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Lead and cadmium sorption in water samples using modified nano-sized cobalt aluminate

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ABSTRACT

A new nanostructure which is surface-modified cobalt aluminate nanoparticles with silica is used for the separation of cadmium and lead prior to its determination by inductively coupled plasma–mass spectrometry was described. For this purpose, at first, ex-situ modification of cobalt aluminate nanoparticles was made, then lead and cadmium were collected on new sorbent by syringe technique. The effects of experimental conditions on sorption of cadmium and lead were investigated. After the optimization of experimental parameters, a successful separation and determination were obtained with high quantitative recovery (>95%) and precision (<10% RSD). Using the proposed technique, the cadmium and lead concentrations in tap water and drinking water could be practically and rapidly determined in the range of 95% confidence level. The detection limit of the described method for cadmium and lead using sample-matching blanks were 0.053 and 0.117 µg L^{-1} (3σ, $N = 10$), respectively. The proposed technique was fast, simple, and economic.

Keywords: Cadmium; Inductively coupled plasma–mass spectrometry; Lead; Nanoparticle sorbent; Solid-phase extraction

1. Introduction

Recent advances in analytical chemistry (e.g. sample pre-concentration, molecular probes, and biological and electrochemical sensing) are using raw and modified nanomaterials. Raw nanomaterials are used as efficient adsorbents for the determination, separation/preconcentration, or removal of heavy metals from water. They exhibit various advantages such as fast kinetics, high capacity, and preferable sorption toward heavy metals in environmental samples, especially in water treatment. The long-term performance of the composite adsorbents, as well as their field application in heavy metal, is applied on contaminated water treatment. In spite of having attracted considerable interest of nanoparticles in analytical chemistry, their physicochemical, surface properties, size, morphology, and impurities significantly affect the sorption of heavy metals [1,2].

On the other hand, selectivity problem is one of the disadvantages of using raw nanomaterials. To overcome and/or to increase the selectivity and adsorption capacity, physical or chemical modifications have often been utilized on the sorbent surface using organic compounds (8-hydroxyquinoline, dithizone, diethyldithiocarbamate (DDTC), dimercaptosuccinic

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acid, and tetraethyl orthosilicate). Besides that, raw or modified nanomaterials are commonly immobilized on different substrates, particularly silica in order to obtain fine grain size, overcome back pressure problem, and prevent the loss of nanomaterials [1].

Transition metal oxide spinels have been used in many industrial applications including semiconductors, magnetic storage media, sensor technology, ion conductors, or heterogeneous catalysts [3–7]. Cobalt aluminate ($CoAl_2O_4$) spinel, also referred to as Thenard's blue, is well known for its thermal and chemical stability, high surface area, and high oxygen anion mobility. Conventionally, cobalt aluminate spinel is micro-sized and it is used as a pigment, owing to its good hiding power and bright blue color. Recent progresses in this metal oxide are synthesis of nano-sized versions, so it provided modified surface and widen its usability [8–10]. Therefore, to increase their usability in different areas, surfaces should be developed for further chemistry while keeping the toxicity as low as possible. Thus, a chemical attachment of a ligand to the $CoAl_2O_4$ surface will be a better strategy to increase usability of cobalt aluminate nanoparticles in different areas.

If the concentration of analyte is too low to be detected and/or the interference effects cannot be eliminated, some sample preparation techniques should be used [11]. One of the common techniques for this purposes are solid-phase extraction. It is a widely used sample preparation system by elements from a mixture to a solid phase according to their chemical properties [12]. Numerous inorganic and organic, natural, and synthetic materials directly or modified with a chelating group, bacteria, etc. have been used as sorbents, all of which have their own advantages and disadvantages [13,14]. Nowadays, raw or modified nanomaterials are successfully used as a sorbent for their above mentioned properties [12,15–17].

In this study, cobalt alumina with silica is functionalized using ex-situ method, in order to obtain sorbent with high capacity, fast determination, and easy usability for removing heavy metals. Moreover, functionalized silica-coated cobalt alumina nanostructures ($CoAl_2O_4@SiO_2$) were used for the sorption of lead (Pb) and cadmium (Cd) by inductively coupled plasma–mass spectrometry (ICP-MS) for the treatment of water samples. The effects of experimental conditions on sorption of lead and cadmium were investigated. As a result, novel, and well-dispersed surface-functionalized $CoAl_2O_4$ NPs coated with silica were obtained and used for the sorption of lead and cadmium from water samples.

