



Triazine-Based Polymeric Network-Modified Magnetic Nanoparticles (NPs) as an Efficient Sorbent to Extract 1-Naphthylacetic Acid in Fruit and Vegetable Samples

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Abstract

In this study, a triazine-based polymeric network-modified magnetic nanoparticles (TPN/MNPs) was synthesized and applied as adsorbent for extraction of 1-naphthylacetic acid (NAA) from the fruit and vegetable samples followed by HPLC determination. The synthesized TPN/MNPs were characterized by the vibrating sample magnetometry (VSM), Fourier-transform infrared spectroscopy (FT-IR), field emission-scanning electron microscopy (FE-SEM) and thermogravimetric analysis (TGA). The factors influencing the extraction efficiency including pH, sorbent amount, salt concentration, extraction time, sample volume and desorption conditions were studied and optimized. Under the optimal conditions, good linearity was obtained in the range of 1.0–500 $\mu\text{g L}^{-1}$. The limit of detection (LOD) and limit of quantification (LOQ) were 0.3 $\mu\text{g L}^{-1}$ and 1.0 $\mu\text{g L}^{-1}$, respectively. The relative standard deviations (RSDs) of intra-day and inter-day were less than 9.5% at 10 and 100 $\mu\text{g L}^{-1}$ of NAA. The method was successfully applied for extraction and determination of NAA in the fruit and vegetable samples including cucumber, tomato and apple and good recoveries were obtained (94.5–96.5%).

Keywords Magnetic solid phase extraction · Triazine-based polymeric network · 1-naphthylacetic acid · Cucumber · Tomato · Apple

Introduction

Naphthylacetic acid (NAA) is a naphthalene-derived plant growth regulator which is widely used in fruits and vegetables. Therefore, its residue in the plant is harmful to human and animal health due to its potential toxicity [1]. Several

methods such as high-performance liquid chromatography with ultraviolet detector [2] and/or fluorescence detector [3], the gas chromatography (GC) with flame ionization detector [4], spectrofluorimetry [5], room temperature phosphorescence (RTP) [6, 7] have been applied for the determination of NAA.

However, sample treatment is still necessary for most applications. Several sample pretreatment methods such as solid-phase extraction (SPE) [8], miniaturized dispersive solid-phase extraction (MDSPE) [9], solid-phase microextraction (SPME) [10], dispersive liquid–liquid microextraction (DLLME) [11] and molecularly imprinted solid-phase extraction (MISPE) have been developed for extraction of NAA [12].

Recently, MSPE, a new type of solid-phase extraction based on magnetic sorbents with high extraction efficiency and convenient operation, has attracted significant attention [13]. In MSPE, the sorbents can be uniformly dispersed into the sample solution by vortexing or shaking that provides sufficiently large contact area between the sorbents and the analytes to ensure a fast mass transfer.

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Therefore, high extraction efficiency in a short time, which is desirable in high throughput sample preparations, can be obtained [14]. Magnetic nanoparticles (MNPs), generally Fe_3O_4 or $\gamma\text{-Fe}_2\text{O}_3$, are used as sorbents in MSPE. Compared to traditional SPE sorbents, MNPs possess high surface area and have unique magnetic properties. When MNPs are introduced to the solution, the equilibrium between sorbents and sample solutions can be reached quickly [16]. After extraction, MNP sorbents enriched with analytes are readily separated from suspension by applying an external magnetic field. Therefore, in contrast to the traditional cartridge SPE, MSPE eliminates the column packing and possible blockage during use. However, bare MNPs can easily aggregate that can alter their stability and extraction capacity [15].

Up to date, functionalized MNPs such as carbon nanotube (CNT) [1], graphene oxide (GO) [17], polypyrrole polymer [18], and β -cyclodextrin (β -CD) [9] have been used for extraction of the analyte. Hence, finding new and suitable functional groups for preparation of efficient MNP-based sorbents for extraction of analytes such as NAA is underway. In recent years, microporous organic polymers (MOPs) that formed by the polymerization of organic building blocks have attracted much research interest due to the combined superiority of porous materials and functional polymers. MOPs have well-defined porosity, high surface area and tunable surface chemistry. Furthermore, they are lightweight and can be easily functionalized [19]. In recent years, MOPs have been utilized to extract the hydroxylated polycyclic aromatic hydrocarbons [20], 5-nitro-imidazoles [21], imidacloprid and 2,4-dichlorophenoxyacetic acid [22], perfluorinated compounds [23] and for removal of methyl orange [24]. Poly(melamine-terephthalaldehyde) network (TPN) is a triazine-based MOP with high amount of amine functional groups that can absorb several cations. Therefore, if the surface areas and porosity of TPNs to be high, interesting applications for such TPNs are expected due to the presence of abundant amine groups on the pore of the walls. Functionalization of MNPs with MOPs could enhance chemical stability of MNPs and introduce porosity on the MNPs surface with proper functional groups that these properties can improve these adsorbents efficiency [24].

