



Magnetic solid-phase extraction based on the Carbonized cotton fabric/zeolite imidazolate framework-71/Fe₃O₄/polythionine followed by atomic absorption spectrometry for cadmium monitoring in water, tomato and cabbage samples

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ABSTRACT

Carbonized cotton fabric/zeolite imidazolate framework-71/Fe₃O₄/polythionine (CCF/ZIF-71/Fe₃O₄/PTh) was fabricated, characterized, and applied as efficient magnetic sorbent in magnetic solid-phase extraction (MSPE) of cadmium from water and food samples before determination by flame atomic absorption spectrometry (FAAS). This modification of carbonized cotton fabric led to making a great surface area and porosity, increase extraction efficiency, and acceptable selectivity. The characterization of this proposed sorbent was performed by X-ray diffraction (XRD), field-emission scanning electron microscopy (FE-SEM), and Fourier transform-infrared (FT-IR) spectroscopy analysis techniques. The impact of several analytical parameters including pH, sorbent dosage, time of extraction, desorption condition, chelating agent concentration, the amount of salt and effect of potentially interfering ions on the selectivity and extraction recoveries of cadmium, were evaluated and optimized. In this proposed methodology, the limit of detection (LOD), the limit of quantification (LOQ), and relative standard deviation (RSD, n = 3) were found to be 0.21 ng mL⁻¹, 0.6 ng mL⁻¹ and lower than 3.0%, respectively. The validation and accuracy of the new advanced procedure were confirmed by applying the proposed procedure for certified reference materials (SRM1570A). Eventually, CCF/ZIF-71/Fe₃O₄/PTh can be utilized as a selective sorbent, for the rapid, accurate and sensitive determination of Cd (II) by magnetic solid-phase extraction tandem flame atomic adsorption spectroscopy (MSPE-FAAS) in water, tomato and cabbage samples.

1. Introduction

Heavy metal ions are classified as toxic contaminants for environmental and life-threatening pollution for human beings. However, some of them like zinc, iron, cobalt, nickel, copper and manganese are considered essential for human health, except when they are

above their maximum acceptable limit concentrations. The other heavy metals for instance As, Cd, Hg and Pb are significantly toxic for living species even at ultra-low concentrations. [1-3] Heavy metals have non-biodegradable nature which is inclined to be concentrated inside the living organisms [3]. One of the most toxic heavy metals is cadmium, which exists in the environmental samples and recent years, because of the developing world, its concentration has

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considerably increased [1]. Cadmium can adversely affect the lungs, liver, and kidneys [2]. It can also cause cancer of the prostate and pancreas [1]. For all these reasons, it is necessary to monitor trace amounts of heavy metals in various real samples [4]. A variety of instrumental methods, such as total reflection X-Ray fluorescence spectroscopy (TXRF) [5], inductively coupled plasma-mass spectrometry (ICP-MS) [6], inductively coupled plasma-optical emission spectrometry (ICP-OES) [7], electrothermal atomic absorption spectrometry (ETAAS) [8], flame atomic absorption spectrometry (FAAS) [9] and inductively coupled plasma atomic emission spectroscopy (ICP-AES) [10], have been employed for the determination of various kind of heavy metals. Real samples have complicated matrices with relatively low concentrations of heavy metals. Therefore, these issues are problematic in the extraction procedure, so for solving these issues, it is required to utilize the preconcentration methods [4]. For preconcentration of heavy metals, the different types of methods including solid phase extraction (SPE) [10], dual-cloud point extraction (d-CPE) [11], dispersive liquid-liquid microextraction (DLLME) [12], and magnetic solid-phase extraction (MSPE) have been applied [13]. MSPE, a more sensitive and practical type of SPE, has a lot of benefits such as low-cost, easier and faster route, decreased consumption of perilous solvent, desirable enrichment factors and better recoveries [13,14]. In addition, the greatest enrichment values and superior recoveries can only be accessed when an advanced sorbent is applied. This sorbent should have reasonable reusability and stability, notable selectivity, huge surface area-to-volume ratio, acceptable porosity and cost-efficient synthesis [14,15]. Fe₃O₄ nanoparticles (Fe₃O₄-NPs) are commonly utilized in hybrid sorbents, which have ultra-high magnetic characteristics and allow the sorbent to be easily separated from the sample solution by external magnetic force [16].

Within carbon-based materials, carbonized cotton fabric (CCF) seems to be a unique element for utilizing as sorbent, due to its notable extraction ability, porous structure, and cost-effective and environmentally-friendly fabrication. [14,17]

Furthermore, its fabrication can be carried out by using cotton, felt or cloth, which are inexpensive and simply available materials and due to their economics and compatibility with green chemistry, have attracted the attention of many researchers [18]. In the literature survey, to increase the performance of the CCF, it has been modified by various materials like Fe₃O₄ [14], cobalt metal-organic framework [19], Co₃O₄/Ni-based MOFs [20], and metal-organic framework/sulfonated polythiophene [21]. Metal-organic frameworks (MOFs) as tunable porous structures have several specific features like large internal surface area, reasonable stability and simple synthesis routes which made them a convenient choice for various utilization in energy and gas adsorption, catalysis, sensor and also separation [21,22]. Zeolitic imidazolate frameworks (ZIFs), a subcategory of MOFs, are composed of metal centers (e.g., Zn, Co) and organic imidazolate linkers with three-dimensional networks. [23,24]. Zeolitic imidazolate framework-71 (ZIF-71), classified among a subclass of ZIFs, offers many attractive properties including high surface to the volume ratio, acceptable chemical and thermal stability, simple, and low-cost synthesis at room temperature [25,26]. Thus, ZIF-71 was selected to be employed as a modifier in this study. Over the last few years, conductive polymers (CPs) have been employed widely in the separation and preconcentration of heavy metals [27-29]. Polythionine (PTh), as part of a large family of CPs, was employed in various studies due to many benefits, for instance large surface area, high thermal and chemical strength, hydrophobicity, good flexibility, and π -interactions [9,30-35]. From our overview of the literature, 2-(2-benzothiazolylazo) orcinol (BTAO) is one of the most popular chelating agents which is utilized for metal ions, has not been used in combination with carbonized cotton fabric to determine and pre-concentrate Cd from real samples [36].

