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ORIGINAL RESEARCH PAPER

Ultra Trace Determination of Lead and Copper Ions in Water Samples using Polyamidoamine Dendrimer Supported on SBA-15 Nanomaterial

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ABSTRACT
In this work, polyamidoamine dendrimer G(1.5) supported on SBA-15 nanoporous is used as a novel sorbent for extraction and determination of Pb^{2+} and Cu^{2+} ions from environmental water specimens utilizing flame atomic absorption spectrometry. FTIR spectrum and thermal analysis were used to represent the existence of dendrimer groups in the silica framework. The various parameters like pH, concentration of eluent, extraction time, and interfering ions on extraction efficiency were studied. Pb^{2+} and Cu^{2+} ions were completely extracted at pH= 5-8 after stirring for 5 minutes. The minimum quantity of acid for stripping the ions from SBA- G1.5 was examined and the pre-concentration factor of the technique was 233 for both of ions. Under the optimized conditions, the linearity of the technique was within 10-40 ng mL^{-1} Pb^{2+} and 2-20 ng mL^{-1} Cu^{2+}. Detection limits for Pb^{2+} and Cu^{2+} were 5.0 and 1.2 ng mL^{-1} and the relative standard deviations (RSD, %, C=15 ng mL^{-1}, n=5) were 2.9 % and 2.1 %, respectively. There was good consistency between the measured and added amount of Pb^{2+} and Cu^{2+} in spiked distilled water which indicates good accuracy of methods. The capability of the method in a real sample was tested in various water samples.

Keywords: *Polyamidoamine dendrimer G(1.5); Preconcentration; SBA-15; Cu2+ and Pb2+; Water samples.*

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INTRODUCTION

Solid-phase extraction is widely employed for trace quantities pre-concentration of the elements in aqueous specimens [1, 2]. Usually, a pre-concentration step before the instrumental measurements is required due to the element's low concentration levels and the complex matrix interfering with the determination [3-5]. The advantages of the solid phase extraction are high concentration factor, simplicity, and low consumption of harmful organic solvents. Up to now, various materials such as green tea leaves [6], composites [7], silanized glass beads [8], silica gel [9], and resin [10] have been used as a solid extractor. These substances involve some

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problems such as weak chemical bonding with metals, low thermal, and mechanical stability. Recently, many researchers have been attracted to nanomaterials due to some of their important physiochemical properties; properties which make them particularly attractive as extraction media. The larger surface area in comparison to bulk particles and materials is one of these properties which increases the nanomaterials adsorption capacity [11-14]. Mesoporous silica materials are one of the nanomaterials that have a great specific surface area, limited pore size distribution range, and high surface concentration of –OH groups that could be easily altered at their silanol groups through grafting with commercial organosilane compounds. These compounds are also useful in aqueous solutions since they possess a hydrophobic surface. Various nanoporous materials have been reportedly used in adsorption applications such as the elimination and pre-concentration of metal ions [15-18], dyes [19-22], radionuclides [23], and anionic species [24,25]. Nevertheless, these instances are inadequate and more studies are required to introduce the new adsorbent or solid-phase extractors.

On the other hand, heavy metals releasing into the environment is still an important issue due to their toxicity and persistence. They impose a considerable threat to the public health and ecosystem. One of the heavy metals is lead which is a possible human carcinogen and a commutative poison. It leads to developing autoimmunity where an individual's cells are attacked by its own immune system. At higher concentrations, lead could cause irreversible brain damage [26,27]. Copper is another heavy metal which is required for the appropriate operating of numerous significant enzyme systems [28], but excess amounts of copper are toxic. For example, Wilson disease is an autosomal recessive disorder resulting in copper toxicity which is the result of copper accumulation in the liver, eyes, and brain [29, 30]. Therefore, Cu^{2+} in water samples is certainly determined by the narrow concentration window between toxicity and essentially. The main sources of lead and copper are mining activities, the textile and leather industries, electric wires, pigments, electroplating, phosphate fertilizers, plumbing manufacturing, wastewater discharge, municipal waste, welding, and galvanized steel [31].

