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Magnetic Nanozeolite-Based Dispersive Solid-Phase Microextraction for Preconcentration and Sensitive Spectrophotometric Determination of Sulfide Ions in Water Samples

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Abstract

In this study, magnetic zeolite was employed as an efficient adsorbent in a dispersive solid-phase microextraction (dSPME) method for the preconcentration and determination of sulfide ions. Detection was based on the formation of a sulfide–methylene blue complex, which was subsequently quantified by UV–Vis spectrophotometry at 656 nm. The structural and functional properties of the synthesized magnetic zeolite were characterized using field-emission scanning electron microscopy (FE-SEM), Fourier-transform infrared spectroscopy (FT-IR), vibrating sample magnetometry (VSM), and energy-dispersive X-ray spectroscopy (EDX).The experimental parameters influencing extraction efficiency and analytical performance were systematically investigated and optimized. The optimal conditions were determined to be pH 6, adsorbent dosage of 30 mg, NaCl concentration of 5% (w/v), sample volume of 10 mL, extraction time of 6 minutes, dimethyl-p-phenylenediamine as the complexing agent, and desorption with nitric acid for 5 minutes. Under these optimized conditions, the method exhibited a linear calibration range of 0.008–0.050 mg L^{-1} ($R^2 = 0.981$). The limits of detection (LOD) and quantification (LOQ) were 0.008 and 0.020 mg L^{-1}, respectively, with a relative standard deviation (RSD) of 4.06 % based on five replicate extractions within the studied concentration range. The developed method was successfully applied to the determination of sulfide ions in tap water, river water, and industrial wastewater samples, yielding satisfactory recoveries in the range of 90–100 %. Owing to its simplicity, cost-effectiveness, sensitivity, high extraction efficiency, and environmentally friendly characteristics, this approach represents a promising analytical method for sulfide ion determination in various aqueous matrices.

Keywords: sulfide ion; dispersive solid-phase microextraction; magnetic zeolite; methylene blue complex.

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Introduction

Sulfur plays a vital role in various fields, including manufacturing, agriculture, medicine, energy production, and environmental protection [1]. It is an essential constituent of several human proteins and is crucial for maintaining the health of skin, hair, and nails. Sulfur also participates in metabolic processes and energy conversion within the human body. In addition, sulfur-containing compounds are widely used in the treatment of rheumatic diseases and arthritis.In the environment, sulfur is commonly present in waste disposal sites, industrial effluents, and soil. Prolonged exposure to elevated concentrations of sulfide ions (S^{2-}) can cause severe adverse health effects, such as gastrointestinal disorders, liver and kidney damage, loss of consciousness [2,3], cardiac arrest [4], and an increased risk of diabetes [5,6]. Therefore, accurate and quantitative determination of sulfide ions in environmental and biological samples is of great importance [7]. In aqueous systems, sulfide mainly exists in the forms of hydrosulfide (HS^-) and sulfide (S^{2-}) ions, which can readily convert into hydrogen sulfide gas (H_2S), a highly toxic compound [8].Exposure to H_2S at concentrations of approximately 20 ppm (~0.89 mg/L) can cause irritation of the eyes and respiratory tract, while exposure to 100 ppm (~4.46 mg/L) may lead to olfactory fatigue. At concentrations exceeding 700 ppm (~31.25 mg/L), H_2S can result in unconsciousness and even death. To minimize these health risks, the Occupational Safety and Health Administration (OSHA) has established a permissible exposure limit of 10 ppm for H_2S [9], and the World Health Organization (WHO) recommends that H_2S concentrations in drinking water should not exceed 15 mg/L [10]. Since 2008, sodium sulfide has been prohibited as a food additive. In humans, abnormal levels of H_2S in blood plasma exceeding the physiological range of 10–100 mg/L may cause symptoms such as dizziness, nausea, and vomiting. Consequently, the rapid, sensitive, and quantitative determination of sulfide ions in both environmental and biological matrices is essential [11]. In recent years, various analytical techniques have been developed for sulfide determination, including gas chromatography, ion chromatography, potentiometric titration [12], colorimetry [13], acid–base titration, fluorescent probes [14,15], flow spectrometry [16], and high-resolution continuous flame molecular absorption spectrometry [17]. Although these methods generally provide high accuracy, they often suffer from disadvantages such as high operational costs, complicated sample preparation procedures, long analysis times, and the requirement for skilled operators. Therefore, the development of a rapid, simple, sensitive, and selective method for sulfide determination remains highly desirable. Ultraviolet–visible (UV–Vis) spectrophotometry is one of the most widely used analytical techniques owing to its simplicity, cost-effectiveness, and ease of operation. However, its relatively low sensitivity limits its direct application for trace-level sulfide determination (below the mg/L level) [18]. To address this limitation, coupling UV–Vis spectrophotometry with an efficient preconcentration step represents a promising strategy for sulfide analysis.

Among various preconcentration techniques, solid-phase microextraction (SPME) has attracted considerable attention due to its simplicity, short extraction time, high enrichment factor, low detection limits, minimal solvent consumption, and compatibility with different detection systems [19,20]. A particularly effective variant is dispersive solid-phase microextraction (dSPME), in which a small amount of solid sorbent is dispersed directly into the sample solution, followed by desorption using a minimal volume of an appropriate solvent prior to analysis [21]. In this technique, the selection of a suitable adsorbent plays a critical role in achieving high extraction efficiency.

Zeolites, owing to their high surface area, excellent adsorption capacity, chemical and thermal stability, and low cost, are promising candidates for dSPME applications [22]. In the present study, magnetic nanozeolite was employed as an adsorbent in a magnetic dSPME method for the extraction and preconcentration of sulfide ions from aqueous samples. Subsequently, the analyte was quantified by UV–Vis spectrophotometry through the formation of a methylene blue complex. The analytical performance of the proposed method was evaluated using natural water samples, and key experimental parameters, including pH, adsorbent amount, sample volume, desorption solvent volume, and extraction time, were systematically optimized.

