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ORIGINAL ARTICLE

Magnetic Solid Phase Extraction of Pb (II) from Water, Rice, and Tomato Samples with Carbonized Cotton Cloth@zeolite Imidazolate Framework-71/ Fe_3O_4/ Polythionine prior to its Flame Atomic Absorption Spectrometric Detection

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KEYWORDS

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Polythionine

ABSTRACT: A sustainable fabricated sorbent, carbonized cotton cloth/ zeolite imidazolate framework-71/ Fe_3O_4/ polythionine (CC@ZIF-71/Fe_3O_4/PTh), was fabricated then utilized for separation and preconcentration of lead in tomato, rice and, water samples applying magnetic solid phase extraction (MSPE) tandem Flame Atomic Absorption Spectrometry (FAAS). The fabrication steps of the sorbent were performed by synthesis of zeolitic imidazolate framework-71 nanocrystalline in attending the carbonized cotton cloth and then thionine was polymerized on the surface of CC@ZIF-71/Fe_3O_4. These nanomaterials were adjusted to enhance the applicability of sorbent. Characterization of sorbent was carried out by using FE-SEM, FT-IR spectroscopy, and XRD technique. The magnetic solid phase extraction efficiency and analytical parameters of this proposed method such as pH, sorbent amount, the effect of interfering ions, desorption condition, extraction time, and the amount of chelating agent were examined. The relative standard deviation (RSD, n=10) of Pb was obtained at 3.5%. The limit of detection (LOD) (n = 10) and limit of quantification (LOQ) were determined at 1.7 and 10.0 µg L^{-1}, respectively. The accuracy of the novel proposed procedure was assessed by analyzing certified reference material. Finally, the proposed process was employed to assess lead in water, tomato, and rice samples.

INTRODUCTION

As a consequence of growing industrial wastes and developing urbanization, environmental contamination grows as well. The toxicity of heavy metals is due to a series of intricate procedures that harm human health and other living species. In this case, a large number of heavy metals present in water or food even if they have low concentrations (<1 mg L^{-1}) can be poisonous [1]. Some heavy metals are necessary for human metabolism. For instance: Zn has an essential role in agglutination and immunity. Whereas, Cr (III) is utilized in the metabolic process of lipid and protein. Also, Fe has a critical role in cell growth and transporting O_2 in the circulatory system. While oxidation of organic compounds is performed by using Mg and Cu. The crucial metal in the human body for convenient function of the liver is Ni, on the other hand, some of the Ni compounds are health hazards and significantly poisonous, like nickel sulfide and nickel carbonyl [2]. Lead, Cadmium, Mercury, and Arsenic are

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among the group of heavy metals, even in very small amounts, which are dangerous for humans' health [3]. In recent decades, analytical chemistry researchers have investigated the area of elemental analysis, particularly analysis of toxic heavy metals [4].

Thus, the direct trace determination of heavy metals that have low-level concentrations in water, food, and other environmental samples is extremely essential. Plus, quantification of low concentrations of heavy metals is hard just by utilizing instrumental methods. In this regard, separation and preconcentration processes of heavy metals are performed by solid phase extraction (SPE), utilizing dispersive liquid-liquid microextraction (DLLME), dispersive solid-phase extraction (DSPE), and solid phase microextraction (SPME) [3-10] Between these methods, SPE is a simple and efficient procedure which can obtain results quickly [2,3,9-12]. Besides, for accurate determination and quantification of heavy metals, different spectrometry methods were utilized in previous literature, including flame atomic absorption spectrometry (FAAS) [13-15], electrothermal atomic absorption spectrometry (ETAAS) [17], laser ablation inductively coupled plasma-mass spectrometry (LA-ICP-MS) [18], inductively coupled plasma mass spectrometer (ICP-MS) [19], inductively coupled plasma optical emission spectrometer (ICP-OES) [20].

Flame atomic absorption spectrometry (FAAS) has provided ease-of-use, cost-effective operation with high performance and it is one of the basic methods for trace determination of components. [13-16, 21]. Magnetic solid-phase extraction (MSPE) has garnered as a novel sort of solid-phase extraction, MSPE has some benefits compared to other techniques which are cost-effective, great recovery, better enrichment factor, diminution of dangerous solvent utilization, acceptable elimination of interfering substances, and also it can be coupled with various techniques [22-24]. The surface property, structure and sort of sorbent are notably influenced by the yield and selectivity of SPE, various sorbents were employed for the determination and quantification of heavy metals such as magnetic-activated carbon cloth [25], graphene oxide/Fe_3O_4@polythionine [26], carbon nanotubes [27] polymer resin [2, 4].

Carbon-based materials have specific chemical and mechanical properties, and because of that they have obtained lots of attention over the last few years [22, 25-27]. Within carbon-based materials, carbonized cotton cloth (CC) is considered, a significant substance, as sorbent to extraction and enrichment of heavy metals from real matrices [25]. CC provides lots of advantages including substantial surface-to-volume ratio, easy modification, and low-cost fabrication. CC is capable of being produced by utilizing cotton, linen, cloth, or felt which has multiple advantages, for example: easily accessible, cost-effective fabricating process, easy and efficient fabrication route, and environmentally friendly [28,29] In addition, the performance of functionalized CC has considerably enhanced in comparison to pure CC. For this purpose, CC has been functionalized by various compounds. For instance: Fe_3O_4 [30], Polycrystalline zirconium metal-organic framework [31], ZnO@MOF@PANI [32], MIL-101(Cr) [33].