2. Materials and methods

2.1. Materials

$CoAl_2O_4$ spinel was produced by Torrecid Turkey (Eskisehir, Turkey); tetraethyl orthosilicate (TEOS) was purchased from Alfa Aeser (MA, USA); diethyl ether and other chemicals were obtained from Merck (NJ, USA). Stock solution ($100\ mg\ L^{-1}$) of Pb and Cd were prepared from Titrisol concentrates (Merck, NJ, USA) and further diluted with distilled–deionized water daily. All chemicals were of highest purity and analytical reagent grade available from Merck and Alfa Aeser.

The pH of the samples was adjusted by $0.01\ mol\ L^{-1}$ NH_3 or $0.01\ mol\ L^{-1}$ HNO_3 and controlled using WTW pH 340-A/SET2 pH meter. Thermo scientific, XSeries2 ICP-MS (MA, USA) was used for the lead and cadmium determination. The characterization of nanomaterial was made using Perkin Elmer, Spectrum65, FTIR spectrometer.

2.2. Methods

2.2.1. Coating of cobalt aluminate with silica

General procedure for modification of $CoAl_2O_4$ was based on a procedure reported by Guo et al. [18], the surface of the nanoparticle was coated with a silica layer. $CoAl_2O_4$ (90 mmol) was mixed with 0.02 mol TEOS and 50 mL diethyl ether in an ice–water ultrasonic bath for about 1 h. The resulting colloidal suspension was precipitated by sedimentation at room temperature. The precipitated nanostructure was rinsed with diethyl ether to remove the excessive TEOS and dried completely in a vacuum oven overnight to remove the solvent.

2.2.2. Procedure of analysis

About 50 mg of dried and cleaned sorbent ($CoAl_2O_4@SiO_2$) was used for the separation of analytes. At first, sorbent was washed for its conditioning. The pH of blank, standard, and sample was adjusted to optimized value using $0.01\ mol\ L^{-1}$ HNO_3 or NH_3 Subsequently, conventional batch method was used to obtain optimum conditions. The lead and cadmium concentration in the supernatant was determined by ICP-MS. Instrumental parameters for the determination of lead and cadmium by ICP-MS are shown in Table 1. In all determinations, blanks, standards, and samples were subjected to same experimental procedure. The schematic diagram for the surface modification of Si-coated $CoAl_2O_4$ and whole separation procedure was shown on Fig. 1.

Table 1
Instrumental parameters for the determination of lead and cadmium by ICP-MS

Parameter	Value
Instrument detector	Simultaneous
Cool gas flow	13.0 L min^{-1}
Plasma flow	18 L min^{-1}
Auxillary flow	0.7 L min^{-1}
Nebulizer flow	0.9 L min^{-1}
RF power	1,400 kW
Stabilization time	60 s
Sampling depth	150 mm
Measurement mode	Peak jumping
Dwell time	10,000 ms
Channels per mass	1
Sweeps	100
Nebulizer quartz micro-concentric	0.4 mL min^{-1}
Number of replicates	3

