Ionic liquid-modified NiTi composite nanosheets coating for efficient solid phase microextraction of octadecylamine in brine

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Abstract: Ionic liquid (IL), 1-dodecyl-3-methylimidazolium-3-hydroxy-2-naphthoate (C_{12}mimHNC) was synthesized and coated on the surface of NiTi as solid phase microextractiom fiber coating for determination the octadecylamine in brine. Prior to modification with IL, the NiTi was hydrothermally treated for in-situ growth of titanium and nickel oxide composite nanosheets (TiO_2/NiOCNSs). The TiO_2/NiOCNSs fibers coating was oriented around the NiTi substrate and presented double-faced open access sites, which provided a desired support framework for the further modification with IL. The extraction performance of C_{12}mimHNC-TiO_2/NiOCNSs fiber coating was evaluated for detection of octadecylamine (ODA) coupled to HPLC with UV detection. As a result, the C_{12}mimHNC-TiO_2/NiOCNSs fiber coating illustrated excellent adsorption and extraction capability for ODA. The main factors affected extraction efficiency were optimized. Under the optimized conditions, good linearity was obtained in the range of 1-150 μg/L with correlation coefficients (r^2) above 0.985. Limits of detection (LODs) for the developed method was 0.280 μg/L. The proposed method was first applied to extract the ODA in brine samples. Relative recoveries varied from 78.3% to 96.5% at spiking level of 15 μg/L and 30 μg/L with the relative standard deviations (RSDs) less than 8.7%.

Keywords: ionic liquid; solid phase microextraction; titanium and nickel oxide composite nanosheets; octadecylamine; high-performance liquid chromatography

1. Introduction

It is well known that majority of potash production is an essential raw material in food, medicine and other chemical industries, especially most being used as fertilizer in agricultural [1]. Over 80% potash productions around the world were produced from salt lake through an efficient flotation technique [2]. Octadecylamine (ODA), an efficacious member of collectors family, was widely used during the process of potash production flotation. The ODA molecule consist of a alkyl chain and a hydrophilic head group with positive charge, which possesses the characteristic of surface activity in solution and forms colloidal particles as well as separates KCl from residual NaCl by forth flotation. However, excessive use of ODA would lead to pollution for salt lake and serious difficulty to KCl for further purity [3]. At present the ODA in brine was mainly detected via traditional methods, which a mass of organic solvent was necessary. Therefore, the efficient adsorption and excellent enrichment of ODA in brine were the key issues.

Solid-phase microextraction (SPME) is a novel technique and integrate sampling, extraction, concentration and direct sample introduction into one step [4]. Due to its special merits, this technique had been successfully applied to different fields such as food, pharmaceutical, environmental and biological analyses [5-8]. In SPME, the fiber was compared of a supporting substrate and a surface sorbent coating. Moreover the sorbent coating was a critical part, which included organic, inorganic or composite materials. To meet the requirements of analysis, many researchers continued to pay more attention and engender innovative approaches to identifying novel fiber coating.

Ionic liquid, as a novel and green solvents, has been widely applied in many fields, such as organic chemistry, inorganic chemistry , electrochemical and analytical chemistry [9,10]. Moreover the applications of ionic liquid in analytical chemistry have been focused on extraction and separation due to their unique properties [11,12]. To the best of our knowledge, there have been no reports on ionic liquid-functioned coating on NiTi wire. In present work, the C_{12}mimHNC was synthesized and successfully modified on the surface of TiO_2/NiOCNSs which were in-situ grown in aqueous NaOH solution. Furthermore the novel C_{12}mimHNC-TiO_2/NiOCNSs-NiTi fiber was used to extraction and determination of ODA coupled with HPLC-UV. To date, this is the first time that SPME technology was applied for determination of ODA.

2. Experimental

2.1 Materials and reagents

Nitinol wires (ϕ0.25 mm O.D.) were purchased from Alfa Aesar (Ward Hill, MA, USA). Nitric acid (HNO_3) was purchased from Yantai Shuangshuang Chemical Ltd (Shandong, China). Sodium chloride (NaCl) and Sodium hydroxide (NaOH) were obtained from Shanghai Hunter Fine Chemicals Ltd. (Shanghai, China). 0.45 μm micropore membrane of polyvinylidene fluoride was supplied by Xingya Purifying Material Factory (Shanghai, China). HPLC-grade methanol was purchased from Yuwang Chemical Company (Shandong, China). A polydimethylsiloxane (PDMS) fiber (100 μm thickness) and polydimethylsiloxane//divinylbenzene (PDMS/DVB) (65 μm thickness) were obtained from Supelco (Bellefonte, PA, USA). Octadecylamine was obtained from Fluka (CA, USA). 1-dodecyl-3-methylimidazolium bromide (C_{12}mimBr) and 3-hydroxy-2-naphthoic acid were purchased from Minxing Chemical Company (Shandong, China), All other reagents were of analytical grade.