Experimental

Chemicals and standard solutions

All reagents employed in this work were of analytical grade. Ferrous sulfate heptahydrate was obtained from Loba Chemie. Iron (III) chloride hexahydrate, concentrated sulfuric acid (98%), nitric acid, ammonia solution, sodium sulfide, and laboratory-grade sodium chloride were purchased from Merck (Germany). Natural clinoptilolite zeolite was purchased from Gohar Khak Khavarmiyaneh Co. (Mashhad, Iran), sourced from mines located in South Khorasan Province, Iran. N,N-dimethyl-p-phenylenediamine sulfate (DPD) and ferric chloride hexahydrate ($FeCl_3·6H_2O$) were used as the color-forming reagent and oxidizing agent, respectively. Both reagents were purchased from Sigma-Aldrich (St. Louis, MO, USA) with a purity ≥ 98%. The reagents are stable for several months when kept in a refrigerator.

Preparation of water samples

Water samples were collected from various sources, including tap water from Mashhad city, river water from Kashaf Rud, and sites within an industrial area. For sulfide analysis, all samples were initially filtered through a 0.45 µm membrane filter to remove suspended solids and minimize potential interferences. Following filtration, the samples were acidified to a pH below 2 using dilute hydrochloric acid (HCl) to prevent sulfide oxidation and inhibit microbial activity. The preserved samples were stored in airtight containers at 4 °C and analyzed within 24 hours to ensure the stability of sulfide species.

Instruments

For measuring absorbance, a single-beam UV-Visible spectrophotometer (USA Liconse, Australia, model Carybio5) was used. The pH of the solutions was measured using a Metrohm pH meter. For weighing, a Sartorius analytical balance (Germany) with an accuracy of 0.0001 g was used. The samples were dried using an oven (Pars Azma.Co). To accelerate phase separation, a centrifuge (Dynamica, Italy; model VELOCITY 18R) was used.

Synthesis procedure of magnetic nanozeolite sorbent

To prepare the magnetic zeolite nanosorbent, an initial acid activation step was carried out. 1 g of raw sodium zeolite was transferred into a round-bottom flask, followed by the addition of 200 mL of 0.1 M sulfuric acid (H_2SO_4) and 200 mL of 0.1 M nitric acid (HNO_3). The suspension was subjected to reflux under continuous stirring at 90°C for 3 hours to enhance surface activity and remove impurities.

After the treatment, the resulting mixture was filtered through standard-grade filter paper. The collected solid was thoroughly rinsed multiple times with deionized water to remove residual acids, and then dried in an oven at 110°C for 24 hours.

Subsequently, 1.6 g of the acid-treated zeolite was dispersed in 100 mL of ethanol and exposed to ultrasonic agitation at 50 W and 20°C for 4 hours to promote particle size reduction and uniform dispersion. The ethanol was then evaporated by drying the sample in an oven at 110°C for another 24 hours. Calcination of the dried material was performed at 800°C for 4 hours in a muffle furnace, yielding 9.86 g of nanozeolite with enhanced crystallinity and thermal stability.

For magnetization, 4.0 g of ferric chloride hexahydrate ($FeCl_3 \cdot 6H_2O$) and 2.8 g of ferrous sulfate heptahydrate ($FeSO_4 \cdot 7H_2O$) were dissolved in 100 mL of distilled water under vigorous stirring. 5g of the prepared nanozeolite was added to the solution and subjected to simultaneous stirring and ultrasonic treatment at 60°C for 10 minutes using an ultrasonic bath (Model W205) [23], ensuring homogeneous dispersion and ion exchange.

The mixture was then stirred magnetically at 80°C for 1 hour at 600 rpm to facilitate the in situ formation of magnetite nanoparticles within the zeolite structure. Aqueous ammonia solution (25%) was added dropwise until the pH reached approximately 11. The color change to black indicated the successful formation of Fe_3O_4 (magnetite) particles [23].

The suspension was left undisturbed for 24 hours to allow complete crystallization. The final product was repeatedly washed with deionized water until the washings reached a neutral pH (~7), then centrifuged and dried at 60°C to obtain the magnetic zeolite adsorbent.

Microextraction process

A 10 mL aliquot of sulfide solution (0.05mg/L) was transferred into a clean flask. Subsequently, 0.2 – 0.4 mL of methylene blue reagent (N,N-dimethyl-p-phenylenediamine sulfate (DPD) 0.1% w/v and ferric chloride ($FeCl_3$, 0.1% w/v) as the oxidizing agent was added to the sample to allow the formation of a pink-colored complex with sulfide ions [20]. The solution was gently stirred and allowed to react for 2 minutes at room temperature to ensure complete complexation.

After complex formation, 0.3 g of magnetic zeolite nanosorbent and 0.5 g of sodium chloride (NaCl, analytical grade) were added to the flask. The sample pH was adjusted using dilute HCl or NaOH solutions, and the resulting mixture was stirred continuously for 6 minutes to facilitate the adsorption of the sulfide–methylene blue complex onto the magnetic sorbent.

Once the adsorption process was complete, the flask was placed on an external magnet to separate the magnetic adsorbent from the solution. The supernatant was carefully decanted or removed using a pipette.

Next, 0.5 mL of 0.1 M nitric acid was added directly to the retained magnetic adsorbent for desorption of the analyte. The mixture was stirred for 5 minutes, and then placed on the magnet once again. The resulting desorption solution, containing the released complex, was collected using a micropipette and transferred into a clean test tube.

To remove any particulate matter, the solution was centrifuged at 3500 rpm for 3 minutes. Finally, the clear supernatant was transferred to a quartz microcell, and the absorbance was measured at 656 nm using a UV-Vis spectrophotometer.

Results and discussion

Characterization of magnetic nanozeolite sorbent

The Field Emission Scanning Electron Microscopy (FE-SEM)

The FE-SEM image (Figure 1) provides detailed insight into the surface morphology and particle size distribution of the synthesized magnetic nanozeolite adsorbent. The micrograph reveals a relatively uniform dispersion of spherical nanoparticles decorating the zeolite substrate. These nanoparticles exhibit a range of diameters, suggesting a polydisperse size distribution.