So, it is clear that determining heavy metals in environmental specimens is necessary. The present work is mainly aimed to provide a practically useful and simple method in order to simultaneously pre-concentrate trace quantities of Pb^{2+} and Cu^{2+} in aqueous specimens. Hence, polyamidoamine (PAMAM) dendrimer G(1.5) supported on SBA-15 nanoporous silica (SBA-G1.5) was synthesized and utilized as a novel compound for extraction and pre-concentration of ultra-trace quantities of Pb^{2+} and Cu^{2+} ions in environmental samples. As we know, it is the first use of G(1.5) dendrimer supported on SBA-15 nanoporous silica for pre-concentration of these ions trace quantities.

EXPERIMENTAL

Reagents

Pluronic P_{123} ($EO_{20}PO_{70}EO_{20}$), tetraethyl orthosilicate (TEOS), 3-aminopropyltriethoxysilane, and methyl acrylate were purchased from Sigma-Aldrich (USA). The solvents such as toluene (purity 99 %), HCl (grade 99.8 %), and ethanol (grade 99.9 %) were attained from Merck (Germany). The substances were utilized with no further purifying. Analytical grade nitrate salts of nickel, cobalt, cadmium, zinc, silver, copper, and lead (all from Merck) were with the greatest available purity and were utilized with no further purifying. All tests were carried out using doubly distilled water (DDW). The stock solutions of the metal ions were 1000 mg L^{-1} solution in DDW and the working standard solutions were made by diluting them to the desired concentration.

Apparatus

Using RAYLEIGH WQF-510A apparatus, the specimen's Fourier transform infrared (FT-IR) spectra were recorded. A TGA Q50 V6.3 Build 189 equipment was used to perform thermogravimetric analysis (TGA) in a normal atmosphere with ambient temperature up to 800 °C with a ramp rate of 20 °C min^{-1} in air atmosphere. The quantitative analysis of the species concentration was performed via measuring the absorbance of the solution on a PG-990 flame atomic absorption spectrometer (England PG Company), with an air-acetylene burner and hollow cathode lamps. The instrumental factors included: wavelengths 273.3 and 324.7 nm for Pb^{2+} and Cu^{2+} respectively, slit width of 0.4 nm and a lamp current of 5.0 mA. The FAAS of other cations was determined under the proposed circumstances for each metal.

Synthesizing the mesoporous SBA-15

SBA-15 was made with Pluronic P123 triblock

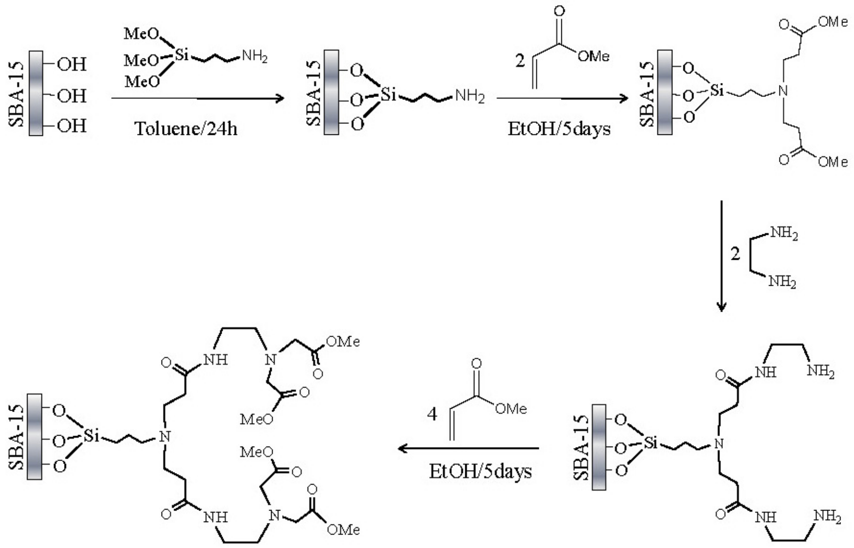

Fig. 1. Preparation of SBA-15 Silica-Supported PAMAM Dendrimers G(1.5)