Magnetic nanocomposite materials, like Fe_3O_4, introduce advantages including increasing the extraction efficiency of target substances by creating a high porous structure, and compared to non-magnetic sorbates, their separation from sample environments doesn't need any special tools. The magnetic nanocomposite is used as a sorbent in the pre-concentration and separation of heavy metals and it can fulfill the principles of green analytical chemistry. [34-36]

Metal-organic frameworks (MOFs), a category of hybrid crystalline substances with hollow structures comprised of clusters with metal ions and organic ligands as their chains, are widely used in separation, sensor, gas storage, catalysis, and drug delivery. Moreover, particular adsorption affinity, large Surface-to-volume ratio, sufficient resistance, and simple synthesis processes are MOFs' great advantages [32,33, and 37]. In the literature survey MOFs are used as sorbent in the preconcentration and determination of heavy metals in real samples because of their significant benefits. [36,38]

Zeolite imidazolate frameworks (ZIFs), a member of the MOFs group, have great stability. ZIFs consist of a tetrahedron frame of metal clusters and an imidazole bridge [37, 39] ZIF-71 is one part of the large family of ZIFs and it can be synthesized by using zinc acetate and 4,5-dichloroimidazole at room temperature [40]. ZIF-71 is a porous crystal substance with notable surface area, permanent hollow structure, great stability, facile synthesis and, cost-efficiency which makes ZIF-71 a great candidate for effective separation and sorbents [41]. The great surface-to-volume ratio causes the better adsorption of target substances on the ZIFs with high efficiency. Thus, for sample preparation process they can be used as a reliable choice [12, 39]

A viable methodology to raise the efficiency of sorbents is a modification of sorbent by using conductive polymers (CPs). The CPs have been extensively used in the extraction and determination of heavy metals, like polythionine, polyaniline, polypyrrole and, polythiophene [13, 42-44]. Polythionine (PTh) illustrates several qualities such as reasonable stability, ease of synthesis, π-π interaction, and great surface area [26, 42, and 45] which make PTh a proper choice to use as a modifier for extraction or isolation of heavy metal in this work.

Organic ligands are frequently employed as chelating agents in order to enhance the separation and preconcentration of heavy metal ions. Among these chelating agents, 2-(2-benzothiazolylazo) orcinol (BTAO) has been extensively utilized in the separation and preconcentration of multiple metal ions from diverse real samples [46].

In the current study, ZIF-71, Fe_3O_4, and PTh were fabricated in the presence of carbonized cotton cloth to prepare the advanced sorbent. BTAO as a chelating agent was applied in MSPE to enrichment and isolation of lead (Pb). Newly fabricated sorbent was subjected to characterization through the utilization of Field-emission scanning electron microscopy (FE-SEM), X-ray diffraction (XRD) spectra, and Fourier Transform Infrared Spectroscopy (FT-IR). Several analytical conditions such as the amount of sorbent, pH level, Desorption condition, and sample volume were investigated and optimized. CC@ZIF-71/Fe_3O_4/PTh, as an MSPE-sorbent, was employed for the purpose of detecting Pb (II) in water and food samples by using flame atomic absorption spectrometry (FAAS).

MATERIALS AND METHODS

Materials

A Shimadzu atomic absorption spectrometry (FAAS) (AA-680 (Kyoto, Japan)) was employed for the purpose of monitoring Pb at 283 during the experiments, utilizing an air-acetylene flame as the atomizer. The carbonization of commercial cotton cloth was achieved by subjecting it to a laboratory tube furnace at a temperature of 1200°C (Exiton, Iran). In order to characterize the fabricated CC@ZIF-71/Fe_3O_4/PTh Fourier transform-infrared (FT-IR) spectra were employed, utilizing a Tensor 27 FT-IR spectrometer (Bruker, Germany). The X-ray diffraction (XRD) spectra were recorded and analyzed using Cu Kα radiation (λ = 1.5406 ˚A) on an X'Pert PRO MPD X-ray diffractometer (PANalytical Company, Netherlands). Field-emission scanning electron microscopy (FE-SEM) was obtained through the utilization of a Mira 3-XMU (Tescan, Czech Republic). All the pH determinations were evaluated by applying a WTW Inolab pH meter (Weilheim, Germany).

Chemicals and reagents

High-purity chemicals and analytical reagent grades were utilized for all fabrication and measurement steps, with no additional purification. A purchase was made of a commercially available cotton fabric, which consisted of uniformly woven 100% cotton fibers using a tabby weave, from the Tehran Grand Bazaar. HPLC grades of nitric acid, hydrochloric acid and, acetic acid were obtained from Merck (located in Darmstadt, Germany). Zinc acetate, phosphoric acid (H_3PO_4) 85%, and 4,5-dichloroimidazole were purchased from the renowned supplier Sigma-Aldrich located in Taufkirchen, Germany. Nitrate salt of Pb (II) (Pb $(NO_3)_2$), iron (II) chloride tetrahydrate ($FeCl_2.4H_2O$), Ethanol (C_2H_5OH), methanol (CH_3OH), chloroform ($CHCl_3$), ammonia (NH_3, 25%), hydrogen peroxide (H_2O_2, 30%), iron (III) chloride hexahydrate ($FeCl_3.6H_2O$), thionine (Th) acetate (85%) and nitric acid (HNO_3) were bought from Merck company (Darmstadt, Germany). Ultrapure water (Millipore, Bedford, MA, USA) was utilized throughout all the experiments. The preparation of 2-(2-benzothiazolylazo) orcinol (BTAO) was carried out by a previously published method [46].

Preparation of sorbent

The fabrication of the sorbent that applied in the current research was performed at the research laboratory of

Islamic Azad University, South Tehran Branch, Iran.

Synthesis of carbonized cotton cloth

For the fabrication of Carbonized cotton cloths (CC), a previously reported procedure was utilized: [47]. a purchased plain weave commercial cotton cloth was cut into squares with a size of 6.4 by 6.4 cm^2. Before the carbonization processes, square pieces of cotton fabric (1 g) were eluted by non-ionic detergent and distilled water, they were stirred for 60 min at 60°C to eliminate impurities. Afterwards, dried by using an oven that was adjusted on vacuum condition at 80°C. Firstly, Cotton clothes were activated chemically by using H_3PO_4. To elaborate, cotton cloths were soaked in a 1.5 impregnation ratio of phosphoric acid for one day and then they were dried by using an oven that was adjusted on vacuum condition at 90°C. Secondly, the chemical-activated cotton fabrics were carbonized by utilizing a tube oven with a running temperature of 500°C for 85 minutes under a nitrogen stream and the heating rate was adjusted to 6°C/min. Thirdly, let the CC be cooled at ambient temperature (23 ± 0.5°C) for one night and they were rinsed with distilled water a couple of times. Finally, they were dried by using an oven that was adjusted on vacuum condition at 80°C for 30 minutes to get CC.