The well-defined spherical morphology of the particles indicates successful synthesis and potential for high surface area, which is beneficial for adsorption processes. Additionally, the absence of significant agglomeration or clustering suggests effective stabilization of nanoparticles on the magnetic nanozeolite surface, likely contributing to improved accessibility of active sites.

This morphological characterization confirms the nanostructured nature of the adsorbent, which is expected to enhance its adsorption capacity and kinetics in applications such as sulfide ion complex extraction.

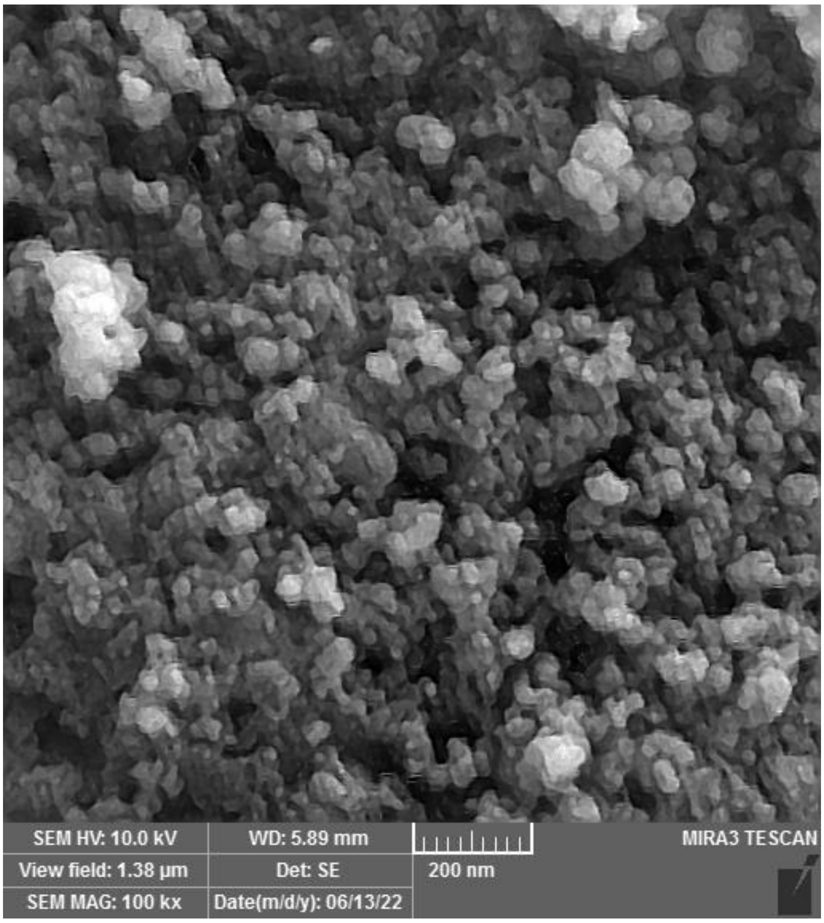

Figure 1. SEM image of the synthesized magnetic zeolite nano sorbent.

FT-IR analysis of synthesized magnetic nanozeolite

The Fourier-transform infrared (FT-IR) spectra of both the pure nanozeolite and the synthesized magnetic nanozeolite were recorded in the 400–4000 cm^{-1} range, as illustrated in Figure 2. The broad absorption band observed around 3440–3500 cm^{-1} corresponds to the O–H stretching vibrations, indicating the presence of hydroxyl groups typically associated with surface-bound water or structural OH groups in the zeolite framework. The absorption band near 1635 cm^{-1} is attributed to the bending vibrations of adsorbed water molecules (H–O–H). A distinct band appearing at 1087 cm^{-1} in the magnetic nanozeolite sample is indicative of Fe–O–Si linkages, suggesting successful incorporation of iron species into the zeolite structure. The absorption peak located at approximately 794 cm⁻¹ is assigned to symmetric Si–O stretching vibrations within the tetrahedral silicate units [24].

Further characteristic peaks are observed at 572 and 470 cm⁻¹, corresponding to Si–O–Al and Al–OH vibrations, respectively, which are consistent with the structural framework of aluminosilicate zeolites. Notably, a sharp and well-defined band at 570 cm⁻¹ in the spectrum of magnetic nanozeolite is assigned to Fe–O stretching, providing strong evidence for the presence of magnetic iron oxide phases in the synthesized material [25].

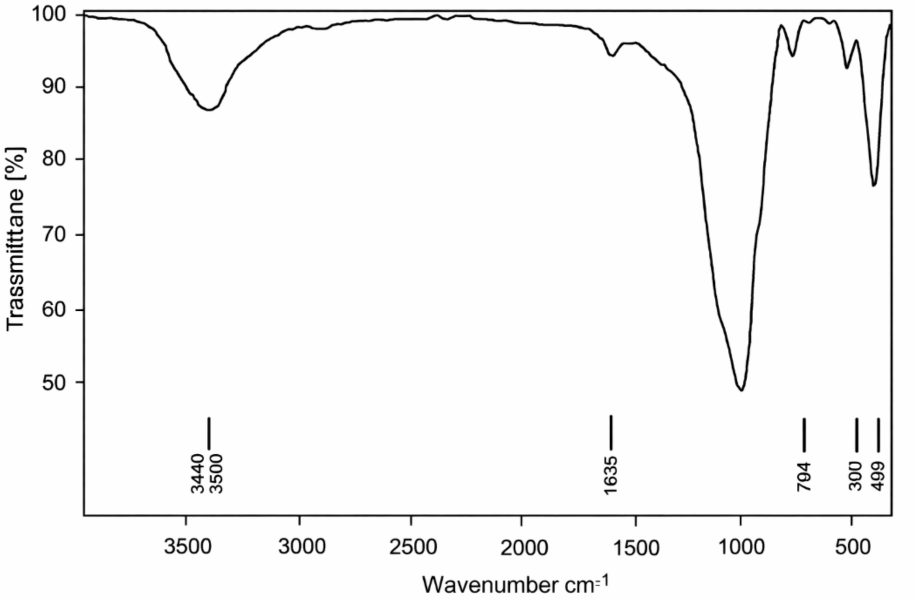

Figure 2. FT-IR Spectrum of Magnetic nanozeolite

Magnetic characterization by VSM

The vibrating sample magnetometer (VSM) analysis depicted in Figure 3 demonstrates that the synthesized magnetic nanozeolite exhibits notable magnetic behavior. The adsorbent shows a saturation magnetization value of 9.7154 emu/g, indicating sufficient magnetic responsiveness. This level of magnetization enables efficient and rapid separation of the adsorbent from aqueous solutions using an external magnetic field. The clear hysteresis loop with negligible coercivity confirms the superparamagnetic nature of the material, which is advantageous for easy recovery without residual magnetization [23].

