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Determination and Speciation of Cd(II) and Pb(II) Ions Using Magnetic Solid Phase Extraction By Flame Atomic Absorption Spectroscopy

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ABSTRACT

In this study, Pb(II) and Cd(II) ions were determined by Fe_3O_4@G2/Napht magnetic dendrimers using the solid-phase extraction (SPE) method by flame atomic absorption spectrophotometer (FAAS). The morphological and chemical properties of magnetic dendrimers were investigated using Fourier Transform Infrared (FTIR) spectroscopy and transmission electron microscopy (TEM) techniques. The magnetic characteristics of the ferromagnetic features of the magnetic nanocomposites were validated by vibrating sample magnetometry (VSM). The heavy metal ion recovery was assessed via flame atomic adsorption spectroscopy (FAAS). To ascertain the ideal adsorption system conditions, the effects of various parameters, including pH, adsorbent dose, adsorbent time, eluent type and amount, etc., were examined. Optimum conditions for heavy metal recovery using Fe_3O_4@G2/Napht magnetic dendrimer were determined as pH 6.5, 1M HNO_3 and 100 mg for Pb(II) and pH 6.5, 1 M HNO_3 and 100 mg for Cd(II). The novel material of Fe_3O_4@G2/Napht magnetic dendrimer for separation and pre-concentration of Pb(II) and Cd(II) was used to natural water.

Keywords: Magnetic dendrimers; SPE; FAAS; Cd(II); Pb(II)

Alevli Atomik Absorpsiyon Spektroskopisi ile Manyetik Katı Faz Ekstraksiyonu Kullanılarak Cd(II) ve Pb(II) İyonlarının Tayini ve Türlendirilmesi

ÖZ

Bu çalışmada, Pb(II) ve Cd(II) iyonları Fe_3O_4@G2/Napht manyetik dendrimerler ile katı faz ekstraksiyon (SPE) yöntemi kullanılarak alevli atomik absorpsiyon spektrofotometresi (AAS) ile tayin edilmiştir. Manyetik dendrimerlerin morfolojik ve kimyasal özellikleri Fourier Transform Infrared (FTIR) spektroskopisi ve transmisyon elektron mikroskobu (TEM) teknikleri kullanılarak incelenmiştir. Manyetik nanokompozitlerin ferromanyetik özelliklerinin manyetik karakteristikleri titreşimli numune manyetometrisi (VSM) ile doğrulanmıştır. Ağır metal iyonlarının geri kazanımı alevli atomik adsorpsiyon spektroskopisi (AAS) ile değerlendirilmiştir. İdeal adsorpsiyon sistemi koşullarını belirlemek için pH, adsorban dozu, adsorban süresi, eluent türü ve miktarı gibi çeşitli parametrelerin etkileri incelenmiştir. Fe_3O_4@G2/Napht manyetik dendrimer kullanılarak ağır metal geri kazanımı için optimum koşullar Pb(II) için pH 6,5, 1M HNO_3 ve 100 mg, Cd(II) için pH 6,5, 1 M HNO_3 ve 100 mg olarak belirlenmiştir. Pb(II) ve Cd(II)'nin ayrılması ve ön konsantrasyonu için Fe_3O_4@G2/Napht manyetik dendrimerden oluşan yeni malzeme doğal suda kullanılmıştır.

Anahtar Kelimeler: Manyetik dendrimerler; SPE; AAS; Cd(II); Pb(II)