In this study, triazine-based polymeric network-modified magnetic nanoparticles (TPN/MNPs), which contain abundant amine groups, were synthesized and applied for the first time for extraction of NAA, as carboxylic acid containing analyte. The factors affecting the extraction efficiency such as pH, sorbent amount, salt concentration, extraction time, sample volume and desorption conditions were optimized. Finally, the proposed method was applied to determine NAA in cucumber, tomato and apple samples.

Experimental

Reagents and Chemicals

1-Naphthylacetic acid (NAA) was purchased from the Sigma–Aldrich (St. Louis, MO, USA). Ferric chloride ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$), ferrous chloride ($\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$), ammonia solution (28%), melamine, terephthalaldehyde, dimethyl sulfoxide (DMSO), tetrahydrofuran (THF), dichloromethane, acetonitrile, methanol, acetone and acetic acid were purchased from Merck (Darmstadt, Germany). Stock standard solution of NAA at 1000 mg L^{-1} was prepared in acetonitrile and kept at $4 \text{ }^\circ\text{C}$ in a refrigerator. The working solution were prepared by proper dilutions of the stock solution with distilled water.

Instruments

Chromatographic analysis was performed on a Knauer HPLC system (Berlin; Germany) consisting degasser, a K-1100 HPLC quaternary pump, a manual injector with $20 \mu\text{L}$ sample loop and a K2600 UV detector. Data were processed by EZChrom software. The separation was performed on an analytical C_8 column ($5 \mu\text{m}$, $4.6 \text{ mm i.d.} \times 25 \text{ cm}$) (Knauer, Germany). Mixture of acetonitrile and water (60:40, v/v) was used under isocratic elution condition as mobile phase at flow rate 1.0 mL min^{-1} . Finally, detection wavelength was set at 220 nm .

Field emission-scanning electron microscopy (FESEM) images were obtained by MIRA3 FESEM (Tescan, Czech Republic). The Fourier-transform infrared (FT-IR) spectra were recorded using a Thermo Nicolet Nexus 870 FT-IR spectrometer (Madison, USA). In addition, Thermogravimetric analysis (TGA) was performed on a NETZSCH TG 209 F1 (Selb, Germany). The magnetic properties were measured by vibrating sample magnetometer (VSM) (Meghnatis Daghigh Kavir, Kashan, Iran).

Synthesis of Triazine-Based Polymeric Network-Modified Magnetic Nanoparticles

Iron oxide nanoparticles were prepared according to previously reported method [25]. Briefly, $2.4 \text{ g FeCl}_2 \cdot 4\text{H}_2\text{O}$ and $5.4 \text{ g FeCl}_3 \cdot 6\text{H}_2\text{O}$ were dissolved in 20 mL deionized water under nitrogen atmosphere with vigorous stirring using a mechanical stirrer. $25 \text{ mL NH}_3 \cdot \text{H}_2\text{O}$ (28 wt%) was added dropwise to the solution. Then, the solution was heated at $70 \text{ }^\circ\text{C}$ for 5 h. The temperature was increased to $85 \text{ }^\circ\text{C}$ for vaporizing residual ammonia. The resulting black dispersion was isolated via a magnet, and washed with deionized water. The magnetic nanoparticles were modified by triazine-based

polymeric network (TPN) through in-situ method as previously reported [24]. Briefly, 0.939 g melamine, 1.5 g terephthalaldehyde and 45 mL DMSO were stirred and degassed by argon bubbling. The mixture was heated to 180 °C under the inert atmosphere. After 48 h, 1.5 g Fe₃O₄ nanoparticles were added and the reaction was continued for another 24 h. After it was cooled to room temperature, the resultant precipitation was collected by magnet, washed one time with 20 mL DMSO, acetone, THF and dichloromethane. Finally, the obtained TPN/MNPs were dried under vacuum at 60 °C. The preparation procedure of TPN/MNPs is shown in Fig. 1.