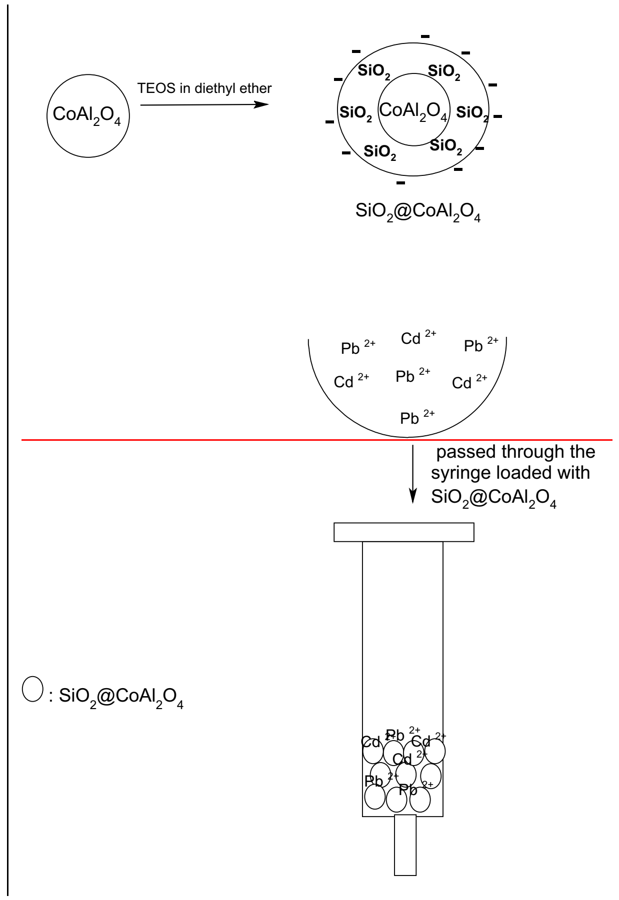

Fig. 1. Schematic diagram for the surface modification of silica coated $CoAl_2O_4$ and whole procedure for the separation.

A model solution of 9.0 mL including 0.1 mg L^{-1} analyte elements was adjusted at pH 8.0. Then, the model solution was passed through the plastic housing of a syringe-mountable filter. The plastic housing of a syringe-mountable filter was filled with 80 mg of dried sorbent using methods of Duana et al. and Akman et al. [11,19]. The filter was closed again and attached to the tip of a 1.0 mL of plastic syringe. At first distilled water was drawn and discharged for conditioning of the sorbent. The pH of blank, standard or sample was adjusted to 8.0 using 0.01 mol L^{-1} HCl or NH_4OH and drawn into syringe manually passing through the sorbent in the filter attached to the syringe with a flow rate of around 20 mL min^{-1} manually and ejected back again at the same flow rate contacting with the sorbent one more time [11,17]. During the draw and discharge of solutions, the analyte, contacting two times with the sorbent in the filter, was retained. 10 mL of distilled–deionized water was passed through the sorbent by means of syringe to remove the non-sorbed matrix components. Finally, the analyte retained by the sorbent in the filter was eluted by drawing and ejecting back 1.0 mL of HNO_3 solution (3.0 mol L^{-1}). The cadmium and lead concentration in the effluent was determined by ICP-MS. In order to enrich the analyte further, different portions of sample solutions were passed and ejected back several times, whereas the analyte collected was eluted only once. After the procedure was completed, distilled water (using 0.01 mol L^{-1} HCl or NH_4OH) was drawn and discharged through the filter for conditioning of the sorbent to prepare it for the subsequent operation. In all determinations, blanks, standards, and samples were subjected to same experimental procedure.

In order to obtain quantitative recovery with high precision, both sorptions were carefully optimized. The effects of experimental conditions with regards to the amount of sorbent, pH of sample, concentration and kind of eluent, foreign ions, flow rates of sample and eluent on the recovery (retention and elution) of the analytes were investigated.

3. Results and discussion

3.1. Characterization of modified $CoAl_2O_4@SiO_2$ nanoparticles

The FT-IR spectroscopy is routinely used for the characterization of nanoparticles. Fig. 2 shows the FT-IR spectra, TEM images and zeta potential of colloidal $CoAl_2O_4$ and $CoAl_2O_4@SiO_2$ nanoparticles.

There is no absorption maximum for the non-coated $CoAl_2O_4$ nanoparticles however, when the

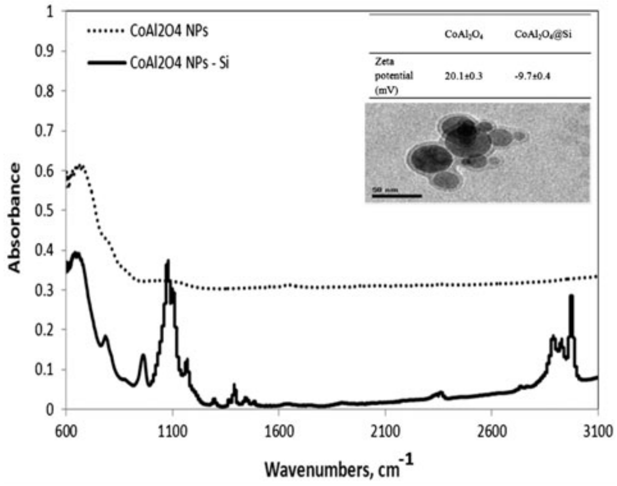

Fig. 2. FTIR spectrum, TEM image and zeta potential of modified and unmodified nano structure.

