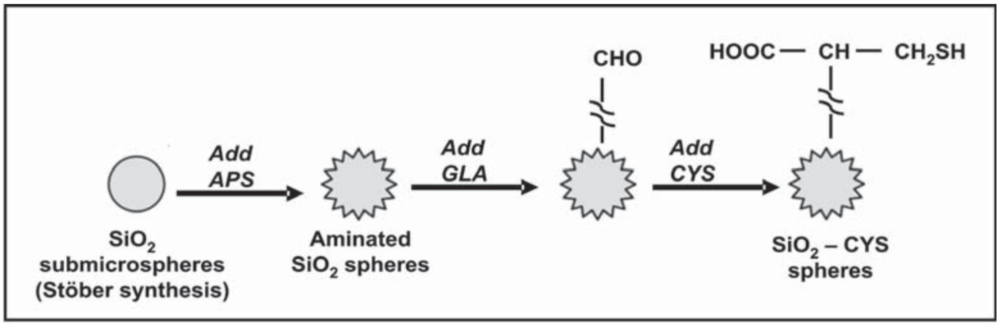

Fig. 1. Scheme of preparation of SiO_2-CYS particles

procedure [20] at optimized reaction conditions as it was described in a previous paper [21]. The reagents were mixed in two starting solutions. Firstly, TEOS (20.3 mL) was dissolved in absolute EtOH (94 mL). A second solution was prepared by mixing of ammonia solution (16.7 mL), distilled water (20.3 mL) and absolute EtOH (209 mL). The second solution was then rapidly added under magnetic stirring to the first solution and mixture was left to react for at least four hours at ambient temperature (22 °C). The final reactant concentrations were 0.25 mol/L TEOS, 0.5 mol/L NH_3, and 5 mol/L H_2O.

The silica particle surface was then functionalized with aminopropyl groups using a modified one-step process similar to that of Wu [22]. At our procedure 4 mL 3-aminopropyltrimethoxysilane (APS) was injected into the above reaction mixture and allowed to react for additional 12 h at room temperature under magnetic stirring. Upon completion of the reaction, a silica surface terminated with amine groups was obtained. For comparison, bare silica spheres without addition of APS were synthesized as well. The particles were then separated by centrifugation and purified by redispersion in ethanol (three times) and DDW (three times). Sonication was used to redisperse the particles in the desired solvents.

L-cysteine modification of aminated silica spheres. The cysteine was immobilized on the SiO_2-NH_2 using the bifunctional reagent glutaraldehyde (GLA). GLA solution (25%, 1 mL) was taken and made up to 40 mL with phosphate buffer (pH 7). SiO_2-NH_2 (1 g) was suspended in this solution and was stirred at room temperature in a nitrogen atmosphere to prevent oxidation. The reaction was allowed to continue for 1 h during which time a brown coloration was observed. The solid product was collected by filtration, washed with water and added to cysteine solution in phosphate buffer (50 mL) at pH 6. Nitrogen was slowly bubbled through the solution for five hours at room temperature (with stirring) and then the solution was left to stay for 2 days. The solid product was filtered and washed several times with DDW and dried under vacuum at room temperature. Four different types of functionalized silica samples were prepared by modification with cysteine using different SiO_2-NH_2 /CYS ratios.

Adsorption studies. Adsorption of Cd(II) and Pb(II) ions from aqueous solutions was studied in batch systems. Aqueous standard solution of (5 mL) containing investigated metal ions (1 µg/mL Cd and 10 µg/mL Pb), 5 mL of a buffer solution and 100 mg of SiO_2-CYS were mixed together in a plastic centrifuge tube. The mixture was stirred with an electric shaker for 15 min and then centrifuged at 3000 rpm for 5 min. In order to investigate the distribution ratio of elements studied, the supernatant was removed and analyzed by FAAS as effluate. The SiO_2-CYS was washed with DDW and trace analytes were eluted from the sorbent particles by 2 mL 2 mol/L HNO_3 for 15 min. In order to investigate the degree of elution, after centrifugation the metal ions contents in the eluate was determined by FAAS.

