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Magnetic Solid Phase Extraction of Triazine Herbicides from Environmental Aquatic Media using Polyaniline/Fe_3O_4 Nanocomposite

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Abstract

Polyaniline/Fe_3O_4 magnetic nanoparticles were synthesized and employed as a sorbent for the magnetic solid phase extraction (MSPE) of seven triazine herbicides from environmental water samples. The properties of the prepared magnetic sorbent were characterized using field emission-scanning electron microscopy (FE-SEM), fourier transform infrared spectroscopy (FT-IR), vibrating sample magnetometer (VSM), X-ray diffraction (XRD) and thermal gravimetric analysis (TGA) methods. Effect of the different parameters influencing the MSPE efficiency, such as sample pH, sorbent amount, and extraction time were investigated and optimized. The amount of enrichment factors for triazines using proposed method were found in the range of 26-49. Calibration curves of triazines showed linearity in the range of 1-1000, 2-1000 and 5-1000 μg/L for analytes. In addition, the detection limits for the analytes were in the range of 0.2-0.9 μg/L. The values of relative standard deviation (RSD%) for n=5 at the concentration level of 10 μg/L were obtained lower than 3.1% for all analytes. Capability of polyaniline/Fe_3O_4 magnetic nanoparticles in extraction of triazines was compared with naked Fe_3O_4 and polyaniline. The proposed method was also successfully applied to the extraction of triazine herbicides from environmental samples and satisfactory relative recoveries were obtained.

Keywords: *Polyaniline/Fe_3O_4 nanocomposite, Magnetic solid phase extraction, Triazine herbicides, Environmental water sample analysis.*

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Introduction

Application of iron oxide magnetic particles in sample preparation field has been reported since 1999 in magnetic solid phase extraction (MSPE) methodology [1]. High sample capacity, ease of sorbent separation using an external magnetic field, and being rapid and inexpensive is the advantages of this methodology. Such benefits lead to the superiority of MSPE technique over conventional solid phase extraction (SPE) method using cartridge or disk [2]. However, the potential of aggregation in naked Fe_3O_4 particles lead to the introduction of modified particles which extend their applications. The developed modifications include incorporation of silica, metal oxides and some polymers [3,4]. In this meanwhile, versatility of conductive polymers has been turned them to one of the most absorbing modified groups [5]. Among conductive polymers, polyaniline (PANI) in particular, has also been corroborated a big attraction due to their multifunctional properties such as their hydrophobicity, acid–base character, π-π interaction, polar functional groups, ion exchange property, hydrogen bonding, and its electroactivity [6-12]. These benefits have been made PANI/Fe_3O_4 particles as a suitable extraction media in sample preparation field [13-15].

Triazine herbicides have been widely utilized in agricultural field. These compounds are extensively used as pre- and post-emergent weed control agents to improve crop yields. The monitoring of these herbicides has been attracted lots of interest. This fact is due to the toxicity and persistency of triazines in ecosystem and their potential of the transformation into more polar compounds [16]. Gas chromatography (GC), high performance liquid chromatography (HPLC), and also capillary electrophoresis have been used for their analysis [17-22]. However, a pre-concentration step is usually mandatory before these analytical systems to meet the essential sensitivity. SPE [23], micro-SPE [24], solid phase microextraction (SPME) [25,26], solvent microextraction (SME) [20,27] have been used for isolation and enrichment of triazines prior to instrumental analysis.

In this work, Fe_3O_4 nanoparticles were synthesized according co-precipitation method and then polyaniline was polymerized on it to form magnetic nanocomposite. Following, the potential of PANI/Fe_3O_4 nanoparticle in MSPE of triazine herbicides from environmental aquatic media was investigated.