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1. INTRODUCTION

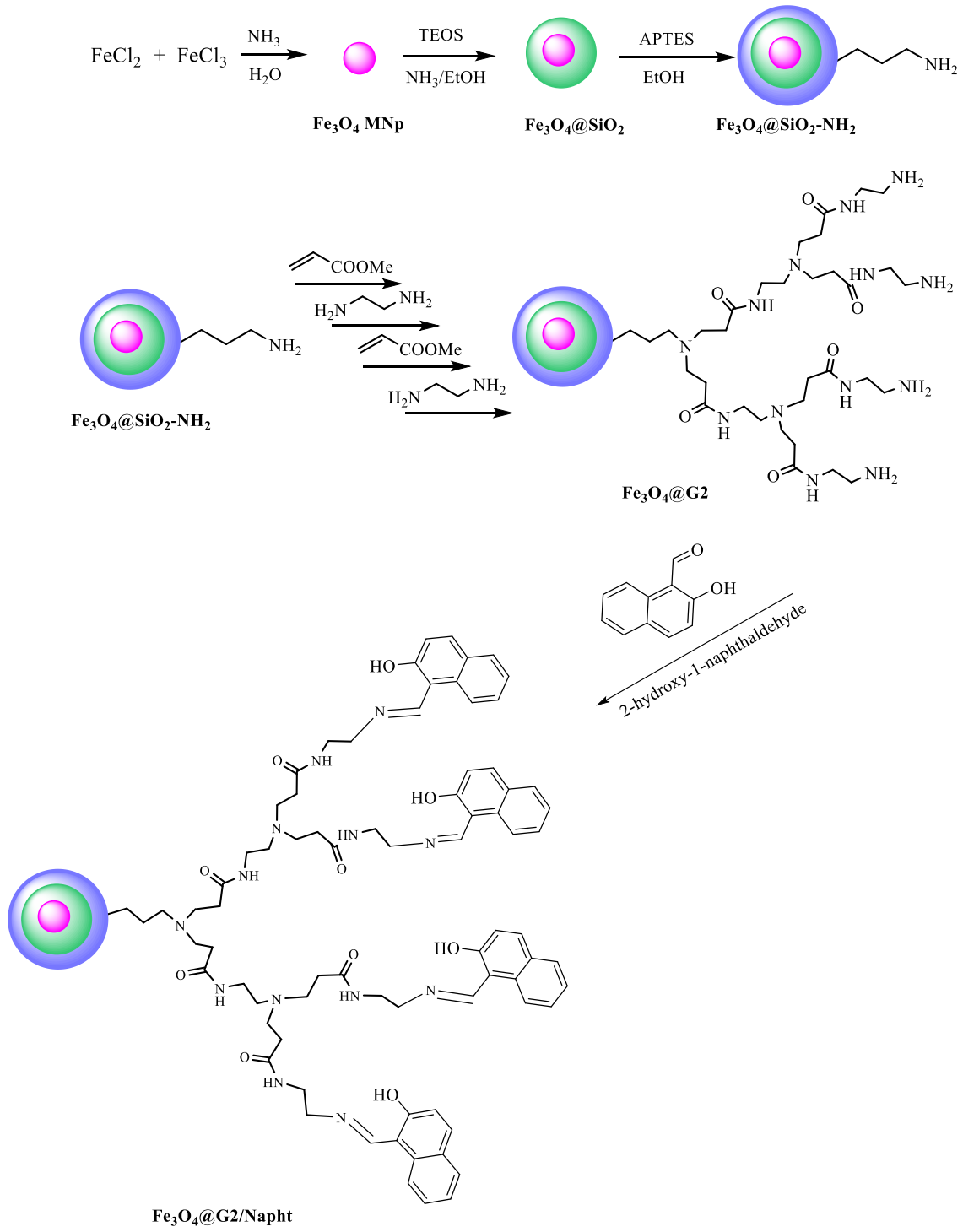
Wastewater contains a large number of toxic heavy metal ions that are extremely harmful to human health. Since it's a useful tool for identifying and tracking harmful compounds in environmental samples, scientists frequently find that determining trace amounts of heavy metals is a significant task. Cadmium is one of the heavy metals in the environment that requires close monitoring due to its sharp rise in concentrations. Being a known carcinogen, lead is among the most hazardous substances to human health. [1-6]. When they build up in different tissues, trace amounts of the metals cadmium and lead can negatively affect the gastrointestinal system, the heart, the blood, the kidneys, and the reproductive system in humans and other living things [7]. Analytical techniques for heavy metal analysis have been developed, including electrothermal atomic absorption spectrometry (ETAAS) [8], flame atomic absorption spectrometry (FAAS) [9-12], inductively coupled plasma-mass spectrometry (ICP-MS) [13-14], and inductively coupled plasma optical emission spectrometry (ICP-OES) [8,14]. Comparing these techniques, it is discovered that FAAS is the analytical technique that is most frequently employed due to its broad linear range, affordability, high accuracy, selectivity, low detection limit, speed, precision, and sensitivity [15]. Nevertheless, because the low detection levels in the materials under examination might exceed the FAAS instrument's detection limit, interference effects from complex matrices could preclude direct heavy metal analysis by this instrument during the analysis of trace heavy metal ions. Thus, before analyzing trace heavy metals using FAAS, a highly accurate and sensitive separation and enrichment technique must be developed.

There are several methods for extracting and preconcentrating heavy metals from natural matrices, such as ion exchange [16], co-precipitation [17], coagulation [18], chemical precipitation, cloud point extraction [19], and liquid-liquid extraction (LLE) [19], reverse osmosis [20], membrane filtration [21], coagulation [18], co-precipitation [17], electrochemical precipitation [22] and SPE have been developed. Among the mentioned methods, SPE is the most widely used method for the pre-concentration of heavy metal ions from environmental samples due to its ease, speed, low cost, and minimal reagent consumption [23].

Dendrimers are one of the materials used as adsorbents in SPE. Dendrimers are good candidates for surface modifications of metal nanoparticles because they can act as structurally and chemically well-defined templates that provide good stabilization. The dendrimer cavities are suitable for transferring the molecules or nanoparticles to any medium [24,25]. The non-covalent interaction between guest and host is effective in such a transfer. By imparting magnetic properties to dendrimers, it is possible to easily remove them from the solution medium [26-28].

In our work, new Fe_3O_4 core magnetic dendrimers were synthesized for the enrichment of Cd (II) and Pb(II), and their structures were characterized by various spectroscopic methods such as FTIR, TEM, and VSM [29-32] (Scheme 1). The applications of adsorbents based on magnetic dendrimer-based nanostructures that we use have unique properties in SPE techniques. Optimum parameters such as pH, eluent

type and concentration, amount of adsorbent, and time, which are important in the enrichment process for SPE of Cd(II) and Pb(II) were determined by flame atomic absorption spectroscopy and optimum conditions were applied to real samples.