The aim of this research was followed by fabricating sorbent based on CCF which is employed in MSPE for preconcentration and determination of Cd from water and some food samples. Firstly, the cotton fabric was carbonized and then the growth of ZIF-

71 nanocrystals on the CCF surface was achieved. Next, Fe_3O_4 was co-precipitated on CCF/ZIF-71 for offering a unique magnetic sorbent, followed by polymerization of thionine to obtain CCF/ZIF-71/ Fe_3O_4 /PTh. Factors that influenced the efficiency of MSPE have been optimized and evaluated in detail. Finally, the proposed procedure was employed for real matrices analysis by flame atomic absorption spectrometry (FAAS).

2. Experimental

2.1. Chemicals and reagents

All chemicals and reagents were analytical grade and were utilized without further purification. 4,5-dichloroimidazole, zinc acetate and phosphoric acid were obtained from Sigma-Aldrich (Taufkirchen, Germany). Iron (III) chloride hexahydrate, Iron (II) chloride tetrahydrate, ammonia, hydrogen peroxide, nitric acid, hydrochloric acid, perchloric acid, chloroform, methanol, ethanol, thionine (Th) acetate (85%) and nitrate salt of analyte (Cd (II)) were bought from Merck company (Darmstadt, Germany). Commercial cotton cloth (100% cotton) with a plain weave was purchased from a nearby market. Double-distilled water was used for preparing all solutions. 2-(2-benzothiazolylazo) orcinol (BTAO) was prepared according to a reported protocol in the literature [36].

2.2. Instruments

A Shimadzu atomic absorption spectrometric device model AA-640-13 (Tokyo, Japan) with an air-acetylene flame burner was employed for the measurement of Cd, with the wavelength of lamp was 228.8 nm. The X-ray diffraction (XRD) spectra were recorded by applying Cu $K\alpha$ radiation ($\lambda=1.5406 \text{ \AA}$) on the X'Pert PRO MPD X-ray diffractometer (PANalytical Company, Netherlands). Fourier transform-infrared (FT-IR) spectra were obtained using A Tensor 27 FT-IR spectrometer (Bruker, Germany). Field-emission scanning electron microscopy (FE-SEM) images were collected by utilizing a Mira 3-XMU (Tescan, Czech Republic). Carbonization of the cotton fabrics was performed by a laboratory tube furnace at 1200°C (Iran).

2.3. Preparation of Carbonized cotton fabrics

Carbonized cotton fabric (CCF) was obtained by Salehi et al [34]. The commercial cotton fabric with square-cut plain weave ($6.4 \times 6.4 \text{ cm}^2$), was washed with distilled water and non-ionic detergent, and stirred for 60 min at 60°C , then dried at 80°C under vacuum. For the aim of chemical activation of cotton fabric, it was soaked in phosphoric acid with a 1.5 impregnation ratio for a day, followed by drying in an oven under a vacuum at 90°C . To prepare carbonized cotton fabric, the carbonization of chemical-activated cotton fabric was performed by a tube oven at 500°C for 85 minutes under nitrogen protection at a heating rate of 1°C min^{-1} . Then CCF was cooled overnight at ambient temperature ($23 \pm 0.5^\circ\text{C}$) and eluted with distilled water repeatedly. Next, it was dried in an oven under a vacuum at 80°C for half an hour, and the carbonized cotton fabric (CCF) was obtained eventually.

2.4. Preparation of CCF/ZIF-71

ZIF-71 nanocrystals were obtained by applying a method reported in the literature [27]. Briefly, a solution of the metal center was obtained by dissolving 0.07 g zinc acetate in 15 mL of methanol, and then 0.2 g 4,5-dichloroimidazole was dissolved in 15 mL of methanol, individually. afterward, the prepared solutions were merged together in a sealed sample vial in the presence of 0.095 g fabricated CCF, and placed at room temperature ($23 \pm 0.5^\circ\text{C}$) for one day. Next, the methanol was drained out from the vial utilizing a pipette. The last synthesis route was completed by soaking the remaining material in chloroform ($3 \times 20 \text{ ml}$) for 72 hours and then drying under a vacuum at 90°C for 60 min.

2.5. Preparation of CCF/ZIF-71/ Fe_3O_4 /PTh

The synthesis of Fe_3O_4 -NPs was done by the chemical co-precipitation method described in reported studies [33]. 0.093 g of CCF/ZIF-71 was weighed and put into a three-necked flat bottom flask. The solution of iron (II) and (III) was prepared by dissolving 0.246 g of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and 0.096 g of $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ in 22.5 mL distilled water. Subsequently, the obtained solution was transferred

to the above-mentioned three-necked flat bottom flask and stirred for an hour at room temperature (23 ± 0.5 °C) under a nitrogen stream. After that, the pH of the solution was adjusted at 10 using ammonia at 25 % v/v, followed by raising the temperature up to 80 °C and stirring for one hour while the nitrogen was still flowing. Eventually, by employing a strong magnet, CCF/ZIF-71/Fe₃O₄ was divided from the media, washed with distilled water and ethanol four times, and dried in an oven under vacuum at 80°C for 20 min. In the next sorbent preparation step, thionine (Th) was polymerized in the presence of CCF/ZIF-71/Fe₃O₄. For this aim, the oxidative chemical polymerization method was demonstrated in previous work [32]. First of all, 0.06 g of Th and

0.03 g of FeCl₃·6H₂O as a catalyst were dissolved in 12.5 mL water in a round bottom flask and then poured with an interval time of 2 min into a beaker containing 0.09g of fabricated CC/ZIF71/Fe₃O₄ and 22.5 mL of water. Subsequently, 0.6 mL of H₂O₂ as an oxidizing agent was slowly added to the resultant mixture, when it was stirred. Then, for the complete fabrication of polythionine, the temperature of the mixture was growing to 50 °C and stirred for an hour to disappear the purple color of the reaction media. Finally, the CCF/ZIF-71/Fe₃O₄/PTh was separated by an external magnet, rinsed by deionized water multiple times, and dried at room temperature (23 ± 0.5 °C) for 12 h. The diagram of all fabrication steps is illustrated in Figure 1.

