Scientific Reports

https://doi.org/10.1038/s41598-026-65372-0

Article in Press

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Received: 16 May 2026

Accepted: 30 July 2026

Published online: 03 August 2026

Cite this article as: Ali B., Büyük M.A., Çakmak E.S. *et al.* Toner@cobalt ferrite nanocomposite based dispersive solid phase microextraction approach for the preconcentration of lead ions in bottled drinking water samples. *Sci Rep* (2026). https://doi.org/10.1038/s41598-026-65372-0

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Toner@cobalt ferrite nanocomposite based dispersive solid phase microextraction approach for the preconcentration of lead ions in bottled drinking water samples

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Abstract

In this method, a dispersive solid phase microextraction (DSPME) method was developed to determine the trace levels of lead (Pb^{2+}) ions with high accuracy in bottled drinking water samples using flame atomic absorption spectrometry (FAAS). Waste toner-based $CoFe_2O_4$ nanocomposite structures, which are expected to contribute to the literature as a newly synthesized sorbent material, were fabricated for the preconcentration of Pb^{2+} ions. The univariate optimization approach was implemented for all parameters that affect extraction efficiency, and under the optimal working conditions, the limit of detection (LOD) and limit of quantification (LOQ) were determined to be 5.0 and 16.5 μg L^{-1} respectively. By comparing the slopes of the calibration plot equations for the FAAS and toner@$CoFe_2O_4$-based DSPME-FAAS methods, it was noted that the sensitivity was improved by 161.1 times. In recovery studies based on spiking with bottled drinking water samples, the recovery results ranged from 86.8% and 116.6% utilizing the matrix matching approach, thereby demonstrating the applicability of the method in drinking water samples. Greenness and practical applicability of the method were supported by BAGI and

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AGREEprep metrics with the scores of 65 and 0.44, respectively. On the other hand, the functionalization of toner particles obtained from waste cartridges and their first-time use as sorbent with a nanocomposite structure for the preconcentration of a metal ion demonstrated the originality and developability of the study.

Keywords: Lead; microextraction; toner; nanocomposite; cobalt ferrite; drinking water

1. Introduction

Potentially toxic elements (PTEs), including metals, metalloids, and non-metals, continue to be the focus of numerous studies due to the disruptive effects they cause in various aquatic media. Such contaminations lead to significant environmental problems, particularly due to the prominent characteristics of metals such as biological accumulation, mobility, and molecular resistance [1]. The presence of PTE in natural water ecosystems may cause lack of dissolved oxygen, algal blooms, and the death of aquatic organisms. Furthermore, when PTEs are introduced into aquatic environments, they can disrupt the overall structure of the food chain, leading to cascading effects on ecological balance [1,2]. Lead (Pb) remains one of the toxic elements that contaminate drinking water today. The presence of Pb in residential areas and even in domestic water supplies is generally linked to old building infrastructure containing lead-alloy pipes [3]. According to current data, it is thought that increased blood pressure in adults and behavioral and neurodevelopmental disorders in children are associated with levels considered safe for Pb. On the other hand, long-term exposure to Pb may result in various types of cancer. The World Health Organization (WHO) guideline for the safe limit of Pb in drinking water has recently been proposed by the Canadian Federal-Provincial-Territorial Committee on Drinking Water (CDW) to be updated from 10 μg L^{-1} to 5.0 μg L^{-1} [4]. Hence, monitoring of Pb levels in drinking water with sensitive and accurate methods is an urgent priority.

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There are various studies currently found in literature for the detection of several metal ions at different levels, including spectroscopic techniques such as ultraviolet-visible spectrophotometry (UV-Vis) [5], inductively coupled plasma mass spectrometry (ICP-MS) [6], inductively coupled plasma optical emission spectrometry (ICP-OES) [7], graphite furnace atomic absorption spectrometry (GFAAS) [8], and flame atomic absorption spectrometry (FAAS) [9], as well as voltametric techniques such as anodic stripping voltammetry (ASV) [10], cathodic stripping voltammetry (CSV) [11], and differential pulse voltammetry (DPV) [12]. Unlike complex, costly, and time consuming methods, FAAS is frequently used not only in scientific studies but also in industrial research due to its prominent advantages such as a simple interface, fast response, and ease of use. However, the determination of target analyte(s) in low concentration in complex matrices may be difficult due to insufficient nebulizer efficiency [13]. As the importance of analytical determination at trace levels increases today, the application of sample preparation methods has become a necessity to overcome these drawbacks.

In the literature, various approaches such as switchable hydrophilicity solvent-based liquid phase microextraction (SHS-LPME) [14], hollow fiber solid phase microextraction (HF-SPME) [15], solidified floating organic droplet microextraction (SFODME) [16], cloud point extraction (CPE) [17], single-drop microextraction (SDME) [18], dispersive liquid-liquid microextraction (DLLME) [19], and dispersive solid-phase microextraction (DSPME) [20] have been frequently reported for the preconcentration/separation of Pb ions. DSPME, which has become quite popular in recent years as a preconcentration method in terms of sorbent diversity, essentially enables the isolation of target analytes from the matrix solution through adsorption onto a micro- or nano-sized solid sorbent [21]. In DSPME, the sorbent material moves by dispersing within the sample solution, and this motion helps the adsorption of more analytes by increasing the surface area.

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Then, a suitable elution solution enables the desorption of analytes collected on the sorbent, and the process is completed with the analysis of the extraction phase [22].