Sorption characteristics of the sorbent

The degree of sorption, adsorption capacity and distribution ratio are calculated using the following equations:

$$E = [(C_i - C_f)/C_i] \,.\, 100$$

$$Q = (C_i - C_f) \,.\, V/m$$

$$D = Q/C_f$$

where: E is degree of sorption (%), Q is the adsorption capacity (µmol/g), D is the distribution ratio (mL/g); C_i and C_f are initial and final concentrations of metal ions (µmol/mL), respectively. V is the volume of the solution (mL) and m is the mass of SiO_2-CYS (g).

RESULTS AND DISCUSSIONS

Characterization of bare and amine-functionalized SiO_2 submicrospheres

The SiO_2 particles synthesized in this study show an X-ray diffraction pattern, typical of amorphous solids (Fig. 2.)

Fig. 3a and b illustrate typical SEM micrograph exemplifying the morphology and size distribution obtained for the bare silica (SiO_2) particles. Table 1 summarizes the main surface characteristics of the bare silica (SiO_2) and amine-functionalized (SiO_2-NH_2) particles.

The SEM image proves that the methodology employed to fabricate bare silica particles provides a

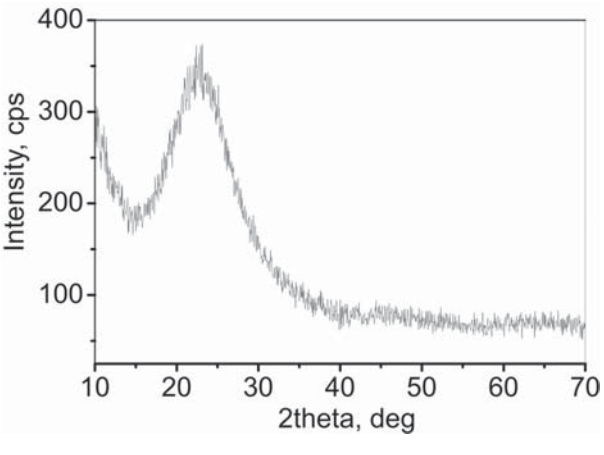

Fig. 2. X-ray diffraction pattern of bare SiO_2 particles

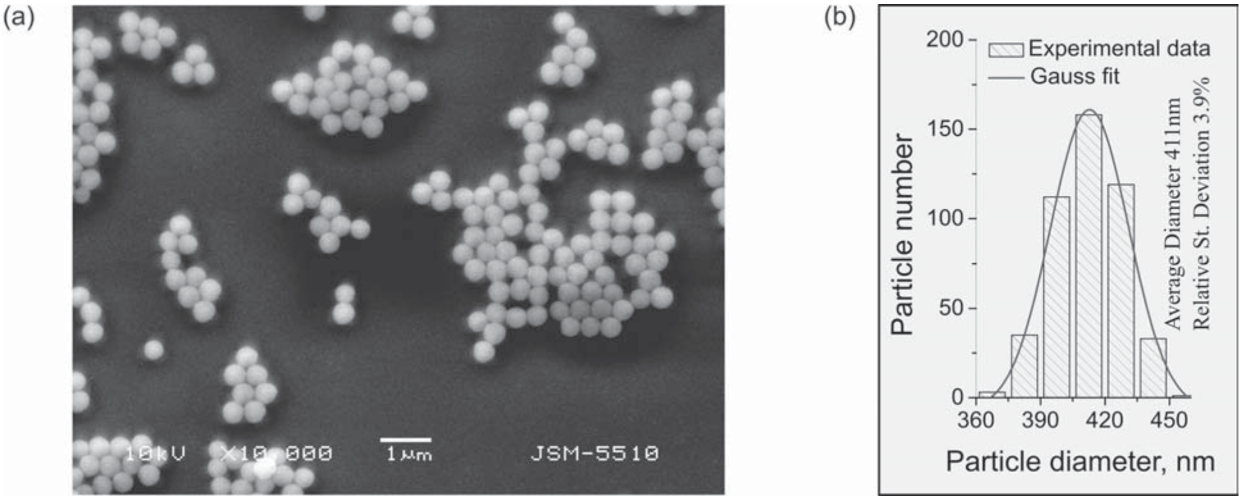

Fig. 3. (a) SEM image showing the representative morphology of synthesized via sol-gel procedure silica submicron-sized particles; (b) particle size-distribution histogram determined by counting of 450 particles from different SEM images using Image J software

reliable control on the particle form and size. Indeed, perfectly spherical and monodispese silica particles with smooth surface can be obtained at the reaction conditions of the implemented sol-gel method. The measured average size of the bare silica spheres was 411±16 nm. The process of amine-functionalization did not change the morphology of silica spheres. As it can be seen from Table 1, there is no difference in the average diameter, size distribution and specific surface area of silica particles before and after the functionalization with APS.