copolymer as a template [32]. By dissolving 4 g of surfactant ($EO_{20}PO_{70}EO_{20}$) in water/HCl 2M solution, subsequently adding some TEOS (tetraethyl orthosilicate), the resultant mixture was agitated at 40 °C for 8 h and later on left at 100 °C for 15 h. The synthesis mixture includes the molar composition as follows: 1 TEOS : 5.854 HCl: 0.0168 P123 : 162.681 H_2O. Subsequently, the white matter was filtered, rinsed, dried, and calcined for 6h at 550 °C in a normal atmosphere. The final product represented the BET surface area of 750 $m^2\ g^{-1}$ and a pore diameter of 6.5 nm, in terms of adsorption-desorption of N_2 at -200 °C.

Synthesis of G(1.5) dendrimer held on SBA-15

In order to eliminate surface humidity, first by drying calcined SBA-15 (15 g) under vacuum at 100 °C for 1 h, it was added to 100 mL of boiling anhydrous toluene. 3-aminopropyltriethoxysilane (9 mL) was inserted into this combination, which was then agitated and refluxed at 110 °C for 12 h. Through filtration, the white amine-functionalized SBA-15 was separated, thoroughly rinsed with toluene, and air-dried. Methyl acrylate (twice the mole number of aminosilane) and aminopropyl-functionalized SBA-15 were agitated in dry ethanol for 5 days at 40 °C. Dry ethanol (3×50 mL) was used to cool, filter, and rinse the mixture. In a vacuum, the residual solvent was eliminated. The product was SBA-G(0.5). Ethylenediamine (13 mL) was additionally inserted to SBA-G(0.5) in dry ethanol, subsequently, the mixture was agitated for 5 days at 40 °C. After cooling, filtration, and rinsing the powder product SBA-G(1), it was dispersed in dry ethanol once more and methyl acrylate (four folds of aminosilane's mole number) was added. For 5 days, the mixture was agitated at 40 °C. The resultant G(1.5) dendrimer supported on SBA-15 was isolated by filtration. Fig. 1 shows the scheme of the prepared sorbent.

Sample extraction procedure

The general extraction procedure using the SBA-G(1.5) involved adding 15 mg of SBA-G(1.5) to suitable volumes of 2 mg L^{-1} solution of Pb^{2+} and Cu^{2+} and stirring the mixture for at least 5 mins. Afterward, the adsorbent was filtered and the extracted ions were stripped utilizing 15 mL of 3.0 mol L^{-1} solution of nitric acid. Ultimately, the Pb^{2+} and Cu^{2+} content in the stripped and the extracted solution was defined by FAAS.

RESULTS AND DISCUSSION

Characterizing SBA-G(1.5)

Fig. 2 indicates the FTIR spectra of G(1.5) dendrimer supported on SBA-15 surface. The broad peaks at 800 and 1180 cm^{-1} are typical of Si–O–Si bands related to the silica network. The weak peaks at 2940 and 2830 cm^{-1} are associated with C-H stretching vibrations. The broad peak at 3380 cm^{-1} is allocated to N-H stretching of the amide groups and O-H of the adsorbed water. Moreover, the bending vibration of -N-H appears

