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# Fast preconcentration and determination of Zn(II) and Fe(III) using phenyl isothiocyanate functionalized nanoporous silica

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**Original Research**

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**Abstract:**

A quick approach to extract and monitor trace amount of Fe(III) and Zn(II) ions by nanoporous silica (SBA-15) functionalized with phenyl isothiocyanate groups and inductively coupled plasma optical emission spectrometry (ICP-OES) is presented. Phenyl isothiocyanate functionalized SBA-15 was constructed based on the process defined in previous studies and was used as a novel adsorbent for Fe(III) and Zn(II) preconcentration. We examined the optimal adsorbent amount, stirring time, pH and the smallest quantity of acid needed for stripping and the volume required to achieve breakthrough. Zn(II) and Fe(III) in 25 mL solution of 4 mg/L were completely extracted at pH = 6 after shaking for 5 min. The highest adsorbent capacity was $1237 \pm 1.0$ µg and $962 \pm 1.4$ µg of Fe(III) and Zn(II) ions/mg functionalized SBA-15. The method's preconcentration factor was determined as 20. The approach detection limit was 3.2 and 5.7 µg/L for Zn(II) and Fe(III). Phenyl isothiocyanate-modified SBA-15 was effectively used as a novel solid extractant to concentrate Zn(II) and Fe(III) ions simultaneously from water samples.

**Keywords:** Nanoporous adsorbent; Functionalized SBA-15; Ferric ions; Simultaneous extraction; Water samples; Zinc ions

## 1. Introduction

Zinc and iron are two of the most prevalent metals in the human body. Zinc is essential for growth and development [1, 2], serving as a co-factor in numerous enzymes and playing a critical role in protein synthesis and cell division [3]. Zinc deficiency can result in stunted growth, impaired DNA synthesis, delayed wound healing, reduced collagen synthesis, and inadequate insulin production [4–6]. Conversely, excessive zinc intake can be toxic, potentially leading to neurotoxic effects such as Alzheimer's and Parkinson's diseases [6]. Moreover, high zinc concentrations can diminish soil microbial activity and are prevalent contaminants in agricultural and food waste [7]. Zinc is naturally found in various foods and soil, released into the environment through the chemical weathering of zinc minerals [1, 3, 8].

Iron (Fe) plays a critical function in cellular metabolism, oxygen transport, and energy production, serving as a vital component in myoglobin, hemoglobin, siderophores, and cytochromes. Imbalances in iron levels can result in serious health issues such as anemia, liver damage, diabetes, hemochromatosis, cancer, and Parkinson's disease. Additionally, the uncontrolled existence of iron in soil and water has significant environmental implications [9, 10], underscoring the significance of monitoring iron levels in biomedical and environmental assessments.

As a result, preparative techniques are often necessary to preconcentration and increase the sensitivity of trace metal or non-metal detection [11–14]. Solid phase extraction (SPE) is extensively utilized for its simplicity, cost-effectiveness, ability to achieve high concentration factors, and full recovery of the analyte [14–17]. The most important component

in a solid phase extraction system is the adsorbent. Today, various types of materials have been synthesized that can be used as an adsorbent. While the application of some of them has been investigated in the field of extraction and adsorption [18–29], many of them have not been investigated in this regard [30–32]. Different adsorbents, containing nanomaterials such as graphene, cellulose, carbon nanotubes, metal oxide nanoparticles, magnetite, and silica, have been successfully employed for extracting, concentrating or catalytic degradation of organic and inorganic species [18–26, 33]. However, many of these adsorbents have problems such as low adsorption capacity, low selectivity, long extraction time, harmful waste and are not environmentally friendly. Therefore, due to the growing complexity of samples and the need for rapid and environmentally friendly analysis, the continuous development of new adsorbents is necessary.