Assuming nonporous particles, the specific surface areas of the particles were calculated on the base of SEM particle size and compared with measured BET surface areas in Table 1. The determined BET surface areas are larger than the calculated values, but these values are on the same magnitude, suggesting nonporous nature of the particles [22].

The Zeta potential measured indicates that bare SiO_2 spheres reach – 56.9 mV at pH 7. It is clearly indicated from measuring of the ζ-potential that the surface charge density of microspheres decreases (in absolute value) with decreasing pH. The ζ-potential data at pH 7 indicate that the negative surface charge on the spheres with APS on their surface is twice reduced. Moreover, the effect of basic amine groups on the silica surface is reflected in the positive value of ζ-potential at pH 2.6, which causes a considerable shift of IEP to higher pH value [22]. The ζ-potential results and data from elemental analysis of SiO_2-NH_2 particles (Table 2) confirm a successful surface functionalization of silica submicrospheres with propylamine groups.

Characterization studies of SiO_2-CYS as a sorbent for SPE

Four different adsorbents were prepared from SiO_2-NH_2 by grafting different quantities of cysteine groups on the surface of silica (Table 2). The elemental analysis was carried out on the SiO_2-NH_2 and SiO_2-CYS sorbents in order to determine C, N and S contents. It is seen that the prepared SiO_2-CYS includes O, N and S donor atoms. The experimental results presented (Table 2) suggest that SiO_2-NH_2

Table 1. Main characteristics of bare and amine-functionalized silica submicrospheres

Sample	ζ^* (mV) (at pH 7)	ζ^* (mV) (at pH 2.6)	Size (nm)	S_{BET} (m^2/g)	S_{calc} (m^2/g)
SiO_2	–56.9	–14.7	411±16	13	7
SiO_2-NH_2	–22.1	+50.8	409±17	12	9

*with 1mM added NaCl at 25 °C.

Table 2. Elemental analysis of the prepared SiO_2-CYS sorbents

Sorbent	SiO_2-NH_2/CYS (g/mmol)	Elemental analysis		
		C (%)	N (%)	S (%)
SiO_2-NH_2	1 : 0	4.2	1.58	–
SiO_2-CYS-0.2	1 : 0.2	7.53	1.98	1.14
SiO_2-CYS	1 : 0.4	10.99	2.57	2.90
SiO_2-CYS-0.6	1 : 0.6	10.35	2.13	2.24
SiO_2-CYS-1.0	1 : 1.0	8.87	2.04	1.25

has been successfully modified by cysteine. The results obtained showed that the sulphur content is highest in SiO_2-CYS (2.90%). The content of nitrogen and sulphur in SiO_2-CYS were estimated as 1.82 and 0.91 mmol/g sorbent, respectively.