Experimental

Chemicals and Reagents

Aniline, HPLC grade acetonitrile, acetone, methanol, ethanol, hydrochloric acid were purchased from Merck (Darmstadt, Germany). Ammonium acetate, ammonium persulfate (APS), Iron (II) sulfate, Iron (III) chloride, sodium dodecyl sulfate (SDS), sodium chloride, sodium hydroxide were also obtained from Merck. HPLC grade water was purchased from Caledon (Ontario, Canada). A solution containing 100 mg/L of seven triazine herbicides (simazine, prometon, atrazine, propazine, ametryne, prometryne, and terbutryne) was obtained from Supelco INC (Bellefonte, PA, USA). Standard solutions were prepared by diluting stock solution with methanol. Moreover, working solutions were prepared daily by dilution of stock solution with double distilled water.

Apparatus

An Agilent 1200 series HPLC system including a G1311A quaternary pump and a UV detector were used for the separation and determination of the analytes. The separation was performed on Zorbax Eclipse XDB-C18 (150 mm× 4.6mm ID, 5µm) column. The solvents used as mobile phase were acetonitrile and 10 mM ammonium acetate buffer (pH=7). The chromatographic data were collected and recorded using ChemStation software. The direct sample introduction was carried out using a Rheodyne manual injector (Rohnert Park, CA, USA) with a 20 µL loop. Column temperature was kept constant at 25 ˚C using a thermostatted column compartment. Chromatographic separations were carried out using the isocratic elution with the mixture of acetonitrile and buffer solution (35:65). The flow rate was 1 mL/min and detection was performed at 220 nm [28].

Synthesis of polyaniline/Fe_3O_4 composite

Firstly, iron oxide magnetic particles were synthesized according to the co-precipitation method [29,30]. In summary, an amount of 2.794 g $FeSO^4.7H^2O$, 3.110 g $FeCl^3$ and 0.85 mL HCl were dissolved in 25 mL degassed deionized water. This solution was added dropwise to the 250 mL sodium hydroxide solution (1.5 mol/L) at 80 ˚C under nitrogen atmosphere while stirring in three necked round bottom. The black colloidal product was collected using a 1.4 T magnet and washed several times by degassed deionized water. This product was kept in degassed deionized water in a 250-mL volumetric flask. Iron oxide magnetic particles concentration estimated 10 mg/mL.

In order to synthesize polyaniline/Fe_3O_4 composite, 0.2 mol aniline was added to 40 mL of acidic magnetic suspension containing 0.26 g SDS. This mixture was inserted in an ultrasonic bath for 10 min, having better dispersion. Following, 5 mL of an aqueous solution containing 0.46 g APS, as an oxidant, was added to the mixture shaking for 1 hr. Eventually, the composite was washed with water and methanol and dimethyl ether. The final product was dried for 6 h at 100 ˚C in a vacuum oven [31]. Polyaniline was also synthesized according the same procedure in absence of Fe_3O_4 particles.

MSPE procedure

In order to perform extraction, a volume of 10.0 mL of aqueous sample containing 50 μg/L triazines (pH=6) and 20% (w/v) NaCl was transferred into the test tube. Following 30 mg PANI/Fe_3O_4 composite was added and the mixture was shaken for 5 min at room temperature. Subsequently the sorbent was isolated from solution using a 1.4 T magnet. After decanting the solution, 1 mL methanol was used to do desorption process in 2 min using vortex mixer. The sorbent was again separated using magnet and the eluent was transferred to the vial and then it was dried using a gentle flow of N_2 gas. The residue was dissolved in 50 μL methanol and then injected into the HPLC system.

Results and discussion

Characterization of PANI/Fe_3O_4 composite

X-ray diffraction pattern for Fe_3O_4 (figure 1a) displayed a sharp peaks at 2θ=30.1, 35.5, 43.1, 53.4 and 57 which is in agreement with literature [32]. Similar X-ray diffraction pattern for composites (figure 1b) was observed for synthesized composite. However, the peak intensities of the composite are significantly lower as a result of Fe_3O_4 coverage by polymer.