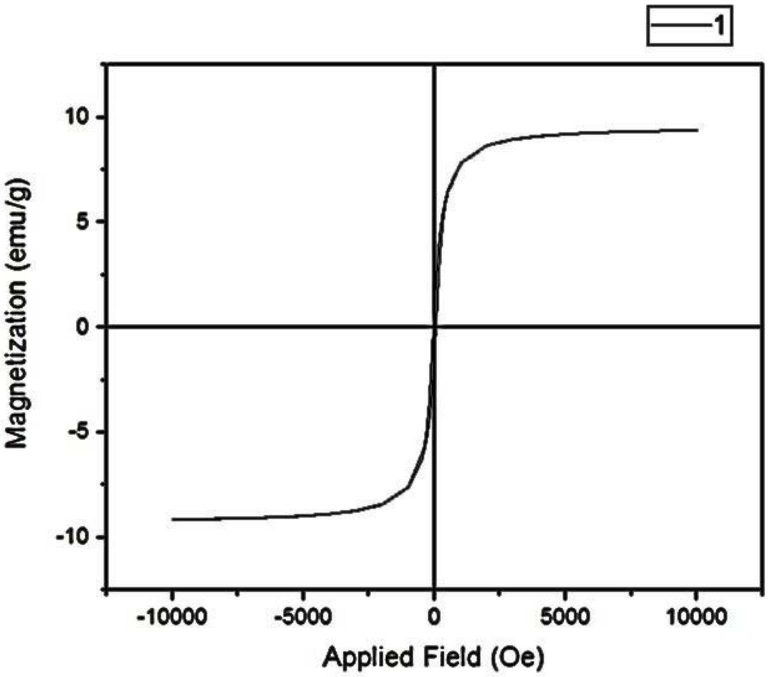

Figure 3. VSM curve of magnetic nanozeolite.

Elemental composition analysis EDX

The Energy-Dispersive X-ray (EDX) spectrum presented in Figure 4 confirms the elemental composition of the synthesized zeolite nanosorbent. The identified elements include iron (Fe), silicon (Si), aluminum (Al), oxygen (O), and magnesium (Mg), reflecting the successful incorporation of magnetic components into the magnetic zeolite framework.

Quantitative analysis reveals that silicon and oxygen possess the highest weight percentages among the detected elements, consistent with the aluminosilicate nature of the zeolite structure [23,24]. The presence of iron further confirms the successful functionalization of the sorbent with magnetic nanoparticles, while traces of magnesium support the natural origin of the zeolite material.

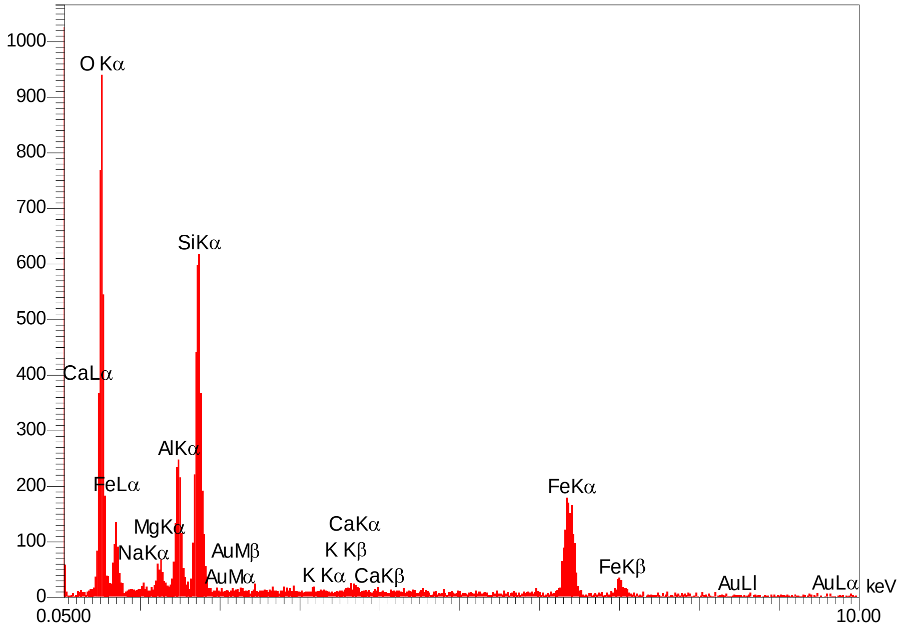

Figure 4. EDX pattern of the synthesized zeolite.

Optimization of microextraction parameters

To enhance the performance of the proposed dispersive solid-phase microextraction (dSPME) technique using the modified zeolite-based adsorbent, a systematic optimization of key experimental variables was carried out. Several influential factors affecting extraction efficiency and analytical accuracy were examined, including: solution pH, adsorbent amount, sample volume, desorption solvent volume, contact time during both adsorption and desorption steps, and the concentration of sodium chloride (NaCl).

Each parameter was independently evaluated under controlled conditions to determine its impact on the extraction process. The optimization aimed to maximize analyte recovery while minimizing time, solvent, and material consumption. The results of this optimization are discussed in detail in the following section.

The choice of desorption solvent is a crucial step that directly influences the efficiency of analyte recovery and the compatibility of the extract with the detection system. The ideal desorption solvent must possess sufficient elution strength to effectively release the analyte from the surface of the sorbent while remaining chemically compatible with subsequent UV–Vis spectrophotometric analysis.