Optimization of the experimental conditions for preconcentration of Cd(II) and Pb(II)

The acidity of sample (pH value) is an important condition for efficient retention of the trace elements on the sorbent. Its influence strongly depends on the nature of the sorbent used. The newly synthesized SiO_2-CYS contains thiol and carboxylic functional groups therefore taking into account that p*K*a values of -SH and -COOH groups in cysteine are about 8 and 2 respectively [23] the sorption of the investigated cations should be strongly affected by pH of the sample solution. The pH influence on the degree of sorption, distribution ratios of Cd (II) and Pb (II) and their adsorption capacities were investigated in the pH range 5–8 by batch equilibrium procedure (Table 3).

The trend observed is an increased sorption and adsorption capacities for investigated cations with increasing pH of the solution. At low pH (around 5-6) the degree of sorption and distribution ratio was generally low for investigated metal ions which might be explained with the protonation of the thiol and carboxylic functional groups thus eliminating their ability to form complexes with metal ions. The degree of sorption for Pb (II) is > 95% in the pH range from pH 7 to pH 8, for Cd (II) quantitative sorption is achieved at pH 8. At higher pH values (>9), the decrease in the degree of sorption can be attributed partly to the formation of metal hydroxide complexes or to the dissolution of the SiO_2-CYS sorbent. Finally, pH 8 could be accepted as optimal for simultaneous sorption of Cd (II) and Pb (II) on SiO_2-CYS sorbent.

The influence of various parameters (sorption and desorption time, eluent volume and concentration) on the solid phase extraction efficiencies of SiO_2-CYS for the preconcentration of Cd(II) and Pb(II) from their solutions at pH 8 was investigated. The kinetics of the Cd(II) and Pb(II) sorption and desorption were examined in a batch system with 100 mg of the SiO_2-CYS particles for 5–40 min. The adsorbed Cd(II) and Pb(II) ions were desorbed by treatment with 2 mol/L HNO_3 at continuous stirring. It was established that the saturation values were gradually reached within 15 min, so the adsorption was sufficiently fast for practical applications. The Cd(II) and Pb(II) ions could be quantitatively eluted for 15 min.

The effect of the eluent volume on the metal desorption was investigated in the range of 1–5 mL 2 mol/L HNO_3 and the eluent acidity influence – in the range of 0.5–4.0 mol/L HNO_3. The full desorption of Cd(II) and Pb(II) was reached when the adsorbed Cd(II) and Pb(II) were eluted with 2 mL 2 mol/L HNO_3.

Table 3. Comparison of the degree of sorption (E), distribution ratio (D) and adsorption capacity (Q) of Cd(II) and Pb(II) extraction by SiO_2-CYS.

pH	Degree of sorption E (%)		Distribution ratio D (mL/g)		Adsorption capacity Q (μmol/g)	
	Cd	Pb	Cd	Pb	Cd	Pb
5	18±3	20±3	22	25	0.35	0.47
6	55±2	87±2	122	674	0.81	4.20
7	75±2	>99	305	9504	2.57	4.75
8	97±1	>99	3197	9504	8.63	4.75
9	89±2	86±2	808	667	7.92	8.2

Table 4. Comparative results for Cd and Pb content in surface waters

Sample	Cd (μg/L) [mean/RSD,%]		Pb (μg/L) [mean/RSD,%]	
	SPE (SiO_2-CYS)	ICP MS*	SPE (SiO_2-CYS)	ICP MS*
Black sea, Krapets	0.05/11	0.06/23	1.8/8	1.5/7
Black sea, Kamchia	0.03/11	<0.05	0.6/8	0.7/16
Varna lake, northwest	0.09/11	0.07/23	2.1/7	1.8/7
Beloslavsko lake, west	0.15/10	0.1/21	1.6/8	1.4/7
River Iskar (Novi Iskar)	0.09/10	0.092/9	0.2/8	0.18/7
River Iantra (V. Tarnovo)	0.03/11	0.024/15	0.1/10	0.11/7