Synthesis of CC@ZIF-71/Fe_3O_4

Nanocrystals of ZIF-71 were fabricated using a procedure elucidated by Lively et al [40]. At first, 0.2 g 4,5-dichloroimidazole was dissolved in 15 mL of methanol. Apart from this, 0.07 g zinc acetate was dissolved in 15 mL of methanol, either. Next, these solutions were mixed in a sealed sample vial which had 0.095 g of the CC and, placed at ambient temperature (23 ± 0.5°C) for a duration of one day. Subsequently, methanol was eliminated from the sealed sample vial utilizing a pipette. Then, the obtained materials were dipped in chloroform (60 ml (3 × 20)) for three days. Finally, the synthesized CC@ZIF-71 was dried by using an oven that was adjusted on vacuum condition at 90°C for 1 hour.

Magnetic nanoparticles (Fe_3O_4-NPs) were prepared by chemical coprecipitation procedure [26]. In the first place, 0.246 g of Iron (III) chloride hexahydrate and 0.096 g of Iron (II) chloride tetrahydrate were dissolved in 22.5 mL of distilled water. Next, the solution was poured into a three-necked flat bottom flask in the presence of 0.093 g CC@ZIF-71. The mixture was stirred for 60 minutes at ambient temperature (23 ± 0.5°C). At this time, a suitable volume of ammonia (25% v/v) was added gently until the pH of the solution was adjusted to 10; subsequently, the temperature was enhanced to 80ºC and stirred for 60 min. All these synthesis routes were carried out under nitrogen flow. Then, the resultant product was separated by placing the three-necked flat bottom flask on an external magnet then supernatant was poured out, and the obtained supermagnetic product was isolated from the reaction media. At last, it underwent elution using distilled water and ethanol multiple times and was subsequently dried in a vacuum oven at a temperature of 80°C for a duration of 20 minutes.

Synthesis of CC@ZIF-71/Fe_3O_4/PTh

The preparation of polythionine is based on an oxidative chemical polymerization technique elucidated in previous scholarly publication [42]. In the first step, 0.09g of prepared CC@ZIF-71/Fe_3O_4 was added to 22.5 mL of water in a beaker. Afterwards, 0.06g thionine (Th) and 0.03 g of $FeCl_3.6H_2O$ (catalyst) were dissolved in 12.5 mL water in a round bottom flask, following that the resulting solution was carefully transferred into the beaker combination at regular intervals of 2 minutes. Next, 0.6 mL of H_2O_2 was gradually poured to the resultant mixture at the time of stirring, to act as an oxidizing agent. Polythionine was formed by elevating the temperature of the aforementioned mixture to 50 °C and subjecting it to stirring for one hour until the purple color disappeared. Finally, CC@ZIF-71/Fe_3O_4/PTh was separated by using a powerful magnet and rinsed plenty of times with deionized water, the subsequent drying process was carried out overnight under ambient conditions at a temperature of 23 ± 0.5 °C. The preparation process of hybrid sorbent is shown in Figure 1.

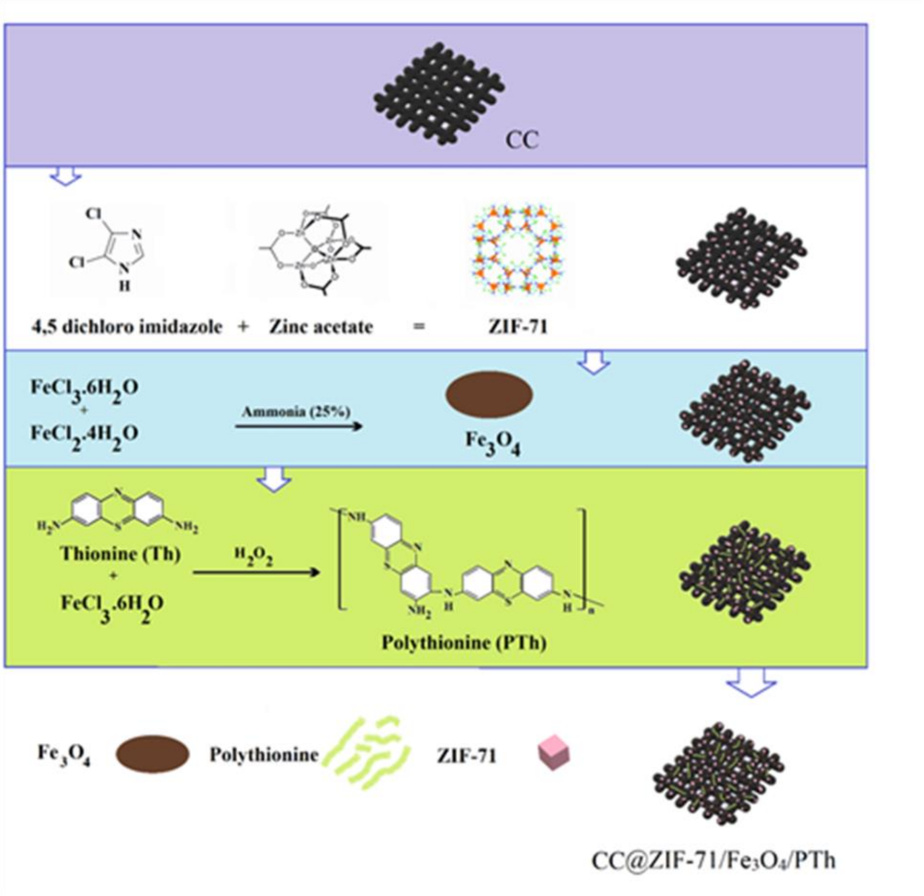

Figure 1. Schematic diagram of all fabrication routes of CC@ZIF-71/Fe_3O_4/PTh.