Today, many types of materials have been synthesized that can be used as absorbents. Among them, nanoporous silica materials like MCM-41 and SBA-15 have a special situation and are well-suited for use as adsorbents in extraction processes [34, 35] due to their narrow pore size distribution, abundance of surface hydroxyl groups, high specific surface area, ease of surface modification and compatibility with the environment [36–38]. Silica is a chemically stable material but can undergo irreversible surface modification through reactions with surface silanol groups and organic species. In general, chemical functionalization of the nanomaterials enhances the efficiency and selectivity of these adsorbents [39, 40]. Mesoporous silica such as SBA-15 is a very porous adsorbent and has a high internal surface area of about $400-900\ m^2/g$ [41]. The high surface area of this compound is a suitable feature in the application of mesoporous materials in the role of adsorbent for the extraction or removal of chemical species. However, researches have demonstrated that if these compounds are left unmodified, their high surface area may not translate into a high adsorption capacity. This could be because the adsorbent lacks selectivity [42]. Consequently, it is imperative to modify mesoporous silica materials using specific modifiers. Nowadays, much attention is paid to this issue. For instance, 1, 4-Diazabicyclo [2.2.2] octane functionalized SBA-15 was recently employed by Larki et al. as a new selective adsorbent for the separation of Cr(VI) from various environmental water samples [43]. Li et al. assessed the modification of 3-[2-(2-aminoethylamino) ethylamino] propyltrimethoxysilane/SBA-15 via phenyl glycidyl ether for the extraction of four acidic nonsteroidal anti-inflammatory medication types (ibuprofen, diclofenac, naproxen, and ketoprofen) in water samples [44]. Functionalized mesoporous silica SBA-15 was created by Sreenu et al. using 2-mercaptobenzaldehyde, and it was successfully used for the preconcentration of Cd (II) in water and vegetable samples [45]. The adsorption capacity of 0.94 mmol/g is demonstrated. In another study, 5-amino-1, 3, 4-thiadiazole-2-thiol was employed by Imran et al. to modify the SBA-15 surface in order to separate Fe(III) from water samples [46]. The limit of detection of 0.32 µg/L was found. These investigations show that the adsorption performance of SBA-15 is significantly impacted by modifications with the organic functional groups. For various contaminants, researchers can create highly selective and effective SBA-15-based adsorbents by carefully choosing the appropriate functional groups. Accordingly, modified mesoporous materials have been employed in various adsorption uses, like the extraction and removal of metal ions [47–49] and organic compounds [50, 51]. These applications are currently limited, and further research is needed to expand the uses of mesoporous silicates.

The present work aimed at developing a straightforward and practical technique for the simultaneous Fe(III) and Zn(II) preconcentration in aqueous samples. To achieve this goal, phenyl isothiocyanate functionalized SBA-15 (depicted in Fig. 1) was synthesized based on the process defined in previous studies and utilized as a novel adsorbent for extracting and concentrating trace amounts of Zn(II) and Fe(III) ions from water samples. To the best our knowledge, this is the first application of phenyl isothiocyanate functionalized SBA-15 for simultaneous extraction of Zn (II) and Fe (III) ions.

## 2. Materials and methods

### Reagents

Phenyl isothiocyanate functionalized SBA-15 was constructed in accordance with the procedure previously reported [32]. Analytical grade salts of manganese, nickel,

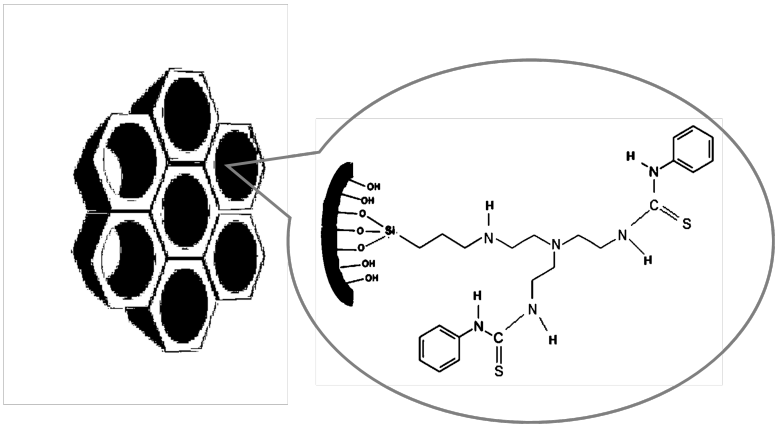


**Figure 1.** Phenyl isothiocyanate functionalized SBA-15.

zinc, cadmium, lead, silver, ferric, ferrous, chromium, copper and cobalt (from Merck) were utilized in their highest available purity without additional purification. Doubly distilled water was utilized exclusively. Stock solutions of metal ions (Zn(II), Fe(III), and others) at a concentration of 1000 mg/L were made by dissolving the nitrate salts in doubly distilled water. The working standard solutions were prepared by diluting the stock solutions with doubly distilled water as required.