MDSPE Procedure

The MDSPE procedure is shown in Fig. 1. Initially, 50 mL of the sample solution containing NAA (100 µg L⁻¹) was transferred to a beaker, and pH was adjusted to 6.5. Then, 10 mg of TPN/MNPs was added. Then, solution was shaken on a shaker at 200 rpm for 10 min to reach the equilibrium. Subsequently, a strong magnet was placed at the bottom of the beaker and TPN/MNPs were isolated from the solution. After about 1 min, the solution became limpid and the supernatant was decanted. The adsorbed analyte was desorbed with 500 µL of acetonitrile by shaking for 5 min. Finally, the supernatant was collected and 20 µL of the solution was injected into HPLC system for analysis.

Sample Preparation

The samples including cucumber, tomato and apple were purchased from local market (Tehran, Iran). The samples were ground and homogenized. 5.0 g of the homogenized samples was accurately weighed and 10 mL acetonitrile:water (20:80, v/v) was added. The samples were sonicated for 10 min and filtered with a 0.45 µm filter. Then, the filtered samples were diluted to 50 mL with distilled water.

For the spiked samples, proper volumes of standard solutions of NAA were added to the blank samples and then prepared as the mentioned procedure.

Results and Discussion

Characterization

Figure 2a shows FTIR spectra of the MNP and TPN/MNPs. In FTIR spectrum of MNPs, the band at 3390 cm⁻¹ is attributed to O–H stretching vibration and a band at 572 cm⁻¹ corresponds to Fe–O bond. The FTIR spectrum of TPN/MNPs showed a broad coupling band around 3400 cm⁻¹ related to N–H groups of TPN and O–H groups in surface of MNPs. The bands at 1554 cm⁻¹