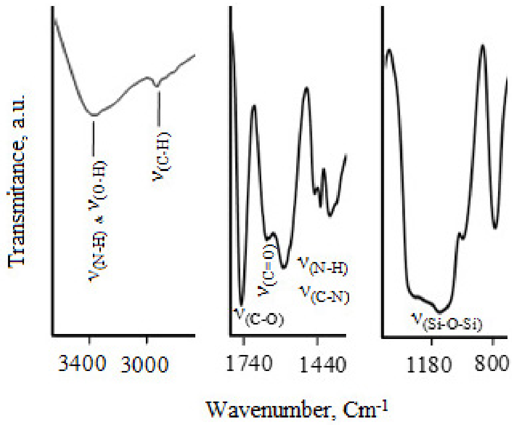

Fig. 2. IR spectrum of SBA-G(1.5)

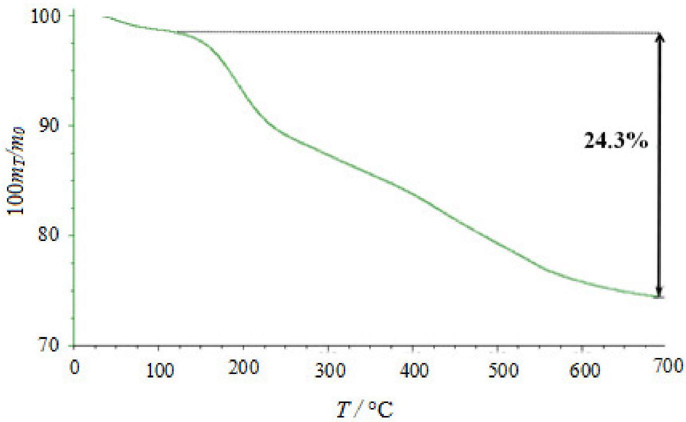

Fig. 3. Thermal analysis curve for SBA-G(1.5)

in 1548 cm^{-1}. A sharp peak at 1740 cm^{-1} is due to the esteric C-O group and another peak at 1645 cm^{-1} shows the presence of the carbonyl group in the structure [33].

The thermal analysis curve for SBA-G(1.5) is represented in Fig. 3. It is obvious that the sample lost weight between 25 and 130 °C, related to the water desorption. The rest of the curve (130-700 °C) indicated continuous and very slow weight loss. To calculate the dendrimer quantity in the sample, the weight loss within 130 and 700 °C was utilized (base on the organic decomposition 24.3 %) which was almost 0.23 mmol (PAMAM) g^{-1} [33].

The effect of pH on the extraction efficiency of Cu^{2+} and Pb^{2+} ions

The pH is a key parameter influencing the metal ions elimination from aqueous solutions. The impact of pH on metal sorption is associated with the ionization state of the adsorbents' functional groups and the metal chemistry in the solution affecting the accessibility of binding sites. The extraction of the Pb^{2+} and Cu^{2+} ions by the SBA-G(1.5) adsorbents was evaluated at different pH values in the range of 2.0 to 8.0. The changes in the solution pH were created utilizing 1 mol L^{-1} solutions of sodium hydroxide or nitric acid, for which the results are provided in Fig. 4. It is observed that Pb^{2+} and Cu^{2+} are quantitatively extracted via the SBA-G(1.5) in the pH range of 5-8, owing to charge-dipole interaction between the nitrogen atoms of SBA-G(1.5) and metal ions. However, at greater acidic media (pH ≤ 5), the adsorbent's nitrogen atoms are protonated while reducing the complexes' stability. Similar results were reported in previous studies [34-36].

Optimization of SBA-G(1.5) amount

In order to determine the best amount of required SBA-G(1.5) for maximum extraction of

