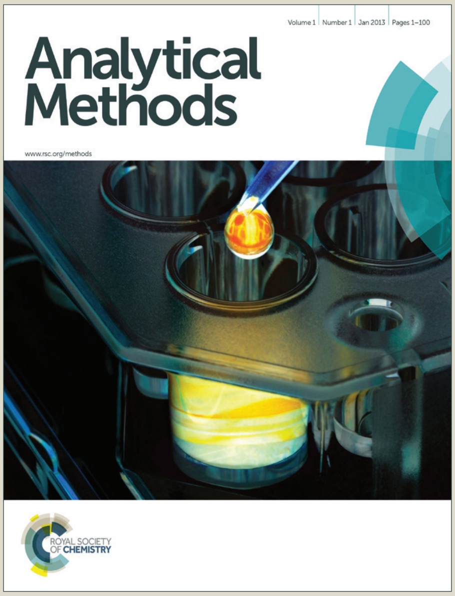
Analytical Methods

Accepted Manuscript



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Magnetic mixed hemimicelles solid-phase extraction based on ionic liquid coated Fe_3O_4 nanoparticles in the analysis of trace organic contaminants in water

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Abstract: Ionic liquid coated Fe_3O_4 magnetic nanoparticles (IL-coated Fe_3O_4 NPs) mixed hemimicelles, as an adsorbent of solid-phase extraction, is proposed for the preconcentration of five organic contaminants (catechol, bisphenol A, 2,4-dichlorophenol, 1,3,5-trichlorobenzene and acrylonitrile) from environmental water sample prior to high performance liquid chromatography (HPLC). In the present study, mixed hemimicelles formed by IL-coated Fe_3O_4 NPs showed a great adsorptive tendency towards the target analytes, and then the analyte-adsorbed mixed hemimicelles can be readily isolated from the sample solution by a magnet. The proposed method could greatly simplify the operation and reduce the whole pretreatment time. Moreover, several parameters affecting the extraction efficiency such as the amounts of Fe_3O_4 and $[C_8MIm]Br$ IL, the type and pH of desorption solvent, extraction time and salt effect were investigated. Under the optimum conditions, satisfactory recoveries for the target analytes were in the range of 90-102 % with 3.3-8.1 % relative standard deviations (RSD, n=6), 90-111 % with 2.1-7.6 % RSD, 92-99 % with 5.5-13.5 % RSD and at 0.01 μg/mL, 0.1 μg/mL and 100.0 μg/mL levels, respectively. And the limits of detections (LODs) for the target analytes were in the range of 0.01-0.07 μg/L.

Keywords: IL-coated Fe_3O_4 NPs hemimicelles, solid-phase extraction, determination, organic contaminants, water sample

1. Introduction

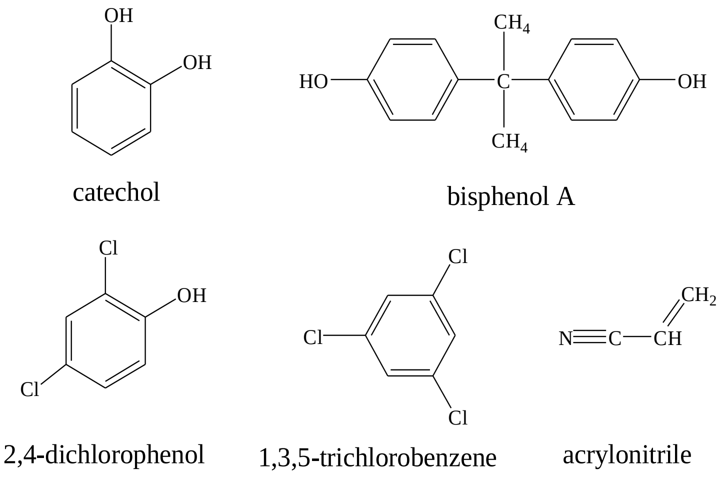
Contamination of water resources by organic contaminants residues is one of the major challenges for the preservation and sustainability of the environment.[1] Although some measures taken have dramatically reduced the presence of many organic contaminants in environmental water over the past years, a large number of potentially organic contaminants can reach the ecological water.[2] Therefore, the monitoring and analysis of the levels of trace organic contaminants in environmental water have increased considerably in recent years to ensure human health.