One of the most critical steps in the DSPME method is the selection of the sorbent that will collect the target analyte(s) with high efficiency. Nanoparticles (NPs) are popular structures with at least one dimension smaller than 100 nm, and have a large application area with characteristics of minimum size, high porosity, and active adsorption sites [23,24]. Up to now, a variety of nanostructures such as metal oxides [25], 2D NPs [26], nanotubes [27], magnetic NPs [28], polymeric NPs [29], silica-based NPs [30], and nanoporous NPs [31] have been synthesized for different purposes in the literature. Moreover, the increasing diversity in scientific research is strengthening the interest of innovative materials. Accordingly, the reusability of waste materials in the production of cost-friendly materials that do not involve complex synthesis procedures is an attractive research topic. Of these, the ink cartridges separated as electronic waste after printing and copying activities contain high amounts of toner powder. On a global perspective, these cartridges, which are widely used all over the world, generate millions of tons of toner powder waste [32]. Generally, the composition of the toner particles varies according to the specific formulations of printer manufacturers, but it basically consists of carbon, iron, silicon, and a binding polymer [33]. Hence, the reuse of toner particles with their magnetic properties and different functional structures not only makes the toner a high value-added product, but also turns it into a suitable material for innovative work within the scope of green chemistry principles [34].

The primary objective of this study is to develop a sensitive, accurate, inexpensive, and innovative analytical method for the determination of trace levels of Pb ions in a vital matrix such as drinking water. Using the hydrothermal synthesis method, the toner based $CoFe_2O_4$ nanocomposite structures were synthesized for the first time in the literature using toner particles with good

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adsorption ability obtained from waste cartridges in our laboratory and were used for the first time for the preconcentration of any analyte as sorbent material. This study, which covers the conversion of waste materials into useful products, an environmentally friendly approach, and previously unreported material synthesis, is expected to offer a good alternative for analytical applications.

2. Materials and Method

2.1.Reagents and Chemicals

All the reagents and chemicals that were used during the experimental process were utilized in analytical grade. Firstly, ultrapure water employed for all sample preparation, synthesis and washing processes was obtained from Elga Pure Flex 3 Ultrapure Water System (High Wycombe, UK) with 18.2 MΩ cm^{-1} resistance. The Pb stock solution was prepared from lead (II) nitrate (≥ 99.5%, Merck, Germany) salt by dissolving in ultrapure water. Buffer solutions were prepared in the range of pH 4.0 – 7.0 by using tris and potassium hydrogen phthalate purchased from Merck (Darmstadt, Germany). The pH 4.0, 5.0, and 6.0 buffers consisted of 0.40 M of potassium hydrogen phthalate, and the pH 7.0 buffer consisted of 0.50 M of tris. The sodium hydroxide (NaOH) and hydrochloric acid (HCl) purchased from Merck (Darmstadt, Germany) were employed for the pH adjustment of buffer solutions. In the synthesis of the toner@$CoFe_2O_4$ nanocomposites, cobalt (II) chloride hexahydrate ($CoCl_2.6H_2O$) and iron (III) chloride hexahydrate ($FeCl_3.6H_2O$) and 25% of ammonia were purchased from Sigma-Aldrich (France) and Isolab (Eschau, Germany), Merck (Darmstadt, Germany), respectively. The nitric acid (65%, v/v) (HNO_3) used as desorption solvent and ethanol used as washing solution were supplied from Merck (Darmstadt, Germany). The toner particles were obtained from Printpen (İstanbul, Türkiye)

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laser printer toner cartridge that had been adapted for use with the Canon printers in our laboratory. The acetylene gas used as fuel was supplied from a local supplier in İstanbul, Türkiye.

2.2.Instrumentation

Pb ions were determined by employing an ATI Unicam 929 AA model flame atomic absorption spectrometer (FAAS) equipped with a deuterium lamp for the background corrections. The continuous light source was provided with the help of the Photron multilamp with a 10 mA current at 283.3 nm wavelength and a bandpass of 0.50 nm. The flame of the FAAS was provided with the stoichiometric ratio of the air-acetylene mixture. An Isolab (Germany) vortex mixer was used for the mixing process of the samples. Additionally, an IKA RCT basic model hot plate with magnetic stirrer (Staufen, Germany), and a Biobase-UC-80A model ultrasonic bath were used to achieve homogeneity during the mixing process and synthesis of the toner@$CoFe_2O_4$ nanocomposites. The pH of the solutions was adjusted with a Mettler Toledo brand pH meter. Also, the hydrothermal synthesis was achieved in the Nuve FN120 model oven (Ankara, Türkiye). The phase separation was carried out by utilizing a Biobased BKC-TL5II model centrifuge (Shandong, China). After synthesis, an Heraeus oven was used to remove moisture from the toner@$CoFe_2O_4$ nanocomposites.

2.3.Synthesis Procedure of Toner@$CoFe_2O_4$ Nanocomposites

First, toner particles were separated from used cartridges obtained from printing/copying devices, washed with ethanol and water to remove any impurities on the surface, and dried in an oven at 50 °C. Next, 100 mg of dried toner particles were placed in a container with a 10 mL of pure water and held in an ultrasonic bath for about 1.0 hour to improve dispersion properties and prevent possible agglomeration. The synthesis conditions reported by Mishra and colleagues for the

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fabrication of $CoFe_2O_4$ nanoparticles were adapted to obtain the toner@$CoFe_2O_4$ nanocomposites [35]. Here, the 1.19 g of $CoCl_2.6H_2O$ and 2.703 g of $FeCl_3.6H_2O$ salts were weighed to achieve a Co:Fe molar ratio of 1:2 and dissolved in a quantity of pure water. 100 mg of toner particles sonicated in other container were added to this solution, and a 25% of ammonia solution was added dropwise to adjust the pH to 11 under constant stirring. The final volume was then completed to 30 mL with pure water. The final solution was transferred to a Teflon container and kept in a hydrothermal furnace at 180 °C for 24 hours. The formed nanocomposite structures were washed several times with an ethanol-water mixture after phase separation and dried in an oven at 50 °C for 24 hours.