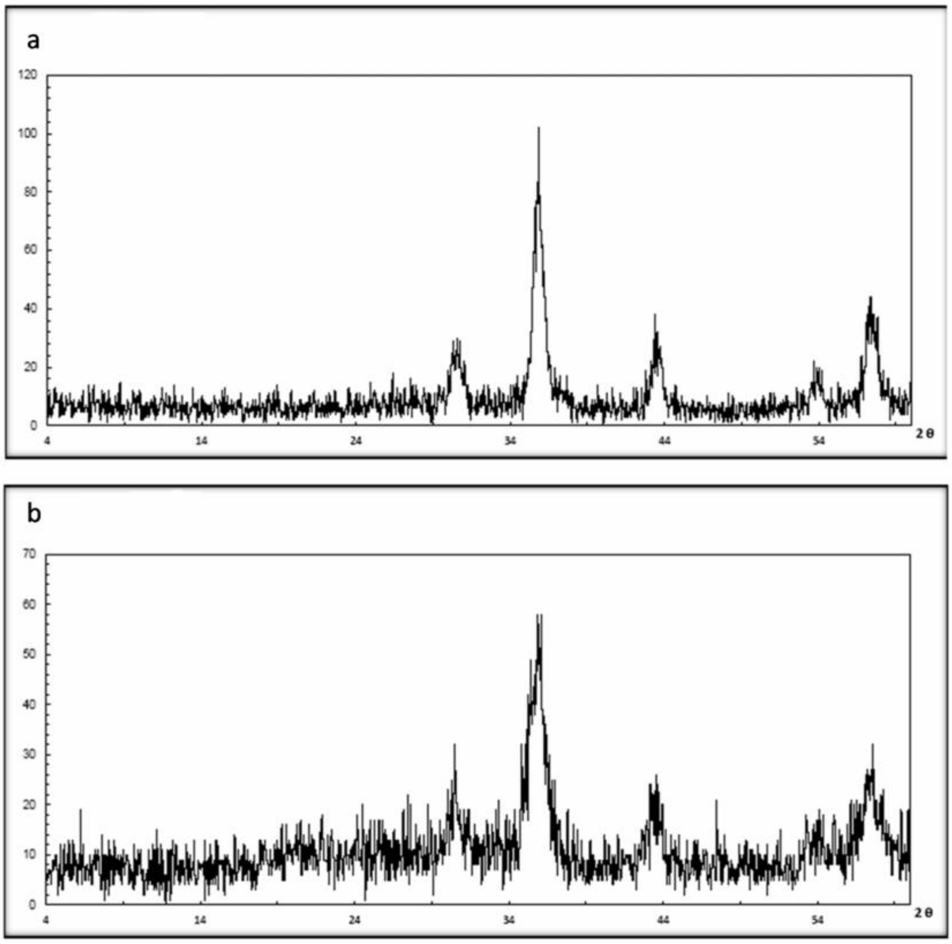

Figure 1. X-ray diffraction patterns for a) Fe_3O_4 and b) PANI/ Fe_3O_4.

According to FT-IR spectrum of composite (figure 2), the observed bands at 1486 and 1561 cm^{-1} correspond to the C-C and C-N stretching modes for the benzenoid and quinoid rings. There was a broad peak at 573 cm^{-1} which is assigned to Fe-O stretching band of Fe_3O_4. Moreover, the observed peak at 1299 cm^{-1} is assigned to the C–N stretching vibration in protonic acid doped PANI, where SO_3 group of SDS is bonded with N of PANI [31, 33].

