http://dx.doi.org/10.5935/0103-5053.20150035

J. Braz. Chem. Soc., Vol. 26, No. 4, 741-747, 2015.
Printed in Brazil - ©2015 Sociedade Brasileira de Química
0103 - 5053 $6.00+0.00

Article

Selective Determination of 2,4,6-Trinitrotoluene in Water Samples Based on Magnetic Imprinted Nanoparticles via Grafting Polymerization

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The magnetic surface imprinted polymer was effectively synthesized based on grafting polymerization for selective determination of 2,4,6-trinitrotoluene (TNT) as template molecule. The "grafting to" procedure was performed by copolymerizing of vinyl modified magnetic substrate with methacrylic acid (MAA) and ethylene glycol dimethacrylate (EGDMA) as functional monomer and cross-linking agent, respectively. The morphology, structure and polymeric properties of imprinting polymers were characterized by scanning electron microscopy (SEM), transmission electron microscopy (TEM) and Fourier transforms infrared spectroscopy (FT-IR). In order to improve on the adsorption capacity amount, the various parameters were considered. The resulting sorbent exhibited a high capacity with appropriate selectivity for TNT molecules. The evaluation demonstrated a linear range of 10-500 μg L^{-1} with the detection limit of 3.0 μg L^{-1}. Moreover, the performance of the present sorbent was studied for extraction and determination of TNT compound in environmental waters and acceptable recoveries ranging from 91.7 to 100.8% were achieved.

Keywords: 2,4,6-trinitrotoluene, molecularly imprinted polymer, surface grafted imprinting, magnetic nanoparticles, water samples

Introduction

Molecularly imprinted polymers (MIPs) have attracted widespread attention owing to the creation of selective artificial recognition sites on the polymer backbone. The MIPs as tailor-made materials are synthesized by copolymerization of the functional monomers and cross-linking agent in the presence of template molecules. Afterwards, the resulted sites are caused by removing of templates from the polymeric substrate. The utilization of MIPs has opened a new window in variety of fields such as in the separation sciences,[1-4] sensor device,[5-7] catalysis study[8,9] and drug controlled release.[10,11] During recent years, the preparation of adsorbent based on imprinted polymers was developed for selective extraction and determination of target analytes. In this regard, the extensive progresses were performed for molecular imprinting technology through different synthetic methods. The bulk polymerization was the traditional procedure for synthesis of MIP, however, it possessed the irregular size and did not generate uniform MIP shell for practical application.[12] To overcome this limitation, surface imprinting polymer was proposed due to formation of imprinted shells on different supporting materials. Therefore, the accessibility to the target molecules and mass transfer difficulty were improved by controlling the position of the templates on the surfaces of materials or close to near them.[13]

Nanoparticles are qualified substrates for surface imprinting that demonstrate significant properties owing to large external surface area to the volume ratio.[14] Accordingly, greater interest was focused on the applying of imprinted polymer layer in nano-size substrates. Among different nanoparticles, magnetic nanoparticles possessed the notable merits like unique magnetic properties and effective capability for modifying.[15] The efficient procedure could be employed for the separation of nanoparticles from the main suspension by magnetic separation. Thus, the collection of target analyte was performed by using of a magnet which avoided time-consuming packing of the solid phase extraction (SPE) cartridge, filtration operation or centrifugation procedure.[15,16] Recently, the coating of imprinting polymer layer on magnetic nanoparticles has introduced a new approach toward separation applications. Therefore, the sorbent of magnetic SPE based on imprinted

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polymer demonstrated a potential method for selective determination and the enrichment of trace analytes in complex matrices.[12,15-18]

The explosive compounds as priority contaminants are often released to the environment through manufacturing activities, chemical industries and loading or packing into munitions items.[19] 2,4,6-trinitrotoluene (TNT) is one of the most explosives which belongs to the nitro-aromatic group. This compound was considered as a carcinogenic agent and the U.S. Environmental Protection Agency (U.S. EPA) has listed it as the toxic pollutant.[20] Because of trace level concentration of TNT and much interference in water samples, the sample clean-up and preconcentration steps were required. However, the various methods were studied and suggested for determination of TNT, the major disadvantage of them was the lack of selectivity for target analytes.[21] Nowadays, the molecular imprinting strategy is as a promising method for selective detection of many contaminants like TNT.[22-25] Hence, the using of imprinted polymers can be a well-suited technique for selective extraction and determination of TNT from water matrices.