2.4.Application of Toner@$CoFe_2O_4$ Nanocomposite based DSPME-FAAS Method

The DSPME-FAAS method developed for the determination of trace levels of Pb ions in drinking water samples involves adding buffer solution and sorbent material to the sample solution, followed by mixing, magnetic separation, decantation, and desorption, and finally FAAS measurements. In a broader scope, pH 7.0 buffer solution (1.0 mL, 0.50 M of tris) was spiked into 40 mL of the sample solution. Then, 25 mg of toner@$CoFe_2O_4$ nanocomposite was added to the solution medium and vortexed for 10 seconds to accelerate the interaction between the sorbent and Pb ions. The phase separation was achieved by external neodymium magnet and supernatant was decanted. 80 µL of 1.0 M of HNO_3 was added onto sorbent phase to release the adsorbed Pb ions. After magnetic phase separation, the extract was measured by FAAS system.

2.5.Samples

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Two bottles of drinking water belong to different brand was bought from a supermarket in İstanbul, Türkiye. Spiking process was performed to obtain a final Pb concentration of 15, 30, and 75 μg L^{-1} without any dilution of drinking water samples.

3. Results and Discussion

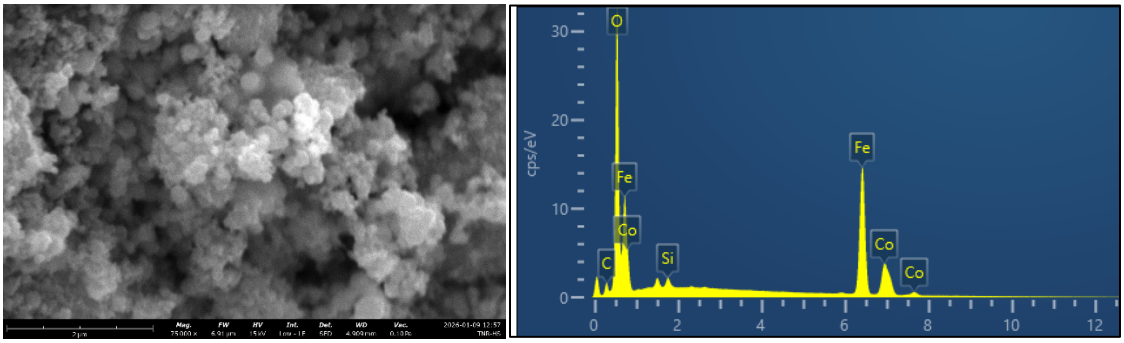
The optimization studies for the proposed toner@$CoFe_2O_4$ nanocomposite-based DSPME-FAAS method for the monitoring of Pb ions at trace levels with high accuracy and sensitivity were carried out with a univariate optimization approach.

3.1.Characterization of toner@$CoFe_2O_4$ nanocomposite

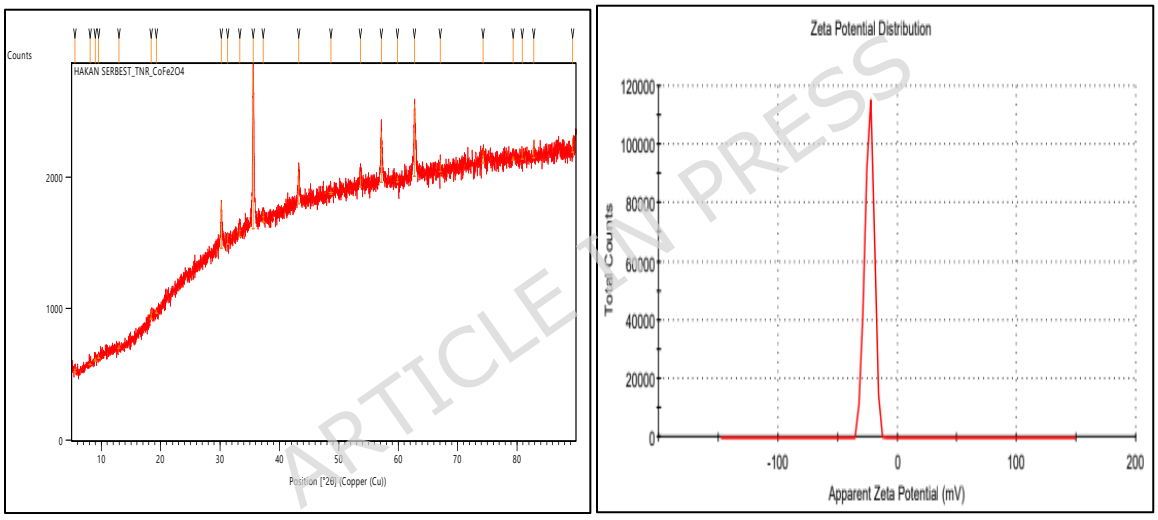
The characterization studies including scanning electron microscope (SEM), energy dispersive X-ray (EDX), zeta potential and x-ray diffraction (XRD) were achieved to investigate the surface morphology, elemental composition, crystalline structures, and particle zeta potential distribution of toner@$CoFe_2O_4$ nanocomposite, respectively. Figure 1a presented the SEM image of synthesized sorbent. In Figure 1b, the EDX results were given with elemental mapping, and the weight percentages of the elements C, O, Fe, Co, and Si were found to be 6.6%, 29.1%, 48.3%, 14.4%, and 0.7%, respectively, and a peak belonging to the sample platform was detected apart from these. The results obtained confirm that the nanocomposite structure was successfully realized. The XRD results are shown in Figure 1c by scanning in the angular range 5.0 – 90° of 2θ angles with a step size of 0.017°. According to the 2θ angles obtained from Cu-K α radiation with a wavelength of 1.5406 Å, the iron oxide (Fe_3O_4) was considered as dominant phase. Moreover, 2θ angles of 30.2, 35.6, 37.1, 43.2, 53.6, 57.2 and 62.8 were in accordance with the Fe_3O_4 phase (JCPDS#19-0629) and $CoFe_2O_4$ phase (JCPDS#22-1086) correspond the lattice parameters (220), (311), (400), (422), (511) and (440), respectively [36,37]. Under the conditions 120.6 of count rate

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(kcps) and 25 °C, the zeta potential given in Figure 1d was measured as -23.4 mV and this result indicated that the surface of toner@$CoFe_2O_4$ nanocomposite was negatively charged.