Scheme 1: Synthesis of Fe_3O_4, Fe_3O_4@SiO_2, Fe_3O_4@G1, Fe_3O_4@G2 and Fe_3O_4@G2/Napht

2. Materials and Methods

2.1. Synthesis of magnetic Fe_3O_4@G2/Napht magnetic dendrimers

Synthesis of Fe_3O_4, Fe_3O_4@SiO_2, Fe_3O_4@G1 and Fe_3O_4@G2 nanoparticles were synthesized by Kurnaz Yetim et al., as shown in Scheme 1 [29-32]. To synthesized Fe_3O_4@G2/Napht;7.5 g Fe_3O_4@G2 and 15 g 2-hydroxy-1-naphtaldehyde in 125 mL dry ethanol dispersed for 30 min. Then, the mixture was heated under reflux for 24 *h*. The final compound was collected from solution using a magnet and the compound washed with ethanol twice. The final product was dried in a vacuum oven 40 °C for 24 *h* (Scheme 1).

2.2. Magnetic solid-phase extraction methodology

50 mg MNPs, 10 mL ultrapure water, 0.25 mL (50 ppm) Pb(II) metal ion solution and 1 mL pH:6 buffer were added into 50 mL test tubes. The total volume was made upto 25 mL with ultrapure water. The samples were then kept in an ultrasonic bath for 10 minutes and centrifuged at 9000 rpm for 10 min. The liquid phase was saved for analysis and 5 mL of the selected acid solution was added to the solid-phase. The samples were first kept in an ultrasonic bath for 10 min and then centrifuged at 9000 rpm for 10 min. The concentration of metal ions remaining in the liquid phase was analyzed by FAAS. In the eluent type optimization step, 0.1-3 M HNO_3 and 1 M HCl acid solutions were used. In pH optimization, pH 5-8 values were used. The buffers used were pH:5.0 (NaH_2PO_4/H_3PO_4); pH: 6 (Na_2HPO_4/NaH_2PO_4); pH: 7.0–8.0 (NaH_2PO_4/Na_2HPO_4). In adsorbent amount optimization, 50-200 mg Fe_3O_4@G2/Napht was used. In eluent volume optimization, 5-30 mL of ultrapure water was used. Finally, the optimum time was studied by keeping the samples in an ultrasonic bath for 5-60 min [33,34].

3. Result and Discussion

3.1. Characterization of magnetic dendrimers

The results of FTIR, XRD, TGA, VSM and different elemental analysis methods of Fe_3O_4@G2 magnetic dendrimer were presented in our previous studies [29,30]. In this study, the characterization of Fe_3O_4@G2/Napht nanocomposites was discussed. Figure 1 presents the FTIR spectrum of Fe_3O_4@G2/Napht nanocomposites. When the FTIR spectrum for Fe_3O_4 MNP was analyzed, the bands observed at about 583 and 456 cm^{-1} were predicted to belong to the intrinsic stress vibrations of the metal in the tetrahedral region (Fetetra↔O) and octahedral region (Feocta↔O) [35]. In the FTIR spectrum of Fe_3O_4@G2 dendrimer, the band at 1524 cm^{-1} was attributed to N-H groups in PAMAM dendrimer and the broad absorption band at 3300 cm^{-1} was attributed to O-H stretching vibration of hydroxy group at Fe_3O_4@G2/Napht and 3073 cm^{-1} peak is belong to aromatic C-H at Napht. The bands at 2933 and 2887 cm^{-1} were attributed to C-H symmetric and asymmetric stretching vibrations of alkane groups, respectively [29].

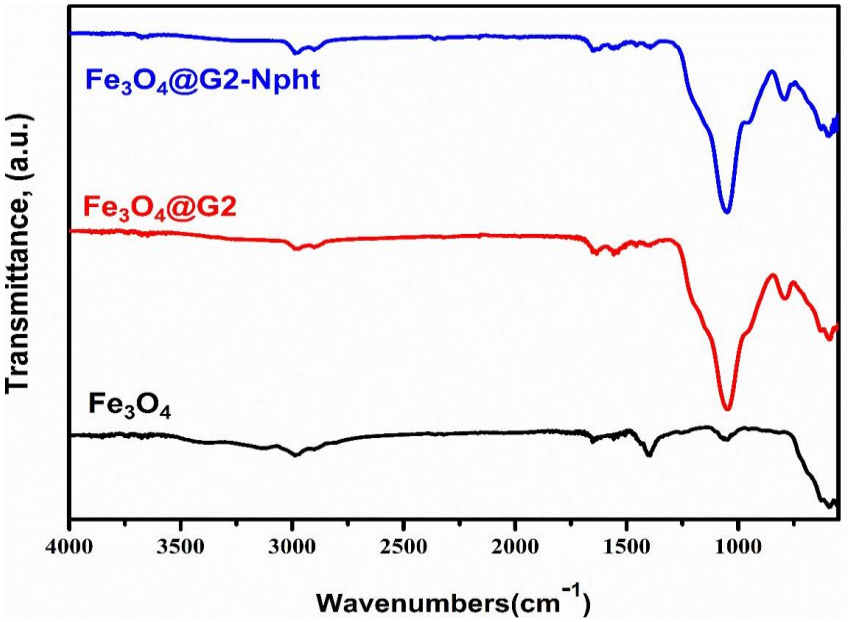


Figure 1: FTIR spectrume of Fe_3O_4, Fe_3O_4@G2 and Fe_3O_4@G2/Napht magnetic nanoparticles

TEM images of Fe_3O_4, Fe_3O_4@G2 and Fe_3O_4@G2/Napht magnetic nanoparticles are presented in Figure 2. When TEM images of Fe_3O_4 magnetic nanoparticles are examined, it is seen that iron nanoparticles are nanosized. Due to their high magnetic properties, the particles are found together. It is clearly seen from the TEM image that the magnetic nanoparticles coated with PAMAM dendrimers have a typical core-shell structure (magnetic core is dark and silica shell is light) (Figure 2b). As seen in the TEM images, it was discovered that the size of the magnetic particles increased as the coating process progressed.