### ICP-OES operating conditions

The ICP-OES was employed using the conditions specified in Table 1 to analyze the concentrations of Zn(II) and Fe(III) in samples. The instrument was configured according to the parameters outlined in Table 1:

### Extraction procedure

The standard procedure for extracting ions using phenyl isothiocyanate functionalized SBA-15 was in this way: A proper volume of a 4 mg/L solution containing Zn(II) and Fe(III) at pH 6 was prepared. Functionalized SBA-15 (20 mg) was mixed with the solution and stirred for 5 minutes. The obtained product was then filtered by a paper filter. Following extraction, the ions captured by phenyl isothiocyanate functionalized SBA-15 were eluted by a 3.0 mol/L nitric acid solution (40 mL). Subsequently, the concentrations of Z(II) and Fe(III) in both the extracted and eluted solutions were determined using ICP-OES.

### Samples preparation

River water samples were gathered from a significant water ecosystem in Iran, located near Tehran and Karaj cities. This river serves as the primary source of drinking water for residents of Tehran and Karaj. We filtered water samples by a 0.45-µm pore size membrane filter to eliminate suspended particles. In some sample solutions totaling 800 mL, 80 µg of Zn(II) and Fe(III) ions were added, while others remained untreated. The prescribed procedure was then applied uniformly to all solutions.

## 3. Results and discussion

### pH Effect on Fe(III) and Zn(II) extraction efficiency

The impact of pH of aqueous samples on the Fe(III) and Zn(II) ions' extraction was studied in 4 mg/L solution (25 mL) of Fe(III) and Zn(II) in the pH range 2.0 – 9.0. The pH was calibrated using either a 1 mol/L sodium hydroxide or nitric acid solution. Subsequently, functionalized SBA-15 (10 mg) was mixed, and the product was stirred for 15 minutes. The Zn(II) and Fe(III) concentration in the extracted solution was then analyzed using ICP-OES. The results are shown in Fig. 2. The most simultaneous extraction of Fe(III) and Zn(II) by the phenyl isothiocyanate functionalized SBA-15 is happened at pH 6.0. The state of ionization of adsorbent functional groups and metal chemistry in solution is completely influenced by pH and affects the availability of binding sites [52]. Changes observed above pH 6.0 may arise from the formation of $Fe(OH)_3$ and $Zn(OH)_2$. Changes observed below this pH arise from the competition of proton ions with Zn(II) and Fe(III) for complex formation between functionalized SBA-15 and ions [49–53]. This change is different for Fe(III) and Zn(II). The proton ions can compete with Zn(II) at higher acidic media and reduces extraction efficiency of Zn(II) ions. However, they cannot compete with Fe(III) as well, and therefore, at lower pH, the extraction efficiency of Fe(III) has decreased much less than that of Zn(II). This could be due to the higher affinity of the phenyl isothiocyanate functionalized SBA-15 for Fe(III) compared to Zn(II).

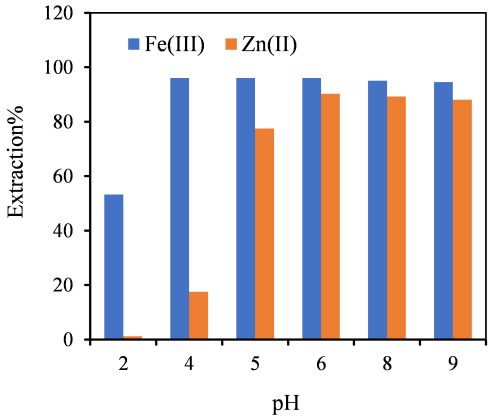


**Figure 2.** pH impact on the extraction of Fe(III) and Zn(II) ions.

**Table 1.** ICP-OES conditions to determine Fe(III) and Zn(II) concentrations.

| Parameters | Conditions |
|---|---|
| Nebulizer | Micro-concentric glass |
| Injector | Quartz injector |
| Detector | Charge-coupled detector (CCD) |
| Plasma gas | Argon gas; flow rate: 5.0 L/min |
| Pressure | 2.5 bar |
| Nebulizer gas | flow rate 0.7 L/min |
| Auxiliary gas | flow rate 0.2 L/min |
| Mode of viewing plasma | Axial mode |
| Integration time | 10 s |
| Replicates | 3 |
| Wavelength | 213.86 nm (Zn(II)) and 238.204 nm (Fe(III)) |