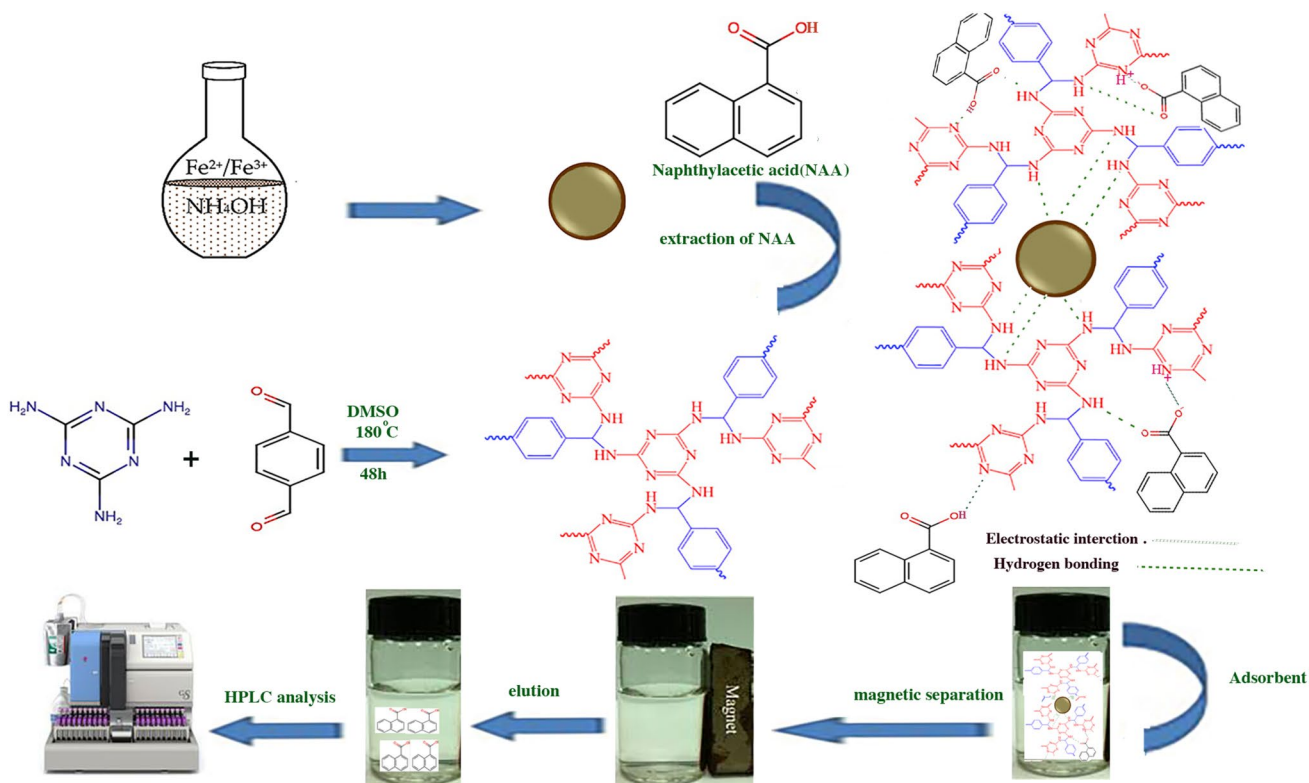


Fig. 1 Synthetic route of TPN/MNPs and its application for the MDSPE

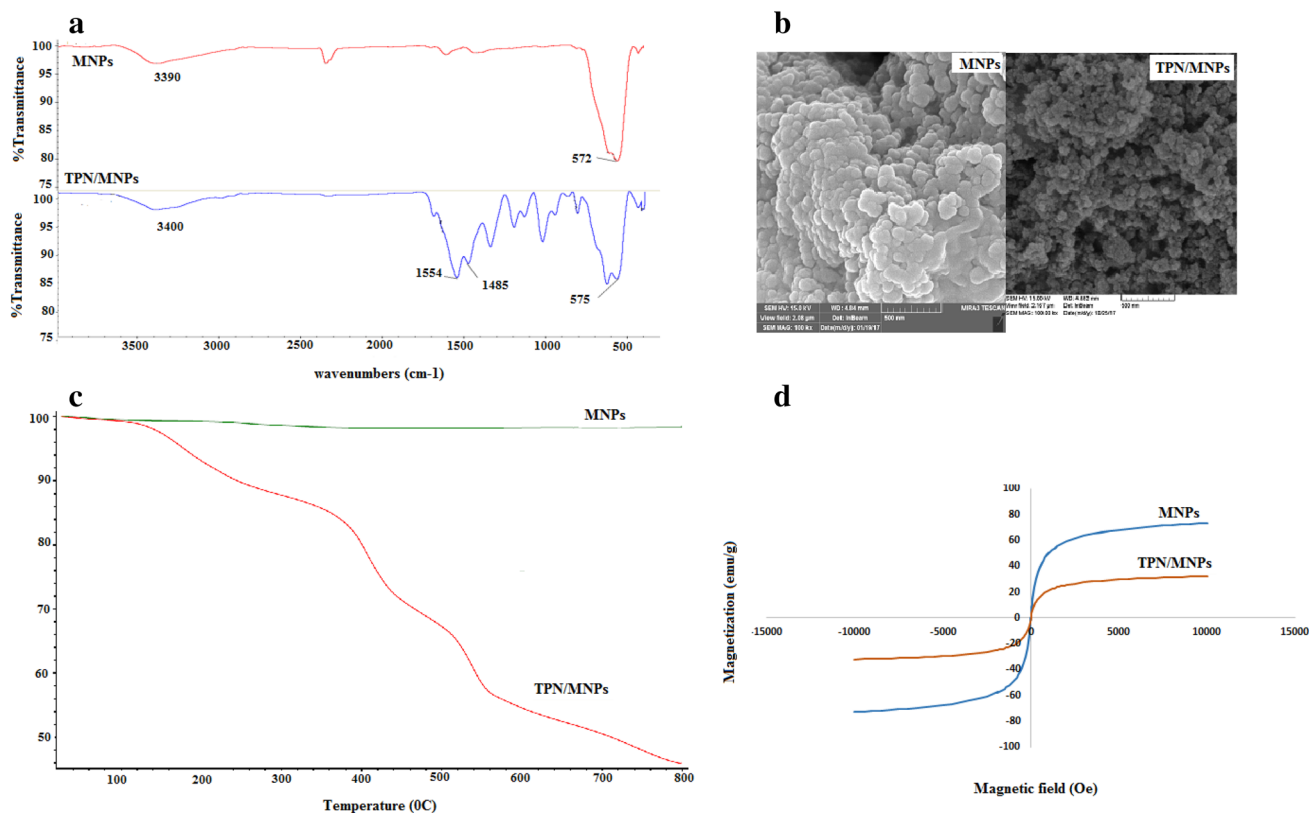


Fig. 2 FTIR spectra (a), FESEM images (b), TGA curves (c) and Magnetization curves (d) of MNPs and TPN/MNPs

and 1485 cm⁻¹ correspond to C=N group of TPN, and a band at 575 cm⁻¹ corresponds to Fe–O [23].

Figure 2b shows FE-SEM images of MNPs and TPN/MNPs. FE-SEM image of MNPs shows the nanoparticles have uniform size distribution. Some particles are agglomerated. The size of nanoparticles is 22–50 nm. It can be seen that TPN/MNPs sizes are 26–70 nm. The size of TPN/MNPs increased that may be attributed to modification with TPN. TGA curves of MNPs and TPN/MNPs are shown in Fig. 2c. In the TGA curve of MNPs, the total weight loss over the full temperature range is 1.6%, due to the loss of absorbed water and dehydration of the surface-OH groups [26]. In the TGA curve of TPN/MNPs, the weight loss 100 °C is attributed to the absorbed water loss. Finally, 53% weight loss in the range of 100–800 °C is probably due to decomposition of TPN.