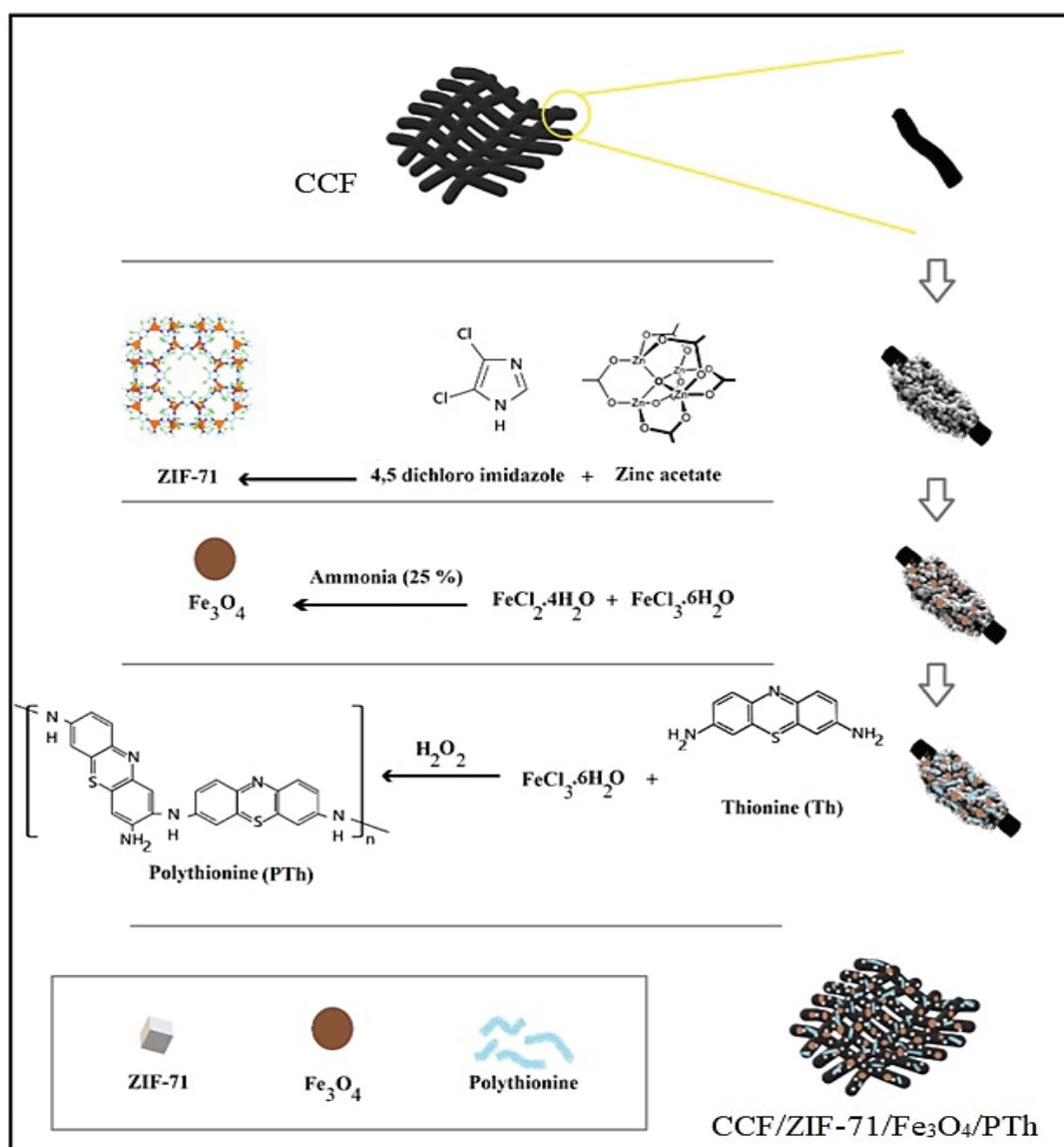


Fig.1. Synthetic pathway for the fabrication of CCF/ZIF-71/Fe₃O₄/PTh

2.6. Preparation of real samples

water samples were prepared to validate the applicability of the novel proposed method. Bottled mineral water was bought from a nearby store and tap water was taken from the water faucet in the research laboratory in Tehran, Iran. Every water sample was filtered applying a 0.45 μm Millipore filter before utilization in the proposed process. Tomatoes and cabbages samples were purchased from a local market in Tehran, Iran. Tomatoes and cabbages were washed with detergent, water and distilled water, respectively. After that, they were cut into small pieces, and then 1 g of each sample was weighed and dried at 120°C to constant weight. The dried samples were put into a muffle furnace, turned to ashes by heating to 400°C and kept at the same temperature for 12 h. After that, the samples were cooled and digested with 10.0 mL concentrated HNO_3 and 3 mL H_2O_2 (30%, w/v), and then remained in a furnace at 400°C once again for four hours. Then, 3 mL concentrated HCl and 3 mL HClO_4 (70%, w/v) was added to the resultant samples and then evaporated to near dryness. Next, they were transferred into a volumetric flask, and their volume were raised to 1 L.

2.7. Magnetic solid-phase extraction procedure

The magnetic solid-phase extraction process was defined in this way: 20.0 mg of $\text{CCF/ZIF-71/Fe}_3\text{O}_4/\text{PTh}$ and washed with distilled water. Then 30.0 mL of the samples/standard solution, containing 55 μM BTAO, with adjusted pH at 7 utilizing buffer was prepared, in addition for real samples, 90 μM of M BTAO was added as an additional dose to eliminate potential interference caused by other species, and added to the glass tube which had the prepared $\text{CCF/ZIF-71/Fe}_3\text{O}_4/\text{PTh}$. The glass vessel was placed into an ultrasonic bath and sonicated for 5 min to make the further adsorption of Cd^{2+} onto the surface of $\text{CCF/ZIF-71/Fe}_3\text{O}_4/\text{PTh}$ sorbent. The $\text{CCF/ZIF-71/Fe}_3\text{O}_4/\text{PTh}$ was collected from sample media via an external magnetic field (neodymium, iron and boron (0.8 tesla) and the water phase was sucked by a pipette. The elution of the isolated phase was carried out by 500 μL of HNO_3 (50%V/V2, M) in ethanol in the presence of ultrasound for 2 min. Finally, the sorbent was separated by employing the external magnet once again and desorbed analyte determined with a FAAS. A Schematic of the MSPE-FAAS process is shown in Figure 2.