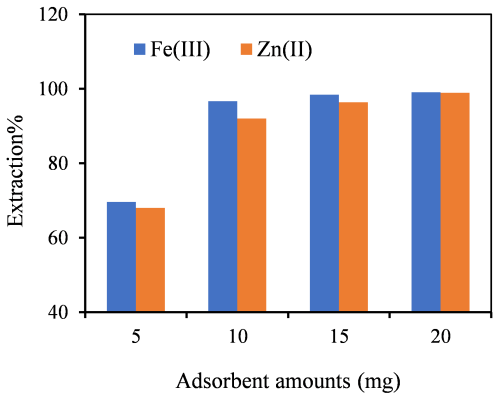


**Figure 3.** Adsorbent amount impact on the extraction of Zn(II) and Fe(III) ions.

### Effect of adsorbent amount on the ion extraction efficiency

For considering the optimal amount of phenyl isothiocyanate functionalized SBA-15 for maximum adsorption of Fe(III) and Zn(II) ions, the extraction was performed using varying quantities of the functionalized SBA-15, ranging from 5 to 20 mg. Various amounts of functionalized SBA-15 was mixed with 4 mg/L solution (25 mL) of Fe(III) and Zn(II) in the pH 6, and the mix was shaken for 15 min. ICP-OES was used to determine content of Fe(III) and Zn(II) in extracted solution. Figure 3 indicates the results. It is noted that, initially, the extraction percentage of ions on phenyl isothiocyanate functionalized SBA-15 is elevated with an increase in adsorbent amount. This was a consequence of a higher number of active sites for the adsorption of Fe(III) and Zn(II) owing to a higher dose of the sorbent [54]. Lastly, the maximum extraction of Fe(III) and Zn(II) ions were achieving with using 15 and 20 mg of adsorbent. Thus, following experiments for extraction were conducted with 20 mg of phenyl isothiocyanate functionalized SBA-15 for simultaneous extraction of Zn(II) and Fe(III) ions.

### The stirring time effect on ion extraction efficiency

The impact of stirring duration on the extraction efficiency was studied using solutions comprising 4 mg/L of Zn(II) and Fe(III) (25 mL), with results illustrated in Figure 4. It was noted that Zn(II) and Fe(III) is extracted completely by phenyl isothiocyanate functionalized SBA-15 within a stirring time of 5 minutes. Therefore, in all experiments, the mixtures were stirred for 5 minutes. The complete extraction in a short time showed that the equilibrium kinetics is very fast [52]. Decreased extraction efficiency at longer stirring times may be due to back extraction.

### Desorption and reuse study

Several experiments were conducted to determine the optimal volume of nitric acid for eluting Zn(II) and Fe(III) ions after their extraction by phenyl isothiocyanate functionalized SBA-15. The ions were removed by applying various volumes of acid. The results, depicted in Figure 5, demonstrated that 3.0 mol/L nitric acid (40 mL) effectively achieved complete elution of Zn(II) and Fe(III) from the adsorbent.

Subsequent experiments were conducted to assess the regeneration capability of the functionalized SBA-15. The adsorbent was employed across several iterations of the adsorption and desorption process [47, 49, 54]. Findings indicated that the recovery rate remained consistent ($97-99\%$) after four cycles of sorption and desorption, gradually decreasing in subsequent cycles of the adsorption and desorption process.

### Break through volume determination

The breakthrough volume of the sample solution was investigated by dissolving 100 $\mu$g each of Zn(II) and Fe(III) in water volumes of 200, 400, 800, 1200, and 1500 mL, following the recommended procedure [49, 53]. The Zn(II) extraction by phenyl isothiocyanate functionalized SBA-15 was quantitative up to 800 mL, while for Fe(III), it was quantitative up to 1200 mL. Hence, the break through volume for Fe(III) measurement must be above 1200 mL and for Zn(II) measurement must be above 800 mL. Since ion recovery was achieved using 40 mL of nitric acid, the preconcentration factor was 30 for Fe(III) measurement and 20 for Zn(II) measurement. However, since the simultaneous measurement of Zn(II) and Fe(III) is desired in this study, the concentration factor of the method was considered 20.