In the present work, an efficient imprinted polymer was developed via "grafting to" method on magnetic nanoparticles and employed for selective determination of TNT from aqueous media. In this regard, the magnetic substrate was first modified by vinyl end groups. The grafting polymerization was performed via co-polymerization of vinyl groups with functional monomers and cross-linking agents in the presence of target molecules. The results confirmed that the present magnetic SPE sorbent was appropriate for trace level detection of TNT from water samples.

Experimental

Reagents and chemicals

All the chemicals and reagents used in this work were of analytical grade. Ethylene glycol dimethacrylate (EGDMA) and acetonitrile were purchased from Sigma-Aldrich (Beijing, China) and Lobachemie (Mumbai, India), respectively. Iron (III) chloride hexahydrate ($FeCl_3.6H_2O$), iron (II) chloride tetrahydrate ($FeCl_2.4H_2O$), ammonium hydroxide (NH_4OH), tetraethyl orthosilicate (TEOS), 3-methacryloxypropyl trimethoxysilane (MPTS), methacrylic acid (MAA), 2,2- azobisisobutyronitrile (AIBN), 4-nitrophenol (4-NP), nitrobenzene (NB), toluene and methanol (HPLC grade) were also obtained from Merck (Darmstadt, Germany). TNT and 2,4-dinitrotoluene (2,4-DNT) were purified by recrystalizing small batches two times from acetone.

Apparatus

The morphology and size of the magnetic molecularly imprinted polymers (MMIPs) were characterized by scanning electron microscopy (S-4160) and transmission electronic microscopy (Philips CM30), respectively. The Bruker VERTEX 70 Fourier transform infrared (FT-IR) spectrometer (Billerica, USA) using KBr pellet was utilized. The high-performance liquid chromatography (HPLC) analyses were performed with the Waters 600 Pump (USA) with Waters 486 UV-Vis detector (Milford, USA).

Synthesis and functionalization of the magnetic nanoparticles

The synthesis of Fe_3O_4 nanoparticles was performed by dissolving $FeCl_3.6H_2O$ (34.6 mmol) and $FeCl_2.4H_2O$ (17.30 mmol) with 160 mL of distillated water while stirring under nitrogen atmosphere. Then, 20 mL of NH_4OH (25%, v/v) was added to the solution while the temperature was elevated up to 80°C (reaction for 30 min). The obtained Fe_3O_4 nanoparticles were separated by applying a magnet and were washed with water and then the resulted nanoparticles were dried in the vacuum. The obtained Fe_3O_4 nanoparticles (900 mg) were redispersed in the mixture of ethanol (240 mL) and water (60 mL) by sonication for 15 min. Subsequently, NH_4OH (15 mL) and TEOS (2.1 mL) were added to the reaction mixture. The reaction was stirred for 12 h at 40°C. The final product was separated by magnet and then five times washed with water.

In order to functionalize with vinyl end groups, 500 mg of $Fe_3O_4@SiO_2$ and 10 mL of MPTS were added to dry toluene. Subsequently, the reaction was refluxed for 24 h under nitrogen atmosphere. The resulted magnetic modified surface was washed with toluene, ethanol and distilled water and then was dried at 55 °C for 3 h.

Imprinting of TNT molecules at the magnetic surface

Prior to polymerization, the prearranged solution was obtained by TNT (0.25 mmol) and MAA (1 mmol) dissolved in 50 mL of acetonitrile. After stirring for 12 h, the magnetic modified surface (200 mg) was added to the reaction mixture, and the mixture was stirred for 3 h. Subsequently, the cross-linking agent EGDMA (5 mmoL) and AIBN (20 mg) were added to the mixture while sonicated for 10 min under purging with nitrogen gas. The polymerization was carried out at 60 °C for 24 h under nitrogen atmosphere. The resulting MMIP nanoparticles were separated from the mixed solution and washed with methanol/acetic acid (9:1, v/v) several times for removing the entrapped TNT. As a reference, magnetic non-imprinted polymers (MNIPs) were synthesized identically under the same procedure in the absence of the template molecules.