Among the emerging organic contaminant, phenolic compounds and volatile organic compounds (VOCs) are co-exist in environmental water and present significant research in interest due to their extended use in several consumers and chemical products, as well as their toxicological and physicochemical properties. Phenolic compounds such as catechol (CC), bisphenol A (BPA), 2,4-dichlorophenol (2,4-DCP), are common by products of large-scale production and the use of man-made organics such as phenolic resins, drugs, dyes, antioxidants, paper pulp and pesticides that cause ecologically undesirable effects.[3-6] VOCs, such as 1,3,5-trichlorobenzene (1,3,5-TCB) and acrylonitrile (ACN), are associated with numerous products and applications, including liquefying agents in fuels, degreasers, adhesives, solvents, polishes, cosmetics, refrigerants, drugs, and dry cleaning solutions. [7-10]

It is well known that the complexity of sample matrices and low concentrations may cause the main difficulty for the analysis of residual compounds, even with the advent of advanced techniques based on chromatography with mass spectrometry. Therefore, sample preconcentration technique has been the main focus on research in environmental analytical chemistry area. Up to now, some treatment methods for the extraction of BPA or 2,4-DCP from environment samples were employed, such as solid-phase extraction (SPE)[11] and dispersive liquid-liquid microextraction (DLLME),[12] etc. However, these methods still have some limitations or shortcomings that have already been discussed in literatures.[13]

Mixed hemimicelles solid-phase extraction (MHSPE) is consistent with the adsorption of ionic surfactants on metal oxides surfaces. It has been proposed for the preconcentration of a variety of organic compounds from complex environmental matrices.[14] Compared with the traditional SPE method, the advantages of MHSPE are favorable to achieve superior extraction efficiency and easy elution of analytes, but it is a laborious and time-consuming procedure. To overcome these problems, Fe_3O_4 magnetic nanoparticles (Fe_3O_4 NPs) have been developed in MHSPE methods owing to its unique properties, namely high surface area, strong magnetism and easiness of surface modification.[15] It can be assumed that its use in pretreatment method can improve the adsorption capacity of analytes, and the phase separation can be isolated readily from sample matrices with an external magnet placed outside the extraction vessel. Additionally, the ionic liquids (ILs) having enough long alkyl chain, are emerging as the alternative to these conventional ionic surfactants such as sodium dodecyl sulfate (SDS) or cetyltrimethylammonium bromide (CTAB) in the Fe_3O_4 NPs mixed hemimicelles SPE process due to their unique and novel physicochemical properties.[16] To date, IL-coated Fe_3O_4 NPs MHSPE method has been proposed for selective extraction of chlorophenols (CPs) from water samples.[17] The new adsorbent combined the advantages of IL and Fe_3O_4 NPs. The results showed that hydrophobic CPs tended to exhibit high distribution coefficients with monocationic IL-aggregates. Although some applications have been reported using IL-coated Fe_3O_4 NPs in MHSPE, to the best of our knowledge, none of the published studies report the simultaneous qualitative and quantitative determination of CC, BPA, 2,4-DCP, 1,3,5-TCB and CAN in water using an integrated method, as fast and cheap, as possible. The simultaneous determination of them would be convenient, which could also give more information in water pollution.

In this paper, IL-coated Fe_3O_4 NPs were used to evaluate the potential application of MHSPE technique for the preconcentration of above five organic contaminants from the actual water sample. The goal of the present study is to improve the mixed hemimicelles SPE technique, using $[C_8MIm]Br$ IL as ionic surfactants coated Fe_3O_4 NPs. Furthermore, several parameters affecting the extraction efficiency such as the amounts of Fe_3O_4 and IL, desorption solvent, ultrasound desorption time and salt effect were investigated.



catechol bisphenol A

2,4-dichlorophenol 1,3,5-trichlorobenzene acrylonitrile

Fig. 1 Chemical structures of five organic contaminants

2. Materials and methods

2.1 Reagents and Chemicals

Methanol (HPLC grade) and acetonitrile (HPLC grade) were purchased from Tedia Co., Ltd (Tedia, USA). Fe_3O_4 (100 nm) was purchased from Beijing boyu materials technology Co., Ltd. 1-Octyl-3-methylimidazolium bromide ($[C_8MIm]Br$) was purchased from the Institute of Chemical Physics of the Chinese Academy of Sciences (Lanzhou, China). Analytical standards of CC (purity > 99%), BPA (purity > 98%), 2,4-DCP (purity > 95%), 1,3,5-TCB (purity > 96%) and ACN (purity > 98%), were bought from Sinopharm Pharmaceutical Co., Ltd. All other chemicals solvent were of analytical grade and were purchased from Xi'an reagent factory (Xi’an China).