Magnetization curves of MNPs and TPN/MNPs are shown in Fig. 2d. The saturation magnetization of the MNPs and TPN/MNPs are 70 and 31 emu/g, respectively. The saturation magnetization of TPN/MNPs decreased which is might be due to the present of TPN. However, it is enough for magnetic separation.

Optimization of MSPE Procedure

The parameters influencing the extraction efficiency including pH, extraction time, salt concentration, amount of adsorbent, and desorption conditions were investigated and optimized. The experiments were performed in triplicate. Distilled water spiked with 100 µg L⁻¹ of NAA was used for optimization of parameters. All quantifications were done based on the peak area.

Effect of pH

The effect of pH on the extraction efficiency was studied in the range of 2.5–8.5. Based on Fig. 3a, when the pH increased from 2.5 to 6.5, the extraction efficiency increased and then decrease gradually at pH higher than 6.5. This result could be interpreted based on the pK_a of the NAA which is around 4.5 [9]. The ionization of analyte occurred when pH exceeds pK_a of the analyte. In the same conditions, amine groups of TPN/MNPs are protonated that causes electrostatic attractions between the NAA and TPN/MNPs surface. When pH increased above 6.5, the positive charge

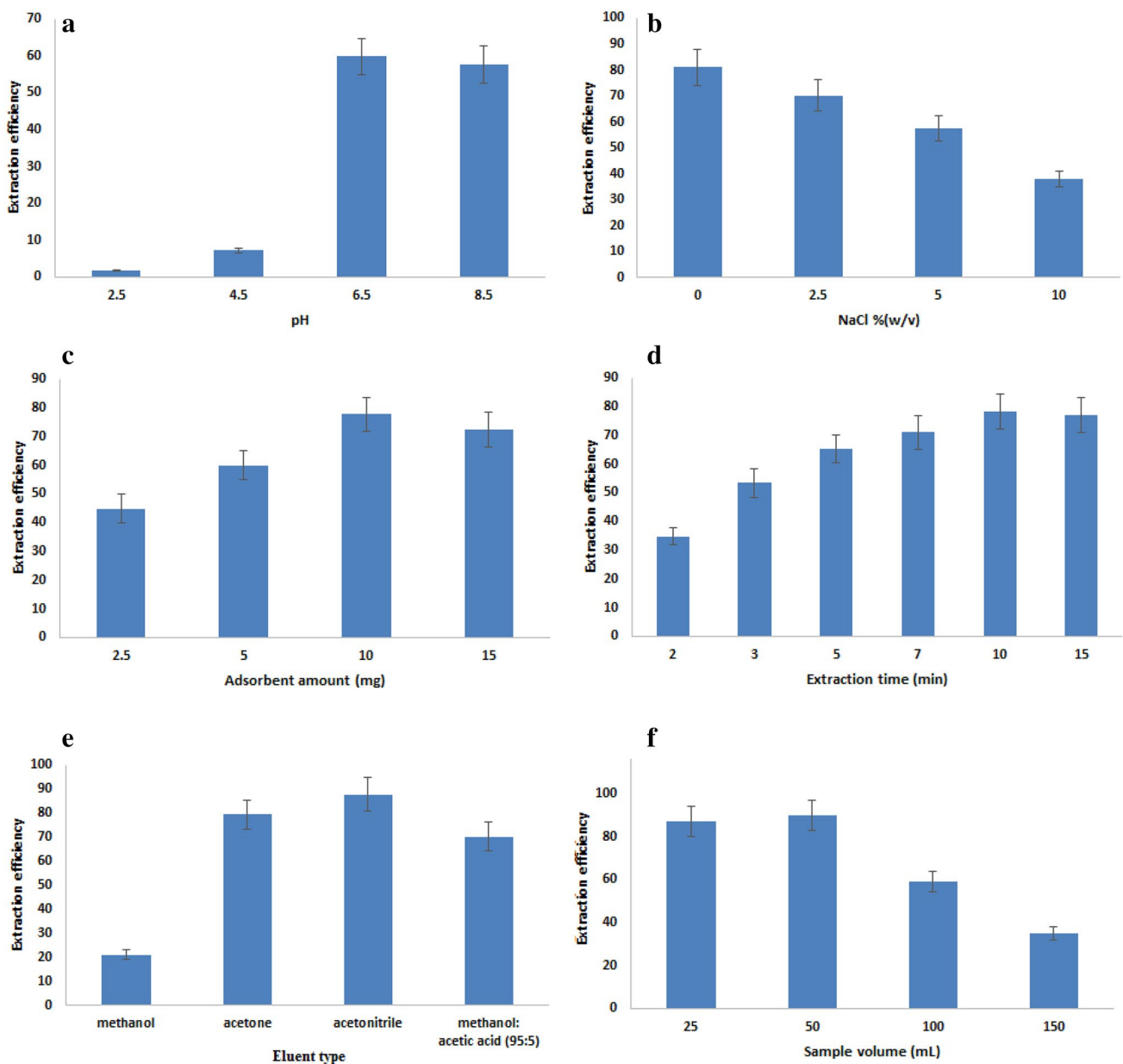


Fig. 3 Effect of pH (a), salt concentration (b), adsorbent amount (c), extraction time (d), eluent type (e), and sample volume (f) on extraction efficiency of the NAA

density on the surface of TPN/MNPs could be decreased which as result of that the extraction efficiency decreased. Moreover, extraction can be driven by hydrogen bonding [24].

Effect of Salt Concentration

The effect of salt concentration was investigated in the range from 0 to 10% (w/v) (Fig. 3b). The results indicated that the extraction efficiency decreased with increasing salt concentrations due to increasing the viscosity of the solution that

causes difficult mass transfer [26]. Moreover, electrostatic interaction of chloride ions with positive sites of adsorbent can reduce the interaction of analyte with adsorbent. Therefore, the extraction efficiency decreased [27]. Therefore, no salt was added into the solution in subsequent experiments.

Effect of the Adsorbent Amount

The effect of the adsorbent amount on the extraction efficiency was studied in the range of 2.5–15 mg. As shown in Fig. 3c, extraction efficiency increased with increasing

absorbent amount up to 10 mg due to increase of accessible sites of the adsorbent. The extraction efficiency decreased with further increasing of the adsorbent amount which is due to incomplete elution of the analyte by the fixed volume of eluent [28]. Therefore, 10 mg was selected for subsequent experiments.