$CoAl_2O_4$ nanoparticles were coated with the Si shell, the FT-IR results show that $CoAl_2O_4$ nanoparticles were successfully functionalized using the procedure (Fig. 2). The bands approximately at 800, 1,100, and 2,400 cm^{-1} proved the functionalization of $CoAl_2O_4$ by Si coating. Also zeta potential results demonstrate that, the surface charge of $CoAl_2O_4@SiO_2$ became negative (-9.7 ± 0.4 mV), whereas bare cobalt alumina surface charge was positive (20.1 ± 0.3 mV).

3.2. Effects of experimental parameters on sorption

The optimization was significant for implementing the method using the sorbent with maximum efficiency. For this purpose, quantitative sorption of analyte element, 0.1 mg L^{-1} for Cd and Pb, onto the sorbent is a prerequisite, which depends on the pH of the sample, sample volume, amount of sorbent, etc. Thus, in order to obtain quantitative recovery with high precision, both sorptions were carefully optimized.

3.3. Effect of pH on the sorption

One of the most important parameters for the quantitative sorption is the pH of sample. The sorption itself is a pH-dependent reaction. Most of the cation removal sorbents are activated up to pH 6 to bind metal ions to the matrix. In order to optimize the sorption conditions for the retention of cadmium and lead on the sorbent, the recoveries of trace metal ions were determined by applying the described procedure by changing the pH of model solutions in the range of 4–8 (Fig. 3). As it is shown in Fig. 3, when the pH of solution was adjusted to pH ≥ 7.0, maximum retentions were obtained and the analyte elements could be quantitatively retained on the sorbent without adding any additional chelating reagent.

3.4. Effect of amount of sorbent

In order to optimize the sorbent amount, different amounts of $CoAl_2O_4@SiO_2$ on the sorption of analyte elements were investigated. From a series of experiments that can be seen in Fig. 4, between 10 and 200 mg of sorbent, it was found that the analytes (0.1 mg L^{-1} Cd and Pb) were quantitatively sorbed above 80 mg of $CoAl_2O_4@SiO_2$. This value was also chosen as a critical parameter throughout the experimental works.

3.5. Eluent type and volume

For desorption of the retained analytes from the syringe-mountable filter, nitric acid was used as eluent. Quantitative recoveries (>95%) were obtained for the analytes with 1.0–4.0 mL of 1.0 and 3.0 mol L^{-1} of HNO_3 respectively. As a result, 1.0 mL of 3.0 mol L^{-1} of HNO_3 was selected as an eluent in all further experiments.

3.6. Effect of sample volume

The effect of sample volume on the sorption of analyte elements using 80 mg of $CoAl_2O_4@SiO_2$ at pH

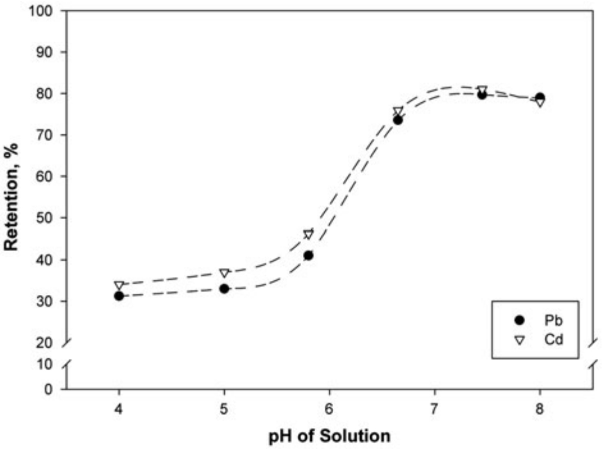

Fig. 3. Effects of pH on sorption of Pb and Cd using silica coated cobalt alimuna nanostructures ($CoAl_2O_4@SiO_2$) (50 mg sorbent, 0.01 mol L^{-1} solution, 8 mL sample volume).