In this study, 0.1 M nitric acid (HNO_3) was selected as the desorption solvent based on its superior performance in preliminary tests, offering higher desorption efficiency compared to other candidates. Its acidic nature facilitates the breakdown of interactions between the sorbent surface and the adsorbed sulfide–methylene blue complex, enabling complete release into the solution phase.

To optimize the desorption solvent volume different ranges 0.5 – 1.0 mLwere investigated. The results indicated that 0.5 mL was sufficient for effective desorption, providing sharp and reproducible absorbance signals without unnecessary dilution of the analyte. This volume was therefore selected as the optimum, balancing efficiency, sensitivity, and solvent consumption.

Selection of desorption solvent type and volume

The choice of desorption solvent is a crucial step that directly influences the efficiency of analyte recovery and the compatibility of the extract with the detection system. The ideal desorption solvent must possess sufficient elution strength to effectively release the analyte from the surface of the sorbent while remaining chemically compatible with the subsequent UV-Vis spectrophotometric analysis.

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To optimize the volume of the desorption solvent, different volumes range **0.5 – 1 mL** were investigated. The results indicated that 0.5 mL was sufficient for effective desorption, providing sharp and reproducible absorbance signals without unnecessary dilution of the analyte. This volume was therefore selected as the optimum, balancing efficiency, sensitivity, and solvent consumption.

Effect of solution pH on the microextraction process

The pH of the sample solution plays a critical role in the efficiency of dispersive solid-phase microextraction (dSPME), as it directly influences both the chemical speciation of sulfide ions and the surface charge of the adsorbent. In this study, the effect of pH was investigated over a range from 5 – 10 by adjusting the solution using dilute hydrochloric acid (HCl) and sodium hydroxide (NaOH). The extraction efficiencies under different pH conditions are presented in Figure 5.

At acidic pH values (below 5), the concentration of free sulfide ions (S^{2-} and HS^{-}) in the solution decreases due to the conversion to hydrogen sulfide gas (H_2S), which is volatile and escapes from the solution. This results in a significant drop in complex formation with methylene blue and a corresponding decrease in extraction efficiency ,At higher pH values (above 7), although the sulfide ions remain in ionic form, the surface of the magnetic zeolite adsorbent becomes increasingly negatively charged due to deprotonation of surface hydroxyl groups. Since the sulfide–methylene, blue complex carries a net positive charge, excessive electrostatic repulsion between the negatively charged surface and competing anions in the solution (e.g., OH^-) can hinder effective adsorption of the complex onto the adsorbent surface.

The optimal extraction was achieved at pH = 6, where the balance between maximum availability of sulfide ions, stable complex formation with methylene blue, and favorable electrostatic interactions between the positively charged complex and the negatively charged zeolitic surface led to the highest extraction efficiency. Beyond this point, any increase or decrease in pH resulted in reduced performance due to the reasons mentioned above. The extraction mechanism is mainly attributed to the interaction between the sulfide–methylene blue complex and the surface of the magnetic nanozeolite. Electrostatic attraction between the positively charged methylene blue and the negatively charged zeolite surface plays a dominant role. In addition, surface adsorption and possible π–π interactions contribute to the efficient retention of the complex.

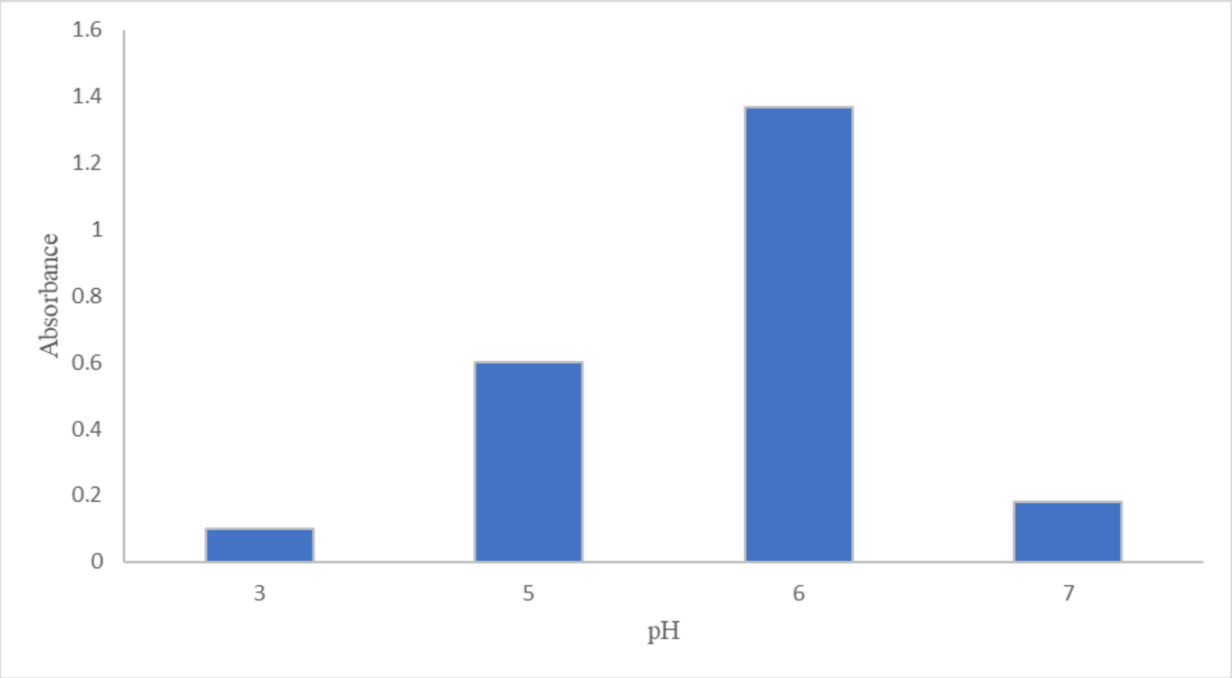

Figure5. Effect of pH. Experimental conditions: 0.03 g nanosorbent; desorption solvent, HNO_3; 10 mL sulfide solution (0.05 mg/L); adsorption time, 6 minutes; desorption time, 4 minutes; desorption solvent volume, 500 µL; NaCl, 0.5 g (5% w/v).