Adsorption capacity and selectivity experiments

To investigate the static adsorption, 20 mg of MMIP or MNIP was dispersed in 10 mL of an aqueous solution with various TNT concentrations (10-500 mg L^{-1}) under continuous mechanical stirring. Following this, the mixture was shaken for 12 h at room temperature and separated by a magnet and supernatant solution by RP-HPLC. The adsorption capacity (Q) was evaluated by the equation (1):

$$Q_e = \frac{(C_0 - C_e)\ V}{m} \qquad (1)$$

where Q_e (mg g^{-1}) is the adsorption capacity; C_0 and C_e (mg L^{-1}) are the initial and equilibrium concentrations of the TNT solution, respectively. V (L) is the volume of solution, and m (g) is the mass of the absorbent MMIP.

The selectivity of MMIP or MNIP for TNT and analogues compounds (2,4-DNT, NB, 4-NP) was studied at 200 mg L^{-1} concentrations. The distribution coefficient was calculated based on the equation (2):

$$k_d = \frac{Q_e}{C_e} \qquad (2)$$

In the equation (2), K_d is the distribution coefficient (L g^{-1}), Q_e (mg g^{-1}) represents the equilibrium adsorption capacity and C_e (mg L^{-1}) is the equilibrium concentration. The selectivity coefficient of MMIP can be obtained from the equation (3):

$$\alpha = \frac{k_d\left(\text{template}\right)}{k_d\,(\text{sc})} \qquad (3)$$

where α is the selectivity factor and K_d (sc) is the distribution coefficient of analogues compounds. In addition, the relative selectivity coefficient α_r (equation 4) can demonstrate the enhanced amount of adsorption affinity of MMIP for the target analyte rather than MNIP.

$$\alpha_r = \frac{\alpha_{MIP}}{\alpha_{NIP}} \qquad (4)$$

HPLC conditions

A C_{18} column (250 mm × 4.6 mm i.d.; 5 μm) was used as the analytical column. The mobile phase consisted of water/methanol mixture (30:70, v/v). The flow-rate of the mobile phase was 1 mL min^{-1}. The oven temperature was set at 25 °C and all compounds were detected at 256 nm. The injection volume was 10 μL.

Analysis of real sample

In order to determine the concentration of TNT in real samples, 20 mg of MMIP powder was added to 10 mL of water samples. After stirring at room temperature, the MMIPs were separated by an external magnetic field and then were eluted with 0.5 mL of methanol solution containing 10% acetic acid. Finally, the concentration of TNT was analyzed in eluted solution by HPLC-UV.

In addition, SPE cartridge with C-18 was employed for comparison with MMIP extraction via eluting with methanol. The extract was evaporated and re-solved in 0.5 mL of methanol and then injected to HPLC.

Results and Discussion

Preparation and characterization of TNT-MMIP

The grafted imprinting polymers on the magnetic nano-components were prepared by the following steps: synthesis of magnetic cores, silica coating on the magnetic nanoparticles, vinyl modification of the magnetic surface, and imprinting of TNT molecules at the surface. The overview of synthesis of the prepared sorbent was schematically represented in Figure 1. The Fe_3O_4 nanoparticles as magnetic cores were prepared by the co-precipitation method. The silica layer on magnetic substrate was obtained by the sol–gel process. In order to create the imprinted sites for TNT, the surface grafting polymerization was employed that nowadays was frequently developed for preparation of surface MIP. In this regard, hydroxyl groups of silica coated Fe_3O_4 were firstly modified with vinyl groups using MPTS and were further copolymerized with MAA and EGDMA in the presence of TNT. Hence, the thin imprinted layers as smart recognition sites were efficiently formed on magnetic nanoparticles for detection of TNT compound.