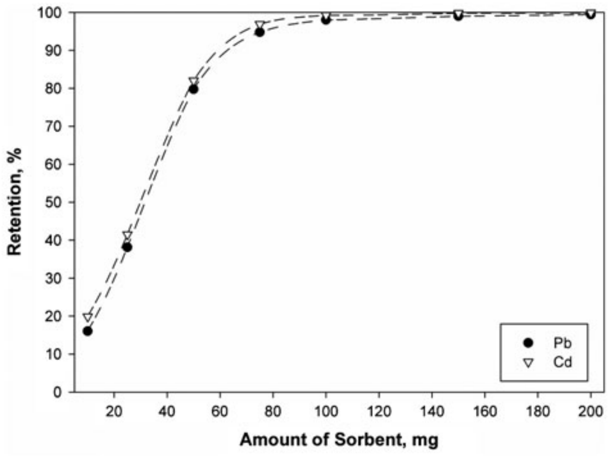

Fig. 4. Effects of the amounts on sorption of Pb(II) and Cd (II) using silica coated cobalt alimuna nanostructures ($CoAl_2O_4@SiO_2$) (pH 7.00, 0.01 mol L^{-1} solution, 8 mL sample volume).

7.0 was investigated for the range of 1.5–15 mL of the model solution. Fig. 5 shows the relationship between the sample volume and the sorption. If the sample volume was between 1.5 and 8.0 mL, quantitative sorption (>90%) of cadmium and lead was obtained. When sample volumes above 8 mL were used, quantitative sorption was decreased. To use minimal sample volume (1.5–8.0 mL) with a maximum sorption, we obtained easy usability, preparation, and handling of sample. Thus, the optimum sample volume was determined as 8.0 mL for the quantitative determination of cadmium and lead ions at pH 7.0. The enrichment factor of the analyzed ions was obtained as 8, since the final volumes of sample and the eluent were 8.0 and 1.0 mL, respectively.

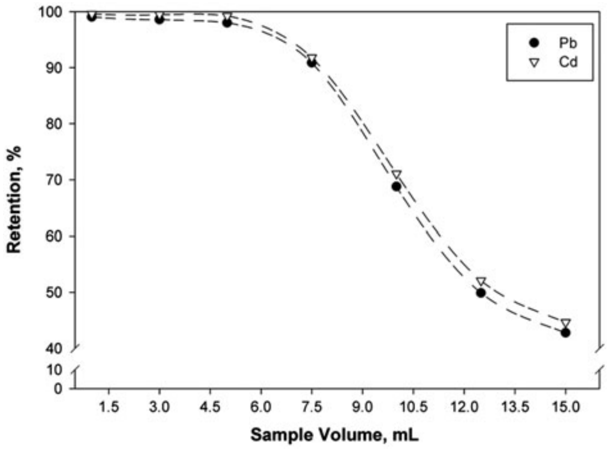

Fig. 5. The effects of the sample volume on retention of Pb(II) and Cd(II) using silica coated cobalt alimuna nanostructures ($CoAl_2O_4@SiO_2$) (pH 7.00, 0.01 mol L^{-1} solution, 8 mL sample volume).

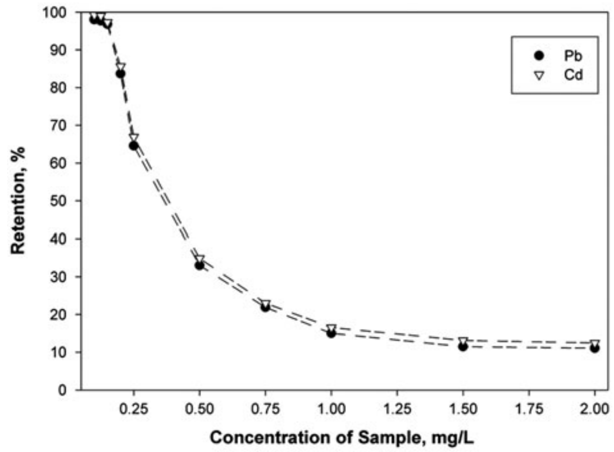

Fig. 6. Loading capacity of the silica coated cobalt alimuna nanostructures ($CoAl_2O_4@SiO_2$) (pH 7.00, 0.01 mol L^{-1} solution, 8 mL sample volume).