Extraction and injection were performed with a 50 μL micro-syringe. A low-thermostat water bath pot (HH-S4, Beijing, China) was used as the analysis of effect of temperature on experiments. An electronic analytical balance (ESG0-4, Shenyang, China) was used for weighing the solid materials, and a rotary evaporator

(RE-52AA, Shanghai, China) was used to remove organic solvents, an ultrasonic cleaning machine (SB4200DTD, Ningbo, China) were also used.

Stock solutions of the target analytes were prepared at a concentration of 1000 μg/mL in ethanol. Mixed standard solutions containing 100 μg/mL CC, BPA, 2,4-DCP, 1,3,5-TCB and ACN were prepared by diluting each stock solution in ethanol, and standard working analyte solutions were prepared daily through appropriate dilution of these mixed standard solutions with ethanol to obtain five different concentrations ranging from 0.001 μg/mL to 100 μg/mL, and all stock solutions were stored in dark at 4 ℃ in a refrigerator.

2.2 Chemical Analysis

The analysis was performed on a Waters 600 Series HPLC system (Waters, USA) equipped with a quaternary pump and a diode array detector (DAD). The separations were carried out with XTerra®RP$_{18}$ C$_{18}$ column (5 μm, 4.6 mm×150 mm i.d.), and the column heater was maintained at 28 ℃. The mobile phase comprised acetonitrile (component A) and water (component B) at a flow rate of 0.6 mL/min. The target analytes were separated by a gradient elute with a total run time of 25 min. The initial mobile phase, was 50/50 (v/v) A/B changed to 60/40 (v/v) A/B for 6 min, then changed to 70/30 (v/v) A/B for another 19 min. The wavelength for DAD detection was set at 280 nm.

2.3 IL-coated Fe_3O_4 NPs MHSPE Procedure

The schematic procedure of the IL-coated Fe_3O_4 NPs MHSPE is illustrated in Fig. 2. A 5.0 mL of water sample with 4 mg/L analytes was put into a 50.0 mL beaker.

Then 30 mg Fe_3O_4 (100 nm) and 0.40 g $[C_8MIm]Br$ were added. The mixture was sonicated for 15.0 min at 30 ℃, the supernatant was discarded. Meanwhile, the sorbent was gathered to the beaker bottom by placing a magnet outside of the beaker. The target analytes were eluted from the isolated particles with 0.5 mL acetonitrile containing 1% glacial acetic acid by an ultrasonic for 20.0 min. Ultimately, the solution was drawn and filtered through a filter (0.22 μm), and 10 μL of the desorption solution was supplied to the HPLC system for analysis.

The extraction efficiency (*E*) of the analytes was calculated by

$$E\ (\%) = C_{IL}V_t/C_0V_{sample} \times 100\ \% \qquad (1)$$

Where C_{IL} and C_0 represent the concentration of analyte in IL in the IL-coated Fe_3O_4 NPs MHSPE and initial concentration of the analyte in the sample, V_t and V_{sample} are volumes of the desorption solution and samples, respectively.