2.2 Experimental

The morphologies of the fabricated fiber were examined by with an Ultra Plus microscope (Zeiss, Oberkochen, Germany) operating at 5 kV, where energy dispersive X-ray spectrometry (EDS) analysis was also carried out at the same time. Separation and determination of octadecylamine were performed on Agilent 1260 Infinity LC system (Waldbronn, Baden-Württemberg, Germany) with a G1314F variable wavelength detector and a Agilent Zorbax SB-C18 column. Data collection was obtained with an Agilent OpenLAB CDS ChemStation. Ultrapure water was obtained from a Pine-tree XYG-60-H water purification system (Beijing, China).

2.3 Synthesis of TiO_2/NiOCNSs coating

Direct hydrothermal growth of TiO_2/NiOCNSs was performed on NiTi wires according our previous report [13]. Briefly the bare NiTi wire was cleaned with acetone and ultrapure water in an ultrasonic bath for 10 min, respectively. One end (1.5 cm long) of the NiTi wire was pretreated in HNO_3 solution of 35% (w/w) for 30 min and subsequently rinsed in a sonicated water bath for 5 min. Thereafter the pretreated wire was immediately dipped into NaOH solution of 2 mol/L held in a Teflon-lined autoclave and kept in an oven at 110 ^{o}C for 10 h.

The as-fabricated fibers were sequentially rinsed with ultrapure water and HNO_3 solution of 0.01 mol/L, and dried in air.

2.4 Preparation of C_{12}mimHCN-TiO_2/NiOCNSs fiber coating

The 1-dodecyl-3-methylimidazolium-3-hydroxy-2-naphthoate (C_{12}mimHNC) was synthesized according to the reference [14]. Briefly, the 20% C_{12}mimBr diluted from the standard solution was exchanged through the anion exchange resin. Then the 10 mL C_{12}mimOH was added to 25% 3-hydroxy-2-naphthoic acid (v/v) and reacted at 30℃ for 2h. The yellow sticky C_{12}mimHCN was obtained after removing of moisture via rotary evaporation. Afterwards, the C_{12}mimHCN was dissolved in ethanol at a 0.85:1 (v/v) ratio. The TiO_2/NiOCNSs fiber was dipped into this solution for 3 min then the coated fiber was withdrawn from solution. The operations were repeated four times to get a homogenous efficacious coating. Finally, the C_{12}mimHCN-TiO_2/NiOCNSs fiber was conditioned in an oven for 30 min at 150℃。

2.5 SPME-HPLC procedure

100 mg/L standard solution was prepared by dissolving the ODA in ethanol. Working solutions were obtained by diluting standard solution with ethanol to requirement concentration. Sample solution of 10 mL was transferred into a 15 mL sample vial with a Teflon septum and a PEEK cap. Typically the fabricated fiber was immersed in the stirred sample solution to reach extraction equilibrium at selected temperature. After extraction, the fiber was withdrawn from the sample vial and immediately introduced into the SPME-HPLC interface for static desorption in corresponding mobile phase. Subsequently the six-port valve was switched from load to inject position for chromatographic analysis. The mobile phase

consisted of methanol and water with the volume ratios of 80/20 at a flow rate of 1 mL/min for HPLC analysis of ODA. Corresponding chromatographic signals were monitored at 280 nm. Prior to next extraction, the fiber was washed with methanol and ultrapure water for 10 min to eliminate possible carryover, respectively.