*ICP MS results obtained in Green Analytical Methods Academic Centre, University of Plovdiv

Application of SiO_2-CYS sorbent

The prepared SiO_2-CYS was used for the determination of Cd (II) and Pb (II) in surface water samples, from defined monitoring stations in Bulgaria and shown in Table 4. After sampling, the water samples were filtered through cellulose filter membranes of 0.2 μm for the removal of suspended matter. The 100 mg SiO_2-CYS particles (placed in a plastic centrifuge tube) were stirred with 50 mL sea water (original pH 8.2) spiked with Cd (1 ng) and Pb (10 ng) for 15 min. After centrifugation, the supernatant is removed and the sorbent is washed twice with DDW. The loaded cations were eluted with 2 mL 2 mol/L HNO_3. The cation amount in the eluate is determined by ETAAS. Recoveries for investigated elements in spiked sea samples varied in the range 93–98%. Results obtained by the proposed analytical procedure were compared with direct ICP-MS measuremenst (Table 4) and very good agreement was observed.

Analytical procedure developed permits quantification of 0.01 μg/L Cd and 0.1 μg/L Pb in various types of water samples. Relative standard deviation for the concentration range 0.01–1 μg/L Cd and 0.1-10 μg/L Pb varied between 4 and 11% for both elements. Model experiments performed showed that proposed preconcentration procedure could be combined with field sampling and next transportation of water samples to the laboratory thus avoiding any sample contaminations due to the additions of conservation reagents .

CONCLUSIONS

Submicrometer silica spheres functionalized with aminopropyl groups are prepared trough a one-step process. Chemical binding of L-cysteine to the functionalized surface of the silica support using glutaraldehyde as a bifunctional reagent are made. It is observed that the density of surface capping by thiol groups can be easily controlled by changing the ratio of SiO_2-NH_2 to L-cysteine. Its optimal value is found to be 1:0.4 g/mmol.

The new sorbent based on cysteine modified silica submicrospheres is found to be suitable for successful separation and preconcentration of Cd (II) and Pb (II) in water samples. The SiO_2-CYS sorbent shows a good efficiency even in the presence of complex matrices such as Black sea water and recommended preconcentration procedure could be combined with field sampling and sample transportation.

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МОДИФИЦИРАНИ С ЦИСТЕИН СУБМИКРОННИ СФЕРИ ОТ СИЛИЦИЕВ ДИОКСИД, КАТО НОВ СОРБЕНТ ЗА КОНЦЕНТРИРАНЕ НА Cd (II) И Pb (II)

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(Резюме)

Силициев диоксид със субмикронни размери и перфектна сферична морфология е синтезиран по зол-гел метода на Stöber и след това е функционализиран с (3-аминопропил)-триметоксисилан (APS). Получените сферични частици са модифицирани чрез химично свързване с L-цистеин (SiO_2-CYS). Съставът, структурата, морфологияга и повърхностните им свойства са охарактеризирани с помощта на елементен анализ, SEM, XRD, измервания на ζ-потенциал и адсорбция на N_2. Показано е, че сорбцията на Cd(II) и Pb(II) върху SiO_2-CYS е бърза и количествена при pH 7, и че този сорбент може да се използва за разделяне на концентриране на Cd(II) и Pb(II) във водни проби. Предложената процедура се характеризира с висок коефициент на концентриране, а границите на откриване в различни типове водни проби за Cd и Pb са 0.01 µg/L и 0.1 µg/L, съответно. Относителното стандартно отклонение в концентрационния интервал 0.01–1 µg/L за Cd и 0.1–10 µg/L за Pb варира между 4 и 11% за двата елемента. Аналитичният метод е приложен за определяне на Cd and Pb в речна, езерна и морска вода и е верифициран чрез ICP-MS анализ.