Effect of Extraction Time

The extraction time was studied in the range of 2–15 min. Because of short diffusion route and magnetically assisted separation of the MNPs from the sample solutions, extraction of analyte can be achieved in shorter time even for larger volumes of samples. As shown in Fig. 3d, the extraction time increased by increasing time up to 10. After that, it remained almost constant. Thus, the extraction time of 10 min was selected [29].

Desorption Conditions

Various solvents such as methanol, acetone, acetonitrile and methanol-acetic acid were used for desorption of analyte from the adsorbent surface (Fig. 3e). Among these solvents, acetonitrile had highest desorption efficiency that might be due to polarity of solvent and the solvent is aprotic [1]. The adsorbent can interact with analyte through electrostatic attraction and hydrogen bonding. Also, acetonitrile can disrupt the interaction between the analyte and the adsorbent.

The volume of acetonitrile was investigated from 200 to 1000 μL . The desorption efficiency increased with increasing of the volume of acetonitrile up to 500 μL and then decreased as a result of dilution effect [28]. Therefore, 500 μL of acetonitrile was selected as the optimum volume. In addition, desorption time was investigated from 1 to 10 min and the results are shown in Fig. S1. The highest desorption efficiency was obtained when time was 5 min.

Effect of Sample Volume

The effect of sample volume on extraction efficiency was studied by different sample volumes (25–150 mL) containing

5.0 μg of analyte. As shown in Fig. 3f, the extraction efficiency decreased with enhancing the sample volume from 50 to 150 mL that can be as a result of more difficult transfer of the analyte from the sample solution to the surface of the sorbent because of decrease in the amount of sorbent in volume unit of the sample [27]. Therefore, sample volume of 50 mL was selected as optimum volume.

Method Validation

The analytical characteristics of the proposed method such as linearity, limit of detection (LOD), limit of quantification (LOQ) and preconcentration factor (PF) are summarized in Table 1. The linearity was in the range of 1.0–500 $\mu\text{g L}^{-1}$ and determination coefficient (R^2) was 0.9973. LOD and LOQ, calculated as 3 and 10 times the signal to noise ratio, were 0.3 $\mu\text{g L}^{-1}$ and 1.0 $\mu\text{g L}^{-1}$, respectively. The PF is defined as the ratio of the aqueous sample volume (50 mL) to the eluent volume (0.5 mL) which is 100. The EF was 90. The relative standard deviations (RSDs) of intra-day (repeatability, $n=6$) and inter-day (reproducibility, $n=3$) were less than 9.5% at 10 and 100 $\mu\text{g L}^{-1}$ of NAA.