Table 2
Effect of foreign ions on the sorption of Pb(II) and Cd(II) (at pH 7.00; sorbent: 50 mg; sample volume: 8 mL; *N*: 5)

Species	Concentration of the diverse ion (μg mL^{-1})	Retention (%)
Na^+	1,150	94
Cl^-	2,485	96
Mg^{2+}	253	96
SO_4^{2-}	676	94
K^+	523	97
NH_4^+	336	96
CO_3^{2-}	566	94

Table 3
Recoveries for Pb(II) and Cd(II) in trace element in water SRM1643e certified reference materials (at pH 7.00; sorbent: 50 mg; sample volume: 8 mL; *N*: 5)

Trace element in water SRM1643e	Pb[a]	Cd[a]
Certified value (μg L^{-1})	19.63 ± 0.21	6.568 ± 0.073
Found value (μg L^{-1})	18.72 ± 0.75	6.494 ± 0.092

[a] Mean ± 95% confidence limits.

3.7. *Loading capacity*

The loading capacity of $CoAl_2O_4@SiO_2$ structure was determined by mixing increasing amounts of

Table 4
Recoveries of Pb(II) and Cd(II) in spiked and unspiked tap water and drinking water (at pH 7.00; sorbent: 50 mg; sample volume: 8 mL; *N*: 5)

	Tap water (μg L^{-1})			Drinking water (μg L^{-1})		
Analyte	Added	Found	Spike recovery (%)	Added	Found	Spike recovery (%)
Pb	0	12.01	–	0	2.41	–
	5.00	16.98	99.3	10.00	12.26	98.5
Cd	0	2.69		0	1.74	–
	5.00	7.77	101.5	10.00	11.78	100.4

Table 5
Literature summary of related investigations

Modified nanomaterial	Analyte	Matrix	Technique	LOD (μg L^{-1})	Refs.
Alumina nanoparticles coated with sodium dodecyl sulfate and modified with Schiff base	Cd	Water, wastewater, biological and food samples	FAAS	0.14	Afkhami et al. [20]
Immobilization of 2,4-dinitrophenylhydrazine on nano-alumina coated with sodium dodecyl sulfate	Pb	Various water, food, industrial effluent, and urine samples	FAAS	0.43	Afkhami et al. [21]
Nanometer-sized alumina coated with chromotropic acid	Pb, Cd	Standard reference materials (water, tomato leaves and rice flour), natural waters	ICP-OES	Pb(0.53) Cd(0.14)	Ramesh et al. [22]
Nanometer ZrO_2 immobilized on silica gel (ZrO_2/SiO_2)	Pb	Water samples	FAAS	5.2	Yang et al. [23]
Nanometer titanium dioxide immobilized on silica gel (immobilized nanometer TiO_2)	Cd	Environmental sample	ICP-OES	0.048	Liu et al. [24]
Dithizone-modified TiO_2 nanoparticles (nanometer TiO_2-DZ)	Pb	Foodstuffs, plants and water samples	ICP-OES	1.72	Lian et al. [25]
Titanate microspheres	Pb, Cd	Water samples	FAAS	Pb(0.072) Cd(0.008)	Zhang et al. [26]
Gammamercaptopropyltrimethoxysilane modified silica-coated Nano-Fe_3O_4	Pb, Cd	Lake sediment, milk powder, seawater	ICP-MS	Pb(56 pg L^{-1}) Cd(24 pg L^{-1})	Huang and Hu [2]
Silver-coated nano-TiO_2 modified with cysteamine	Pb	Certified wastewater, spiked sea water	FAAS	0.38	Baysal et al. [17]
Nano-TiO_2 core–Au shell nanoparticles modified with 11-mercaptoundecanoic acid	Cd	Tap, sea, mineral, bottled drinking water	FAAS	0.15	Gunduz et al. [27]
Recent work—silica coated $CoAl_2O_4$ nanostructure	Pb, Cd	Water samples	ICP-MS	Pb(0.117) Cd(0.053)	–