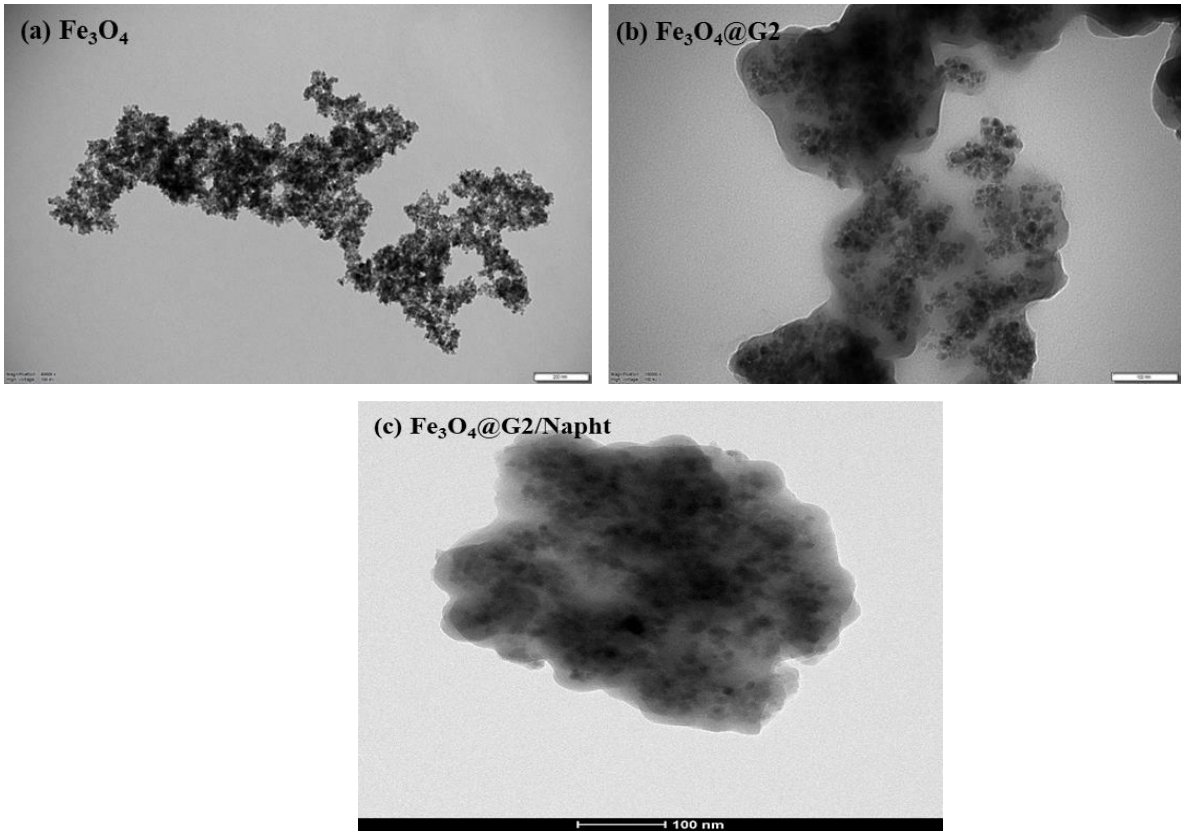


Figure 2: TEM images of Fe_3O_4 **(a)**, Fe_3O_4@G2 **(b)** and Fe_3O_4@G2/Napht **(c)**

The magnetization curves of Fe_3O_4, Fe_3O_4@G2 and Fe_3O_4@G2/Napht magnetic nanoparticles are presented in Figure 3. When the magnetization curve of Fe_3O_4 nanoparticles was examined, it was determined that their saturated magnetization value was 63.7 emu/g. The saturated magnetization value of Fe_3O_4@G2 dendrimer obtained by attaching PAMAM dendrimers to MNPs was found to be 34.7 emu/g, while the saturated magnetization value of Fe_3O_4@G2/Napht magnetic nanoparticle obtained by attaching 2-hydroxy-1-naphtaldehyde to magnetic dendrimers was 10.8 emu/g.