Analysis of Real Samples

The proposed method was applied for the determination of NAA in cucumber, tomato, and apple. The results are summarized in Table 2. 6.1 $\mu\text{g L}^{-1}$ of NAA was detected in the apple sample. The trueness of the method was evaluated by analysis of the samples spiked with the analyte known amounts of the analyte. Samples analysis was performed before and after spike three times. The recoveries were in the range of 94.5–96.5% with RSDs in the range of 3.6–9.8. Figure 4 shows the chromatograms of NAA in the apple sample prior to and after the spiking with 20 and 40 $\mu\text{g L}^{-1}$ of NAA.

Table 1 Analytical parameters of proposed method

Linear range ($\mu\text{g L}^{-1}$)	Regression equation	R^2	LOD ^a ($\mu\text{g L}^{-1}$)	LOQ ^b ($\mu\text{g L}^{-1}$)	PF ^c	Intra-day RSD% ^d ($n=6$)		Inter-day RSD% ($n=3$)	
						10 $\mu\text{g L}^{-1}$	100 $\mu\text{g L}^{-1}$	10 $\mu\text{g L}^{-1}$	100 $\mu\text{g L}^{-1}$
1.0–500	$y=14,387 C+41,113$	0.9973	0.3	1.0	100	8.0	6.2	9.2	8.3

^aLimit of detection

^bLimit of quantification

^cPreconcentration factor

^dRelative standard deviation

Table 2 Determination of NAA in cucumber, tomato and apple

Sample	Added ($\mu\text{g L}^{-1}$)	Found ($\mu\text{g L}^{-1}$)	Recovery (%)	RSD (%) ($n=3$)
Cucumber	–	–	–	–
	20.0	19.1	95.5	7.2
	40.0	37.8	94.5	6.5
Tomato	–	–	–	–
	20.0	19.1	95.5	6.4
	40.0	38.3	95.8	5.7
Apple	–	6.1	–	9.8
	20.0	25.1	95	5.3
	40.0	44.7	96.5	3.6

Conclusion

In the present study, triazine-based polymeric network-modified magnetic nanoparticles (TPN/MNPs) were successfully synthesized and applied as efficient adsorbent for extraction of NAA. TPN/MNPs contains amine groups

and can form hydrogen bond and electrostatic interaction with NAA. The adsorbent possess porosity, high surface area and good chemical stability. The magnetic separation greatly improved the separation rate and reduced the analysis time. The results indicated that TPN/MNPs can be used as efficient adsorbent for extraction of NAA in fruit and vegetable samples.

The proposed method was compared with other published methods. As shown, based on the results in Table 3, this the method has wide linear range. In addition, this method has lower LOD in comparison with other methods [8–10, 12]. The advantage of magnetic separation is easy separation and adsorbent can be isolated from the sample solution rapidly by applying an external magnetic field. The method is simple and requires low amount of organic solvent. The proposed method has lower extraction time in comparison with the other reported methods [9, 10]. Also, the adsorbent has high adsorption capacity.