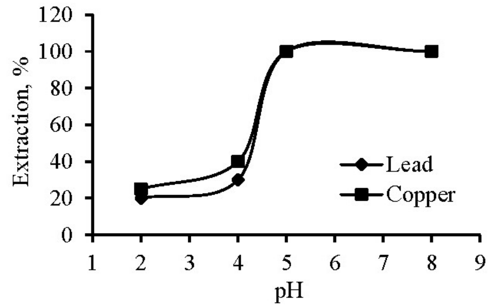

Fig. 4. Effect of pH on the percent of Pb^{2+} and Cu^{2+} ions extraction

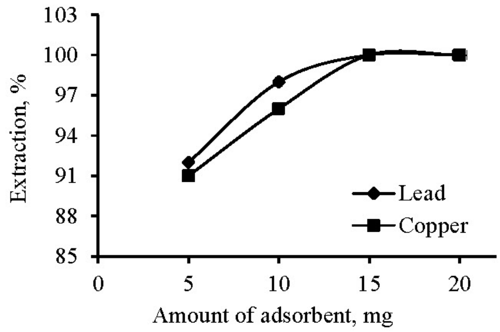

Fig. 5. Effect of the amount of SBA-G(1.5) on the percent of Pb^{2+} and Cu^{2+} ions extraction.

Pb^{2+} and Cu^{2+} ions, experiments were conducted using different amounts of the adsorbent. As seen from the results in Fig.5., initially, the extraction efficiency of Cu^{2+} and Pb^{2+} ions were increased with the amount of SBA-G(1.5) and finally, this reaches just about a constant value. This could be attributed to the higher number of available adsorption sites with the adsorbents increasing amount from 5 to 15 mg. At adsorbent dosages of 15 mg, Pb^{2+} and Cu^{2+} ions could be quantitatively extracted and extraction efficiency reaches about 100%. At higher adsorbent dosages (>15mg), there is significant unsaturation of adsorption sites and the number of available adsorption sites is more than the number of Pb^{2+} and Cu^{2+} ions in solution. Similar results have been observed in the previous study on the extraction of Pb^{2+} and Cu^{2+} ions with functionalized mesoporous silica materials [13,14,37]. The later extraction tests were carried out using the minimum optimal value of 15 mg of SBA-G(1.5) since Pb^{2+} and Cu^{2+} could be quantitatively extracted utilizing 15 mg of the adsorbent.

The impact of the extracting time on extracting efficiency

The impact of time on the extraction efficiency was studied using the addition of 15 mg of SBA-G(1.5) to 25 mL of some solutions including 50 mg of Pb^{2+} and Cu^{2+} ions at pH= 6 and ambient temperature. The solutions were stirred from 3 to 20 mins. The findings are presented in Fig. 6 and it is easy to note that the removal rapidly increases during the initial stage, but this trend lessens over time. The fast adsorption procedure could be ascribed to the occurrence of numerous active sites on the SBA-G(1.5) and robust attraction forces between Pb^{2+} and Cu^{2+} ions and the adsorbent's active functional groups. These findings were consistent with the previous study [13,14,37]. Based on the data, before 5 mins, the extraction efficiency of Pb^{2+} is more than Cu^{2+}, but after 5 mins more than 98 % of the total Pb^{2+} and Cu^{2+} content is extracted. It seems that in a very short time there is a competition between Pb^{2+} and Cu^{2+} ions. But, over time, both ions could be completely extracted and therefore 5 mins were chosen as the optimal contact time for further evaluations.

The impact of stripping solution volume on the extraction efficiency

An appropriate volume of nitric acid was selected using some tests for recovering Cu^{2+}

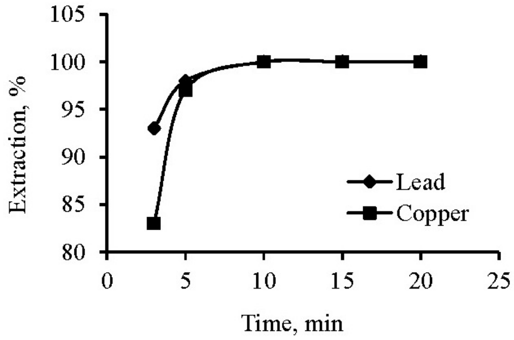

Fig. 6. Effect of contact time on the percent of extraction of Pb^{2+} and Cu^{2+} ions