cadmium and lead through the sorbent. As can be seen in Fig. 6, when the loading capacity of the sorbent was exceeded, the retention of cadmium and lead began to decrease. The loading capacity was calculated from the differences of cadmium and lead concentrations between the beginning and remaining amounts in the supernatant (Fig. 6). 1.9 mg g^{-1} was found as a surface capacity of the mentioned nanostructure for both Pb and Cd, which was high enough compared to other sorbents in the literature [19–27].

Regeneration or reusability of the sorbents may not be necessary in some situations, especially during removal of mercury or other high toxic metals. In other way, it is important for regeneration to increase the utility. For this purpose, sorbent was treated with HCl and HNO_3 with different durations and concentrations. The sorbent was washed with various acid solutions at the range of 0.1–2.0 M, and nearly >90% of sorbed Cd and Pb were recovered. Approximately 100 times of use, $CoAl_2O_4$ spinel mixed that was coated with silica and SiO_2 still remains on the surface. The SiO_2 coating remained unchanged on the surface even after three months of its preparation.

3.8. Effects of common diverse ions

The effect of various diverse ions on the sorption of analytes was investigated. Instead of testing the effects of each diverse ion on the recoveries of the analytes separately, the recoveries of the analytes (1 μg mL^{-1}) in a model solution prepared by dissolving 100 mg of NaCl, Na_2SO_4, KCl, NH_4Cl, Na_2CO_3, and $MgCl_2$ in water and completed to 100 mL were investigated. The analytes were satisfactorily recovered between 94 and 100% in a quite complicated matrix of the most common ions. The results are shown in Table 2. Obviously, $CoAl_2O_4$@SiO_2 nanosorbent could be successfully used for the determination of Cd and Pb in the presence of foreign ions at their concentrations. The concentrations of foreign ions are higher than those in most commonly studied samples with very heavy matrices, e.g. sea water, serum, etc.

3.9. Validation of method

The limit of detection (LOD) of the method for lead and cadmium was 0.03 and 0.02 μg L^{-1} (3σ, $N = 10$), respectively. LOD was calculated according to 3σ of 10 replicate of blank.

The optimized method was applied for the determination of lead and cadmium concentrations in Certified Reference Materials (Trace Element in Water SRM1643e). The analytical results are shown in Table 3. In addition, the optimized method was applied for analysis of tap water taken from laboratory in Istanbul and drinking water that was purchased from markets in Istanbul (Table 4). The proposed method was applied to real samples using standard addition method. The spiked amounts of water samples were successfully determined in the range of 95% confidence level ($N = 5$).

Table 5 presents a summary about the application of some modified nanomaterials or nanoparticles and recent work in separation of heavy metals. The LODs of the methods using modified nanomaterials or nanoparticles in the literature was found between 0.072–5.2 μg L^{-1} and 0.008–0.14 μg L^{-1} for cadmium and lead, respectively. The recoveries and detection limits of analytes using $CoAl_2O_4$@SiO_2 used in this study outperforms the most of the literature studies in the same field [19–27].

4. Conclusions

In this study, a sorbent using ex-situ modification of silica-coated cobalt aluminate nanostructures for the determination of Cd and Pb and removal from water samples by ICP-MS is reported. It was crucial to consider and measure all influencing factors for the sorption to demonstrate that the new sorbent could be used successfully for determination and removal of Cd and Pb from water samples with high recoveries, sensitivity and accuracy. In addition to high capacity and good recovery of the method, regeneration of the sorbent is obtained effectively using suitable acid (HCl). Furthermore, the modification and uses of cobalt alumina spinel mixed in the sorption was applied for the first time in the literature. Besides that, the methods are easy, fast, economic, environmental friendly, and they do not require high sample volume to remove and detect analyte elements from water samples.

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