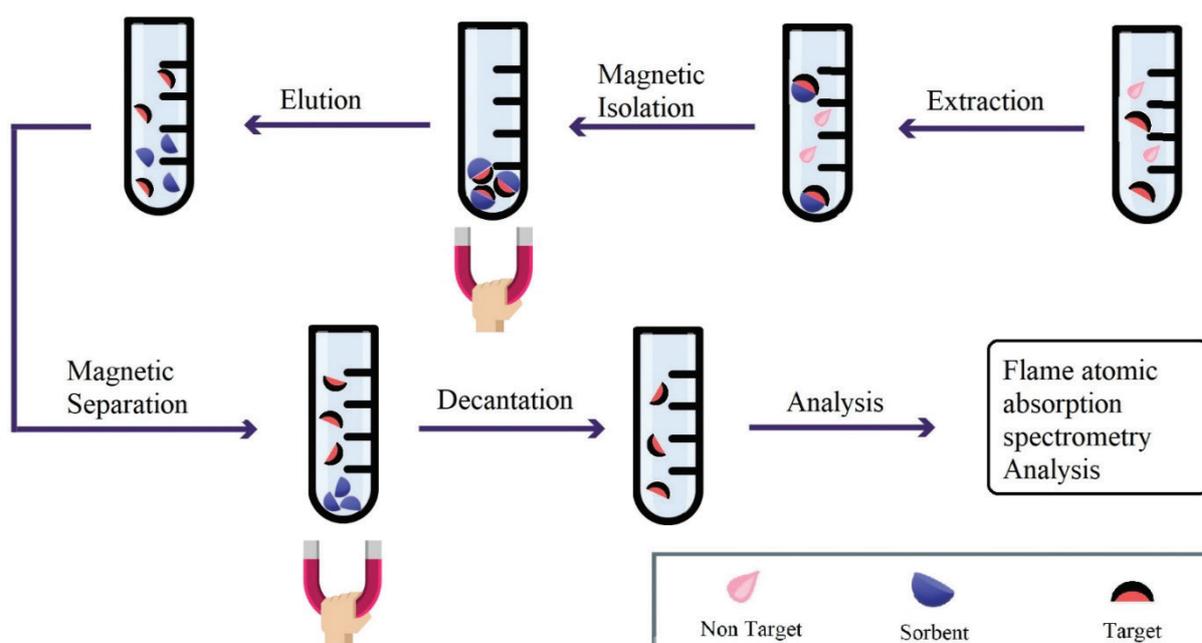


Fig.2. Graphical representation of the MSPE - FAAS procedure for determination of Cd .

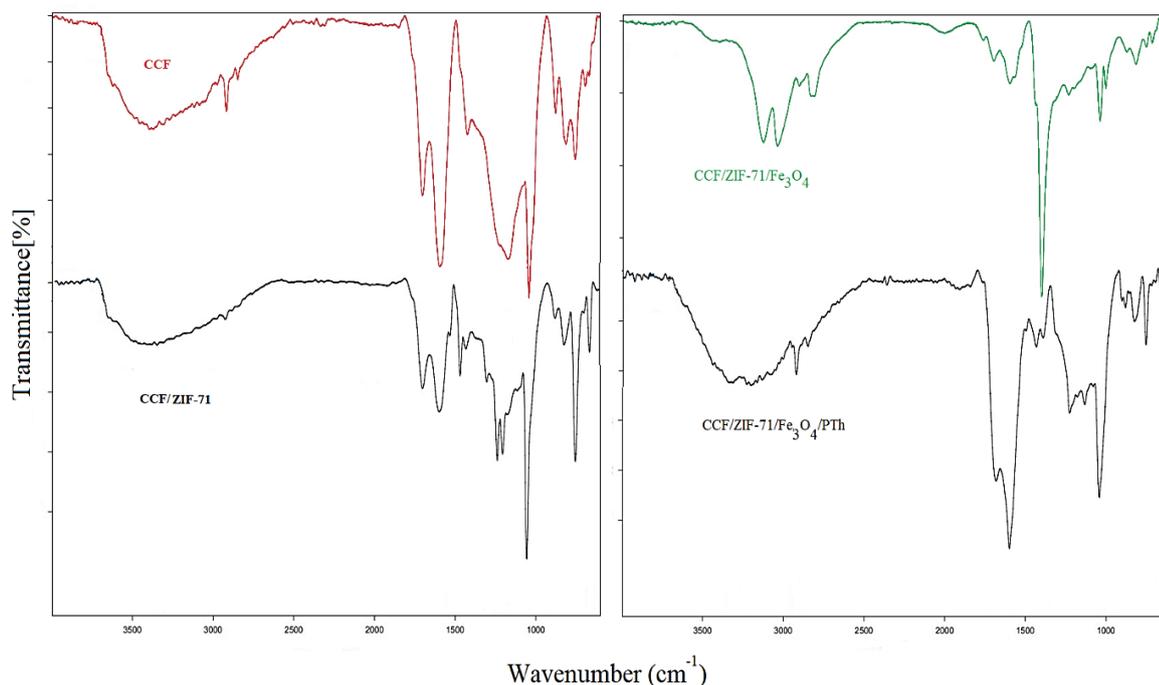


Fig.3. FTIR spectra of sorbent through all the preparation steps.

3. Results and discussion

3.1. Characterization studies

3.1.1. Fourier transform-infrared spectra analysis

For the aim of chemical confirmation of the sorbent structure and the surface modification of that: The CCF, CCF/ZIF-71, CCF/ZIF-71/Fe₃O₄ and CCF/ZIF-71/Fe₃O₄/PTh structures were investigated by employing the FT-IR spectroscopy in the range of 400–4000 cm⁻¹ (Fig. 3). The band of O–H stretching vibration of CCF was situated at 3393 cm⁻¹; While, a stretching vibration of the ester group, asymmetric and symmetric stretching vibrations of carboxylate groups in the structure of CCF are laid at 1702 cm⁻¹, 1595 cm⁻¹, and 1423 cm⁻¹, respectively. a band at 755 cm⁻¹ was associated with methylene's (-CH₂-) bending vibrations of CCF. the imide's peaks in ZIF-71 structure revealed at 1300 cm⁻¹, 1594 cm⁻¹, and 1697 cm⁻¹ were referred to as C–N, symmetric C=O, and asymmetric C=O stretches, respectively. The medium band for C–

Cl stretching vibration of 4,5-dichloroimidazole ligand in the ZIF-71 structure appeared at 663 cm⁻¹. In addition, the band at 3342 cm⁻¹ was attributed to free non-hydrogen bonded N–H bonds and the bands at 1428 and 1464 cm⁻¹ were assigned to N–H bonds of secondary amine nanocrystalline formation of ZIF-71. Two peaks were evident in the range 623–660 cm⁻¹ and 3039 cm⁻¹ which linked to the stretching vibrations of Fe–O in the magnetic nanoparticles. The IR spectrum of CCF/ZIF-71/Fe₃O₄/PTh indicates the presence of PTh, by revealing the peak at 3198 cm⁻¹ due to the N–H stretching vibration and the C–S group revealed a peak at 800 cm⁻¹. The presence of 1041 and 2918 cm⁻¹ bands, characterize C–N stretching vibrations and aromatic C–H stretching vibrations of polythionine, respectively. The peaks at 1680 and 1598 cm⁻¹ were attributed to the N–H scissoring of the primary amino moieties and also the peaks at 1431 cm⁻¹ were associated with the aromatic C=C stretching vibration of polythionine.