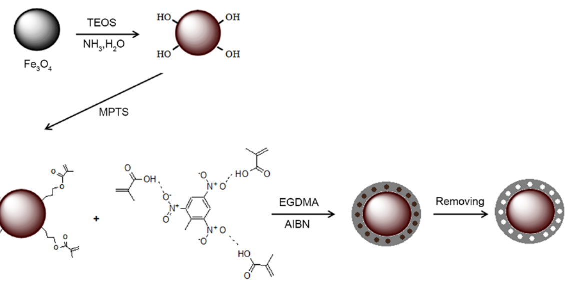

Figure 1. Synthesis route of TNT-MMIP by surface grafting polymerization.

To confirm the presence of functional groups on magnetic substrate, FT-IR spectroscopy (Figure 2) was applied. The formation of silanol groups on the surface of Fe_3O_4 was exhibited in Figure 2a. The peaks at 954 and 1096 cm^{-1} were attributed to the stretching of Si–O–H and Si–O–Si, respectively. In this regard, the vinyl modified magnetic surface showed the characteristic peaks of carbonyl groups at 1716.7 cm^{-1}. In addition, the existence of methyl groups in the structure of modifier was proved by symmetry and asymmetry stretching bonds in the region of 2800–3000 cm^{-1}. As can be seen from Figure 2b, the shift of carbonyl group peak to 1732.6 cm^{-1} has been indicated that the MIP layer was successfully formed on the surface of Fe_3O_4 nanoparticles.

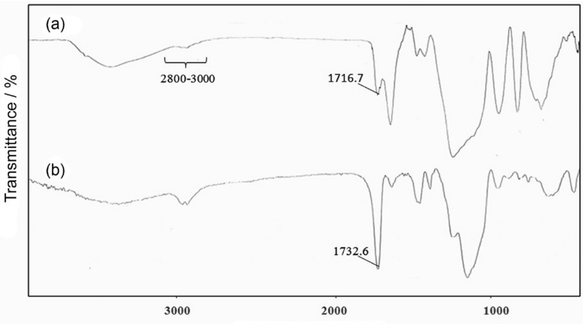

Figure 2 FT-IR spectra of Fe_3O_4@MPTS (a) and TNT-MMIP (b).

The morphology and structure of TNT-MMIP nanoparticles were evaluated by SEM and TEM technique. As shown in Figure 3, the core-shell structure and spherical shape can be observed by electron microscope images. The TEM micrograph also revealed that the imprinted polymer layer was acquired with thickness lower than 25 nm.

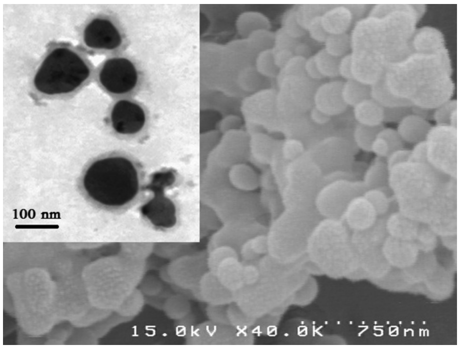

Figure 3. SEM (a) and TEM (b) images of TNT-MMIP.

Optimization of extraction conditions

The influence of pH solution, salting out and sample volume

The influence of pH on the adsorption capacity of TNT was studied by adjusting the pH of the solution from 3.0 to 11.0. The results showed no significant difference in adsorption amount of the analyte. Thus, there was no necessity for adjustment of pH in further experiments. The salting out effect was widely evaluated for effective extraction of analytes with low solubility in water media. For investigation of salt effect, sodium chloride (NaCl) was added to the samples to elevate the adsorbed analyte. Figure 4a indicated that the adsorption capacity was increased from 0 to 10%. Therefore, salt addition can partly improve extraction of TNT from water matrices.

To evaluate the influence of the sample volume, a series of different volumes of aqueous solutions ranging from 5-20 mL were examined with 20 mg of the sorbent. The effect of volume quantity was presented in Figure 4b. According to the results, it could conclude that 10 mL was appropriate as sample volume and was considered as the optimized volume of solution.