3. Results and discussion

3.1 Characterization of C_{12}mimHCN-TiO_2/NiOCNSs fiber

The surface morphology of C_{12}mimHCN-TiO_2/NiOCNSs fiber coating was characterized by SEM. As compared with original NiTi wire, the etched NiTi (Fig. 1b) exhibited similar surface microscopically. Moreover, EDS analysis revealed that the surface ingredients of these fibers consisted of the Ti、Ni、C and O elements. However, the etched fiber (Fig. 2b) presented slight decreased surface content of Ni and O because a thin native oxide layer was formed on the surface of original wire to corrosion resistance [15]. To modify its surface properties, the etched NiTi wire was hydrothermally treated in NaOH solution. As shown in Fig. 1c, crosslinked nanosheets were radially oriented around the NiTi substrate, and a homogeneous and porous nanosheets were formed on the external surface of pretreated NiTi supports. EDS analysis (Fig. 2c) exhibited that the content of O element was remarkable increased and the content of Ni element was slight decreased. This results illustrated that a newly and thicker TiO_2/NiOCNSs was in-situ grown. The robust TiO_2/NiOCNSs coating provided a large surface area and desired supporting substrate for subsequent fabrication of C_{12}mimHCN-TiO_2/NiOCNSs fiber coating. As shown in Fig. 1d, a homogenous and uniform coating was obtained by sol-gel technology. Furthermore a number of C_{12}mimHCN nanoparticles appeared on the surface of new fiber. Fig. 2d illustrated significant carbon peak but sharply decreased Ti and Ni peaks from the C_{12}mimHCN-TiO_2/NiOCNSs fiber coating. This result revealed the C_{12}mimHCN-TiO_2/NiOCNSs fiber coating was successfully fabricated.