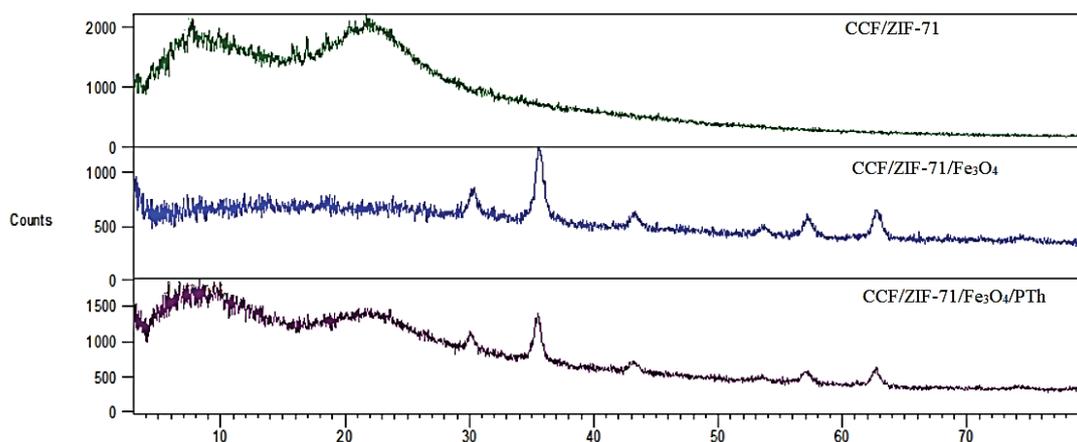


Fig. 4. XRD patterns CCF/ZIF-71 (green colour), CCF/ZIF-71/Fe₃O₄ (blue colour) and CCF/ZIF-71/Fe₃O₄/PTh (purple colour).

3.1.2. X-ray diffraction analysis:

The XRD patterns of the CCF/ZIF-71, CCF/ZIF-71/Fe₃O₄ and CCF/ZIF-71/Fe₃O₄/PTh are demonstrated in Figure 4. The diffraction peaks at 2θ values at 9° and 22.2° are attributed to the graphite carbon and the peaks are about $2\theta = 5^\circ$ and 15° ascribed to nanocrystal structures of zeolitic imidazolate framework-71 in CCF/ZIF-71 pattern. In addition, seven obvious diffraction peaks corresponded to pure cubic spinel crystal of Fe₃O₄-NPs (at 2θ values 30.30° , 35.63° , 53.64° , 57.20° , 62.76° and 74.42°). By comparing CCF/ZIF-71/Fe₃O₄ and CCF/ZIF-71/Fe₃O₄/PTh patterns, it is observed the remarkable diffraction peak of CCF shifted down to 8.2° 2θ , which indicated the great magnetic property of fabricated sorbent. That makes the fabricated sorbent a great choice for applying in magnetic solid-phase extraction.

3.1.3. Field-emission scanning electron microscopy:

A Field-emission scanning electron microscopy (FE-SEM) was utilized for the purpose of verification of the surface morphology of fabricated samples. FE-SEM images of the products in different zooms are shown in Figure 5 (A, B, C and D), respectively. The FE-SEM image of CCF (Fig. 5A) shown that the plain weave fabric structure of CCF had uniform surface morphology. After the crystallization of ZIF-71 on the CCF, the surface of CCF was not smooth anymore and the crystals of ZIF-71 were formed on the surface of

CCF with size of about 91-118 nm and appropriately distributed which can be clearly seen in Figure 5B. Also, Figure 5C was depicted, the cubic spinel crystal Fe₃O₄-NPs framed with the around particle size of 20 nm were properly composed on the CC/ZIF-71 with a less aggregate and more. According to the Figure 5D, the average particle size changed to about 30 nm, so it can be concluded PTh was successfully coated on CCF/ZIF-71/Fe₃O₄. These outcomes illustrated that the modification of CCF by ZIF-71, Fe₃O₄-NPs, and PTh can be the cause of the jagged surface of prepared sorbent which prepared a good condition for applying this sorbent in enrichment, isolation, and determination of cadmium.

3.2. Effect of sorbent amount

A suitable amount of sorbent is absolutely essential for the favorable quantitative recoveries of analytes due to interaction between analytes and sorbent in the reaction media [34]. Because of this, the various amounts of CCF/ZIF-71/Fe₃O₄ /PTh between the range from 1 to 40 mg were utilized in recoveries to determine the best sorbent amount. Figure 6 indicated that the quantitative recoveries for metal ions in the range of 1 to 20 mg were enhanced significantly with the grow of the dosage of sorbent, at amounts higher than 20 mg the signals remained constant with slightly decreasing which is due to insufficient desorption of the analyte from the CCF/ZIF-71/Fe₃O₄ /PTh surface. So, 20 mg of CCF/ZIF-71/Fe₃O₄ /PTh was enough to gain a reasonable outcome.