Effect of adsorption and desorption time

Adsorption time refers to the period during which the analyte is transferred from the sample solution to the surface of the dispersed adsorbent. To determine the optimal duration, various adsorption times ranging from 4 to 6 minutes were evaluated.

The results demonstrated that extraction efficiency increased steadily with time, reaching a maximum at 6 minutes. Beyond this point, a decline in signal was observed, likely due to deeper diffusion of analyte molecules into the inner structure of the adsorbent, which hinders effective, desorption. Consequently, an adsorption time of 6 minutes was selected as optimal.

In parallel, desorption time was studied by exposing the analyte-loaded adsorbent to the desorption solvent for varying durations (5–9 minutes). The data indicated that 5 minutes was sufficient to achieve complete desorption, and longer durations did not result in significant improvements. Therefore, a desorption time of 5 minutes was considered ideal.

Effect of nanosorbent amount

The quantity of adsorbent significantly influences extraction performance. To identify the optimal dosage, different amounts of magnetic nanozeolite (0.01–0.03 g) were tested. The data revealed that increasing the amount to 0.03 g enhanced analyte recovery, whereas lower amounts, such as 0.01 g, led to insufficient extraction due to limited surface area and weak analyte interaction. Hence, 0.03 g (30 mg) of the magnetic zeolite adsorbent was established as the most effective amount, as shown in Figure 6.

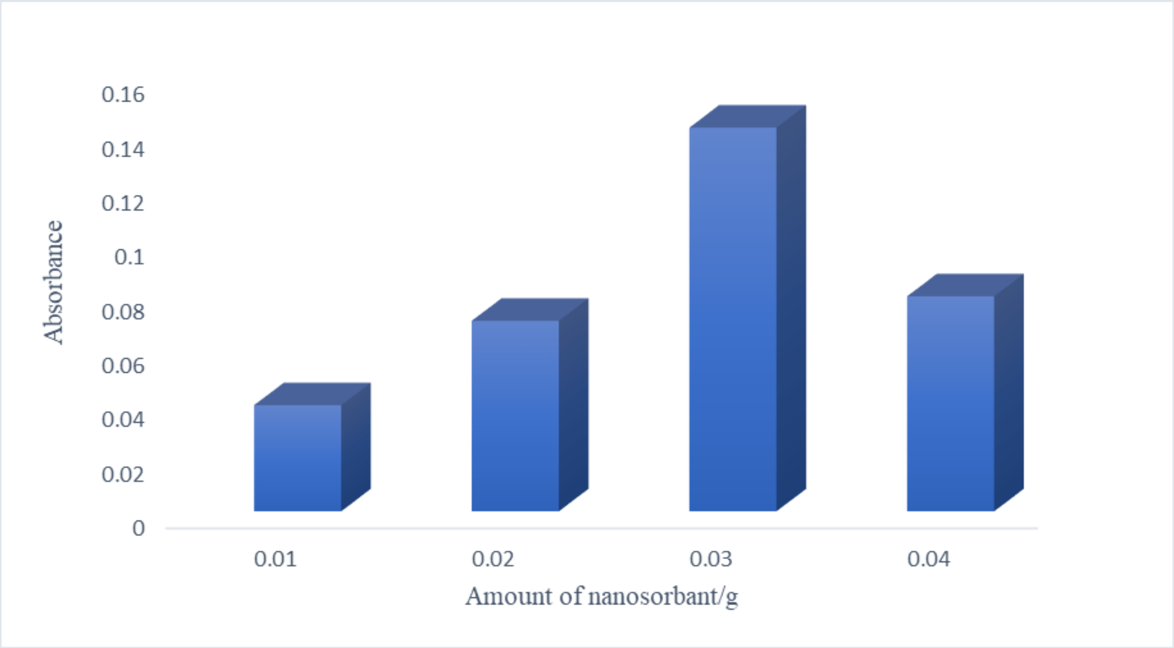

Figure 6. Effect of nanosorbent amount. Experimental conditions: pH = 6; desorption solvent, HNO_3; 10 mL sulfide solution (0.05 mg/L); adsorption time, 6 minutes; desorption time, 4 minutes; desorption solvent volume, 500 µL; NaCl, 0.5 g (5% w/v).

Desorption solvent volume

The volume of the desorption solvent must be optimized to ensure complete analyte recovery while avoiding unnecessary dilution. In this study, solvent volumes between 500 and 800 µL were evaluated. It was observed that increasing the volume beyond 500 µL led to a decrease in analytical response due to dilution effects that lowered analyte concentration in the eluted phase.

Accordingly, a volume of 500 µL was chosen as the optimal desorption solvent volume, as shown in Figure 7.