(a) (b)



(c) (d)

Figure 1. The characterization results of toner@$CoFe_2O_4$ nanocomposite a) SEM image, b) EDS image, c) XRD patterns, d) Zeta potential

3.2.Impact of pH and Buffer Volume

In DSPME methods, the extraction efficiency of metal ions is primarily affected by the acidity or alkalinity of the sample solution [38]. A decrease in pH corresponds to an increase in the concentration of H_3O^+ in the sample media. Lower pH values lead to poor adsorption efficiency due to the repulsive behavior between analyte ions and positively charged adsorption sites.

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However, as the pH of the medium increases, donor atoms in the adsorption sites become deprotonated and the surface of the sorbent becomes favorable for the transfer of target analytes to the sorbent surface and complex formation. On the other hand, in alkaline solutions, the presence or addition of hydroxide into the medium may result in the precipitation and complex formation of various metals. Hence, above a certain pH, any increase in pH may lead to a decrease in adsorption efficiency on the sorbent [39]. This may be explained by the fact that in aqueous solutions, Pb exists predominant in the form of $Pb(OH)^+$ or $Pb(OH)_2$ when pH>7.0, and in the form of Pb^{2+} when pH<6.0. In a preconcentration based approach, Pb^{2+} transferred to the sorbent surface in the alkaline region, as well as $Pb(OH)_2$, may significantly contribute to extraction yields [40]. However, in such a case, tests conducted with and without the sorbent are crucial for comparing the sorbent's performance. For this goal, pH of solutions was tested in the range of 4.0 – 7.0 to determine the optimum acidity of medium. As seen in Figure 2, the highest mean absorbance values were recorded at pH 7.0. Furthermore, the extraction procedure was performed without using sorbent at the same pH values to test if any precipitation occurred. The mean absorbance value measured in the absence of sorbent corresponded to 6.0% of the mean absorbance value measured in the presence of sorbent. This result demonstrated that the contribution of precipitation to the analyte signal was minimal under the specified conditions. Hence, pH 7.0 was decided to be the optimum pH. The types of interactions between the analyte and the sorbent have generally been reported as ion exchange, electrostatic interactions, dipole-dipole and π-π interactions, chemical bonding, complex formation in the inner and outer spheres, hydrogen bonding, and van der Waals forces [41,42]. In the literature, the formation of surface complexes has been reported as the primary adsorption mechanism for Pb^{2+} on $CoFe_2O_4$ at pH < 7.0 and inner sphere complexation has been observed at pH > 7.0 [43]. In addition, the fact that the surface is negatively

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charged according to the zeta potential result also suggests that electrostatic interactions likely to contribute to the transfer of Pb^{2+} ions to the sorbent surface.

Next, the buffer solutions were added with the different volumes between 0.25 and 1.0 mL with 0.25 mL of increments. The mean absorbance values recorded were close each other. 1.0 mL was chosen as optimum buffer solution with high repeatability.

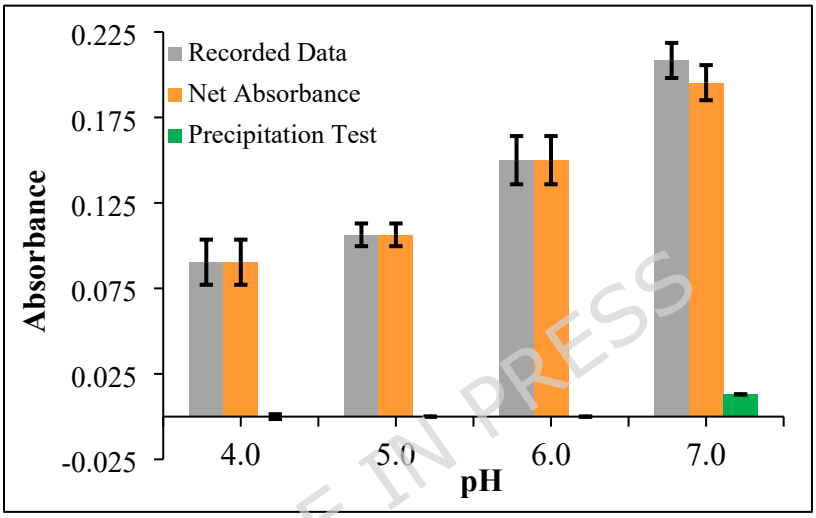


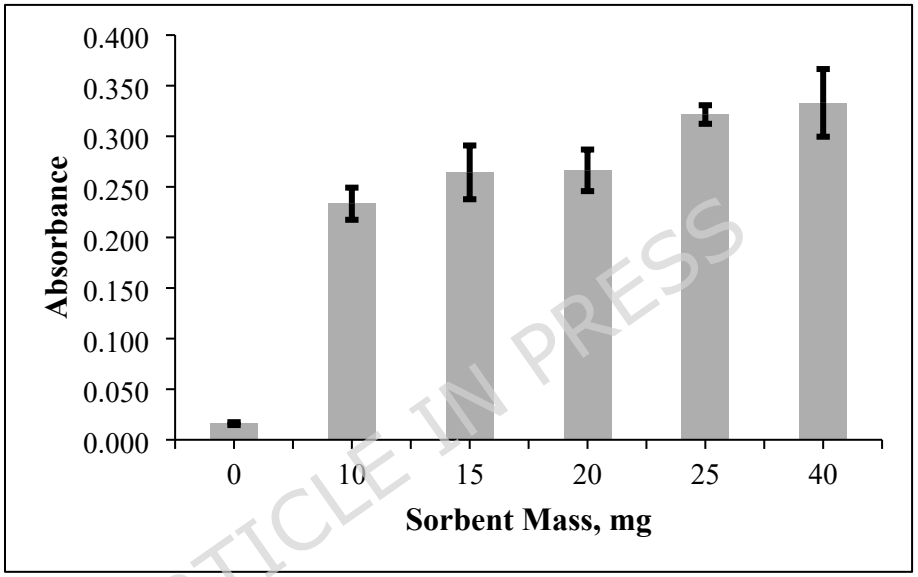
Figure 2. Influence of pH (20 mL of 0.50 mg L^{-1} Pb solution, 30 s vortex, 20 mg of toner@$CoFe_2O_4$ nanocomposite, 150 µL of conc. HNO_3) (n=3)