Magnetic solid-phase extraction procedure

The experimental scheme of the MSPE-FAAS for extraction, preconcentration, and trace determination of Pb (II) is demonstrated in Figure 2. The preconcentration and extraction of the target substance are illustrated as follows: First, CC@ZIF-71/Fe_3O_4/PTh was washed by deionized water, followed by a subsequent drying step in an oven at a temperature of 60 °C for a duration of 1h. 20 mg of dried sorbent was put into the test tube and 0.09 mM 2-(2-benzothiazolylazo) orcinol (BTAO) was put as an extra amount of chelating agent to omit the species that may cause interference in real samples. Separately, adjusting the pH of the spiked sample solution was carried out by adding a buffer, and the desired pH was selected at 7. Next, 0.055 mM BTAO was added as a chelating agent and they were transferred to the test tube and then sonicated for 5 min for the aim of improvement in Pb absorption. Afterward, Strong magnet (Nd-Fe-B-Nd, 0.8 tesla) was placed in the vicinity of the test tube for isolation and separation of the Pb-loaded nanosorbent from the solution, and the upper phase was decanted. In order to remove the analyte from the extraction phase, it was eluted using a volume of 0.5 ml of 2M nitric acid (50% V/V) while ultrasound was radiated for 2 min to enhance the desorption process. Then, the strong magnet was applied once again and the solution which contains the desorbed heavy metal was separated from the sorbent. In the end, the flame atomic absorption spectrometer was employed to determination of the extracted analyte in the final solution.

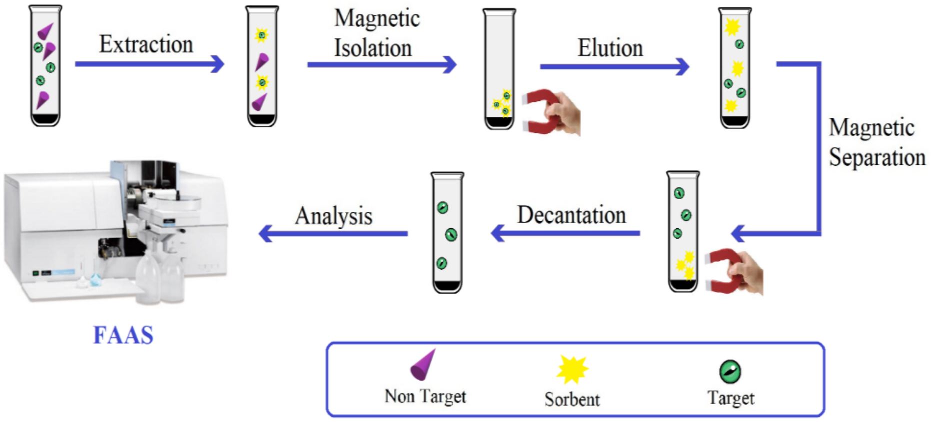

Figure 2. The MSPE-FAAS is depicted in a schematic diagram to assess the concentration of lead.

Preparation of real samples

Some water samples were prepared to validate the applicability of the recommended method in this study. We purchased the Bottled mineral water from a store near the research laboratory in Tehran, Iran. For tap water, we took it from the water faucet in the research laboratory in Tehran, Iran. For the filtering step, we applied a 0.45 µm Millipore filter for each water sample before using it in the recommended procedure.

The fabricated sorbent was utilized for quantification and determination of Pb^{2+} in rice and tomato samples. The rice and tomato were obtained from the local shop in Tehran, Iran. The tomato was cleaned with detergent, water and distilled water, respectively. The rice underwent a process of washing using both water and distilled water. Following this, the tomato was finely chopped. Subsequently,1 g of tomato and 1 g of rice samples were weighed and put in an oven at 120°C to dry at constant weight, subsequently, these constant weight samples were placed into a muffle furnace, then put and kept them in an oven for 12 h in 400°C to turn the samples to ashes. Next, the samples were put at room temperature (23 ± 0.5°C) to cool down. The digestion was carried out by using 10.0 mL of concentrated HNO_3 and 3.0 mL of H_2O_2 (30%), afterward placed again in the oven for 4 h at 400°C. At last, the obtained samples were mixed with 3 mL of 70% $HClO_4$ (w/v) and 3mL of HCl, and they were almost vaporized to dryness. The volume of samples was raised to 1 Liter after putting them in a flask.

RESULTS AND DISCUSSION

Characterization of hybrid sorbent

The developed hybrid structure of sorbent was examined with the aid of FT-IR spectroscopy within the interval of 400–4000 cm^{-1}. The sorbent's FT-IR spectrums are depicted in Figure 3. The bending vibrations of methylene ($-CH_2-$) in the carbonized cotton cloth structure appeared at 755 cm^{-1}. Moreover, the peaks observed at 3393 and 1702 cm^{-1} were assigned to the stretching vibration of the O–H group and the stretching vibration of the ester group within the CC structure, respectively. The carboxylate groups in the CC exhibit asymmetric and symmetric stretching vibrations, with respective frequencies of 1595 and 1423 cm^{-1}. In addition, the spectral band that appeared at 663 cm^{-1} was referred to as the C–Cl stretching vibration of the 4,5-dichloroimidazole ligand, and the C–N in imide structure was located at 1300. Plus, the peak at 3342 cm^{-1} was attached to the frequency of free non-hydrogen bonded N–H bonds, was observed in the nanocrystalline structure of ZIF-71. As you can see, the stretching vibrations of Fe-O detected at approximately 640 cm^{-1} and 3039 cm^{-1} which illustrated this fact, the sorbent has been satisfactorily modified with Fe_3O_4-NPs. Owing to the FT-IR spectrum, the observed peaks at1041 and 2918 cm^{-1} were attributed the stretching vibrations of the C-N bond and the aromatic C-H bond, respectively, in the polythionine compound. Additionally, the N-H scissoring of the primary amino moieties was revealed at 1680 and 1598 cm^{-1}. Furthermore, the peaks at 1431 and 800 cm^{-1} were marked to the aromatic C=C stretching vibration and C-S group of polythionine, respectively. The FT-IR spectra confirmed that the CC@ZIF-71/Fe_3O_4/PTh was successfully fabricated which provides suitable adsorption abilities for the separation of heavy metals.