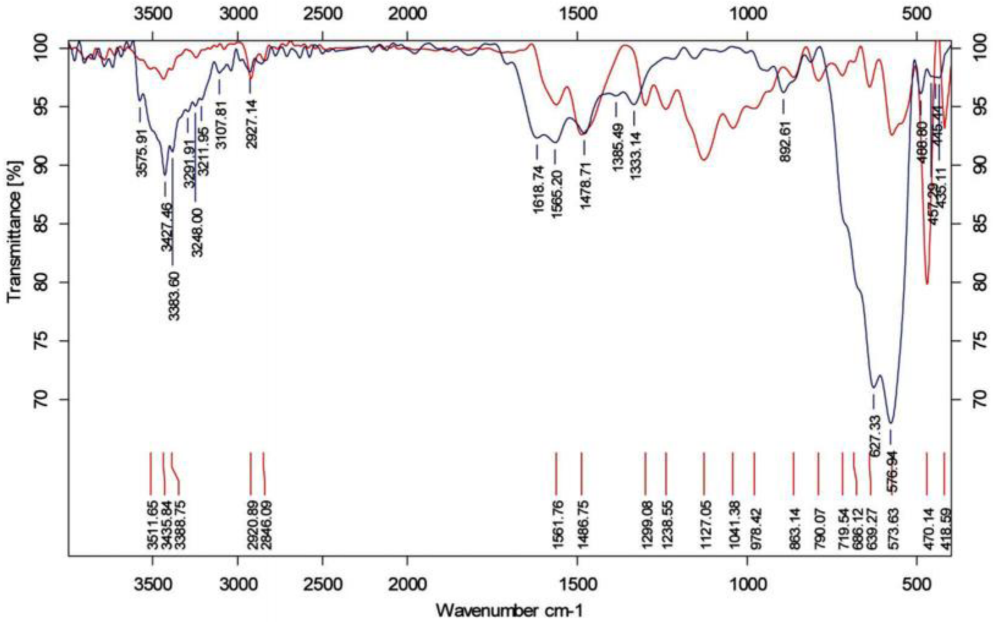

Figure 2. FT-IR spectra of a) Fe_3O_4, and b) PANI/Fe_3O_4 composite.

Figure 3 display FE-SEM images of Fe_3O_4 and PANI/Fe_3O_4 composite. These images confirm formation of nanosized particles of composite which resulted in high surface area sorbent.

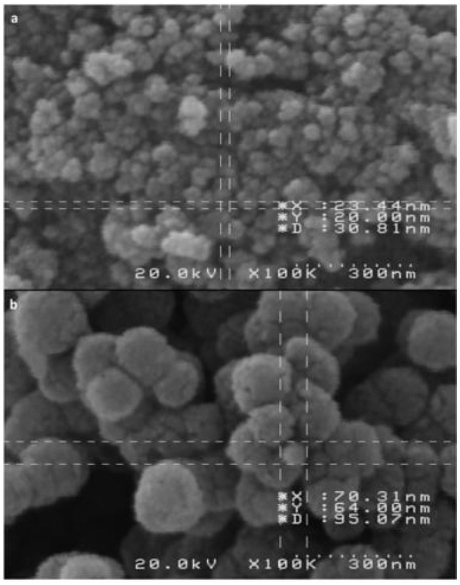

Figure 3. FE-SEM images of a) Fe_3O_4 and b) PANI/Fe_3O_4 composite.

In order to estimate the contribution of organic moiety in the composite, a thermal gravimetric analysis was performed. According to the TGA analysis, the portion of conductive polymer in this structure is about 47.33%.

In order to measure magnetic properties of Fe_3O_4 and PANI/Fe_3O_4 composite, a VSM analysis was also performed (figure 4). Magnetic saturation for Fe_3O_4 is obtained 50 emu/g and it was 15 emu/g for coated Fe_3O_4. Magnetic properties of composite enable simple isolation of composite from solution by a magnet [34]. Lower amount of magnetic saturation for synthesized composite prove noticeably presence of PANI in magnetic nanocomposite [35].