3.3.Impact of Sorbent Mass

In an extraction process, the amount of sorbent used affects not only the interaction between the analyte and the adsorbent, but also other conditions such as operating costs, environmental approach, and waste management. Specifically, when the amount of sorbent used for analyte ions at a certain concentration is low, the total surface area may be insufficient to achieve effective extraction. On the other hand, using excessive amounts of sorbent to ensure sufficient surface area may lead to infeasible situations such as requiring a larger volume of eluent for desorption, increased synthesis costs, and the accumulation of more sorbent waste [13,44]. For this purpose, 10, 15, 20, 25 and 40 mg of toner@$CoFe_2O_4$ nanocomposite were added to the solutions to

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determine the optimum sorbent mass under equal conditions. The mean absorbance values presented in Figure 3 increased from 10 mg to 25 mg linearly, and close between 25 mg and 40 mg. Considering the high repeatability, 25 mg was determined as optimum sorbent mass. Moreover, the experiments were carried out without using sorbent under same conditions and it has been confirmed that the precipitation with hydroxyl form of Pb^{2+} contributed approximately 5.0% to the signals obtained for 25 and 40 mg, where the analyte-sorbent interaction was highest.



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Figure 3. Influence of sorbent mass (40 mL of 0.25 mg L^{-1} Pb solution, 1.0 mL of pH 7.0 buffer, 30 s vortex, 150 µL of conc. HNO_3) (n=3)

3.4.Impact of Sample Volume

The initial sample volume is critical to determine the preconcentration factor as well as to evaluate the extraction capacity of sorbents for analytes at different concentrations. Theoretically, it may be advantageous to operate at lower sample volumes in terms of the potential matrix effects and extraction periods; however, it is known that extraction efficiency and preconcentration factors generally may be improved as the sample volume increases [45]. Furthermore, since the number of analyte(s) transferred to a given total sorbent surface area increases with an increase in sample

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volume, the initial volume of the sample significantly contributes to the sensitivity of the method and the achievement of low detection limits [46]. In light of this information, the extraction procedure was performed under the same conditions with different sample volumes ranging from 8.0 to 40 mL in increments of 8.0 mL. Considering the shape of the tube, the use of samples exceeding 40 mL could not provide effective operation for the analyst; therefore, 40 mL was determined as the maximum sample volume. As seen in Figure 4, the mean absorbance values were increased linearly from the lowest volume to the highest volume tested, and 40 mL was selected as the optimum one.

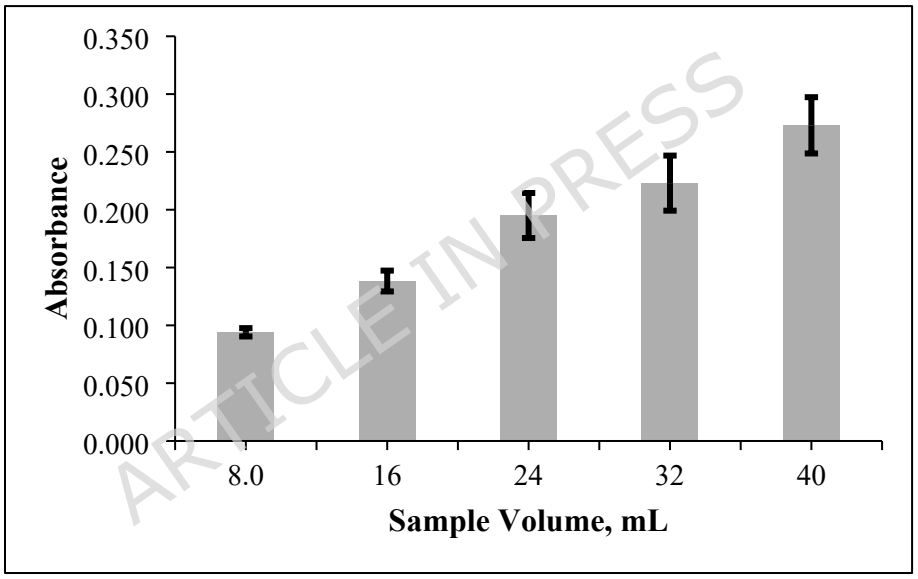


Figure 4. Influence of sample volume (pH 7.0 buffer (1.0 mL), 30 s vortex, 25 mg of toner@$CoFe_2O_4$ nanocomposite, 150 µL of conc. HNO_3) (n=3)

3.5.Impact of Vortexing Period

In DSPME, the efficient dispersion of the adsorbent within the sample solution and the enhancement of effective interaction with the analyte are significantly dependent on the mixing process [47]. Vortexing is an agitation method that rapidly and homogeneously disperses the adsorbent in the solution and increases its interaction with the analyte. To investigate the effect of

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mixing time on extraction outputs, vortexing periods ranging from 0 to 45 seconds (0, 5, 10, 15, 30, and 45 seconds) were tested under equal conditions.

The recorded measurement results revealed that Pb ions rapidly transferred to the sorbent surface even during very short contact times (Figure 5). The mean absorbance values showed a slight increase from 0 s to 10 s, reached the highest value at 10 s with high repeatability, and then began to decrease linearly towards 45 s. Accordingly, 10 s was selected as the optimal vortexing period, and these results showed that Pb^{2+} ions interacted with the adsorbent surface within a short period of time. The decrease in the results observed at longer vortexing periods (15, 30 and 45 s) may be attributed to partial desorption of Pb^{2+} ions or aggregation of the sorbent, reducing the effective surface area.