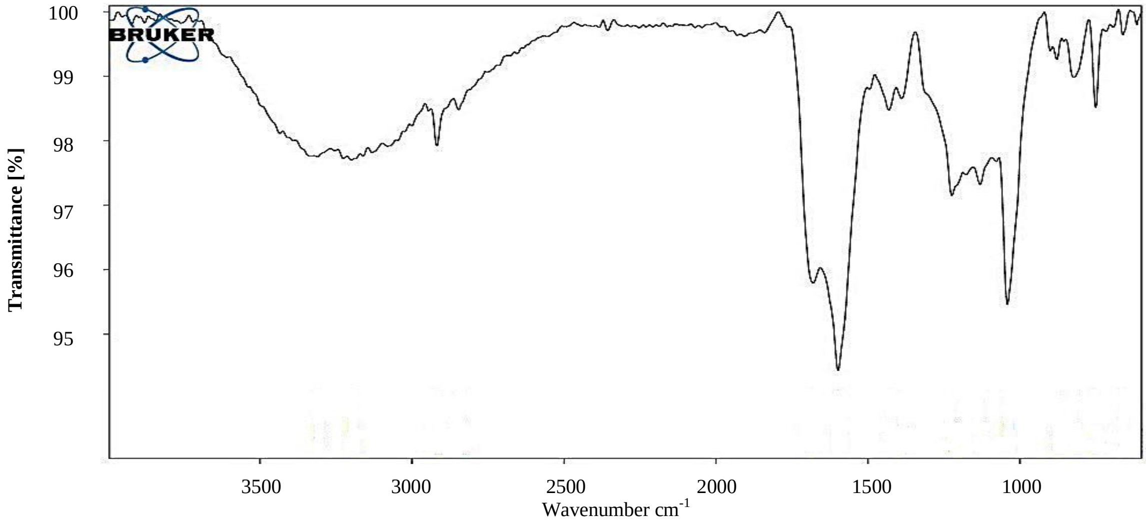

Figure 3. Fourier transform infrared spectra of CC@ZIF-71/Fe_3O_4/PTh.

For additional corroboration of the surface modification of the novel sorbent structure, the last fabricated substances of the synthesis step (CC@ZIF-71/Fe_3O_4/PTh), were analyzed with the aid of an X-ray diffraction technique. As depicted in Figure 4, it is evident that the diffraction peaks of the crystalline reflection of ZIF-71 were at about 5° and 15° 2θ. Furthermore, seven remarkable peaks at 30.30°, 35.63°, 43.31°, 53.64°, 57.20°, 62.76° and 74.42° 2θ which are related to pure cubic spinel crystal of Fe_3O_4 nanoparticles. It has to be pointed out that the notable peaks of Fe_3O_4 -NPs were not influenced by PTh.

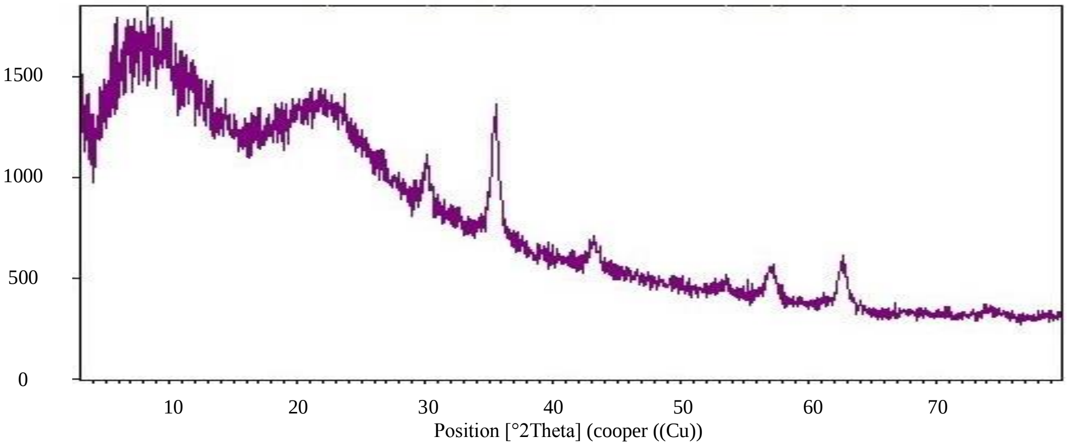

Figure 4. XRD pattern of CC@ZIF-71/Fe_3O_4/PTh.

The surface morphology of pure CC together with CC@ZIF-71, CC@ZIF-71/Fe_3O_4, and CC@ZIF-71/Fe_3O_4/PTh were surveyed using a Field-emission scanning electron microscopy (FE-SEM). As demonstrated in Figure 5a. The CC exhibits uniform and even surface folds, besides the fiber surface seems to be rough. ZIF-71 nanocrystals, possessing a diameter of around 100 nm, were incorporated onto the CC substrate, displaying a commendable dispersal throughout various regions of the CC (Figure 5b). Figure 5c shows that the Fe_3O_4-NPs with an average particle size of 20 nm were efficiently assembled on the CC@ZIF-71 and an agglomeration of Fe_3O_4-NPs was also observed. As evidenced in Figure 5d, the modification of CC@ZIF-71/Fe_3O_4 by PTh was successfully carried out, due to converting the size of them to 30 nm. The FE-SEM results pointed out that the jagged surface of the fabricated sorbent can be attributed to the distribution of

ZIF-71, Fe_3O_4 and PTh nano substances which can increase the surface-to-volume ratio and then separation and preconcentration of heavy metals.