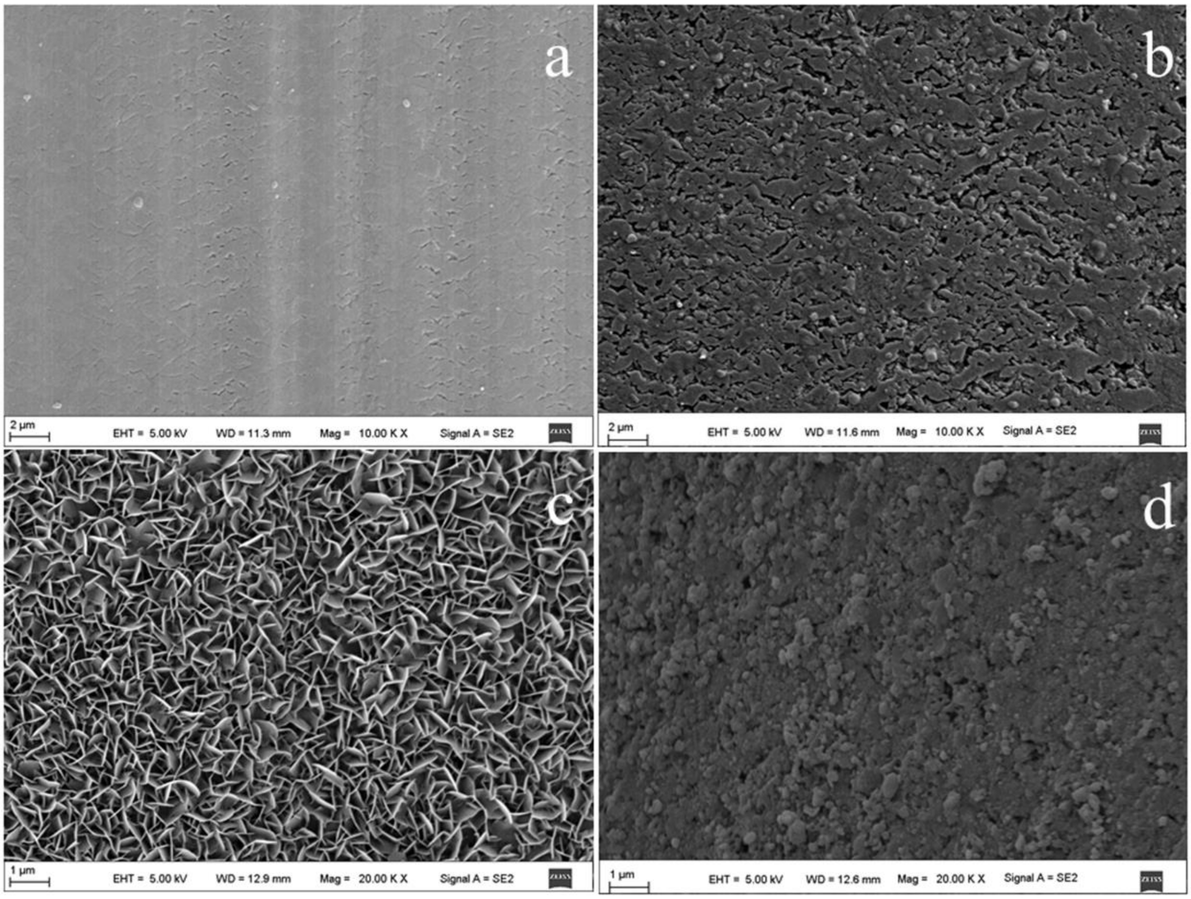

Fig. 1 SEM images of treated NiTi wires (a) Bare NiTi wire (×1000); (b) Etched NiTi wire (×1000); (c) TiO_2/NiOCNSs-NiTi fiber (×20,000); (d) C_{12}mimHCN-TiO_2/NiOCNSs-NiTi fiber (×20,000).