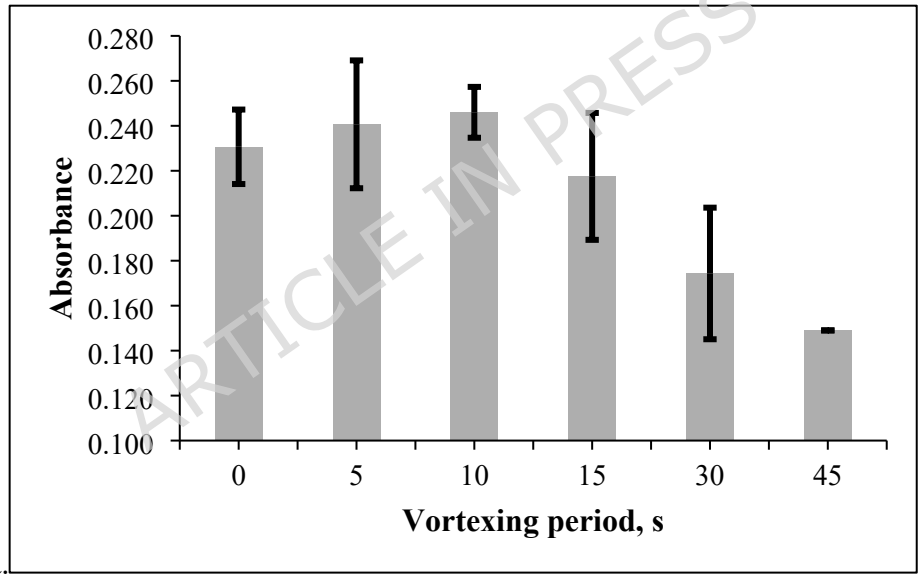


Figure 5. Influence of vortexing period (40 mL of 0.25 mg L^{-1} Pb solution, 1.0 mL of pH 7.0 buffer, 25 mg of toner@$CoFe_2O_4$ nanocomposite, 150 µL of conc. HNO_3) (n=3)

3.6.Impact of Desorption Solvent Concentration and Volume

In DSPME, the desorption process not only affects the overall efficiency of the method but also plays a decisive role for the determination of the preconcentration factor. In this step, the type, concentration, and volume of the preferred desorption solvents also play a critical role in the

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effective release of metal ions from the sorbent surface [48]. Acidic solvents, which tend to positively charge the adsorbent surface, facilitate the removal of cationic species such as Pb^{2+} from the sorbent surface [49]. For this reason, nitric acid (HNO_3) was selected as the desorption solvent throughout this study.

Next, to investigate the influence of HNO_3 concentration on desorption efficiency, a series of HNO_3 concentrations ranging from 0.50 to 14.4 M were tested. The mean absorbance values increased from 0.50 M to 1.0 M, were close to each other between 1.0 and 5.0 M, and showed a decreasing trend from 5.0 M to 14.4 M. Considering the environmentally friendly approach and effective desorption efficiency, 1.0 M concentration was selected as the optimal acid concentration. It is thought that the increasing acid viscosity at increasing concentrations is responsible for the decrease in mean absorbance values since changes in viscosity have a primary effect on the nebulizer aspiration rate, aerosol transport efficiency and altering the amount of analyte reaching the atomizer unit [50,51].

The final volume is crucial in DSPME method to achieve high preconcentration factor. For this goal, different volumes between 80 and 200 µL of 1.0 M of HNO_3 were tested. As shown in Figure 6, the highest mean absorbance was recorded at 80 µL. Experiments performed with this volume showed both efficient Pb^{2+} desorption and good repeatability. A linear decrease occurred towards 200 µL. This decrease was thought to cause a significant decrease in signal, likely due to dilution of the analyte desorbed in a higher final volume. Hence, 80 µL of 1.0 M HNO_3 was recorded as the optimal condition for effective release of Pb^{2+} from the sorbent surface.

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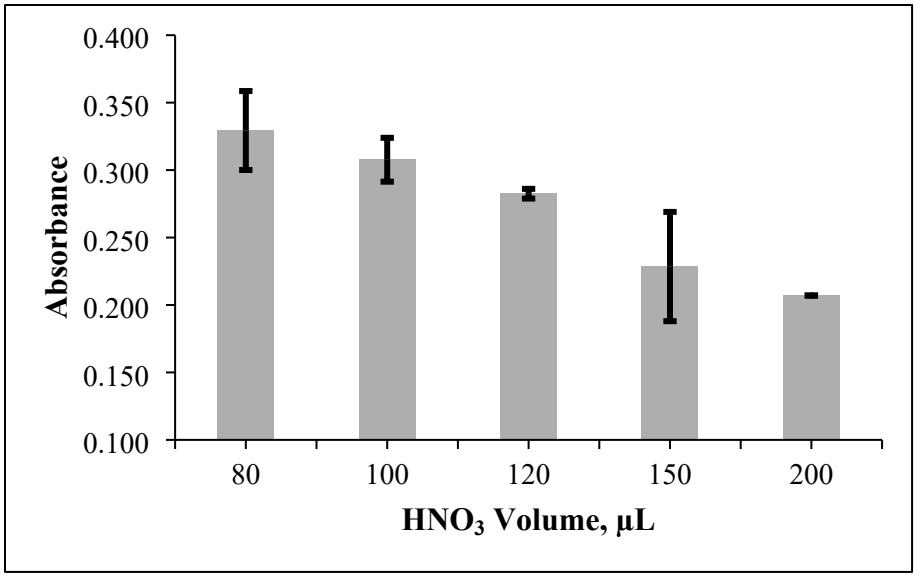


Figure 6. Influence of HNO_3 volume (40 mL of 0.10 mg L^{-1} Pb solution, 1.0 mL of pH 7.0 buffer, 10 s vortex, 25 mg of toner@$CoFe_2O_4$ nanocomposite) (n=3)