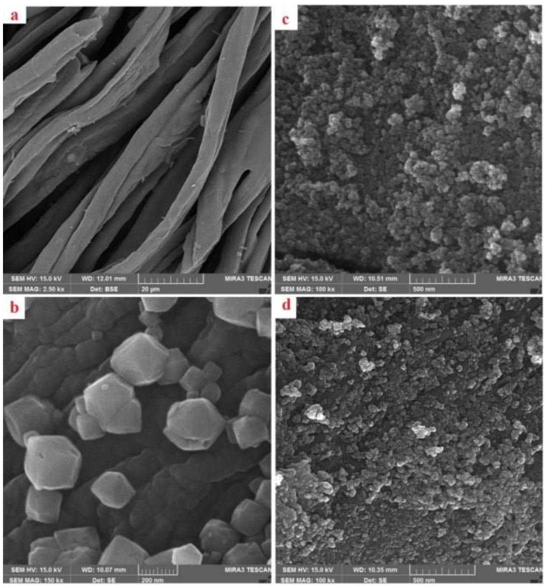

Figure 5. (a) FE-SEM images of CC, (b) CC@ZIF-71, (c) CC@ZIF-71/Fe_3O_4, (d) CC@ZIF-71/Fe_3O_4/PTh.

Development of SPE method

The effect of several analytical factors including sorbent amount, sample pH, amount of chelating agent, desorption condition, interfering ions, extraction time, and ionic strength were studied in this study. To achieve better yield, the optimum procedure for adsorption and extraction of heavy metal ions is performed, which should increase the analytical performance and sensitivity of the method.

Effect of sorbent amount

The impact of the amount of hybrid sorbent on the recuperation of analytes during the process of extraction is an influential determinant. [4] For this reason, the different amounts of CC@ZIF-71/Fe_3O_4/PTh in the range of 1.0 - 40.0 mg were assessed. According to the results which are reported in Figure 6, the recovery of Pb^{2+} climbed with increasing the amount of fabricated hybrid sorbent. However, when the amount of sorbent was raised to more than 20 mg, a slight change in analyte recovery was observed and it decreased slightly. To achieve a high recovery yield and the best adsorption capacity, 20 mg of CC@ZIF-71/Fe_3O_4/PTh was chosen as the optimal quantity of hybrid sorbent for the rest of this work.

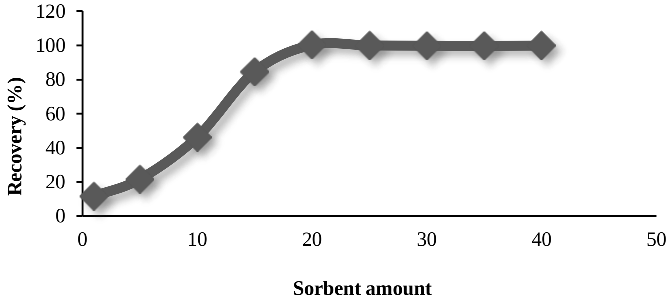

Figure 6. Effect of sorbent amount on extraction recovery of Pb (II).

Impact of sample pH

The pH of the sample solutions [26] has a significant effect on controlling the structure of the metal chelation and determination of the analyte recovery. According to this point, within the specified range of 2.0 - 12.0, an examination was conducted to analyze the influence of the pH of the working sample media on the recoveries of Pb (II). The outcomes are illustrated in Figure 7. Based on data, between pH 2.0 to 4.0 the amount of recovery yield remains stable and after that, the percentage of recovery is claimed to be its highest value at pH 7.0 and then decreased. So, the optimum amount of pH was 7.0 to achieve the greater sensitivity for SPE of Pb (II) and it was picked for all experiments of this work.

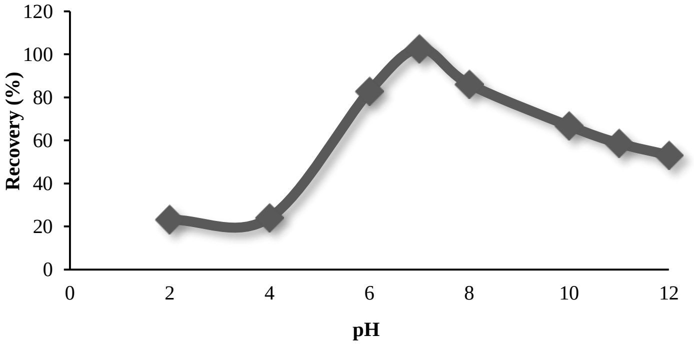

Figure 7. Effect of pH on extraction recovery of Pb (II).

Effect of chelating agent concentration

Utilizing chelating agents is another important factor for the quantification of heavy metal ions which has considerable influence on extraction efficiency in solid phase extraction studies. In the current MSPE, 2-(2-benzothiazolylazo) orcinol (BTAO) was picked as a chelating agent for Pb (II). The amount of BTAO was investigated from 0.005 to 0.07 mM. The outcomes are presented in Figure 8, while the quantitative recoveries were achieved in 0.055 mM of BTAO. So, 0.055 mM of BTAO was adequate for the separation and preconcentration of Pb (II).

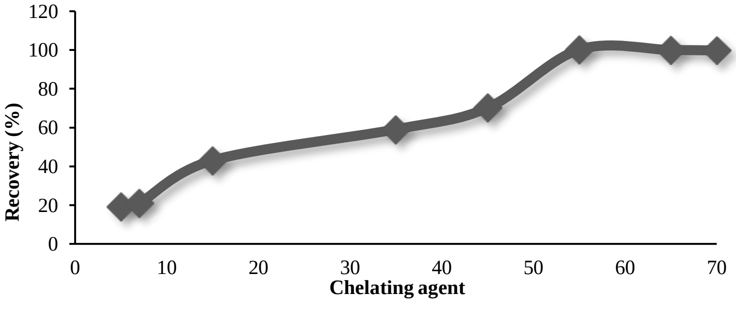

Figure 8. Effect of chelating agent amount on extraction recovery of Pb (II).