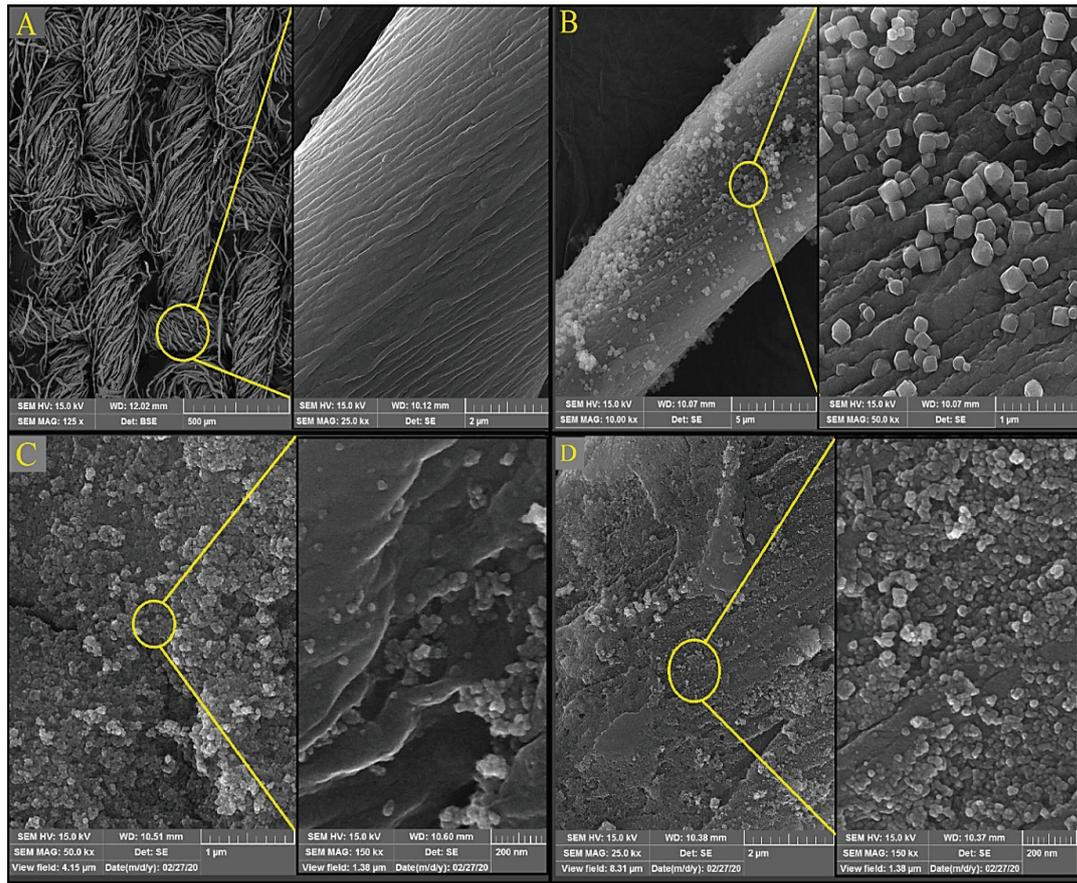


Fig. 5. Field-emission scanning electron microscopy (FE-SEM) images of (A) CCF (B) CCF/ZIF-71 (C) CCF/ZIF-71/Fe₃O₄ (D) CCF/ZIF-71/Fe₃O₄/PTh. Inset: The enlarged view of the nano-array substances and CCF.

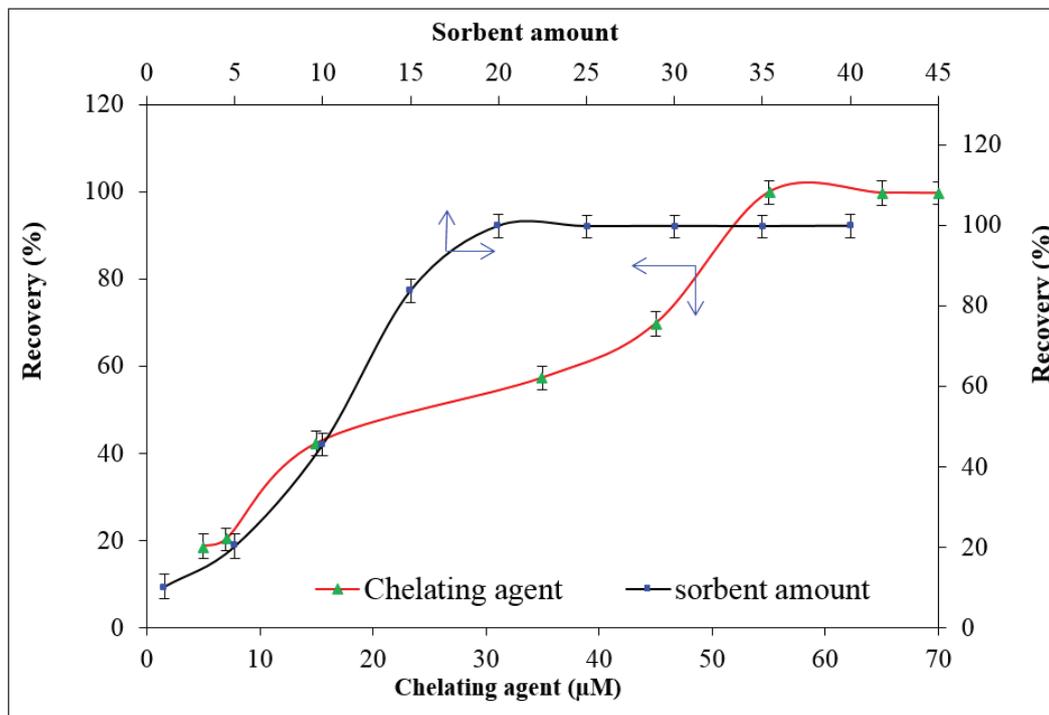


Fig. 6. Effect of CCF/ZIF-71/Fe₃O₄/PTh amount and chelating agent (BTAO) dosage on extraction recovery.

3.3. Effect of pH

In solid-phase extraction studies, the pH of the aqueous solutions is an important parameter which has influence in the formation of metal complexes. To identify the optimum pH value, the impact of pH on the recovery value of cadmium was studied over the pH range 2.0 -12.0. The results are shown in Figure 7 indicated that the recoveries of cadmium were considerably influenced by pH. Between the pH range of 2.0 to 4.0 the adsorption quantity of cadmium was noticeably low, but when the pH exceeded than 4.0, the adsorption of analyte rises considerably and reached a peak at pH 7.0 which was considered as an optimal quantity, after that steady decline was observed. Therefore, the pH at 7.0 was selected as the optimum value for the rest of the study.

3.4. Effect of amount of chelating agent

The amount of chelating agent is an important parameter for following determinations which have influenced extraction efficiency [17]. In the

current magnetic solid-phase extraction protocol, 2-(2-benzothiazolylazo) orcinol (BTAO) was chosen as the capable chelating agent. The amount of chelating agent was investigated in the range of 5–70 μM . Fig.6 demonstrated that the recoveries of cadmium were go up by increasing the amount of BTAO, however after 55 μM BTAO the recoveries of Cd declined steadily. Eventually, cadmium recovery in the 55 μM BTAO is optimal, and all further work was carried out by 55 μM BTAO.