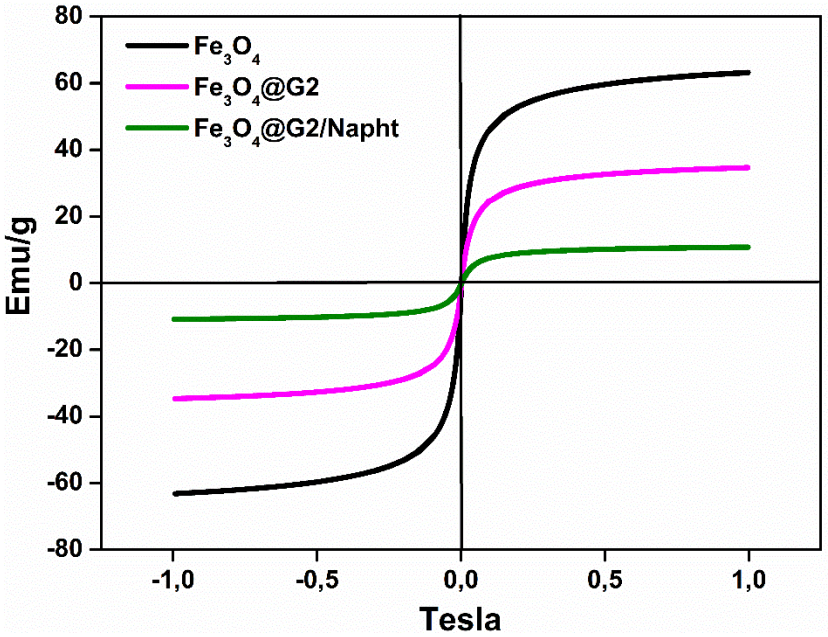


Figure 3: Hysteresis curves of Fe_3O_4, Fe_3O_4@G2 and Fe_3O_4@G2/Napht magnetic nanoparticles

3.2. Removal of heavy metals (Cd(II), Pb(II))

3.2.1. Effect of pH

In adsorption-separation investigations, the main factor examined is the impact of pH on the recovery of analyte ions. In order for trace amounts of heavy metal ions to be adsorbed onto the freshly manufactured adsorbent, pH optimization is essential. Direct effects on the solubility and chemical forms of metal ions are caused by the solution's acidity or alkalinity. In an acidic environment, metal ions usually exist as free, hydrated species, but they can also precipitate form hydroxide complexes or in a basic solution. In order to find the ideal pH, we created model solutions and used buffer solutions to investigate the pH range of 5 to 8. The results of three parallel runs were averaged to determine recovery values. Figure 4 displays the pH and recovery values. Pb(II) and Cd(II) were both quantitatively recovered at pH 6.5.

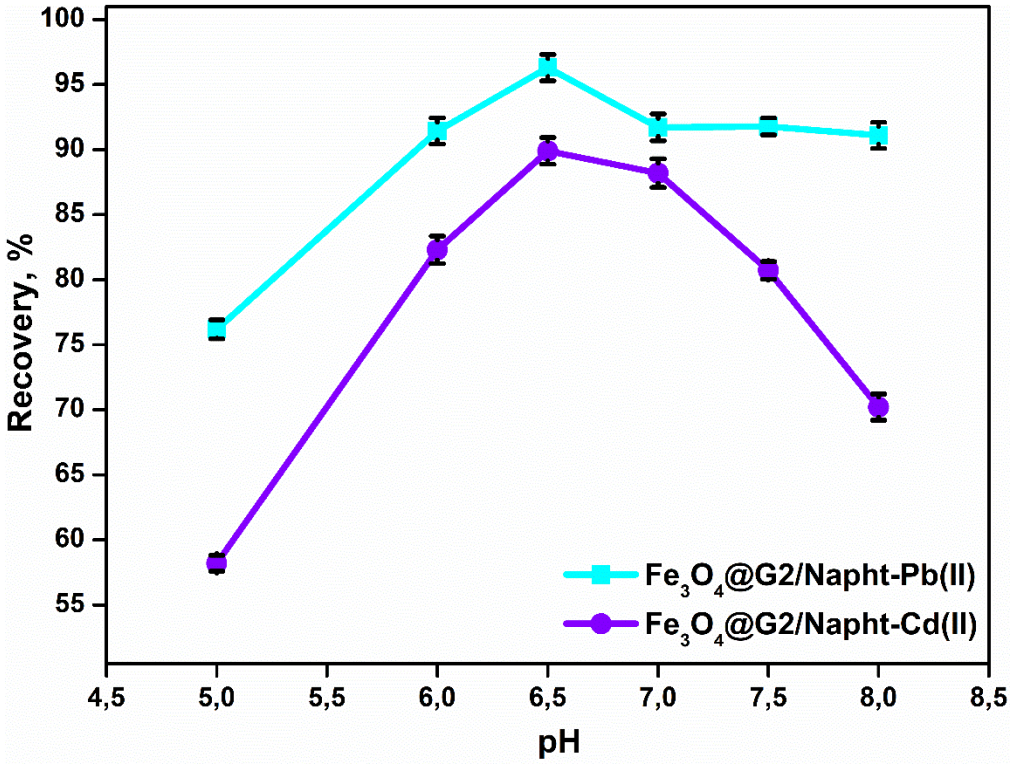


Figure 4: Effect of pH on recovery values

3.2.2.Eluent Type and Concentration

The kind and concentration of the eluent is another important factor affecting the recovery outcomes. The properties of the analytes, the solid-phase material, the intended analytical method, and the eluent's capacity to efficiently release the target analytes from the solid-phase while minimizing interference from other sample components are all taken into consideration when selecting the elution solution in SPE. When choosing the eluent, factors including selectivity, solubility, and compatibility with downstream analysis procedures should be taken into account.

Different concentrations of HNO_3 (0.1-3.0 mol L^{-1}) and 1 M HCl acid solution were used for the elution of trace amounts of Pb(II) and Cd(II) adsorbed on magnetic dendrimers. The results are given in Figure 5. In the graph; the best recovery of Pb(II) metal ion was found to be in 1 M HNO_3 with 98.27 % efficiency, while the best recovery of Cd(II) metal ion was found to be in 1 M HNO3 with 91.35 % efficiency and these eluents were used in all subsequent studies.