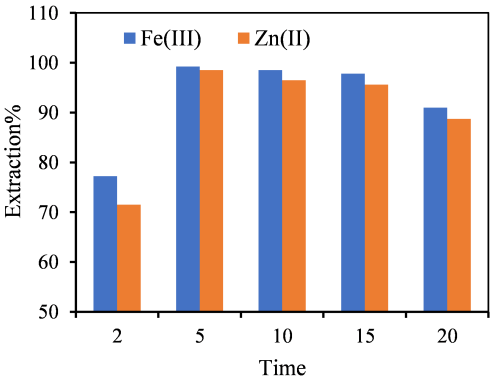


**Figure 4.** Impact of stirring time on the extraction of Fe(III) and Zn(II) ions.

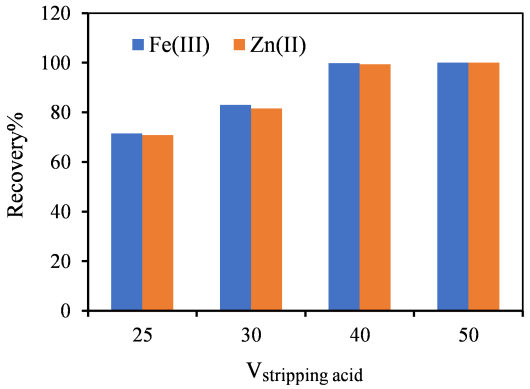


**Figure 5.** Impact of volume of stripping acid on the extraction of Fe(III) and Zn(II) ions.

### Capacity of phenyl isothiocyanate functionalized SBA-15

The amount of adsorbent needed to quantitatively extraction a given quantity of metal ions from the solutions is determined by the adsorbent's capacity, which makes it a crucial factor. Different metal ions likely have different adsorption capabilities because of their size, degree of hydration, and binding constant with the functional groups of adsorbents [53]. The highest capacity of phenyl isothiocyanate functionalized SBA-15 was specified by the addition of 20 mg of the adsorbent to 25 mL portions of an aqueous solution with 1500 mg/L of Zn(II) and Fe(III). The product was stirred for 5 minutes, filtered via a paper filter, and the reserved metal ions were quantified using ICP-OES. The highest capacity was measured to be $962 \pm 1.4$ µg of Zn(II) and $1237 \pm 1.0$ µg of Fe(III) ions per milligram of phenyl isothiocyanate functionalized SBA-15. The higher adsorption capacity of the phenyl isothiocyanate functionalized SBA-15 for Fe(III) can indicate the greater affinity of the adsorbent for Fe(III) than zinc(II).

### Extraction of Fe(III)and Zn(II) ions in mixtures

For investigating the selective preconcentration and extraction of Fe(III) and Zn(II) ions from water with different metal ions, an aliquot of aqueous solution (25 mL) with 100 µg Zn(II), 100 µg Fe(III) and different quantities of other cations were used, and the prescribed procedure was followed. Table 2 presents the results. As observed, the proposed adsorbent effectively extracts Zn(II) and Fe(III) ions completely, up to a satisfactory extent in the presence of other cations.

An important point is that in the most cases, the interference of other ions on the Fe(III) extraction is less than their interference on the Zn(II) extraction. This issue can be due to the greater tendency of the adsorbent to Fe(III) compared to Zn(II).

**Table 2.** Extraction of Fe(III) and Zn(II) ions from mixtures.

| Diverse ions | Amount taken (µg) | Extracted Zn(II) (%) | Extracted Fe(III) (%) |
|---|---|---|---|
| $Cu^{2+}$ | 250 | 98.9 | 99.3 |
| $Cu^{2+}$ | 500 | 92.6 | 98.6 |
| $Cd^{2+}$ | 500 | 98.2 | 98.8 |
| $Cd^{2+}$ | 2000 | — | 95.8 |
| $pb^{2+}$ | 500 | 98.1 | 99.5 |
| $Ag^{+}$ | 500 | 98.2 | 99.9 |
| $Ag^{+}$ | 2000 | 14.2 | 95.3 |
| $Mn^{2+}$ | 500 | 12.1 | 93.8 |
| $Ni^{2+}$ | 500 | 99.0 | 99.9 |
| $Ni^{2+}$ | 2000 | 3.0 | 99.4 |
| $Cr^{3+}$ | 250 | 12.5 | 96.5 |
| $Cr^{3+}$ | 100 | 96.1 | 98.6 |
| $Co^{2+}$ | 100 | 98.3 | 98.0 |
| $Fe^{2+}$ | 100 | 96.5 | 97.3 |