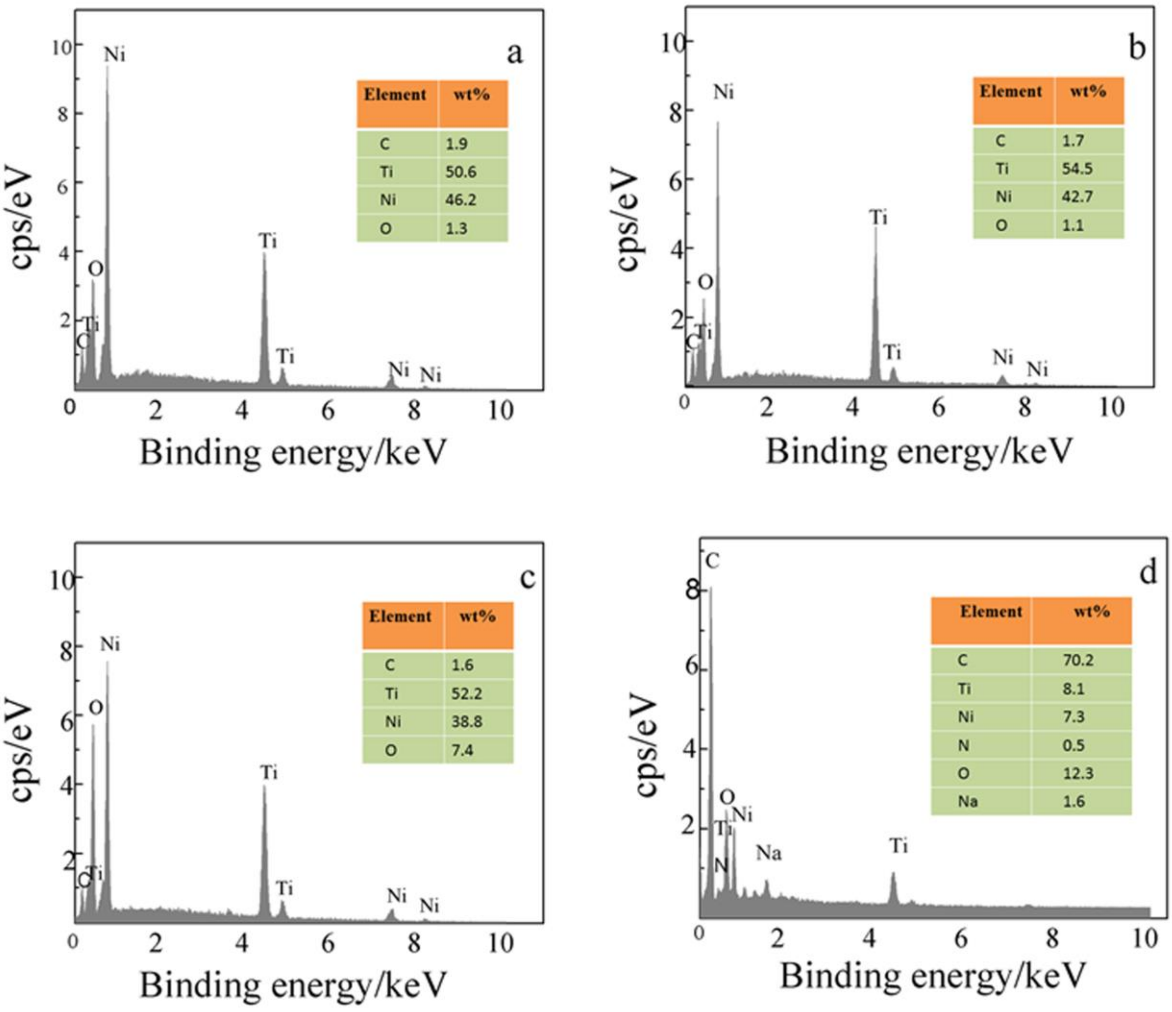

Fig. 2 EDS spectra of treated NiTi wires. (a) Bare NiTi wire; (b) Etched NiTi wire; (c) TiO_2/NiOCNSs-NiTi fiber; (d) C_{12}mimHCN-TiO_2/NiOCNSs-NiTi fiber.

3.2 Optimization of SPME conditions

Generally SPME is subjected to thermodynamic and kinetic factors in practical applications [12]. In order to obtain better extraction performance, the main experimental conditions were further optimized for SPME of ODA in aqueous samples with the C_{12}mimHCN-TiO_2/NiOCNSs-NiTi fiber. Fig. 3 illustrated the dependence of extraction efficiency on extraction temperature, stirring rate, extraction time and ionic strength. Under the optimized conditions, SPME can be accomplished at 65 ^{o}C for 55 min with a stirring rate of 450 r/mim. The C_{12}mimHCN-TiO_2/NiOCNSs fiber coating showed the best extraction capability for ODA . Typically, addition of NaCl to sample solution can increase ionic strength and decrease the solubility of ODA in an aqueous phase. However, the extraction efficiency (Fig. 3d) was monotonically decreased with the increasing concentration of NaCl. This result may be due to the increased viscosity of aqueous phase in the presence of NaCl, which decreased the mobility of ODA [3, 16]. As a result, a negative effect of sodium chloride on the extraction occured. In this study, addition of salt was not recommended in SPME procedure. Constant desorption was achieved in the methanol/water of 80/20 within 6 min.