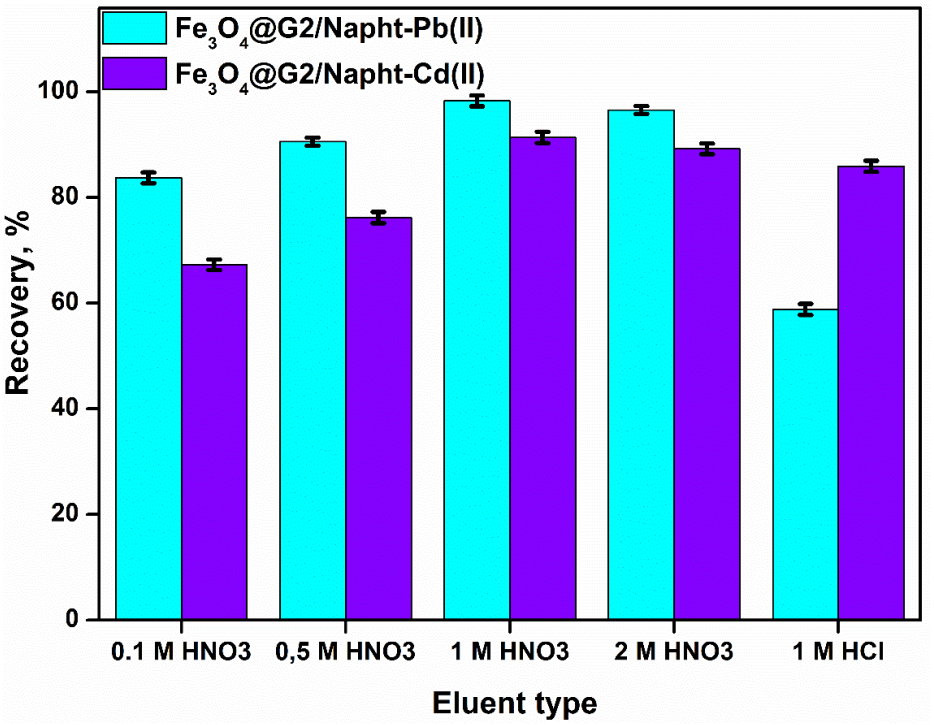


Figure 5: Effect of eluent type and concentration on recovery values

3.2.3. The Effect of Magnetic Dendrimer Amount

Different amounts of magnetic dendrimer used as adsorbent for the recovery of lead and cadmium were investigated. When choosing the ideal amount of adsorbent for SPE, a number of factors must be taken into account, including the analyte's concentration, volume of sample, capacity and properties. To determine the ideal ratio between maximizing adsorption and minimizing adsorbent waste, optimization experiments are also required. The amount of adsorbent was tested in the range of 25-200 mg and the results are given in Figure 6. According to the results obtained, all amounts used gave quantitative recoveries of Pb(II) and Cd(II). Figure 6 shows that the best recovery of Pb(II) metal ion was determined at 100 mg adsorbent with 99.58 % efficiency, while the best recovery of Cd(II) metal ion was determined at 100 mg adsorbent with 95.85 % efficiency.

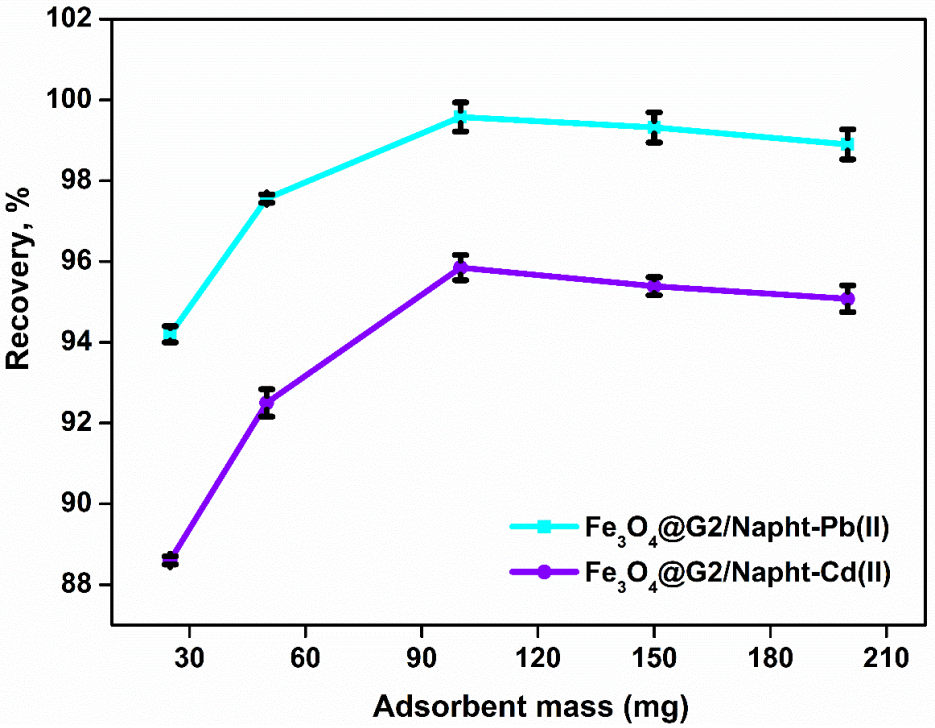


Figure 6: Effect of magnetic nanoparticles on recovery values

3.2.4. The Effect of Solution Volume

Solution volume optimizations were performed to obtain the best recovery values with minimum solution volume. The effect of sample volume on Pb(II) and Cd(II) recoveries on magnetic dendrimers was investigated in the range of 5-30 mL sample volume. Figure 7 shows that the best recovery of Pb(II) was found to be at 10 mL with 99.9 % efficiency and for Cd(II) at 10 mL with 95.73 % efficiency.