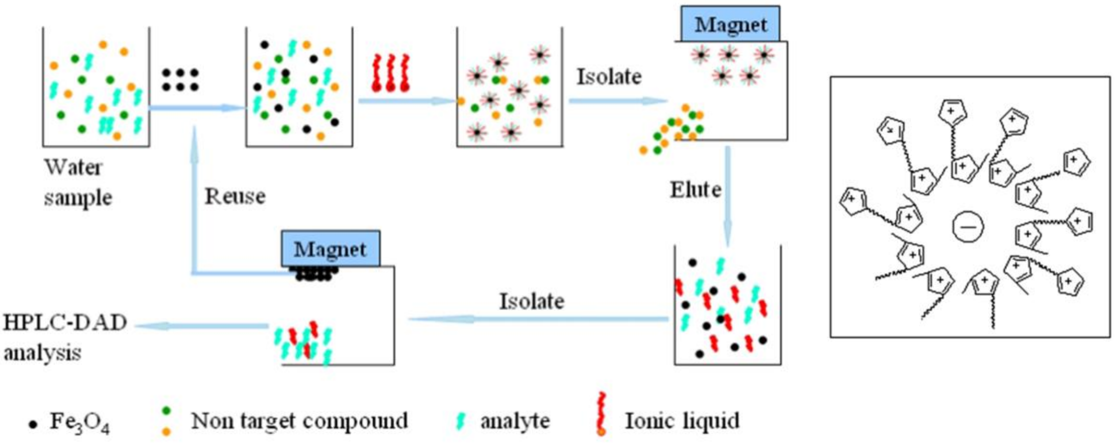


Fig. 2 Schematic illustration of IL-coated Fe_3O_4 NPs MHSPE procedure and analysis

3. Results and discussion

3.1 FTIR characteristics of Fe_3O_4 NPs

Fourier transform infrared spectroscopy (FTIR) has been employed to qualitatively determine adsorption of [C_8MIm]Br onto Fe_3O_4 NPs surface. Fig. 3 displays the FTIR spectra of the Fe_3O_4 NPs (a) and the [C_8MIm]Br coated Fe_3O_4 NPs (b). The strong peak at 570 cm^{-1} is related to the vibration of the Fe-O functional group, and the peaks at 1089, 991 and 862 cm^{-1} in the spectrum of [C_8MIm]Br coated Fe_3O_4 NPs derive from deformation vibration in-plane and bending vibration of C-H bond in aromatic rings of the [C_8MIm]Br. In addition, the peaks at 1652 and 1562 cm^{-1} are attributed to the stretching vibration of C=C bond, which match with those from the standard spectrum,[18] All of these bonds revealed that [C_8MIm]Br was successfully modified on the surface of Fe_3O_4 NPs.

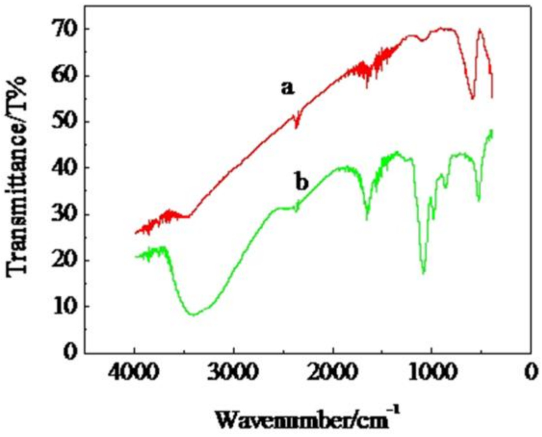


Fig. 3 FT-IR spectra of Fe_3O_4 NPs (a) and IL-coated Fe_3O_4 (b)

3.2 Optimization of condition for IL-coated Fe_3O_4 MHSPE

In order to evaluate the feasibility of IL-coated Fe_3O_4 MHSPE for the extraction of the target analytes from the water sample, some parameters (the amounts of Fe_3O_4 and IL, the type and pH of desorption solvent, ultrasound desorption time and salt effect) that might affect the performance of the IL-coated Fe_3O_4 MHSPE need to be optimized.

3.2.1 Effect of the amount of Fe_3O_4 NPs

Fewer amounts of nano-adsorbents may be achieved more agreeable consequences than micro-adsorbents thanks to their greater surface areas. To ensure the optimized amount of adsorbent for the extraction, the amount of Fe_3O_4 NPs should be carefully taken into account. As shown in Fig. 4A, with the increase of the amount of Fe_3O_4 NPs, the extraction efficiencies for the target analytes increased at first, and then went down. The electrostatic attraction between the cations of the ILs and oppositely charged groups on the Fe_3O_4 surface resulted in the formation of mixed hemimicelles assemblies,[19-20] which was beneficial to the adsorption and desorption of analytes. However, when the amount of Fe_3O_4 NPs was beyond 0.03 g, all the Fe_3O_4 NPs were not separated effectively, which led to a decrease in the extraction efficiencies of analytes. Ultimately, 0.03 g Fe_3O_4 NPs was selected in the following experiments.