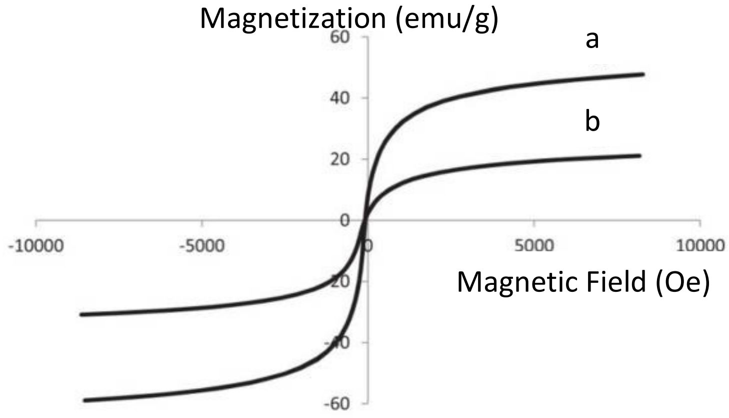

Figure 4. Magnetization curves of a) Fe_3O_4 and b) PANI/Fe_3O_4.

Optimization Process

The effect of the influential parameters on the extraction efficiency of MSPE including pH effect, sorbent amount, extraction time, ionic strength, type and volume of eluent, desorption time was studied. A univariate approach was employed to the optimization of affective factors. Moreover, the peak area was used to assess the extraction efficiency under investigated condition.

pH effect

Sample pH is a key parameter that could affect both forms of analytes and surface charge density of sorbent; therefore this parameter was assessed in the range of 2-10. As depicted in figure 5a, the best results were obtained at pH 6. The behavior of analytes in different sample pH is accordance with pKa of triazines which range 1.6-4.3 [36]. Charged analytes are formed below pH 6 which is responsible for lower results. This study was proved that the sorbent possess no influence in extraction performances.

Sorbent amount

Sorbent amount is one of the parameters that influence the extraction capacity and sensitivity of the method. As illustrated in figure 5b, the extraction efficiencies were increased up to

30 mg and no marked changes were observed afterward. So an amount of 30 mg sorbent was used as the optimum value and it was used in further experiments.