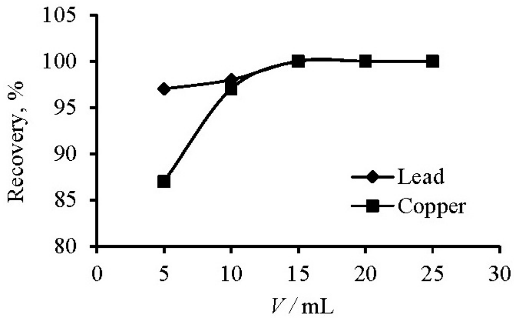

Fig. 7. Effect of stripping acid volume on the percent of Pb^{2+} and Cu^{2+} recovery

and Pb^{2+} ions followed by extracting through the SBA-G(1.5). The ions were exposed to changing acid volumes. The findings indicated that (Fig. 7) with 5 mL of 3.0 mol L^{-1} nitric acid solution, 97 % Pb^{2+} and 87 % Cu^{2+} are recovered while the quantitative elution of both Cu^{2+} and Pb^{2+} ions from the SBA-G(1.5) could be accomplished by 15 mL of 3.0 mol L^{-1} nitric acid solution.

Determination of breakthrough volume

The sample's breakthrough volume of the solution was investigated by dissolving 50 µg of Cu^{2+} and Pb^{2+} ions in 1000, 500, 2000, 3000, and 3500 mL of water, following the proposed process. In all cases, it was found that extracting by SBA-G(1.5) was quantitative. Therefore, the breakthrough volume for the technique needs to be higher than 3500 mL. Considering the recovery of Pb^{2+} and Cu^{2+} ions with 15 mL nitric acid, the pre-concentration factor is 233.

Extraction of Pb^{2+} and Cu^{2+} ions in binary mixtures

The extraction of Cu^{2+} and Pb^{2+} ions from water solutions including diverse metal ions was investigated by taking an aliquot of aqueous solution (25 mL) including 50 µg of Pb^{2+} and Cu^{2+} ions and different quantities of other cations and following the proposed process, for which the outcome is presented in Table 1. It is clear that Cu^{2+} and Pb^{2+} ions in all mixtures are completely retained via the SBA-G(1.5). The adsorbent's high affinity for Cu^{2+} and Pb^{2+} ions is probably related to the complex reactions of Pb^{2+} and Cu^{2+} as intermediate acids with the ligand's amine groups as intermediate bases.

Possible mechanism of ions adsorption onto SBA-G(1.5)

The surface of SBA-15 has a negative charge because of its silanol groups. This negatively charged surface causes a strong attraction to the positively charged ions due to Coulombic interactions. When SBA-15 was functionalized with polyamidoamine dendrimer G(1.5), the selectivity of adsorbent was increased and nitrogen atoms inside SBA-G(1.5) pores (as a relatively soft atom) caused more adsorbent affinity to Pb^{2+} and Cu^{2+} ions (as a soft atom). The adsorbents amine groups as intermediate bases have a high affinity for complex formation with Pb^{2+} and Cu^{2+} as intermediate acids. Depending on the pH, surface groups of the adsorbent (N and O) may change

Table 1. Extraction of Pb^{2+} and Cu^{2+} from binary mixtures

Divers ions	Amount taken, µg	Extraction of Cu^{2+}, %	Extraction of Pb^{2+}, %
Ag^{+}	375	100.0 (1.9)[b]	99.9 (2.5)[b]
Co^{2+}	750	98.7 (1.9)	99.5 (1.7)
Ni^{2+}	750	100.0 (1.7)	100.0 (1.9)
Cd^{2+}	500	98.1 (2.0)	99.0 (2.2)
Zn^{2+}	500	99.4 (1.9)	100.1 (1.9)
Co^{2+}, Ni^{2+}	100	100.0 (2.4)	99.6 (2.4)
Cd^{2+}, Zn^{2+}	100	95.8 (2.1)	99.5 (1.6)
Co^{2+}, Ni^{2+}, Cd^{2+}	100	98.7 (1.8)	99.9 (2.3)
Co^{2+}, Ni^{2+}, Ag^{+}	100	98.2 (2.2)	96.5 (1.8)
Cd^{2+}, Zn^{2+} ,Ag^{+}	100	97.0 (1.9)	98.5 (2.1)

[a] Initial samples contained 50 µg Pb^{2+} and Cu^{2+} in 25 mL water; [b] Values in parentheses are RSDs based on three replicate analysis.