**Table 3.** Overview of the analytical properties of the method.

| | Zn(II) | Fe(III) |
|---|---|---|
| Limit of detection ($n$ = 4 µg/L) | 3.2 | 5.7 |
| Relative standard deviation (% RSD), ($n$ = 5, $C$ = 0.1 mg/L) | 3.56 | 3.97 |
| Linear range (mg/L) | 0.025 – 0.5 | 0.025 – 0.5 |
| Correlation coefficient ($R^2$) | 0.995 | 0.996 |
| Calibration function | $I$ = 2E+07 $C$ + 68237 | $I$ = 3E+07 $C$ + 172507 |

### Analytical characteristics of the methods

Table 3 presents various features of the proposed approach. Parameters such as precision, linear range, limit of detection (LOD), correlation coefficient, and regression equations were utilized for validating the method.

The LOD for Zn(II) and Fe(III) was specified by passing a blank solution through phenyl isothiocyanate functionalized SBA-15 in optimum empirical conditions. The LOD values, calculated using the equation LOD = $K_b \times S_b/m$ (where $K_b$ = 3 as a numerical factor) [49, 52], were found to be 3.2 µg/L for Zn(II) and 5.7 µg/L for Fe(III). Here, $S_b$ represents the SD of the blank solution, and m denotes the calibration curve's slope.

Method precision was assessed using five solutions comprising 0.1 mg/L of Zn(II) and Fe(III). The relative SD (% RSD) across five preconcentration tests was determined to be 3.56% for Zn(II) and 3.97% for Fe(III).

The regression equations for determining metal concentration were established as follows:

$$\begin{aligned} &-\text{For Zn(II)} : I = 2\text{E}+07 \times C + 68237 \\ &-\text{For Fe(III)} : I = 3\text{E}+07 \times C + 172507 \end{aligned} \quad (1)$$

where $I$ represent the intensity and $C$ (mg/L) denotes the metal concentration in the solution.

Calibration graphs exhibited linearity within the range of 0.025 to 0.5 mg/L for both Zn(II) and Fe(III) under the optimal conditions of the general procedure.

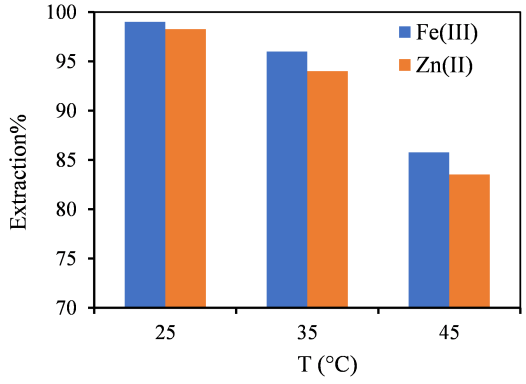


**Figure 6.** Temperature impact on the extraction efficiency of Fe(III) and Zn(II) ions.

### Effect of thermodynamic parameters and Temperature

Metal ion adsorption was investigated across three temperatures ranging from 25 to 45 °C, using solutions containing Zn(II) and Fe(III) ions at a concentration of 4 mg/L. Figure 6 illustrates the impact of temperature on the efficiency of ion extraction using phenyl isothiocyanate functionalized SBA-15. The extraction decreased with increasing temperature, indicating that the sorption of Fe(III) and Zn(II) ions were exothermic processes and favorable at lower temperatures. This could be attributed to the increased tendency of these ions to escape from the solid phase to the bulk phase as the temperature rises [55].