3.5. Effect of elution conditions on recovery

The type of desorption solvent is another essential aspect in the efficiency of the preconcentration process in order to achieve the best desorption of analyte, various eluents (nitric acid (50%V/V, 2M) in ethanol, methanol, and acetonitrile) were examined and the more acceptable desorption efficiency was obtained using nitric acid (50%V/V, 2M) in ethanol. In all subsequent studies, HNO_3 (50%V/V,2 M) in ethanol was used as the suitable eluent that could desorb cadmium effectively.

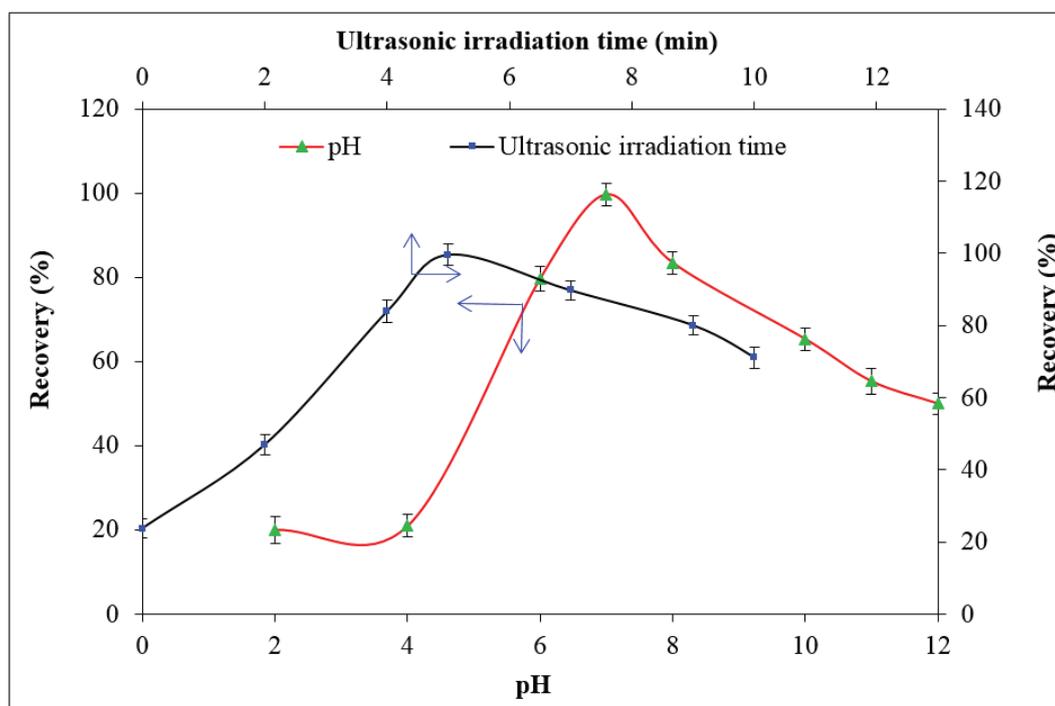


Fig. 7. Effect of ultrasonication time and pH on extraction recovery.

3.6. Effect of ionic strength

It is well known that adding NaCl as an electrolyte in the sample solutions leads to improving the extraction efficiency which is because of the salting-out effect. [37] In the current study, the influence of ionic strength in an aqueous solution on the recovery values of the analyte was evaluated by adding NaCl. By growing the amount of electrolyte, the extraction efficiency of cadmium has been dropped. The explanation for plummeting in recovery percentage is that by enhancing in electrolyte amount in sample media solution, active sites of sorbent were employed by the salt ions. Hence, no NaCl was added for the rest of the study.

3.7. Effect of ultrasonic time

The Cd ions need a particular time and ultrasonic bath to desorption from the CCF/ZIF-71/Fe₃O₄/PTh in MSPE studies. The time of ultrasonic irradiation bath is considered as the extraction time which has an important role in the recovery percentage of analyte and extraction performance. Ultrasonication was applied to the dispersion of fabricated sorbent through sample solution media and interacted with target analytes. Thus, the effect of extraction time was examined in the range from 0 to 10 min. As illustrated in Figure 7, 5 min was adequate for the quantitative determination of Cd. However, after 5 min, a steady decrease in the recovery percentage of the analyte was demonstrated which is due to the return analyte back to the aqueous solution from the sorbent. Accordingly, 5 min was selected as the optimum value.

3.8. Effect of interfering ions

There are various ions in the real samples that may cause interference in the selectivity and reduce the extraction recovery of the analyte in the proposed method [14]. The impact of different interfering ions that may react with BTAO was studied to determine the selectivity of CCF/ZIF-71/Fe₃O₄ / PTh. Therefore, different amounts of interfering ions were added to the standard solutions containing 10.0 ng mL⁻¹ of cadmium, individually. The ratio of tolerance for interfering ions is shown in Table 1, The tolerance limit was determined as the largest number of interfering ions that caused alterations on the recovery percentage of the analyte less than ±5%. For the purpose of eliminating interfering ions resulting from real samples, 90 μM BTAO was used as an extra amount.

3.9. Validation of the advanced method

Several analytical aspects of the proposed method include a limit of detection (LOD), limit of quantification (LOQ), relative standard deviation (RSD), determination coefficients (r^2), and preconcentration factor (PF) were investigated and the obtained results are listed in Table 2. The LOD and LOQ, were calculated based on $LOD = 3S_b/b$ and $LOQ = 10S_b/b$ which b is the calibration graph's slope and the standard deviation of blank solutions is illustrated as S_b , [35] were determined 0.21 and 0.6 ng mL⁻¹, respectively. The calibration curve was constructed by using the spiked sample of cadmium obtained in linear ranges from 0.6-40 ng mL⁻¹ and also 0.9991 was achieved for the coefficient of

Table 1. Interference study of the interfering ions on the determination of 10 ng mL⁻¹ cadmium using MSPE-FAAS

Foreign Species	Tolerance Ratios [Interference-to-Cd (II) ratio ^a]
K ⁺ , Li ⁺ , Na ⁺ , CO ₃ ²⁻ , SO ₄ ²⁻ , NO ₃ ⁻ , F ⁻ , Cl ⁻	800
Ca ²⁺ , Mg ²⁺	500
Al ³⁺ , Pb ²⁺ , Fe ²⁺	70
Co ²⁺ , Fe ³⁺ , Cu ²⁺ , Ni ²⁺ , Cd ²⁺	25