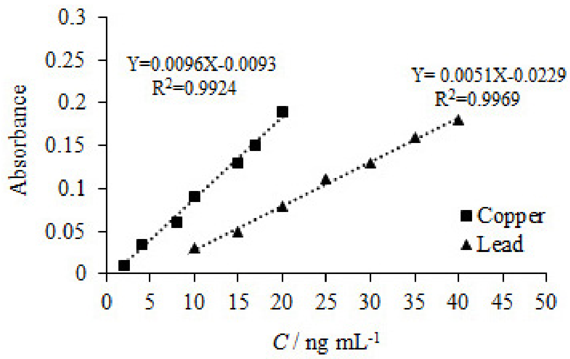

Fig. 8. The calibration graphs of the proposed method for Pb^{2+} and Cu^{2+} ions determination

their charges. At greater acidic media (pH ≤ 5), the adsorbent surface becomes more protonated due to the increase in H^{+} concentration, which decreases the electrostatic interaction between Pb^{2+} and Cu^{2+} ions and adsorbent surface as well as the adsorption efficiency. With increasing pH levels of the ions solution, the surface groups will be deprotonated, resulting in an increase of negatively charged sites which favors the sorption of Pb^{2+} and Cd^{2+} cations due to electrostatic attraction.

Analytical features of the technique

The detection limit, limit quantitation, accuracy, precision, regression, and linear range equations were the parameters utilized for the validation of the technique.

The limit of detection (LOD) for Pb^{2+} and Cu^{2+} was defined by passing a blank solution through the SBA-G(1.5) under the optimum empirical circumstances. The LODs attained from $C_{LOD}=K_bS_bm^{-1}$ for a numerical factor $K_b=3$, were 5.0 and 1.2 ng mL^{-1} for Pb^{2+} and Cu^{2+} respectively. "S_b" shows the blank solution's standard deviation and "m" represents the calibration curve's slope. The quantitation limit, determined as 10 times the S values of blanks, were computed as 6.4 and 1.9 ng mL^{-1} for Pb^{2+} and Cu^{2+} respectively.

The repeatability was assessed to study the accuracy of the technique. For this aim, 5 replicate standard specimens, 15 ng mL^{-1} of Pb^{2+} and Cu^{2+} ion were measured. RSD, % value were found to be 2.9 % and 2.1 % for Pb^{2+} and Cu^{2+}, respectively.

The calibration graphs (Fig. 8) were linear within the range 10-40 ng mL^{-1} Pb^{2+} and 2-20 ng mL^{-1} Cu^{2+} under the optimal circumstances of the general process. The regression equations for Pb^{2+} and Cu^{2+} determination were A=0.0051C-0.0229 (R^2=0.9969) and A=0.0096C+0.0093 (R^2=0.9924) respectively, in which A shows the absorbance and C represents the metal concentration in solution (ng mL^{-1}).