Furthermore, the dependence of extraction efficiency on temperature has been elucidated by considering thermodynamic parameters like entropy change ($\Delta S^\circ$), Gibbs free energy change ($\Delta G^\circ$), and enthalpy change ($\Delta H^\circ$), which were specified using the equations [56]. The $\Delta G^\circ$ of the process is associated with the equilibrium constant ($K_C$) by the following relatin:

$$K_C = \frac{C_{Ae}}{C_e} \tag{2}$$

where $C_{Ae}$ and $C_e$ represent the solid phase and equilibrium liquid phase concentrations at equilibrium (mg/L) and $K_C$ denotes the equilibrium constant.

$$\log K_C = \frac{\Delta S^\circ}{R} - \frac{\Delta H^\circ}{RT} \tag{3}$$

$$\Delta G^\circ = -RT \ln K_C \tag{4}$$

The $\Delta H^\circ$ and $\Delta S^\circ$ were gained from intercept and slope of the Van't Hoff plot (Eq. (3)) of $\log K_C$ versus $1/T$ (Fig. 7). $R$ is the gas constant and $T$ shows the temperature in Kelvin. Table 4 gives these parameters' values.

The negative standard enthalpy change ($\Delta H^\circ$) values across the temperature ranges indicate that the adsorption process is exothermic in nature. The estimated values of $\Delta H^\circ$ for the present system for Zn(II) and Fe(III) was −31.696 kJ/mol and −37.023 kJ/mol. The negative $\Delta G^\circ$ values confirm the feasibility and spontaneous nature of the extraction process for Zn(II) and Fe(III) ions onto phenyl isothiocyanate functionalized SBA-15 [56].

### Proposed mechanism of interaction

According to the mechanisms described in previous studies on similar compounds [52, 57, 58], adsorption most likely would result from the formation of coordination interactions between heteroatoms of phenyl isothiocyanate functionalized SBA-15 (nitrogen and sulfur) and Zn(II) and Fe(III) ions. The Fe(III) ion most likely only interacts with nitrogen atoms that are harder than sulfur since it is a harder ion than Zn(II). While Zn(II) ion may interact with both nitrogen and sulfur atoms [59, 60].

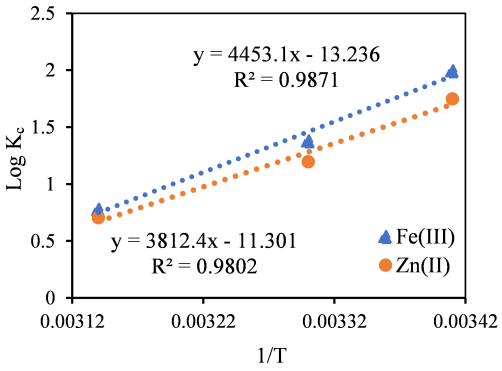


**Figure 7.** Van't Hoff Plot for the extraction of Zn(II) and Fe(III) by functionalized SBA-15.

Remarkably, the adsorption of Fe(III) demonstrated a higher adsorption capability when compared to Zn(II). The reason behind this could most likely be the different ionic diameters; the ionic radius of Fe(III) is less than that of Zn(II) [0.065 nm for Fe(III) vs. 0.074 for Zn(II)] [61]. Due to this size difference, Fe(III) ions have greater accessibility to the material's adsorption sites than Zn(II) ions because they are less susceptible to sterical hindrances [58].

### Application to real samples

The proposed approach was employed for extracting and quantifying Zn(II) and Fe(III) in two types of water: distilled water and Karaj river water. Table 5 demonstrates a close correspondence between the measured and added concentrations of spiked samples, indicating the method's effectiveness for the determination and preconcentration of these metal ions. Additionally, the method was validated by comparing its results with those obtained by ICP-OES after concentration through evaporation. Table 5 shows good consistency of the results.

### Comparison of proposed adsorbent with some previously studied

The maximum adsorption capacity, extraction time and usable pH range of the phenyl isothiocyanate functionalized SBA-15 were compared with some previous studies adsorbents used for extraction of Zn(II) and Fe(III) (Table 6). The findings obviously imply that the proposed adsorbent is su-

**Table 4.** The thermodynamic parameters for extraction of Zn(II) and Fe(III) by phenyl isothiocyanate functionalized SBA-15.

| Metal ion | Temperature (°C) | $\Delta G^\circ$ (kJ/mol) | $\Delta S^\circ$ (kJ/mol. K) | $\Delta H^\circ$(kJ/mol) | $K_C$ |
|---|---|---|---|---|---|
| Zn(II) | 25 | -8.452 | -0.094 | -31.696 | 30.257 |
| | 35 | -6.287 | | | 11.635 |
| | 45 | -4.123 | | | 4.752 |
| Fe(III) | 25 | -9.736 | -0.110 | -37.023 | 50.792 |
| | 35 | -7.203 | | | 16.634 |
| | 45 | -4.670 | | | 5.845 |