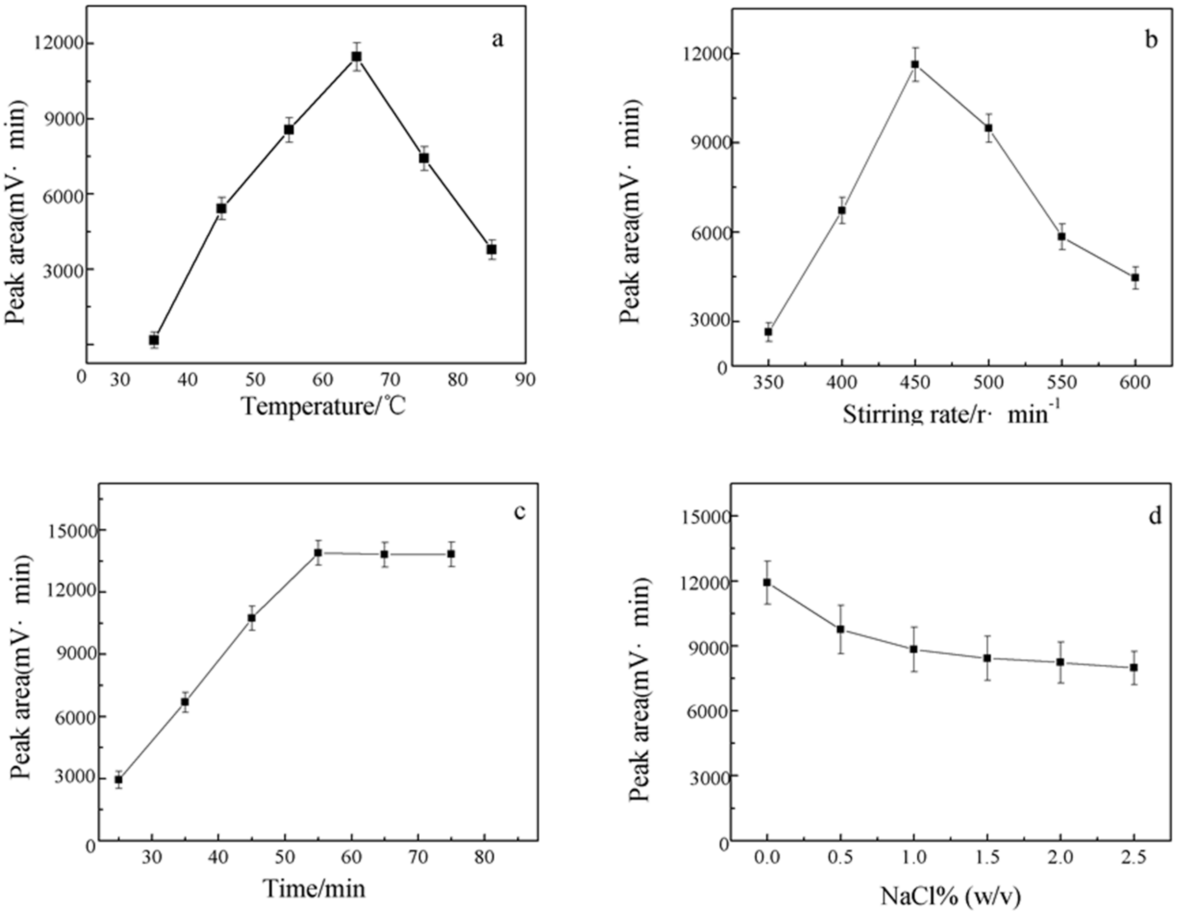

Fig. 3 Effect of (a) temperature; (b) stirring rate; (c) extraction time and (d) ionic strength on the extraction efficiency.

3.3 Extraction efficiency of the C_{12}mimHCN-TiO_2/NiOCNSs fiber coating

Under the optimized conditions, the extraction capability of the C_{12}mimHCN-TiO_2/NiOCNSs-NiTi fiber was further evaluated using ODA at 50 μg/L. The TiO_2/NiOCNSs-NiTi fiber (Fig.4c) exhibited some extraction capability for ODA due to its large surface area, however no chromatographic peak were observed at retention position of ODA for bare NiTi-SPME-HPLC (Fig. 4b) and direct HPLC (Fig. 4a). After modification by C_{12}mimHCN coating, the best extraction efficiency was achieved. Compared with commercially available 65-μm PDMS/DVB (Fig. 4e) and 100-μm PDMS fibers (Fig. 4f), the C_{12}mimHCN-TiO_2/NiOCNSs-NiTi fiber exhibited higher extraction capability for ODA. This result revealed that the C_{12}mimHCN-TiO_2/NiOCNSs coating was mainly hydrophobic due to the long chain groups covalently bonded onto TiO_2/NiOCNSs [14]. In addition, IL with unique and fascinating properties may also contributed to good coupling physicochemical affinity [9,10]. As a result, the C_{12}mimHCN-TiO_2/NiOCNSs fiber coating provided a potential approach to adsorption and extraction of ODA from complex brine samples.