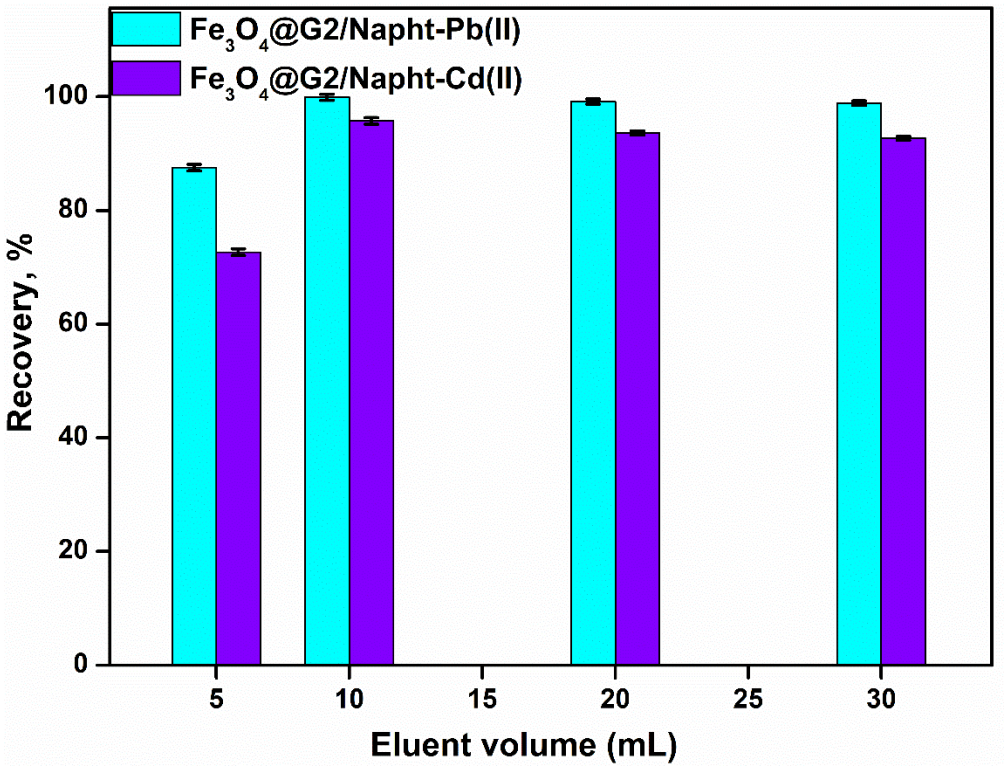


Figure 7: Effect of sample volume on recovery values

3.2.5. Effect of Extraction Time

The characteristics of the analytes, the solid phase, and the makeup of the sample matrix all affect how long the adsorption process takes to complete and how many analytes are absorbed by the solid phase. For the adsorption of analyte ions onto magnetic dendrimers, stirring in an ultrasonic bath was applied. The effect of sonication time on Cd(II) and Pb(II) recovery was investigated in the range of 5-60 min and presented in Figure 8. As shown in Figure 8, 10 min was sufficient for the recoveries. 10 min was determined as the optimum time for extraction as there was no further increase in recoveries at the end of the min. During this time, the best Pb(II) metal ion recovery was realized with 99.8 % yield, while for Cd(II) 96.8 % yield was observed.