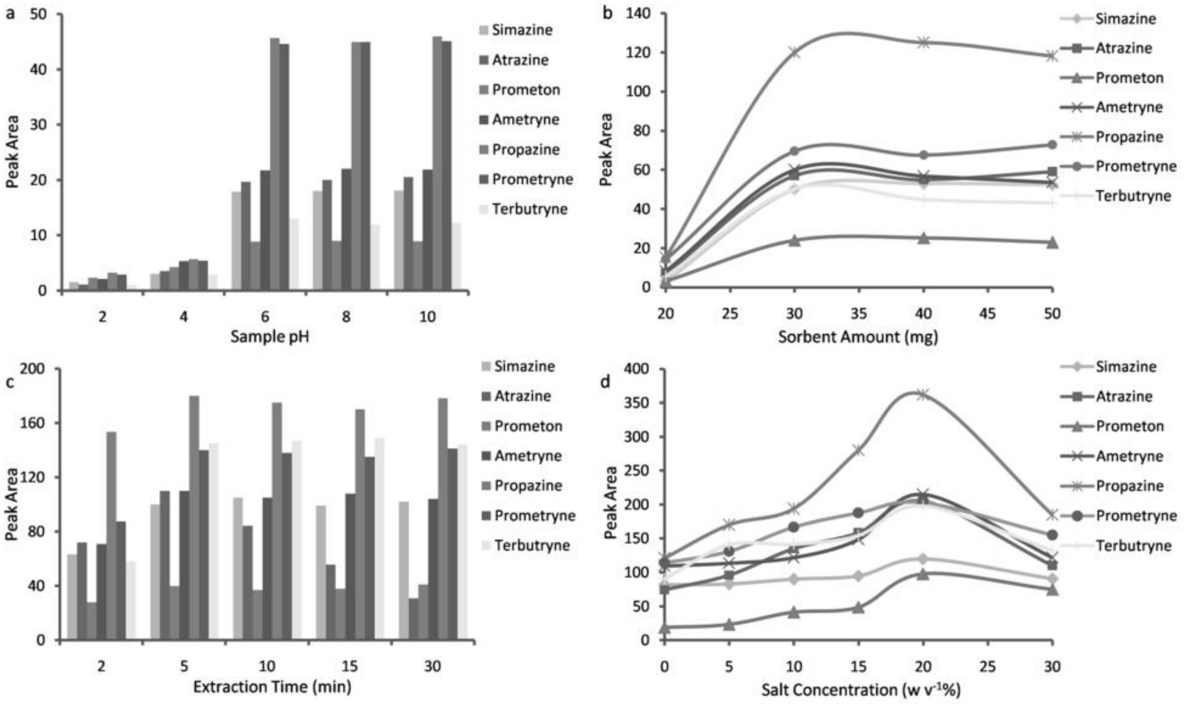

Figure 5. Effect of a) sample pH, b) sorbent amount, c) extraction time, and d) ionic strength on MSPE efficiency.

Extraction time

Extraction process was investigated in the range of 2 to 30 min. Extraction time is considered from the sorbent exposure point to the magnetic removal step. As demonstrated in figure 5c, the best results were obtained in 5 min.

Ionic strength

Generally, engagement of water molecules in the hydration spheres around the ionic salt would affect solubility of organic solutes in the aqueous solutions. Reduction of the available water concentration for dissolving analyte molecules is responsible for this phenomenon. To investigate the effect of solution ionic strength on the extraction efficiency, several solutions containing different concentration of sodium chloride salt including 0 to 30% (w/v) were prepared and extraction process was conducted. For all compounds, an increase in the extraction efficiency was seen up to the 20% NaCl and a drop is observed afterwards (Figure 5d). The enhancement in solution viscosity could be led to this decline. Thus, the value of 20% salt was used for subsequent extraction.

Desorption conditions

In order to select the most suitable eluent for desorption process; methanol, ethanol, and acetonitrile were utilized. The best results were obtained from acetonitrile that could be attributed to greater solubility of the analytes in this solvent, regarding the presence of nitrile groups. Study on the volume of the eluent showed a dramatic increase up to 1000 µL for all triazines (figure 6a). Further volume increase resulted in the decreasing extraction efficiency due to the dilution of analytes. Thus desorption process was carried out using 1000 µL of acetonitrile.

Desorption time was studied in the range of 1 to 10 min. According to the figure 6b, desorption time of 2 min was quite suitable. Agglomeration of nanoparticles and therefore trap of the analytes in the middle space of sorbent particles could be responsible for these decreases.

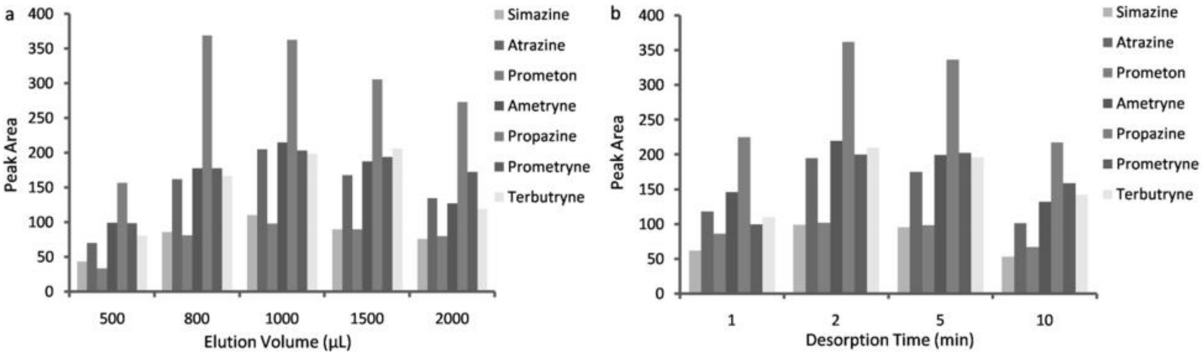

Figure 6. Optimization of desorption process, a) eluent volume, and b) desorption time.