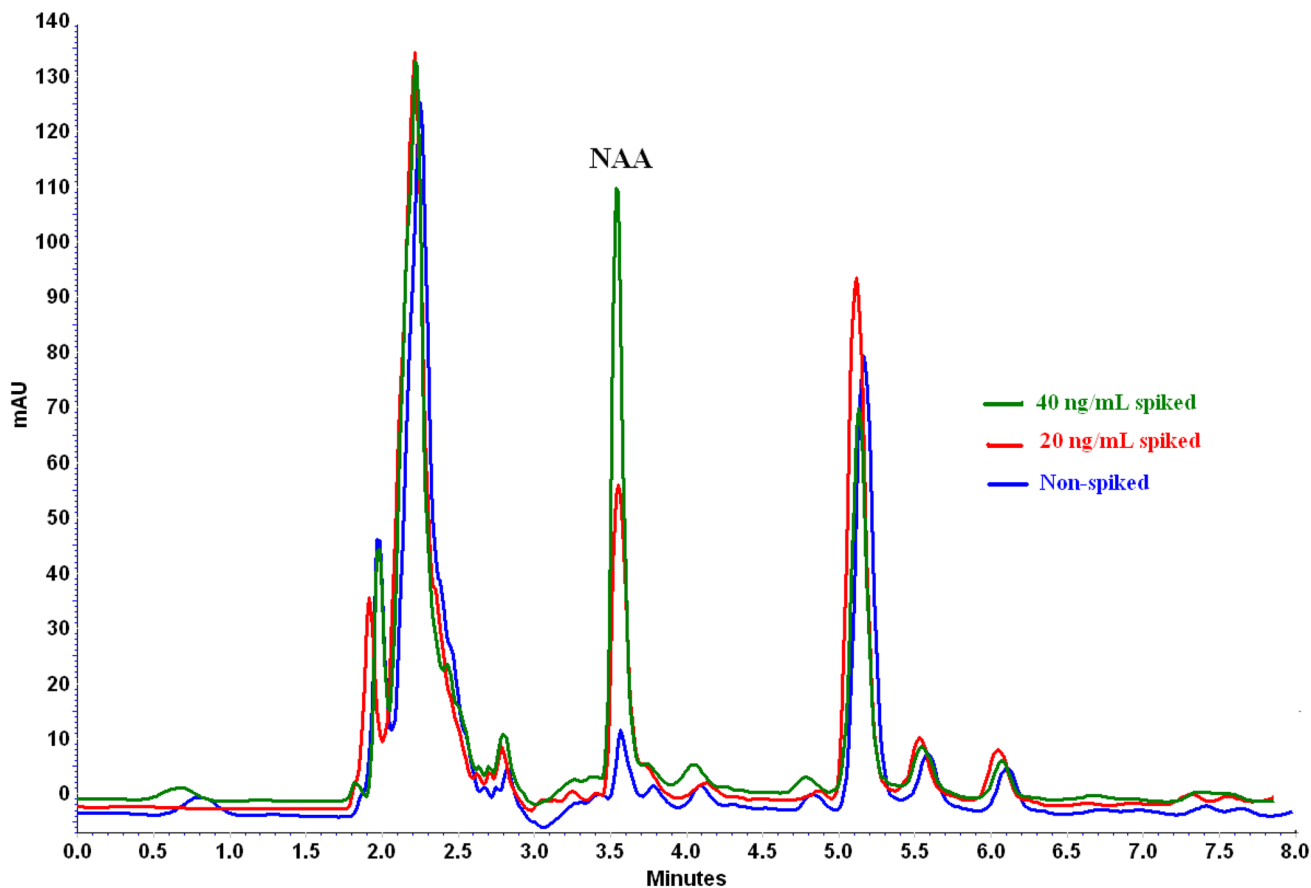


Fig. 4 Chromatograms of non-spiked and spiked (20 and 40 $\mu\text{g L}^{-1}$) apple sample

Table 3 Comparison of the proposed method with other methods for determination of NAA

Matrix	Extraction method	Detection	Linear range	LOD	References
Plant samples	SPE ^a	HPLC–UV	5–200,000 $\mu\text{g L}^{-1}$	1.2 $\mu\text{g L}^{-1}$	[8]
Tomatoes	MDSPE ^b	HPLC–UV	2–600 $\mu\text{g kg}^{-1}$	0.67 $\mu\text{g kg}^{-1}$	[9]
<i>Chlorella vulgaris</i>	DLLME ^c	HPLC–FLD	0.05–5.0 $\mu\text{g L}^{-1}$	0.02 $\mu\text{g L}^{-1}$	[11]
Banana	MISPE ^d	HPLC–UV	40–4000 $\mu\text{g kg}^{-1}$	3.0 $\mu\text{g kg}^{-1}$	[12]
Tomatoes	N-doped CNTs–HF–SPME ^e	HPLC–PDA	3–1500 $\mu\text{g kg}^{-1}$	1.0 $\mu\text{g kg}^{-1}$	[10]
Cucumber, tomato and apple	MDSPE	HPLC–UV	1.0–500 $\mu\text{g L}^{-1}$	0.3 $\mu\text{g L}^{-1}$	Present work

^aSolid-phase extraction

^bMiniaturized dispersive solid-phase extraction

^cDispersive liquid–liquid microextraction

^dMolecularly imprinted solid-phase extraction

^eN-doped carbon nanotubes-reinforced hollow fiber solid-phase microextraction

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Compliance with Ethical Standards

Conflict of interest Sepideh Moradi Shahrebabak would declare that she would not have any conflicts of the interests. Mohammad Faraji would also declare that he would have not any conflicts of the interests. Moreover, Mohammad Saber-Tehrani would disclose that he would not have any conflicts of interests. In addition, Meisam Shabaniyan discloses that he would not have any conflicts of interests. Finally, Parviz Aberoomand-Azar would declare that he would not have any conflicts of interests.

Ethical approval The present paper did not include any research on the humans or animals subject.

Informed consent Not applicable.

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