3.2.2 Effect of the amount of IL

In the light of Fig. 4B, the amount of IL is the most influential parameter in all cases. It can be observed that the efficiencies of extractions at 0.4 g IL are significantly higher than those obtained at other amounts. The probable reason for this phenomenon is that the progressive formation of hydrophobic mixed hemimicelles (hemimicelles and admicelles) on the surface of Fe_3O_4 NPs made the target analytes been preconcentrated gradually as well as not easy to break away from Fe_3O_4 NPs. The results suggested that the adsorption behaviors of the target analytes were related to the hydrophobic interactions between the aromatic rings or chlorine groups and the alkyl chain of the IL, as well as hydrogen bonds of most target analytes. However, when IL amount was above 0.4 g, the IL molecules began to form micelles in the bulk aqueous solution and the micelles caused the analytes to redistribute into the solution again,[17] and the adsorption of the analytes decreased. Given these findings, 0.4 g IL was recommended for the satisfactory extraction efficiencies of the target analytes from the sample solution.

3.2.3 Effect of ultrasound desorption time

As shown in Fig. 4C, when the ultrasound desorption time was increased from 5 to 20 min, the extraction efficiencies of the target analytes increased dramatically. However, when the ultrasound desorption time was changed from 20 to 25 min, the extraction efficiencies of the target analytes decreased rapidly. These reasons can be according to the follows: On the one hand, the ultrasound reduces the viscosity of ionic liquids, which shortens the equilibrium of the extraction and desorption, and makes the analytes-adsorbed IL separated readily from Fe_3O_4 NPs. On the other hand, too long ultrasound time will make a part of analytes-adsorbed IL again attached on the surface of Fe_3O_4 NPs, which results in the decrease of the extraction efficiency.[21] In order to prove the explain, we designed experiments to examine the effect of ultrasound desorption time on UV-Vis absorption spectra of IL from desorption solution without target analytes. It was observed that with the increasing of ultrasound desorption time, the absorption intensity of the peaks of IL at 204 nm and 226 nm decreased gradually, which implied that the amount of IL from desorption solution decreased. Therefore, this value was fixed at 20 min for all the experiments.

3.2.4 Effect of the type and pH of desorption solvent

Generally speaking, the types of desorption solvent play an important role that can affect the extraction efficiency. Therefore, the effects of common desorption solvents such as methanol containing 1 % glacial acetic acid, ethanol containing 1 % glacial acetic acid, acetonitrile containing 1 % glacial acetic acid on the extraction efficiencies of the target analytes were shown in Fig. 4D. Obviously, the best extraction efficiency was obtained when acetonitrile containing 1 % glacial acetic acid was used. This phenomenon may be attributed to the fact that its pH value was less than the isoelectric point (IEP) of Fe_3O_4 NPs, the negative charge on Fe_3O_4 NPs surface was weak, which is advantageous to make the analytes-adsorbed IL separated from Fe_3O_4 NPs in the IL-coated Fe_3O_4 mixed hemimicelles.[22] Hence, acetonitrile containing 1 % glacial acetic acid was used in the following experiments.