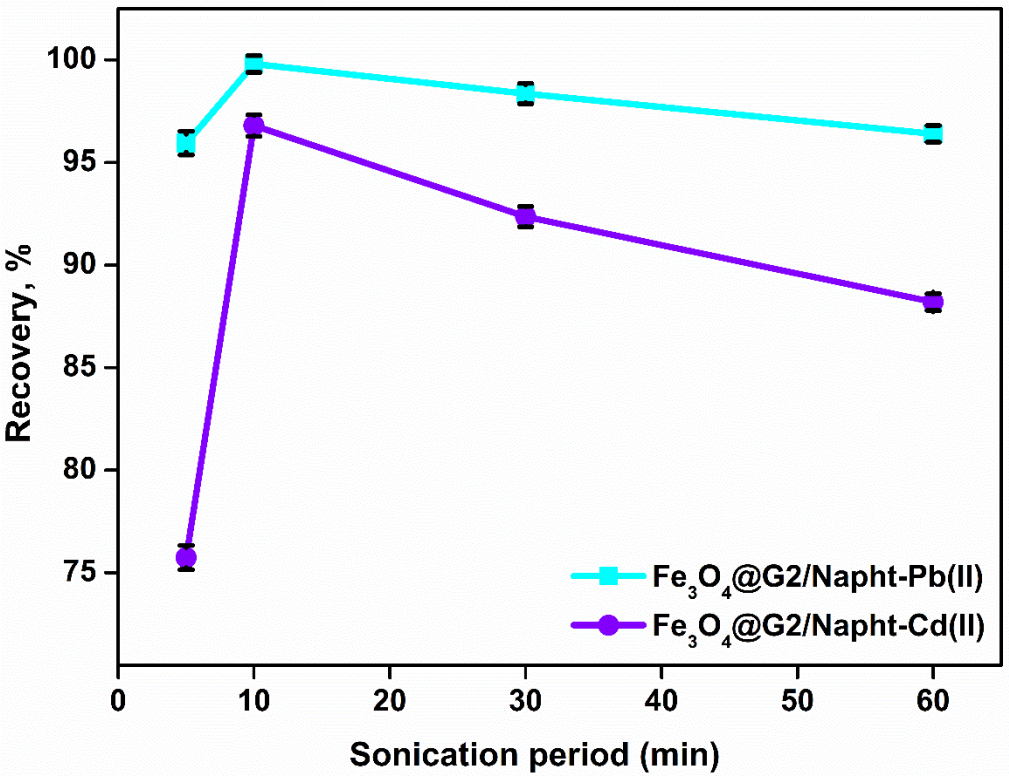


Figure 8: Effect of sonication time on removal of Cd(II) and Pb(II).

3.2.6. Effect of foreign ions on recovery

The interference of foreign ions is a major problem in the detection of trace levels of certain analytes. In this study, the effect of matrix ions of real samples on the recovery of Pb(II) and Cd(II) in wastewater by magnetic dendrimers was investigated and given in Table 1.

Table 1. Effect of other ions on the recovery efficiency of Pb and Cd ions (matrix)

Ions	Added as	Concentration (mg/L)	Recovery for Pb, %	Recovery for Cd, %
K^+	KCl	1000	99.9 ± 0.1	98.9 ± 0.6
Na^+	NaCl	100	102 ± 3	98.4 ± 0.2
Ca^{2+}	$CaCl_2$	25	100 ± 3	98.8 ± 0.9
Mg^{2+}	$Mg(NO_3)_2$	5	102 ± 2	100 ± 3
Zn^{2+}	$Zn(NO_3)_2.6H_2O$	5	99.3 ± 4	99.2 ± 0.6
Cu^{2+}	$Cu(NO_3)_2$	5	103 ± 3	98.9 ± 0.9
Mn^{2+}	$Mn(NO_3)_2$	5	99.2 ± 0.9	97.8 ± 0.5
Cr^{3+}	$Zn(NO_3)_2.6H_2O$	1	98.9 ± 0.5	98.5 ± 0.3
Fe^{3+}	$Fe(NO_3)_3 9H_2O$	5	99.3 ± 2	99.2 ± 0.2

No interference effect of the ions given in Table 1 was observed in the model solutions containing 0.5 mg/L Pb^{2+} and Cd^{2+} ions. In addition, optimum conditions were applied to real samples and verified by standard addition method.

Table 2. Aplication of the method for water samples using standard addition method.

	Pb (II)			Cd (II)		
Sample	Added, mg/L	Found mg/L	Recovery %	Added, mg/L	Found mg/L	Recovery %
Tap water	0	ND	-	0	ND	-
	0.5	0.48 ± 0.009	95	0.5	0.49 ± 0.006	98
	1.0	0.98 ± 0.006	98	1.0	0.99 ± 0.006	99
River water	0	ND	-	0	ND	-
	0.5	0.48 ± 0.011	96	0.5	0.51 ± 0.006	101
	1.0	0.98 ± 0.007	98	1.0	0.99± 0.006	99

With the method applied to tap water and river water samples as real samples, 4-fold and 1.5-fold enrichment was achieved in Pb(II) and Cd(II) ions, respectively. We suggest that the used magnetic nanomaterial will contribute to the waste removal procedure in battery factories where lead metal is used intensively.

4. CONCLUSION

A new magnetic adsorbent, Fe_3O_4@G2/Napht nanoparticle, was synthesized and characterized. The optimum conditions for pH, eluent type, sonication time, etc. which are important parameters in solid-phase extraction for Pb (II) and Cd (II) were determined with the synthesized magnetic nanoparticle. An effective, fast, and easy solid-phase extraction and precipitation process was carried out to separate and enrich Pb and Cd in natural water samples and analyzed by FAAS. Maximum recovery of 99.8% and 96.8% was achieved for magnetic nanoparticles Pb (II) and Cd (II), respectively. It can be suggested that our study is much more effective in lead recovery and can be used for recovery in wastewater.

CONFLICT OF INTEREST STATEMENT

There is no conflict of interest among the authors.

ACKNOWLEDGEMENT

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CONTRIBUTIONS OF AUTHORS

F.A.: N. KURNAZ YETİM designed the experiments and contributed to the interpretation of the results, writing-

original draft preparation.

S.A.: E. HASANOĞLU ÖZKAN performed the FAAS experiments, formal analysis, visualization, writing-review & editing, validation, and resources.

T.A.: N. AKKURT carried out the experiments depending on synthesis and written original draft preparation.

F.A.: C. OZCAN carried out and assessment the FAAS experiments.

Each author contributed to the final manuscript and discussed the findings.

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