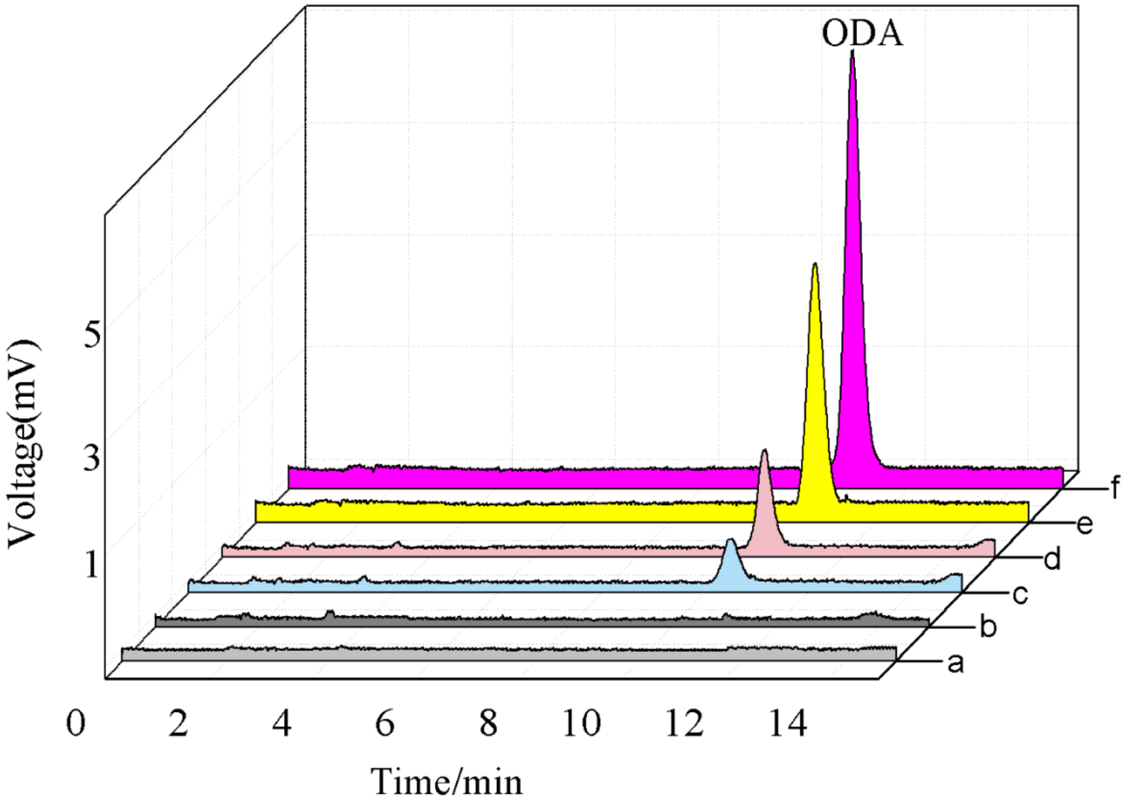

Fig. 4. Typical chromatograms of direct HPLC and SPME-HPLC for ODA at 50 μg/L. (a) Direct HPLC and (b) SPME-HPLC with the bare NiTi fiber; (c) SPME-HPLC with the TiO_2/NiOCNSs-NiTi fiber; (d) the 65-μm PDMS/DVB fiber; (e) the 100-μm PDMS fiber and (f) the C_{12}mimHCN-TiO_2/NiOCNSs-NiTi fiber.

3.4 Method validation

The analytical performance of the proposed method with the C_{12}mimHCN-TiO_2/NiOCNSs-NiTi fiber was investigated for ODA under the optimized conditions. Good linearity was achieved in the range of 1-150 μg/L with correlation coefficients (r^2) above 0.985. Limits of detection (LODs), calculated based on a signal-to-noise ratio of 3 (S/N=3), were 0.280 μg/L (S/N=3). Relative standard deviations (RSDs) for five replicate extractions of ODA at the spiking level of 50 μg/L were less than 7.16% for the single fiber. These data indicated that satisfactory accuracy, precision and sensitivity were obtained for this method. Moreover the C_{12}mimHCN-TiO_2/NiOCNSs-NiTi fiber could be prepared in a reproducible manner.

3.5 Analysis of real sample

To estimate the feasibility of the proposed method, the fabricated fiber was applied for the detection of target ODA in real brine samples collected in local lake salt. In order to improve the solubility of ODA in water sample, 1mL ethanol was added into brine. Then real sample were filtered through 0.45 μm micropore membrane to remove any suspended particulate matter. Satisfactory results were obtained. To evaluate the accuracy of the results, standard ODA were spiked into the real sample at the levels of 15 μg/L and 30 μg/L, respectively. The relative recoveries ranged from 78.3% to 96.5% with the RSDs less than 8.7% for target ODA. These results demonstrated that the novel fiber was reliable and suitable for adsorption and sensitive detection of ODA in brine sample.

4. Conclusions

The TiO_2/NiOCNSs fiber coating oriented around the NiTi substrate was in-situ obtained via hydrothermal growth, which provided remarkable available framework for further modification of IL. Then the C_{12}mimHCN with good surfactivity was synthesized through a simple and green method and was successfully assembled on the surface of TiO_2/NiOCNSs. Moreover the fabricated C_{12}mimHCN-TiO_2/NiOCNSs fiber coating exhibited uniform and porous structure, which contributed to the adsorption and extraction of target analyte from sample solution to fiber coating. The novel fiber exhibited higher extraction capability for target ODA due to its excellent property and desired nanostructure. In addition, the fabricated

C_{12}mimHCN-TiO_2/NiOCNSs-NiTi fiber was first successfully applied for the detection of ODA in real brine sample. Meanwhile the innovative SPME-HPLC technology was also first used in the salt lake fields. Furthermore the proposed method opened up a new pathway for adsorption and detection of ODA in brine in the future.

Acknowledgements

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