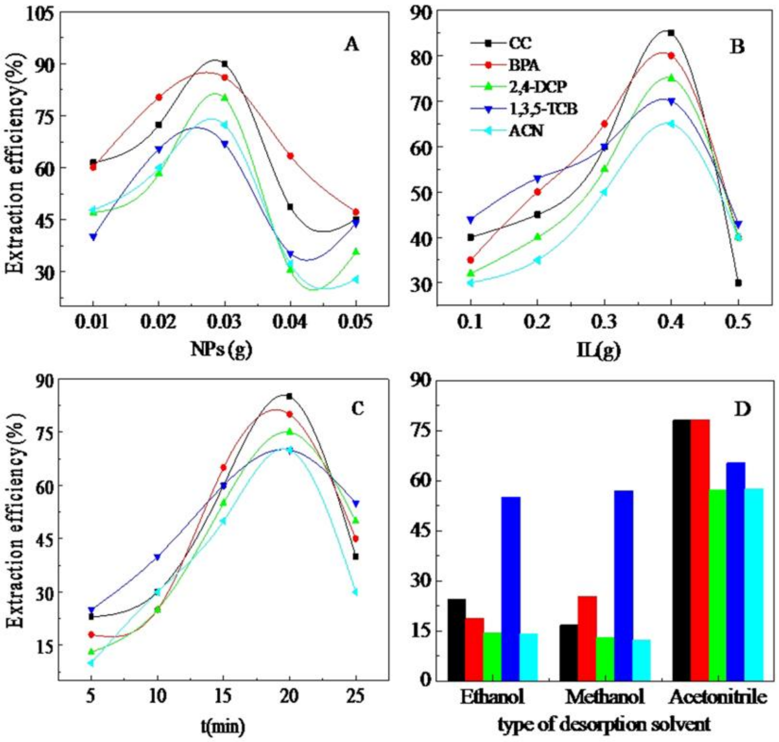


Fig. 4 The effect of the amount of Fe_3O_4 NPs (A), the amount of ionic liquid (B), ultrasound desorption time (C), and type of desorption solvent (D) on the extraction efficiency of five organic contaminants

Further, the effect of the acetonitrile with different pH values ranging from 3.0 to 6.0 on the extraction efficiencies of the target analytes was studied. It was found that the extraction efficiencies decreased with the increasing of pH value. Therefore, in the following experiments, the pH of desorption solution (acetonitrile containing 1 % glacial acetic acid) was adjusted at about 3.0.

3.2.5 Effect of ionic strength

The salt concentration could suppress the electrical adsorption layer, and weaken formation of IL mixed hemimicelles on the Fe_3O_4 NPs surface. In order to evaluate the influence of the ionic strength of the solution on extraction efficiency of the target analytes, various experiments were performed by adding different amounts of sodium chloride, potassium nitrate and sodium sulfate (0.000 g, 0.0050 g, 0.0100 g, 0.0150 g and 0.0200 g), respectively, it was found that the extraction efficiencies of the target analytes decreased with the increasing of the amounts of salt. The results indicated that the role of electrostatic attraction in the adsorption process was important. In addition, the competition between Na^+/K^+ ions and $[C_8MIm]^+$ for the Fe_3O_4 NPs substrates led to low enrichment performance.[24] Hence, salt was adopted for not use.

3. 3 The lifetime of Fe_3O_4 NPs

The lifetime of Fe_3O_4 NPs is also important for practical application and recycling. Under optimal extraction conditions, the lifetime testing of Fe_3O_4 NPs was investigated by extracting five target analytes from spiked samples. As shown in Table 1, the results indicated that the extraction efficiencies of five target analytes did not decline after being extracted 2 times, whereas the extraction efficiencies of five target analytes began to drastically decrease after 3 times. Due to its long-term use, IL spontaneously coated Fe_3O_4 NPs surface to form a monolayer coverage becomes more difficult by electrostatic attraction, which makes the adsorption capacity decrease. As a result, the reuse degree of Fe_3O_4 NPs was 3 times.

Table 1 The lifetime of Fe_3O_4 NPs

Recovery / Analytes	One time	Two times	Three times	Four times	Five times
CC	90.00 %	91.00 %	87.00 %	77.00 %	66.00 %
BPA	95.00 %	93.00 %	84.00 %	74.00 %	61.00 %
2,4-DCP	96.00 %	90.00 %	85.00 %	70.00 %	65.00 %
1,3,5-TCB	89.00 %	90.00 %	79.00 %	65.00 %	55.00 %
ACN	92.00 %	88.00 %	83.00 %	66.00 %	54.00 %

3. 4 Quantitative calibrations and reproducibility

Table.2 summarizes some analytic characteristics of IL-coated Fe_3O_4 MHSPE method. Each analyte exhibited a good linearity in the range of 0.001-100.0 μg/mL with correlation coefficient (r) ranging from 0.9987 to 0.9999. The LODs were in the range of 0.01-0.07 μg/L for the five target analytes (S/N=3). High recoveries for the target analytes were in the range of 90-102 % with 3.3-8.1 % relative standard deviations (RSD, n=6), 90-111 % with 2.1-7.6 % RSD, 92-99 % with 5.5-13.5 % RSD and at 0.01 μg/mL, 0.1 μg/mL and 100.0 μg/mL levels, respectively. The comparison results demonstrated that the recoveries by the proposed procedure were higher than those in references.[24-27] Additionally, the developed method was more convenient and faster than other methods.