**Table 5.** Determination of Fe(III) and Zn(II) ions in water samples.

| Sample | Metal | Added amount of each ion (µg/L) | Found, µg/L (RSD)[a] | |
|---|---|---|---|---|
| | | | (SPE-ICP-OES) | (Ev-ICP-OES)[b] |
| Distilled water | Zn(II) | 100 | 99.3 (2.5) | 100.2 (2.8) |
| | Fe(III) | 100 | 99.5 (3. 1) | 99.7 (3.3) |
| Karaj river water | Zn(II) | 0.0 | 15.3 (2.6) | 14.9 (2.2) |
| | Fe(III) | 0.0 | 20.6 (3.4) | 21.2 (2.6) |
| Karaj river water | Zn(II) | 100 | 115.7 (3.6) | 115.1 (2.4) |
| | Fe(III) | 100 | 119.7 (3.0) | 120.5 (2.7) |

[a]RSD based on three replicate analyses.

[b]Measurements were done after twenty times concentration by evaporate.

**Table 6.** Comparison of the proposed adsorbent and the previously reported adsorbents.

| Adsorbent | Ion | MAC[a] (mg $g^{-1}$) | Extraction Time (min.) | pH | Ref. |
|---|---|---|---|---|---|
| 5-Amino-1,3,4-Thiadiazole-2-Thiol-SBA-15 | Fe(III) | 45.79 | — | 9 | [46] |
| Silica gel modified with curcumin | Fe(III)<br>Zn(II) | 25.69<br>24.19 | 2 | 4 | [53] |
| Triethylenetetramine/SBA-15 | Zn(II) | 13.6 | 180 | 4 | [57] |
| SBA-15 silica functionalized with 4-amino-2-mercaptopyrimidine | Zn(II) | 0.85 | 360 | 5-6 | [58] |
| 5-methyl-2-thiophenecarboxaldehyde Schiff base-immobilised SBA-15 | Zn(II) | 33 | 360 | 6.5 | [62] |
| Thiosalcylic acid | Fe(III) | 275.78 | 15 | 2.5 | [63] |
| Phytate-polyaniline hydrogel | Fe(III) | 46.96 | — | 7 | [64] |
| Phenyl isothiocyanate functionalized SBA-15 | Fe(III)<br>Zn(II) | 1237<br>962 | 5 | 6 | This work |

[a]Maximum Adsorption Capacity

perior to the reported previously in terms of the adsorption capacity and contact time. Phenyl isothiocyanate functionalized SBA-15 can afford very high adsorption capacity and is better than other adsorbents [46, 53, 57, 58, 62–64]. Regarding the contact time, the proposed method is better than most reported earlier for other methods [57, 58, 62, 63] and is close and comparable to the best method reported previously for Zn(II) and Fe(III) ions [53]. Also, it is noticeable that present study can afford simultaneous determination of Zn(II) and Fe(III).

## 4. Conclusions

Chemical functionalization of silanized nanoporous materials is an effective approach to enhance the selectivity and efficiency of extraction processes in a short timeframe. Therefore, in this study, phenyl isothiocyanate functionalized SBA-15 was utilized successfully as a novel solid extractant for the rapid preconcentration of trace amounts of Zn(II) and Fe(III) ions in water samples. The adsorbent exhibited a remarkably high maximum capacity owing to its substantial specific surface area. Proposed method was characterized by its speed (extraction time of 5 minutes), sensitivity, efficiency, and simplicity. Also, since the adsorption capacity of phenyl isothiocyanate functionalized SBA-15 was good, even a small amount of the absorbent is enough to ensure high efficiency extraction. Therefore, the proposed methodology can be considered as a cost-effective analysis method. Reusability of the adsorbent, clean extraction procedure and no use of organic solvents put this method in the category of environmentally friendly methods.

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**Authors contributions**
Authors have contributed equally in preparing and writing the manuscript.

**Availability of data and materials**
The data that support the findings of this study are available from the corresponding author upon reasonable request.

**Conflict of interests**
The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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