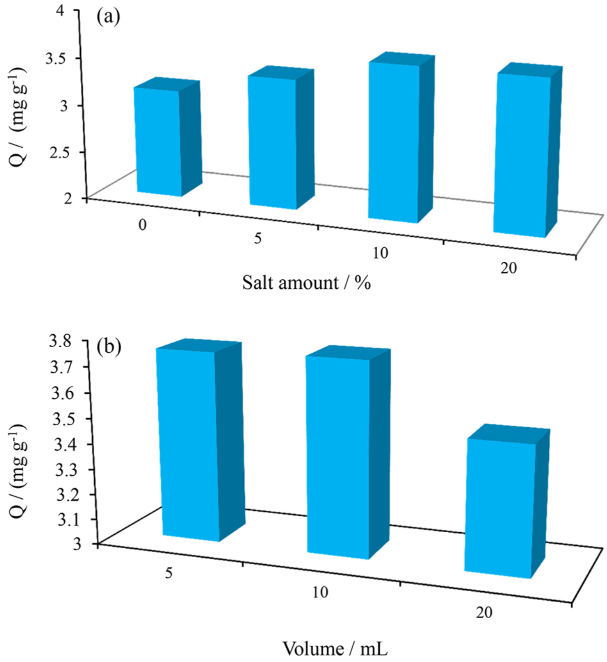

Figure 4. The influence the salt addition in (a) and sample volume solution on adsorption of TNT molecules containing the 20 mg L^{-1} of TNT solution (n = 3) in (b).

The influence of adsorption time

The kinetic of adsorption is one of the important properties for explaining the efficiency of adsorption. In this regard, the several contact times were examined for evaluation of adsorption kinetic. As can be seen from Figure 5, the adsorption capacity reached to equilibrium at 120 min for the target analyte. Hence, 120 min was selected as an appropriate time for adsorption of TNT.

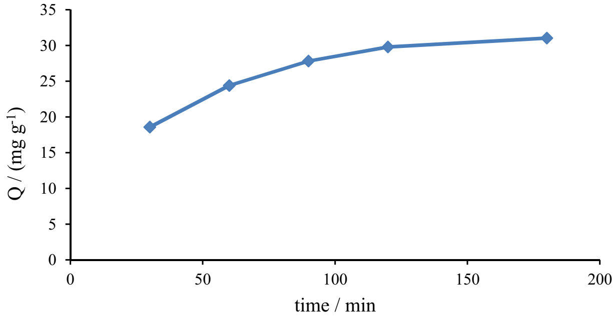

Figure 5. Kinetic adsorption curve for TNT adsorption at 200 mg L^{-1} of concentration (n = 3).

Adsorption isotherms

The adsorption capacity is an essential parameter to be evaluated in the adsorption behavior of a sorbent. In order to recognize the specificity and affinity of imprinted structure, the adsorption experiments were performed at various initial concentrations of TNT in the range of 10-500 mg L^{-1}. As exhibited in Figure 6, it was observed that MMIP nanoparticles had a stronger memory function and higher adsorption capacity than MNIP for the template molecules. The maximum adsorption capacities obtained were 40.39 mg g^{-1} and 18.45 mg g^{-1} for MMIP and MNIP, respectively. The results confirmed that recognition sites were generated on the magnetic substrate for adsorption of TNT molecules.

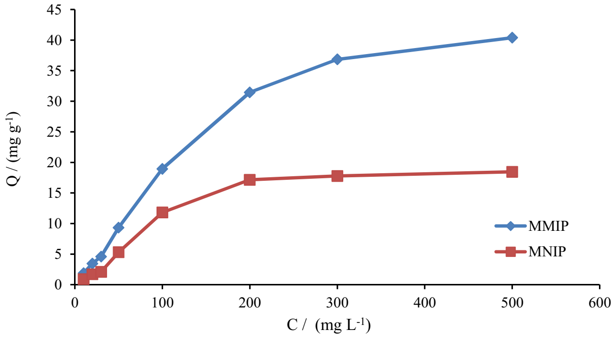

Figure 6. Adsorption equilibrium isotherm of MMIP and MNIP for TNT molecule (n = 3).