Table 2 Analytical performance data of IL-coated Fe_3O_4 MHSPE

analytes	Spiked level (μg/mL)	Mean recovery (%)	Spiked level (μg/mL)	Mean recovery (%)	Spiked level (μg/mL)	Mean recovery (%)	LODs (μg/L)
CC	100	97	0.1	95	0.01	90	0.01
BPA	100	95	0.1	111	0.01	102	0.03
2,4-DCP	100	96	0.1	106	0.01	98	0.07
1,3,5-TCB	100	99	0.1	90	0.01	93	0.06
ACN	100	92	0.1	93	0.01	95	0.03

3.5 Analysis of real sample

To demonstrate the applicability of IL-coated Fe_3O_4 MHSPE method, the water sample from the reservoir located in Shan Dong in China was analyzed, which was analyzed in six replicates. Fig.5 presents the HPLC chromatograms of actual water sample and the mixed standard solution obtained after IL-coated Fe_3O_4 MHSPE method. The results in Table 3 showed that five target analytes were all found in the actual water sample. The target analytes may result from chemical plant in the reservoir upstream, which emissions of wastewater containing high levels of chemicals and flows into the downstream reservoir.

To further confirm the identity of five target analytes in actual water sample, we conducted a series of additional experiments. If the actual sample contained five target analytes, the same chromatographic peaks which corresponded to CC, BPA, 2,4-DCP, 1,3,5-TCB and CAN would increased. The experiment results indicated that the peaks were consistent with those of the CC, BPA, 2,4-DCP, 1,3,5-TCB and CAN. Meantime, the spectrum which corresponded to each target analyte of the actual sample was same as that of the spiked water sample in the DAD full wavelength spectrum. The observation results meant the actual water sample contained above five target analytes.

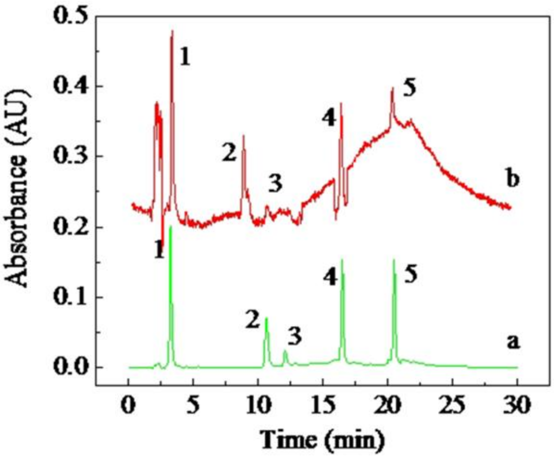


Fig. 5 High performance liquid chromatogram of the analyzed sample (a) the mixed standard solution of 100 μg/mL each of organic contaminants (b) IL-coated Fe_3O_4 MHSPE, Peak identification: (1) CC; (2) BPA; (3) 2,4-DCP; (4) 1,3,5-TCB; (5) CAN

Table 3 Concentration of five organic contaminants detected in actual water samples

analytes	Water sample in Shandong (μg/mL)
CC	1.87
BPA	2.47
2,4-DCP	0.67
1,3,5-TCB	2.08
ACN	0.89

4 Conclusions

A novel MHSPE method based on IL-coated Fe_3O_4 mixed hemimicelles combined with HPLC-DAD was developed for the preconcentration and quantification of five organic contaminants in environmental water sample. Mixed hemimicelles formed by IL-coated Fe_3O_4 NPs showed a great adsorptive tendency towards the target analytes, and rapid extraction can be achieved. Compared with the conventional SPE methods, the strong hydrophobic interactions between the mixed hemimicelles and the target organic contaminants make the proposed MHSPE method have the advantages of convenience and high extraction efficiency. Herein, IL-coated Fe_3O_4 MHSPE technique will have a great broad prospect in the determination of trace organic contaminants from the water samples.

Acknowledgments

The authors appreciate the support from the National Natural Science Foundation of China (No. 50830303), The Projects in the National Science & Technology (No. 2012BAC04B02), overall Innovation Project of Science & Technology in Shaanxi Province (No. 2011KTCG03-07), and the Research Achievements Foundation of Xi′an University of Architecture and Technology (No. ZC1004).

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