3.7.Evaluation of System Analytical Performance Values

The analytical figures of merit are highly valuable for understanding, evaluating, and comparing the analytical performance values of both the instrument and the developed analytical method with literature findings. Table 1 shows the optimal operating conditions for the developed toner@$CoFe_2O_4$ nanocomposite-based DSPME-FAAS method. Key parameters such as the limit of detection (LOD), limit of quantification (LOQ), linear working range, and regression coefficient (R^2) were assessed under optimal conditions. The LOD and LOQ calculations were carried out by multiplying the ratio of the standard deviation of at least six replicated measurements of the lowest concentration in the calibration plot obtained to calibration plot slope by 3 and 10, respectively and found to be 5.0 and 16.5 µg L^{-1}, respectively. The sensitivity of FAAS was improved as 161.1-fold by making a comparison the slope of the FAAS ($y=0.0101x + 0.0028$, unit in mg L^{-1}) and toner@$CoFe_2O_4$ nanocomposite-based DSPME-FAAS ($y=1.6268x + 0.0055$, unit in mg L^{-1}). The dynamic linear range was between 10 and 100 µg L^{-1} and R^2 was found to be 0.9967.

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Table 1. The optimal conditions of toner@$CoFe_2O_4$ nanocomposite-based DSPME-FAAS protocol

Parameters	Condition
pH / volume of buffer	pH 7.0 (tris) buffer / 1.0 mL
Sample volume	40 mL
Amount of toner@$CoFe_2O_4$ nanocomposite	25 mg
Vortexing period	10 s
HNO_3 volume / concentration	80 µL / 1.0 M

The analytical performance indicators of the proposed method were compared in Table 2 with the findings of other sorbent types synthesized for Pb^{2+} preconcentration and the methods described in the literature. In a preconcentration study reported by Tarley et al., the Pb^{2+} ions in various food matrices were enriched utilizing an adsorbent based modified rice husks, resulting in a 46-fold increase in calibration sensitivity [52]. Barabi et al. synthesized magnetic iron/graphene oxide nanosorbents coated with dimethylglyoxime-functionalized silica for the determination of Pb^{2+} in nail, water, and hair samples and recorded a 15.5-fold preconcentration factor in the FAAS system [53]. Matoso et al. presented an analytical method that provides 30-fold enrichment in an FAAS system for the determination of Pb^{2+} in river and wastewater samples using silica gel sorbents chemically modified with zirconium phosphate [54]. Borges et al. synthesized magnetite incorporating orange peel and developed a method for the preconcentration of Pb ions in commercial fruit juices through direct sampling without using eluent. Although the LOD was calculated to be 2.6 µg L^{-1}, the sensitivity of FAAS was improved only 14-fold [9]. Shan et al. obtained a 25-fold enrichment of Pb ions in various water samples by using humic acid-modified magnetite, with a limit of detection (LOD) of 4.9 µg L^{-1} [55]. Although the evaluated preconcentration methods have LOD values comparable to or competitive with the 5.0 µg L^{-1} of LOD value we reported, they generally demonstrated limitations in the analyte enrichment

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capabilities of the sorbent materials. In contrast, the toner@$CoFe_2O_4$ nanocomposite showed superiority over these methods in terms of high preconcentration factor, thanks to good adsorption capacity. Hence, toner@$CoFe_2O_4$ nanocomposites as a newly synthesized sorbent provide a good alternative to the literature for the preconcentration of Pb^{2+} with high efficiency and the achievement of low detection limits.

Table 2. A comparison for proposed toner@$CoFe_2O_4$ nanocomposite-based DSPME-FAAS and literature outputs.

Sorbent	LOD, (µg L^{-1})	LOQ, (µg L^{-1})	Linear Range, (µg L^{-1})	ECS/PF*	Reference
Toner@$CoFe_2O_4$ nanocomposite [a]	5.0	16.5	10-100	161.1	This Study
Modified rice husk	14.1	47.0	0-2000	46	[52]
DMG-Si@Fe_3O_4/GO [b]	7.0	20	20-600	15.5	[53]
Silica gel - Zr(IV) phosphate [c]	6.1	16.7	-	30	[54]
Magnetic orange peel powder	2.6	8.0	10 – 300	14	[9]
Humic acid@ Fe_3O_4	4.9	16.3	30 – 500	25	[55]

[a] *Toner-cobalt ferrite nanocomposite*

[b] *Dimethylglyoxime functionalized silica-coated magnetic iron/graphene oxides*

[c] *Silica gel modified with zirconium phosphate*

**Enhancement in calibration sensitivity / Preconcentration factor*

3.8.Recovery Studies

The recovery experiments have an importance to assess the feasibility of a developed analytical method. Real sample matrices consumed by humans are good media to apply the optimal working

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conditions of the method. In this study, the bottled drinking water samples were utilized as real samples. Firstly, the presence of Pb^{2+} ions was investigated with sample analysis, but there was no analytical signal observed. Next, spiking process was achieved using drinking water samples to get final volumes of 15, 30, and 75 µg L^{-1} Pb concentrations. After FAAS measurements, the recorded results were evaluated in external calibration plot obtained with aqueous Pb^{2+} solutions. The recovery results obtained using the external calibration method were calculated to be in the range of 96.8% and 121.9% and were analytically acceptable. The matrix matching calibration strategy was also applied to obtain more reliable results and increase the accuracy of measurements by minimizing the effects of potential interference from the sample matrix on the analyte signals. With this objective, two different calibration plots were generated for each drinking water sample at the specified concentrations, and the % recovery results for each drinking water matrix were determined using the calibration plot equation of the other matrix and calculated between 86.8% and 116.6%. The summarized results are given in Table 3 and these numerical expressions demonstrated that the proposed analytical approach was applicable for bottled drinking water samples.

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Table 3. The recovery results of bottled drinking water samples employing matrix matching and external calibration (n=4).