The Langmuir and Freundlich isotherms were also applied in description of the adsorption behavior of the prepared sorbent which were expressed by the following equations (5), (6) and (7):

$$\frac{1}{Q} = \frac{1}{Q_{max}} + \frac{1}{bQ_{max}C_e} \quad (5)$$

$$Q = \alpha C_e^m \quad (6)$$

$$\log Q = \log \alpha + m \log C_e \quad (7)$$

In Langmuir equation, Q_{max} (mg g^{-1}) and b (L g^{-1}) are the saturation capacity and the adsorption equilibrium constant, respectively. In the equation (6) and (7), α is the Freundlich constant and m represents the heterogeneity factor. Fitting of the experimental data on the Langmuir model demonstrated more suitable R^2 value for MMIP and MNIP with amounts of 0.998 and 0.970, respectively. Besides, theoretical Q_{max} and b were 76.92 and 13.0 for MMIP while they were obtained 58.82 and 2.43 for MNIP. The higher amount of b constant for MMIP than MNIP proved higher affinity toward TNT molecules.

The Freundlich model was also investigated for fitting the experimental data and the obtained R^2 value was less than the Langmuir model (R^2 = 0.904 for MIP and R^2 = 0.885 for NIP).

Adsorption selectivity of TNT-MMIP

In order to verify the selectivity performance of TNT toward the synthesized sorbent, the adsorption extent of TNT was compared with similar nitroaromatic compounds. The selectivity experiment was carried out for TNT and three analogous compounds like 2,4-DNT, 4-NP and NB. Figure 7 demonstrated that TNT-imprinted polymer possessed remarkably higher adsorption capacity to template molecule when compared to the other compounds. In addition, the selectivity coefficients were calculated and listed in Table 1. Based on the results, the relative selectivity factors were more than one which expressed higher selectivity for target analyte. Therefore, it was obvious that the imprinted sites indicated proper selectivity to the TNT molecules.

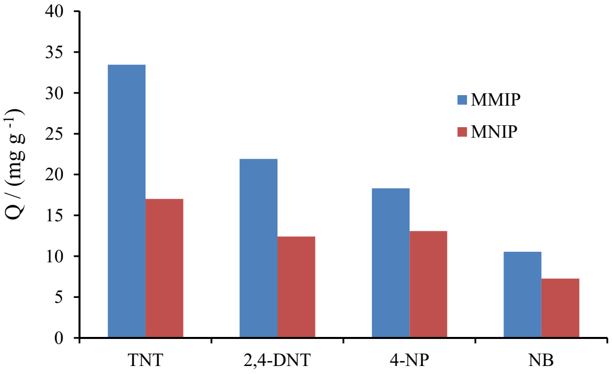

Figure 7. Adsorption selectivity for TNT and similar compounds by MMIP and MNIP under the optimized conditions at 200 mg L^{-1} of concentration.

Reusability and reproducibility experiments

The stability and potential regeneration of the synthesized sorbent were studied. In order to investigate

Table 1. The selectivity parameters of MMIP and MNIP (n = 3)

Sample	MMIP		MNIP		
	K_d / (mL g^{-1})	α	K_d / (mL g^{-1})	α	α_r
TNT	251.30		102.63		
2,4-DNT	140.53	1.79	71.04	1.44	1.24
4-NP	112.14	2.24	75.25	1.36	1.65
NB	59.04	4.26	39.14	2.62	1.63

Table 2. The related recoveries of TNT in water samples by using of MMIP, MNIP and C-18 SPE (n = 5)