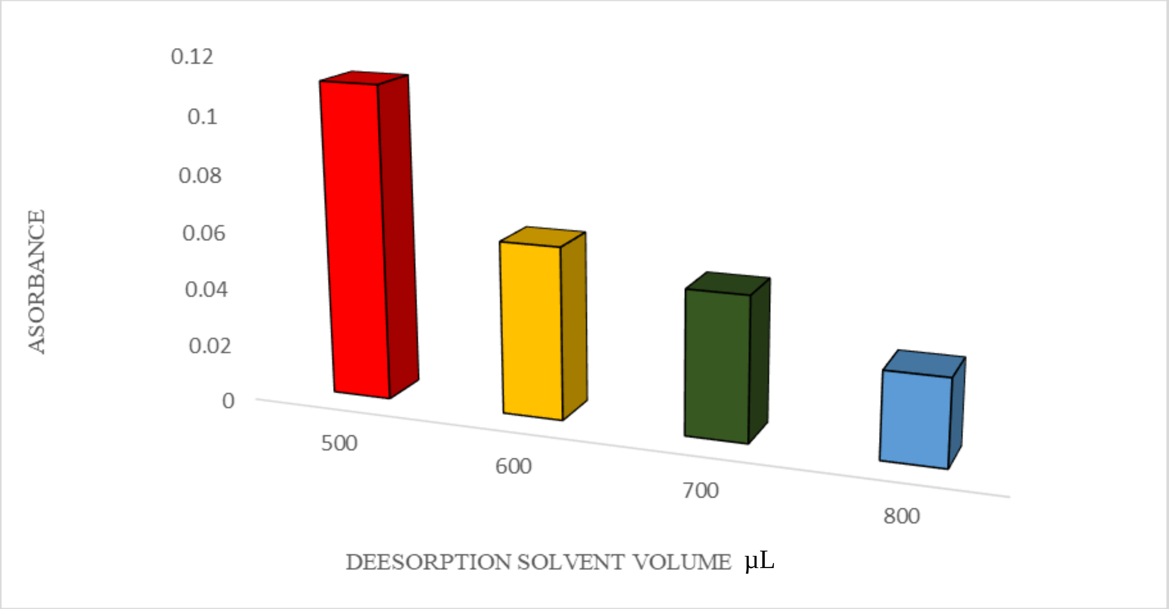

Figure 7. Effect of desorption solvent volume. Experimental conditions: pH = 6; desorption solvent, HNO_3; 10 mL sulfide solution (0.05 mg/L); adsorbent, 0.03 g; adsorption time, 6 minutes; desorption time, 4 minutes; NaCl, 0.5 g (5% w/v).

Effect of salt addition (NaCl)

The presence of salt in the sample can affect analyte transfer through the salting-out effect. Addition of NaCl reduces the solubility of the analyte in the aqueous phase, thereby promoting its migration to the adsorbent surface. However, excessive salt concentrations can increase solution viscosity and hinder mass transfer.

To study this effect, samples were prepared with and without the addition of 5% NaCl. The results showed that salt addition enhanced extraction efficiency, while its absence led to a noticeable decrease in performance. Thus, 5% NaCl was selected as the optimal concentration, as illustrated in Figure 8.

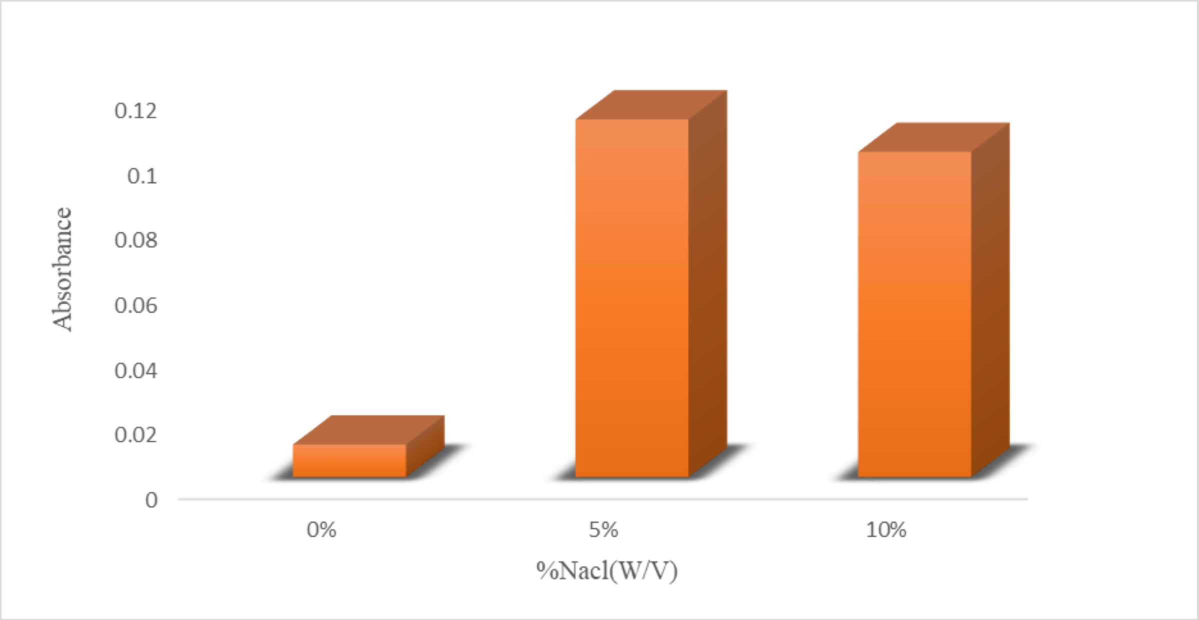

Figure 8 - Effect of Salt Addition. Experimental conditions: pH = 6; desorption solvent, HNO3; 10 ml sulfide solution, 0.05mg/L; 0.03 g adsorbent; adsorption time, 6 minutes; desorption time, 4 minutes; desorption solvent volume, 500 µL.

Calibration curve and statistical evaluation

A calibration curve for sulfide ion determination was constructed under optimized experimental conditions. The method exhibited a linear response within the concentration range of 0.008 –0.050 mg/L, in accordance with the Beer–Lambert law. The linear regression using equation (1) obtained was:

$$A = 21.025C + 0.1704 \qquad (1)$$

Where *A* represents the absorbance and *C* is the sulfide ion concentration in mg/L. The method showed excellent linearity, with a correlation coefficient (R^2) of 0.9801.

The limit of detection (LOD), calculated, as three times the standard deviation of the blank after the preconcentration step, was determined to be 0.008 mg/L. The limit of quantification (LOQ), defined as ten times the standard deviation of the blank, was found to be 0.030 mg/L.

The method's precision was evaluated by calculating the relative standard deviation (RSD**)** for multiple measurements within the studied concentration range, yielding an RSD of 4.06%. This demonstrates acceptable repeatability and reliability of the proposed method. The results are summarized in Table 1.

Table 1 . Analytical parameters of the proposed method for sulfide ion measurement

Parameter	Analytical Value
Linear range (mg/L)	0.008 – 0.050
Correlation coefficient (R^2)	0.9801
Limit of detection (LOD, mg/L)	0.008
Limit of quantification (LOQ, mg/L)	0.030
Relative standard deviation (RSD, %)	4.060

Selectivity and interference study

Selectivity and interference studies were carried out to evaluate the applicability of the proposed dSPME method in complex water matrices. The effect of common inorganic ions including Cl^-, SO_4^{2-}, NO_3^-, CO_3^{2-}, Ca^{2+}, Mg^{2+}, Mn^{2+} , Na^+, K^+, and Fe^{3+} as well as selected organic compounds were investigated. Each potential interfering species was added at concentrations up to 100-fold higher than that of sulfide (Table 2). The results showed no significant interference (signal deviation < ±5%), indicating that the magnetic nanozeolite exhibits high selectivity toward the sulfide–methylene blue complex under the optimized experimental conditions.