Effect of desorption conditions

The higher extraction yield and the maximum quantitative recoveries of heavy metal depend on various parameters, one of the extremely important parameters is the selection of suitable eluent type and volume. [45] Towards achieving the highest recoveries of Pb (II) ion by applying the lowest volume of desorption solvent, hydrochloric acid, nitric acid, and acetic acid were used as eluent. The results which shown in Table.1 indicated that 0.5 mL of 2 M nitric acid presented a higher elution performance thus it was picked as optimal eluent.

Table 1. The influence of different solvents on the recoveries of lead ion (N=3).

Eluent type	Recovery, %
1.0 mol L^{-1} CH_3COOH	90±3
2.0 mol L^{-1} CH_3COOH	95±2
3.0 mol L^{-1} CH_3COOH	92±2
1.0 mol L^{-1} HNO_3	92±5
2.0 mol L^{-1} HNO_3	100±3
3.0 mol L^{-1} HNO_3	96±4
1.0 mol L^{-1} HCl	79±3
2.0 mol L^{-1} HCl	81±5
3.0 mol L^{-1} HCl	87±5

Impact of ultrasonic time

Interaction between analyte and sorbent has required a certain period, time and some other processes. For instance, ultrasonic irradiation time, which is expressed as the extraction time, is applied to improve the adsorption of the analyte on the sorbent. extraction time is one of the important parameters that effects the adsorption efficiency and extraction performance. This parameter was surveyed within the range of 0 – 10 minutes. The results shown in Figure 9 demonstrate that the CC@ZIF-71/Fe_3O_4/PTh has a desirable dispersion capability and provides a relatively short extraction time to obtain optimal efficiency. On the other hand, when ultrasonic irradiation was employed for more than 5 min, a substantial decrease was observed in extraction efficiency. Consequently, 5 min was picked for all experiments.

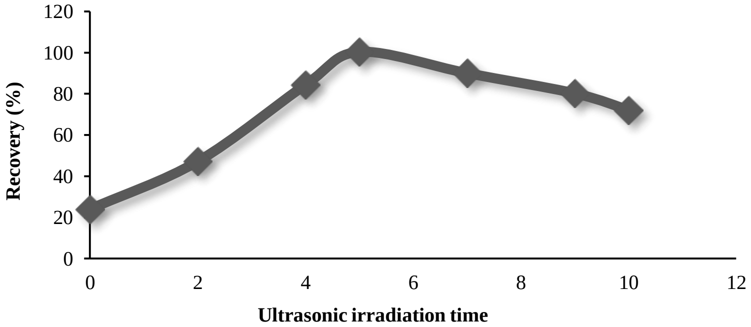

Figure 9. Effect of ultrasonication time on extraction recovery of Pb (II).

Effect of sample media ionic strength

It is a well-known fact that by adding an electrolyte to the sample media, the sensitivity of signals and extraction yields increase which is owing to the salting out effect [45]. In this work, the influence of ionic strength on the recovery percentage of Pb (II) was examined by applying various concentrations of NaCl as a chosen analyte. The results indicate that the peak area of Pb (II) descends gradually by increasing the dosage of the analyte. The reason for this condition is that the active sites of the CC@ZIF-71/Fe_3O_4/PTh were engaged by the salt ions and as a result, the recovery percentage declined. Thus, no NaCl was employed as the optimal amount in all quantification steps.

Tolerance levels for the foreign ions

The existence of various ions in food samples is common which may have reactions with chelating agents and cause interference in the extraction process as well as reducing the recovery of target analyte. Thus, the effect of possible interfering ions on lead-chelate formation was examined by adding various concentrations of metal ions. The tolerance limits were defined as the largest values of the interfering ions which caused variation lower than 5% in the quantification of Pb (II). Table 2 demonstrates the degree of tolerance of each interfering ion. FAAS is known as a selective technique that has a low interference in comparison with the other methods. However, to remove interfering ions from real samples, 0.09 mM BTAO was employed as an excess amount. So, the selectivity of the current procedure is acceptable and can be utilized for extraction and preconcentration of Pb (II) in real samples.

Table 2. Interference study on the determination of lead using MSPE-FAAS.

Foreign Species	Concentration (mg L^{-1})	Recovery (%) [a]
Na^+ ($NaNO_3$)	20000	96±2
K^+ (KCl)	15000	98±2
Cl^- (KCl)	10000	101±2
CO_3^{2-} (Na_2CO_3)	5000	100±2
Ca^{2+} ($Ca(NO_3)_2.4H_2O$)	2000	98±2
SO_4^{2-} (Na_2SO_4)	2000	99±2
Mg^{2+} ($Mg(NO_3)_2$)	1000	99±2
Al^{3+} ($Al(NO_3)_3.9H_2O$)	50	98±2
Co^{2+} ($Co(NO_3)_2.6H_2O$)	50	97±2
Fe^{3+} ($FeCl_3$)	50	97±2
Cr^{3+} ($Cr(NO_3)_3.9H_2O$)	40	100±2
Mn^{2+} ($MnSO_4.H_2O$)	20	99±2
Cu^{2+} ($Cu(NO_3)_2.3H_2O$)	10	98±2
Ni^{2+} ($Ni(NO_3)_2.6H_2O$)	10	99±2
Cd^{2+} ($Cd(NO_3)_2.4H_2O$)	10	100±2
Zn^{2+} ($Zn(NO_3)_2.3H_2O$)	10	98±2
Cu^{2+} ($Cu(NO_3)_2.3H_2O$)	10	98±2

a: Mean ± standard deviations

Analytical performance data

Under the optimized experimental conditions, the Pb (II) ion was determined by employing the proposed procedure. The limit of detection (LOD), limit of quantification (LOQ), preconcentration factor (PF), relative standard deviation (RSD) and, determination coefficients (r^2) were evaluated as the main analytical figures of analyte which are presented in Table 3. The limit of detection (LOD) was evaluated based on the equation [7].

$$LOD = (3\times SD)/m$$

Where: SD is the standard deviation of ten blank readings, and m is the slope of the calibration curve. The LOQ was assessed according to the 10SD/m. PF is calculated as the ratio of sample volume divided by desorption solvent volume. In this study, PF was obtained at 80. The linearity range (LR) of Pb (II) was within the 10.0-700.0 µg L^{-1} in initial concentrations. The coefficients of determination (r^2) after employing the preconcentration process was determined 0.9991, respectively. the LOD (1.7 µg L^{-1}) and LOQ (10.0 µg L^{-1}) provide convenient sensitivity and functionality of the method.