Method Validation

In order to evaluate proposed method using PANI/MNPs, quantitative analysis was performed considering optimized conditions. As tabulated in the table 1, wide dynamic ranges of

1-1000 µg/L, for propazine, 2-1000 µg/L, for atrazine, ametryne, prometryne, terbutryne, and 5-1000 µg/L, for simazine and prometon, along with good R^2 values were acquired. Reproducibility of the method based on RSD% (n=5) values were assessed. These values were ranged between 1.8 and 3.1% at the concentration level of 10 µg/L. The amounts of limit of detection (LOD) and limit of quantifications (LOQ), based on the signal to noise ratio of 3 and 10 were ranged from 0.2-0.9 µg/L and 0.6-2.8 µg/L, respectively. The amounts of enrichment factors were from 26, for prometone, to 49 for propazine.

Table 1. Analytical data obtained from MSPE/HPLC-UV of triazine herbicides using PANI/MNP sorbent.

Compound	LDR (µg/L)	R^2	LOD (µg/L)	LOQ (µg/L)	RSD% (n=5)	EF
Simazine	5-1000	0.996	0.9	2.8	2.2	29
Atrazine	2-1000	0.994	0.6	1.9	3.1	35
Prometon	5-1000	0.994	0.9	2.8	1.7	26
Ametryne	2-1000	0.994	0.6	1.9	1.9	36
Propazine	1-1000	0.996	0.2	0.6	2.9	49
Prometryne	2-1000	0.995	0.6	1.9	1.8	32
Terbutryne	2-1000	0.996	0.6	1.9	2.7	33

In a comparison study, the extraction performances of selected triazines were evaluated using MNPs, synthesized PANI and PANI/MNPs. As expected, the extraction efficiencies of all analytes were negligible using naked MNPs due to the simplicity of surface and aggregation [37] of MNPs. However the extraction performances were shown about 1.2 times improvement for seven triazines using PANI/MNPs compared with PANI. This phenomenon could be attributed to the higher surface area of this sorbent more than just interaction of analytes with PANI moiety [38].

The figures of merit of proposed method were measured against solid phase membrane tip extraction (SPMTE)-micro-LC-UV method [39] and MSPE-HPLC-DAD using Graphene/Fe3O4 [40] for extraction of triazines (table 2). As tabulated, the proposed method demonstrates wider dynamic ranges, lower RSD% values and 4-times lower extraction time. However, the amount of LODs using Graphene/Fe3O4 has been more desirable.

Table 2. Comparison of the proposed method with two other sorbent-based extraction methods for the determination of triazines in water samples.

Method	LDR (µg/L)	LOD (µg/L)	RSD%	Extraction Time (min)	Reference
SPMTE-micro-LC-UV	1-100	0.2-0.5	5.7-8.5	20	[39]
MSPE-HPLC-DAD using Graphene/Fe_3O_4	0.1-50	0.025-0.040	3.4-5.2	20	[40]
MSPE-HPLC-UV using PANI/Fe_3O_4	1-1000	0.2-0.9	1.7-3.1	5	Proposed method

To evaluate the applicability of the proposed method, experiments were performed using Caspian Sea, Zayandeh Rood River and Shahr-e-Rey well water samples. The chromatograms for three samples confirmed the absence of triazines in non-spiked samples. Figure 7 is typically demonstrated the chromatogram for Zayandeh rood river water sample. In order to evaluate the matrix effect on extraction performance, the samples were spiked at the concentration level of 10 µg/L of triazines and they were analyzed using developed method.

As tabulated in Table 3, the amounts of relative recoveries were ranged 80-99% and the RSD% values were calculated less than 5%. The results reveal water matrices, in our present had little effect on MSPE-HPLC-UV method using PANI/Fe_3O_4 sorbent.