Table 2. Effect of interfering ions on the relative recovery of **0.05**mg/ L S^{2-}. (Recovery: mean ± standard deviation; n = 3).

Interfering ions	Added as	Concentration (mg L^{-1})	Relative Recovery (%)
Na^+	Na_2S0_4	50	96±0.2
K^+	KNO_3	50	98±0.4
Mg^{2+}	$Mg(NO_3)_2.9H_2O$	50	97±0.2
Ca^{2+}	$Ca(NO_3)_2.6H_2O$	50	98±0.3
Fe^{3+}	$Fe(SO_4)_2.NH_4.12H_2O$	50	95±0.5
Mn^{2+}	$MnSO_4.H_2O$	50	97±0.9
NO_3^-	$Na(NO_3)_2$	50	98±1.0
Cl^-	NaCl	50	99±0.9
CO_3^{2-}	$Na(CO_3)_3.9H_2O$	40	96±0.6
SO_4^{2-}	K_2SO_4	75	95±0.8

Stability and reproducibility of the adsorbent

The stability and reusability of the magnetic nanozeolite were evaluated to assess its practical applicability. The adsorbent was stored under ambient conditions, and its extraction efficiency was periodically tested. No significant loss in performance was observed over 12 weeks of storage.

Furthermore, the adsorbent could be reused for at least 6 consecutive extraction cycles after simple magnetic separation and washing, with extraction efficiency remaining above 89% of the initial value.

Application to real samples

To validate the practical applicability of the developed method, it was employed for the detection and quantification of sulfide ions in various real water samples, including tap water (Mashhad city), Kashaf Rud River water, and industrial wastewater. Samples were filtered through 0.45 µm membranes and acidified to pH < 2 using HCl to prevent sulfide oxidation. Stored in airtight containers at 4°C and analyzed within 24 hours. Each sample (10 mL) was subjected to the optimized microextraction procedure, and analyses were performed in triplicate.

To assess recovery, the samples were spiked with 0. 01 mg/L of sulfide ion, followed by extraction and measurement under optimized conditions. The recovery results, summarized in Table 3, confirmed the method’s accuracy and effectiveness in complex matrices. The high and consistent recovery rates affirm the method’s suitability for environmental monitoring of sulfide in diverse aqueous samples.

Table 3. Extraction and measurement of sulfide in water samples

Sample	**Added Concentration (mg/L)**	**Measured Concentration (mg/L)**	**Recovery Percentage (%)**
Mashhad Municipal Water	0.000	Not detected	---
	0.010	0.009 ± 0.004	90
Kashafroud River Water	0.000	Not detected	---
	0.010	0.010 ± 0.003	100
Industrial area Water	0.000	0.003	---
	0.010	0.012 ± 0.004	92

Comparison of the proposed method with other sulfide determination techniques

The developed methylene blue microextraction method for sulfide determination at low concentrations (0.05 mg/L) demonstrates competitive analytical performance when compared with established techniques [2 6-30]. As shown in Table 4, the method offers a suitable linear range and a low limit of detection (LOD) comparable to traditional spectrophotometric methods, while achieving excellent precision with a relative standard deviation (RSD) below 5%.

Compared to electrochemical sensors and gas chromatography, this method requires simpler instrumentation and minimal sample preparation, making it more accessible for routine laboratory analysis. Although chromatographic methods provide superior sensitivity, they involve higher operational costs and complexity. Furthermore, iodometric titration, while straightforward, has a higher LOD and poorer precision than our microextraction approach. Fluorometric methods demonstrate very high sensitivity but require specialized reagents and fluorescence detection systems. In summary, the proposed microextraction coupled with methylene blue spectrophotometry balances sensitivity, accuracy, and simplicity, making it a practical and reliable choice for sulfide monitoring in environmental water samples, especially at trace levels.

Table4. Comparison with Other Sulfide Determination Techniques.

Method	Linear Range mg/L	Limit of Detection mg/L	Reference
Spectrophotometry	0.32–19.2	-	26
Spectroflouremetry	3.2– 48	0.176	27
Spectrophotometry	0.02–1.5	0.016	28
Spectrophotometry	0.50–1.0	0.02	29
Spectrophotometry	Up to 4640	3.2	30
Spectrophotometry	0.008–0.05	0.008	this method

Conclusion

The findings of this study demonstrate that integrating magnetic zeolite with dispersive solid-phase microextraction provides a practical and effective platform for sulfide ion analysis in aqueous environments. By forming a stable colored complex with methylene blue prior to adsorption, high extraction efficiency and enhanced sensitivity were achieved without the need for sophisticated instrumentation or labor-intensive procedures.

The method’s ability to detect low concentrations of sulfide with satisfactory precision and repeatability highlights its potential for routine environmental analysis. Moreover, its successful application to real samples from urban, river, and industrial water sources confirms the robustness and adaptability of the technique to complex matrices.

One of the key strengths of this method lies in its simplicity and environmental friendliness, it avoids extensive use of toxic solvents, requires only small amounts of adsorbent, and enables rapid analysis, making it suitable for on-site or resource-limited settings. Despite these advantages, the proposed method has some limitations: at very high sulfide concentrations or in highly complex matrices, matrix effects may slightly influence extraction efficiency. Additionally, the procedure is optimized for trace-level determination and may require sample dilution when sulfide levels are exceptionally high.

While the method exhibited excellent performance, future research could focus on enhancing its selectivity toward sulfide in the presence of interfering species or adapting the approach for portable, field-deployable detection systems. Overall, this technique offers a viable alternative to more complex analytical methods and contributes significantly to water quality monitoring and environmental protection efforts.

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