^a Tolerance limit was defined as the largest ratio causing a relative error less than 5% in concentration level of cadmium.

determination. 60 was found as the preconcentration factor and the relative standard deviation (RSD), which was assessed from three replicates of the Cd standard solutions, was 3.0%. These results signified that the advanced procedure is a proper choice for determination of cadmium in water and food samples which has great sensitivity and acceptable accuracy. To assess the applicability and accuracy of the novel proposed methodology in real matrices, different food (tomato and cabbage) and water (tap and mineral) samples were utilized to determination

and preconcentration of cadmium. These aspects were carried out by analyzing the spiked samples with varying amounts of cadmium and a certified reference material of food samples (SRM1570A). The recoveries from spiked samples and standard reference material are revealed in Table 3, as it can be seen, desirable agreement was observed between the obtained values and the certified values which pointed out that the fabricated sorbent as well as proposed method can be utilized for determination and preconcentration of Cd (II) in natural samples.

Table 2. Analytical Parameters of Cd (II) determination by of MSPE-FAAS

Parameter	Analytical data
Linear range (ng mL ⁻¹)	0.6-40
Determination coefficients (r ²)	0.9991
Limit of quantification (ng mL ⁻¹)	0.6
Limit of detection (ng mL ⁻¹)	0.21
Repeatability (R.S.D., %) (n = 3) (C _{Ca(II)} = 10.0 ng mL ⁻¹)	3.0
Preconcentration factor (PF) ^a	60
Sample volume (mL)	30

^a Preconcentration factor is defined as the ratio of sample volume to desorption solvent volume

Table 3. The determination of cadmium in water, tomato and cabbage samples by the proposed method

Sample	Added (μg g ⁻¹)	Found (μg g ⁻¹) ^a	RSD (%)	Recovery (%)
SRM1570A ^b	-	2.80 ± 0.09	3.2	96.9
Tomato	-	<LOQ	-	-
	5.0	4.6 ± 0.2	4.3	92.0
	10.0	8.9 ± 0.3	3.4	89.0
	15.0	14.1 ± 0.5	3.5	94.0
Cabbage	-	<LOQ	-	-
	5.0	4.3 ± 0.1	2.3	86.0
	10.0	10.2 ± 0.4	3.9	102.0
	15.0	13.7 ± 0.6	4.4	91.3
Sample	Added (ng mL ⁻¹)	Found (ng mL ⁻¹) ^a	RSD (%)	Recovery (%)
Bottled Mineral water	-	<LOQ	-	-
	5.0	4.8 ± 0.2	4.1	96.0
	10.0	10.1 ± 0.4	4.0	101.0
	15.0	13.5 ± 0.5	3.7	90.0
Tap water	-	<LOQ	-	-
	5.0	4.4 ± 0.2	4.5	88.0
	10.0	9.3 ± 0.4	4.3	93.0
	15.0	13.9 ± 0.7	5.0	92.7

^aMean ± standard deviation (n=3),

^bCertified value: SRM1570A concentration, 2.89 μg g⁻¹

Table 4. The comparison of analytical parameters of the developed MSPE-FAAS method with other reported methods from some recent studies

Instrumental technique	Extraction method	Extraction phase	LOD (ng mL ⁻¹)	RSD (%)	sample	Refs.
FAAS	SPE	multiwalled carbon nanotubes impregnated with 4-(2-thiazolylazo) resorcinol	2.8	< 5	Macaroni, Rice and lentil	38
FAAS	US-assisted in-syringe D μ SPE	Nitrogen doped nano porous graphene	0.3	4.38	human plasma, urine and saliva	39
FAAS	SPE	activated carbon cloth impregnated with PAN	1.1	NR	Soil and water	4
FAAS	SPE	poly[prothymosin-alpha-co-divinylbenzene-co-2-acrylamido-2-methylpropane sulfonic acid] (PTMA-co-DVB-co-AMPS)	1.4	≤ 2	Dried vegetable and water	40
FAAS	SPE	poly[2-(4-methoxyphenylamino)-2-oxoethyl methacrylate-co-divinylbenzene-co-N-vinylimidazole] (MPAEMA-coDVB-co-VIM)	1.4	≤ 2	Tea and herbal plants	41
FAAS	MSPE	CCF/ZIF-71/Fe ₃ O ₄ /PTh	0.21	3.0	Water, tomato and cabbage	This work

solid-phase extraction (SPE), magnetic solid-phase extraction (MSPE), flame atomic absorption spectrometry (FAAS), ultrasonic-assisted in-syringe dispersive micro solid-phase extraction (US-assisted in-syringe D μ SPE), not reported (NR).

3.10. Comparison with other methods

The performance of the advanced MSPE-FAAS method employing CCF/ZIF-71/Fe₃O₄/PTh sorbent was compared with reported methods in the literature of cadmium. Table 4 presents the comparison data, this proposed methodology has simple and faster operation, cost-effective, efficient and better performance. In addition, the proposed method does not require applying much sorbent and is also more sensitive. Due to a lower detection limit (LOD) and higher surface-to-volume ratio, the surface of CCF/ZIF-71/Fe₃O₄/PTh has plenty of active sites, for this reason, the fabricated sorbent has a great adsorption capability. In conclusion, the MSPE method based on a CCF/ZIF-71/Fe₃O₄/PTh coupled with FAAS utilizes as a viable choice for the determination of cadmium in real matrices.

4. Conclusion

In the current study, a novel magnetic sorbent, a sensitive, fast, and selective magnetic solid-phase extraction procedure followed by flame atomic

adsorption spectroscopy, for pretreatment and determination of cadmium from water, cabbage, and tomato samples has been performed. The fabricated solid phase has notable and inherent properties like large surface area and great porous volume, simple isolation process, and cost-effective fabrication route. The fabricated novel hybrid sorbent was characterized by FT-IR, FE-SEM, and XRD. The recovery results revealed that the proposed method has excellent selectivity, satisfactory accuracy, acceptable enrichment factor, low limit of detection (LOD=0.21 ng mL⁻¹), and essential preconcentration ability. Lastly, the proposed method can be a great offer to utilize successfully in the selective extraction, preconcentration, and determination of heavy metals in water and food samples.

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6. Conflict of interest

The authors declared no conflict of interest.

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