	Final Concentration, µg L^{-1}	**EC Recovery ± SD, %**	**MMC Recovery ± SD, %**
	Sample	ND	ND
DW 1	15	121.9 ± 14.2	99.4 ± 13.3
	30	100.3 ± 7.3	86.8 ± 6.9
	75	96.8 ± 2.4	88.1 ± 2.3

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	Sample	ND	ND
DW 2	15	116.7 ± 12.5	99.1 ± 13.3
	30	121.2 ± 10.5	116.6 ± 11.2
	75	110.8 ± 4.6	113.0 ± 4.9

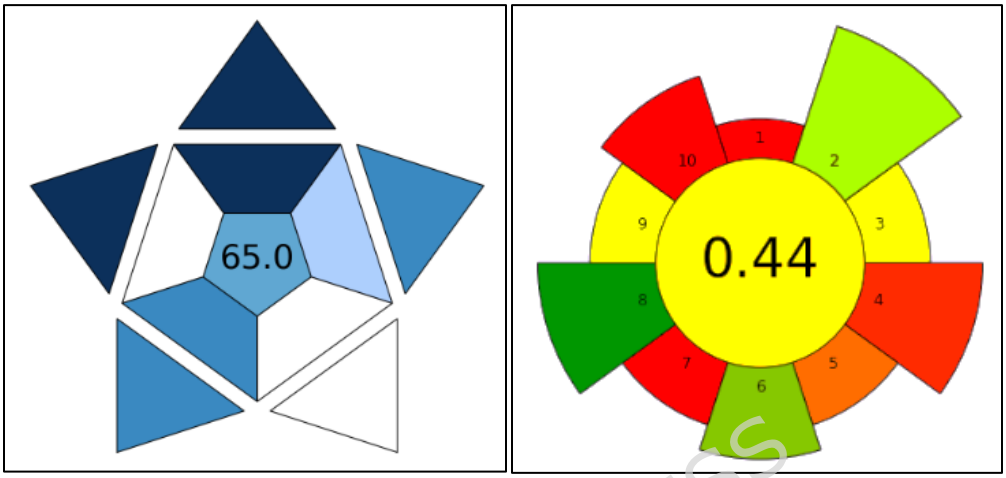
**DW: Drinking Water, EC: External Calibration, MMC: Matrix Matching Calibration, SD: Standard Deviation, ND: Not Detected*

3.9. Evaluation of Greenness of Toner@$CoFe_2O_4$-DSPME-FAAS Method

Green chemistry compatibility is an important topic that many researchers have focused on. In current studies, environmental sensitivity and analytical feasibility are now considered just as important as experimental results. Accordingly, various tools such as AGREEprep [56], blue applicability grade index (BAGI) [57], and Eco-Scale [58] have started to be frequently reported in order to ensure objective environmental evaluation in the sustainability of scientific research, as human health and environmental protection are top priorities. For this purpose, the BAGI analysis was carried out with the evaluation of the analytical applicability of developed method and the BAGI score was found to be 65 (Figure 7a). This result supported that the developed method was practical applicable. The scores for each criterion were evaluated using the AGREEprep tool within the framework of green chemistry. Despite the red findings in criteria 1 (placement of sample preparation), 4 (waste), 7 (integration and automation), and 10 (operator's safety), an acceptable score of 0.44 was recorded (Figure 7b). It is believed that this score was recorded as a result of the sample volume, the amount of waste generated, and the hazard class of the reagents. In addition, since DSPME methods inherently require multiple steps for sample preparation, the scores assigned for ex situ analysis and lack of automation were as expected. In this context, further

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studies could focus on practices encouraging the utilization of lower volumes of chemicals and control the waste generation in the procedure, with the aim of improving the environmental performance of the current method.



(a) (b)

Figure 7. (a) BAGI pictogram, (b) AGREEprep pictogram

4. Conclusion

Pb as a health- hazardous metal is encountered in many areas of our lives, both as a natural resource and in man-made products. Widespread presence of Pb^{2+} poses a significant risk to human health and the environment due to its potential to enter the water sources. In the method developed for the determination of trace levels of Pb^{2+} in the FAAS system, toner-based $CoFe_2O_4$ nanocomposite structures were synthesized and used for the first time in the literature for the preconcentration/separation of Pb^{2+}. The developed toner@$CoFe_2O_4$-DSPME-FAAS method provided a LOD of 5.0 µg L^{-1} under optimal conditions and improved the FAAS sensitivity by 161.1 times. The applicability and reliability of method was examined by recovery tests using bottled drinking water samples and % recovery results calculated between 86.8% and 116.6% by

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matrix matching calibration method. The BAGI and AGREEprep scores were found to be 65 and 0.44, respectively. The presented results showed that the proposed method was applicable and feasible for the determination of Pb^{2+} at legal limits indicated by official authorities. The toner@$CoFe_2O_4$-DSPME-FAAS method also has low operational cost, ease of implementation, and the use of waste-toner-derived material as the adsorbent not only contribute to sustainability but also make this approach a promising alternative for the removal and determination of Pb^{2+} in complex water matrices. In addition, the investigation of sorbent performance in various water and food matrices and preconcentration of other heavy metal ions will be the subject of future studies. It should also be noted that variations in the composition of toner particles depending on the manufacturer may affect the analytical findings.

Acknowledgement

This study is dedicated to all researchers who strive to turn their dreams into reality with persistence, dedication, and passion, while upholding ethical and moral principles, and who never give up despite the challenges encountered.

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Funding

This study was supported by The Scientific and Technological Research Council of Türkiye (TUBITAK) under 1002-A Short-term Support Module with an application number of number 125Z877.

Conflict of interest

The authors declare that they have no conflicts of interest.

Data Availability

Data will be made available with reasonable request.

Author Contributions

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Büşra Ali: Writing – original draft, Validation, Methodology, Formal analysis, Data curation.

Muhammed Ali Büyük: Writing – original draft, Validation, Methodology, Formal analysis, Data curation

Elif Sevim Çakmak: Writing – original draft, Validation, Methodology, Formal analysis, Data curation.

Hakan Serbest: Writing – original draft, Visualization, Validation, Methodology, Formal analysis, Data curation, Conceptualization.

Sezgin Bakirdere: Writing – review & editing, Methodology, Investigation, Conceptualization.

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