Table 3. The analytical characteristic of MSPE-FAAS in the determination of lead (II).

Parameter	Analytical data
Linear range (µg L^{-1})	10.0 – 700.0
Determination coefficients (r^2)	0.9991
Limit of quantification (µg L^{-1})	10.0
Limit of detection (µg L^{-1})	1.7
Repeatability (R.S.D., %) (n = 10) ($C_{Pb(II)}$ = 100.0 µg L^{-1})	3.5
The preconcentration factor (PF)[a]	80

[a] Preconcentration factor is delineated as the ratio of the volume of the sample and the volume of the desorption solvent.

Application of the proposed method

To demonstrate the validation and applicability of the suggested method, the advanced SPE procedure was examined with certified reference material and spiked samples before being employed in varied food and water samples. The recovery results from certified reference material (GSBZ50009-88) and spiked samples are presented in Table 4 which reveals an acceptable agreement was achieved between the recovered amounts and the certified results. The suggested method was employed for tomato, rice and, water samples and then its accuracy was approved. The founded recoveries were in an adequate range of 88–99% which can be ascribed to suitability of applying the fabricated sorbent separation and accuracy of magnetic solid-phase extraction followed by flame atomic absorption spectrometry for the determination of Pb (II) in food and water samples.

Table 4. The determination of Pb in certified reference materials, water, and food samples by the proposed method (n=3).

Sample	Added ($\mu g\ L^{-1}$)	Found ($\mu g\ L^{-1}$) [a]	Recovery (%)
GSBZ50009-88[b]	10.58 ± 0.68	10.06 ± 0.63	94.5
Mineral water	0.0	<LOD	-
	5.0	4.78 ± 0.22	91.0
	10.0	9.77 ± 0.61	93.0
	20.0	19.54 ± 0.56	96.7
Tap water	0.0	<LOD	-
	5.0	4.12 ± 0.23	88.0
	10.0	9.47 ± 0.63	91.0
	20.0	19.46 ± 0.72	98.0
Sample	**Added ($\mu g\ g^{-1}$)**	**Found ($\mu g\ g^{-1}$) [a]**	**Recovery (%)**
Tomato	0.0	<LOD	-
	5.0	4.74 ± 0.17	91.0
	10.0	8.83 ± 0.34	89.0
	20.0	18.92 ± 0.65	96.0
Rice	0.0	<LOD	-
	5.0	4.98 ± 0.01	93.0
	10.0	8.87 ± 0.53	91.0
	20.0	19.89 ± 0.73	99.0

[a] Mean ± standard deviation, [b] Certified reference ($\mu g\ L^{-1}$)

Comparison with other methods reported in the literature

The obtained analytical figures from the current developed method were compared with different sample preparation, determination, and quantification of Pb (II) from previously reported analytical methodologies and the results were demonstrated in Table 5. As can be seen, the proposed advanced method exhibits adequate accuracy and the LOD comparable with those listed methods. It is worth mentioning that the MSPE-FAAS method has lots of benefits, for instance: cost efficiency, ease of use, quick extraction time, and high performance. In addition, the CC@ZIF-71/Fe_3O_4/PTh exhibited better adsorption capacity and higher extraction performance than most sorbents of other techniques.

Table 5. The present method's analytical features are compared with previously reported methods in the literature for the determination of lead.

Instrument	Extraction method and phase	LOD ($\mu g\ L^{-1}$)	LOQ ($\mu g\ L^{-1}$)	PF	RSD (%)	Refs.
FAAS	SPE, aminothioamidoanthraquinone silica	22.5	NP	NP	≤ 9	[48]
FAAS	Pseudomonas aeruginosa immobilized on multiwalled carbon nanotubes	2.6	NP	50	<10	[49]
FAAS	SPE, Octadecyl silica membrane disks modified with Schiff's base	75	NP	>100	2	[50]
FAAS	SPE, silica gel-immobilized 5-aminoisophthalohydrazide	3.5	11.8	7	1.6	[51]
FAAS	SPE, multiwall carbon nanotubes	2.6	8.6	44.2	<7.7	[15]
FAAS	MSPE, CC@ZIF-71/Fe_3O_4/PTh	1.7	10.0	80	3.5	This work

FAAS: flame atomic absorption spectrometry, SPE: solid-phase extraction, MSPE: magnetic solid-phase extraction, CC@ZIF-71/Fe_3O_4/PTh: carbonized cotton cloth/zeolite imidazolate framework-71/Fe_3O_4/polythionine, NP: not provided

CONCLUSIONS

In this work, first of all, the CC@ZIF-71/Fe_3O_4/PTh was fabricated and then characterized by FT-IR, XRD, and FE-SEM analysis. This fabricated sorbent not only has the benefits of carbonized cotton cloth but also the advantages of utilized modifying agents, like great surface-to-volume ratio, accessibility, substantial reusability, and acceptable mass transfer ability. This practical sorbent was applied for the efficient separation and preconcentration of the Pb (II) ion by utilizing magnetic solid phase extraction in combination with FAAS in water, tomato, and rice samples. The results demonstrate that the spongy structure of fabricated sorbent in combination with FAAS leads to desirable recovery, adequate enrichment factor, and a low limit of detection achieved from water and food samples. In addition, owing to the advantages of the prepared sorbent introduced a cost-effective, easy to use and fast approach for trace screening of heavy metal ions and it also can be applied in other real samples and expect a great adsorption capability for Pb.

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Conflict of interest

The authors declared no conflict of interest.

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