Sample		MMIP			MNIP			C-18 SPE		
	Added / (μg L^{-1})	Found / (μg L^{-1})	Recovery / %	RSD / %	Found / (μg L^{-1})	Recovery / %	RSD / %	Found / (μg L^{-1})	Recovery / %	RSD / %
Tap water	0	N.D.[a]	-	-	N.D.	-	-	N.D.	-	-
	200.0	198.6	99.3	3.16	65.8	32.9	6.10	180.4	90.2	4.59
Water well	0	N.D.	-	-	N.D.	-	-	N.D.	-	-
	200.0	201.6	100.8	4.43	64.4	32.2	5.74	177.2	88.6	4.01
Sea water	0	N.D.	-	-	N.D.	-	-	N.D.	-	-
	200.0	183.4	91.7	4.25	53.6	26.8	7.33	167.0	83.5	5.32

N.D.: not detected.

the reusability, the TNT adsorbed imprinted polymer was placed in the desorption medium and the results showed that the prepared imprinted polymer can be used 7 times without obvious decrease in adsorption efficiency. Therefore, the synthesized sorbent can provide the regeneration adsorption efficiency for TNT molecules.

In addition, the investigation of reproducibility was performed via batch-to-batch experiments for the synthesized sorbent in five different batches at the Q_{max} concentration. The obtained RSD was 7.94%, which indicated proper reproducibility for TNT analysis.

Performance data and real sample analysis

The analytical methodology was also evaluated by description of linearity and detection limit for the synthesized sorbent in the determination of TNT. The results expressed proper linearity in the range of 10-500 μg L^{-1} with a correlation coefficient (R^2) 0.995 for target analyte. The limit of detection (S/N=3) was also obtained, 3.0 μg L^{-1}. Furthermore the preconcentration factor (19.85) of the resulted procedure was obtained by division of final elution concentration to first concentration of analyte. In order to investigate the applicability and reliability of the present method for real samples, it was utilized for some aqueous samples consist of tap water, water well and seawater. The studied TNT was not detected in the water samples. For determination of the accuracy, the relative recoveries were investigated by spiking the water samples at concentration levels of 200 μg L^{-1}. The results of recovery for synthesized MMIP, MNIP and C-18 SPE were also listed in Table 2. Figure 8 illustrated non spiked and spiked seawater samples by the proposed procedure. It demonstrated that the proposed sorbent was qualified and efficient for the trace analysis of TNT in water samples.

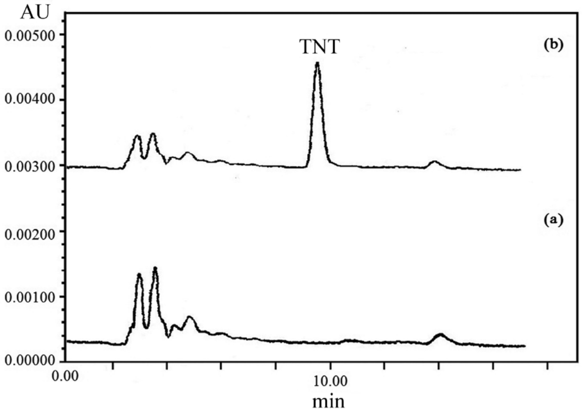

Figure 8. Chromatograms of extracted TNT from seawater (a) and spiked sample with 200 μg L^{-1} of TNT by MMIP (b).

Conclusions

A selective imprinted polymer was prepared via "grafting to" procedure on magnetic nanoparticle. Tailor-made recognition sites were applied for selective extraction of TNT molecules from aqueous media. The resultant MIP could be easily isolated from the liquid medium by an external magnetic field without additional centrifugation or filtration. The obvious advantages of the MMIP like proper adsorption capacity and selectivity with fast kinetic binding were achieved for target molecules. The imprinted polymer-SPE sorbent was successfully utilized for efficient enrichment and determination of TNT in environmental samples of water. According to the obtained results, the recoveries were attained more than 91.7% for template molecules. The figures of merit and the obtained results of the synthesized sorbent demonstrated that the proposed magnetic SPE was an efficient sorbent for selective determination of TNT at trace-level concentrations in aqueous media.

Acknowledgments

The authors wish to thank Malek Ashtar University of Technology Research Council for providing support for this work.

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Submitted: September 11, 2014