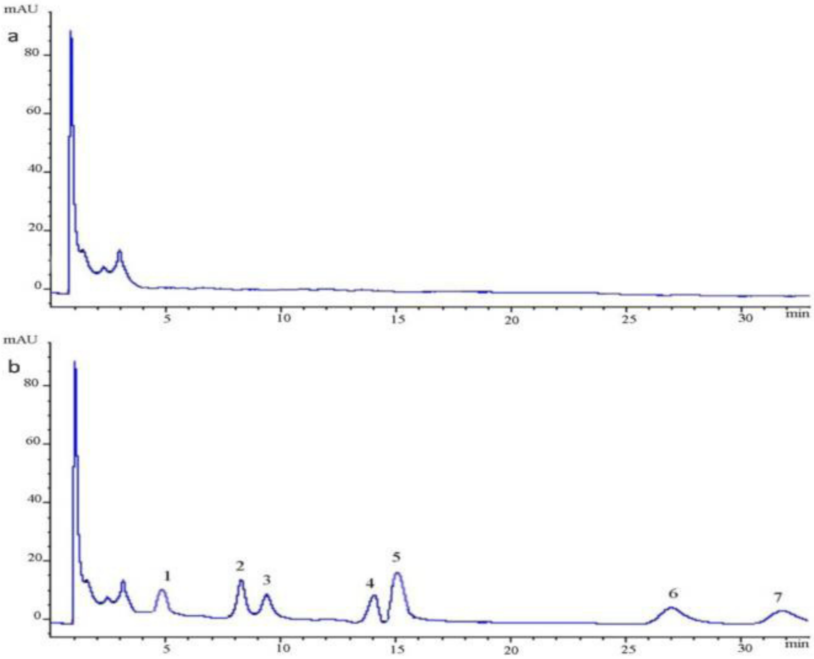

Figure 7. Chromatograms obtained from Zayandeh rood river sample a) before and b) after being spiked with triazines at concentration level of 10 µg/L. 1) Simazine, 2) Atrazine, 3) Prometon, 4) Ametryne, 5) Propazine, 6) Prometryne, and 7) Terbutryne. MSPE conditions: 10 ml sample solution (pH=6) containing 20% NaCl, 30 mg sorbent, extraction in 5 min, desorption using 1000 µL acetonitrile in 2 min.

Table 3. MSPE-HPLC-UV analysis of triazines in three environmental water samples after being spiked at concentration level of 10 µg/L.

Sample		Simazine	Atrazine	Prometon	Ametryne	Propazine	Prometryne	Terbutryne
Caspian Sea water	Initial concentration*	-	-	-	-	-	-	-
	Found concentration*	8.5	8.3	8.7	8.1	9.3	8.0	8.8
	Relative recovery (%)	85	83	87	81	93	80	88
	RSD%	3.2	3.7	2.9	3.0	3.7	4.2	5.0
Zayandeh Rood River water	Initial concentration	-	-	-	-	-	-	-
	Found concentration	9.1	9.3	9.0	9.1	9.3	8.9	9.2
	Relative recovery (%)	91	93	90	91	93	89	92
	RSD%	3.4	3.9	3.1	2.4	3.4	4.0	3.6
Well water	Initial concentration	-	-	-	-	-	-	-
	Found concentration	9.8	9.9	9.7	9.8	9.8	9.7	9.7
	Relative recovery (%)	98	99	97	98	98	97	97
	RSD%	2.9	3.7	2.8	2.4	3.5	4.1	3.7

* All concentrations are in µg/L.

Conclusion

Polyaniline/Fe_3O_4 magnetic nanoparticles have been synthesized and characterized. The nanocomposite was used as a sorbent in magnetic solid phase extraction along with HPLC-UV system. The developed method proved good sensitivity and reproducibility along with appropriate enrichment factor for seven studied triazines. The experiments demonstrate the superiority of PANI/MNPs against naked MNPs and PANI in extraction of the analytes. Short extraction time, long dynamic range and low RSD% values were the strong points of proposed method. Furthermore, relative recoveries data obtained from the extraction of triazine herbicides from three environmental water samples reveal robustness of developed method.

Possessing high surface area and consequently high loading capacity of polyaniline/Fe_3O_4 magnetic nanoparticles along with the capability of the chemical structures of polyaniline for contribution in π-π interaction between the analytes and the sorbent, makes PANI/Fe_3O_4 composite sensitive for fast extraction of compounds having aromatic moiety.

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