Applying to real sample

In order to study the proposed method applicability in real specimens, it was tried to define Pb^{2+} and Cu^{2+} in different water kinds containing spiked distilled water and river and well water. To 3500 mL of some sample solutions,

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Table 2. Determination of Pb^{2+} and Cu^{2+} ions in various water samples

Sample	Metal	The added amount of each ion, ng mL^{-1}	Found, ng mL^{-1} (RSD, %)[a] (Proposed method)	(Ev-AAS)[b]
Distilled water	Pb^{2+}	30.0	30.1(2.1)	29.7(1.6)
	Cu^{2+}	10.0	9.9 (1.8)	9.8(0.9)
Distilled water	Pb^{2+}	20.0	20.0(2.4)	19.6 (1.9)
	Cu^{2+}	5.0	5.0(2.0)	4.8(1.5)
Karaj river	Pb^{2+}	0.0	<LOD	<LOD
	Cu^{2+}	0.0	4.0(1.6)	3.9(1.0)
Karaj river	Pb^{2+}	30.0	29.9(2.2)	30.1(2.3)
	Cu^{2+}	10.0	13.8(2.0)	14.0(1.9)
Well water	Pb^{2+}	0.0	<LOD	<LOD
	Cu^{2+}	0.0	6.1(2.0)	6.3(1.5)
Well water	Pb^{2+}	30.0	30.2(1.8)	30.2(1.7)
	Cu^{2+}	10.0	15.8(2.0)	16.1(2.1)

[a] RSD, % based on three replicate analysis; [b] Measurements were done after 233 times concentration by evaporate

Table 3. Comparison of the proposed method with the previously reported Pb^{2+} and Cu^{2+} ions determination methods using modified SBA-15

Adsorbent	Ion	*PF*[a]	*ET*[b] / min	*LOD*[c] / ng mL^{-1}	pH	Ref.
SBA-15/Diphenyl Carbazon/ SDS	Cu^{2+}	100	15	0.21	7-8	1
SBA-15/ Guanidin	Cu^{2+} Pb^{2+}	100	10	0.6 4.5	3-8	2
SBA-15/Diethylenetriamine	Cu^{2+} Pb^{2+}	100	15	1.4 5.5	3-8	14
SBA-15/8-Hydroxyquinoline	Cu^{2+}	50	15	1.0	4.5-7	30
SBA-15/ G(1.5) dendrimer	Cu^{2+} Pb^{2+}	233	5	1.2 5.0	5-8	This work

[a] Preconcentration Factor; [b] Extraction Time; [c] Limit of Detection

specified amounts of Pb^{2+} and Cu^{2+} ions were added and nothing was added to some solutions. For all solutions, the proposed process was followed.

According to Table 2, there was a good consistency between the measured and added quantity of ions in the spiked samples that indicates the methods capability for pre-concentration and determination of Cu^{2+} and Pb^{2+} ions in various water types.

The method was validated by comparing the findings obtained by the recommended technique and determined by the flame atomic absorption spectrometry followed by concentration through evaporation. According to Table 2, there is a satisfactory agreement confirming the precision of the recommended technique and its independency from matrix impacts.

Comparing the recommended technique with the formerly reported Pb^{2+} and Cu^{2+} ions retention approaches through modified SBA-15

The capability of the present technique was verified by comparing with comparable previous studies outlined in Table 3. As can be seen clearly, the findings imply that the current work could afford very fast extraction time, high pre-concentration factor, satisfactory pH ranges, and acceptable detection limit [1,2,14,30]. Therefore SBA-G(1.5) could be considered as an excellent adsorbent for the extraction of Pb^{2+} and Cu^{2+} ions.

CONCLUSION

The present work is mainly aimed to develop a simple, practically useful, and fast pre-concentration method in determining the trace quantity of Cu^{2+} and Pb^{2+} ions in water samples. Hence, polyamidoamine dendrimer G(1.5) supported on SBA-15 nanoporous silica as a novel solid extractor for the pre-concentration of these ions was applied successfully. The proposed technique had an enrichment factor of 233 for both ions. The recommended technique was used to determine the ultra-trace quantities of Pb^{2+} and Cu^{2+} ions in distilled water, river, and well water. The main benefits of the current extraction process include low usage of harmful organic solvents, very short sample processing time, and high pre-concentration factor.

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CONFLICT OF INTEREST

Author declares no conflict of interest.

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