



Poly (indole-co-thiophene)@Fe₃O₄ as novel adsorbents for the extraction of aniline derivatives from water samples



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ABSTRACT

For the first time, Fe₃O₄ nanoparticles modified by poly(indole-co-thiophene) (PIn-co-PTh@Fe₃O₄) via in situ emulsion polymerization used for magnetic-solid phase extraction (MSPE) of the aniline derivatives from water samples. After extraction, the aniline derivatives were detected using gas chromatography–flame ionization detector (GC–FID).

The resultant core–shell magnetic solid-phase extraction nanoparticle sorbent was characterized by scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray diffraction (XRD), Brunauer–Emmett–Teller (BET), vibrating sample magnetometer (VSM) and Fourier transform-infrared (FT-IR) spectroscopy. The dominant parameters affecting enrichment efficiency were investigated and optimized. Under the optimum conditions detection limits and linear dynamic ranges were achieved in the range of 0.005–0.02 ng mL⁻¹ and 0.02–200 ng mL⁻¹, respectively. The relative standard deviations (RSDs) for five replicates at three concentration levels (0.05, 5 and 100 ng mL⁻¹) of analytes were ranged from 3.8 to 7.0%. Ultimately, the applicability of this method was successfully confirmed by analyzing tap, well, sea and waste water samples and satisfactory results were obtained.

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1. Introduction

Aromatic amines are widely used in the manufacture of pesticides, rubber chemicals, pharmaceuticals, dyes, photographic chemicals and as intermediates in many chemical syntheses [1,2]. During production, use, and disposal emissions of aromatic amines may occur. In the recent years, because of the potential carcinogenic of aromatic amines, considerable growing attention has been paid to human exposure to them [3]. As a consequence, it is necessary to determine these compounds in environmental water by a rapid and sensitive analytical technique [4].

Among the sample preparation methods, solid-phase extraction (SPE) is the most popular one. SPE has many obvious advantages, such as high extraction efficiency, low consumption of organic solvents, and convenience of operation [5,6]. However, long operation time is required when large volumes of water samples pass through the SPE column; also there is probability of the SPE cartridge blockage in analyzing the samples containing particles or microorganisms. Therefore, it is necessary to develop novel sorbents with high extraction efficiency and *anti*-interference ability. In order to overcome these limitations of SPE, a magnetic SPE (MSPE) method has been developed based on the use of magnetic

nanoparticles (MNPs) [7,8]. In MSPE, the sorbent is dispersed in a sample solution instead of being packed into a SPE cartridge, improving the contact area between the sorbent and the sample and therefore increasing the extraction rates. Also, after the extraction the sorbent recovery is easily performed by the application of an external magnetic field which is a simpler alternative compared to filtration or centrifugation. Among the most widely used magnetic adsorbents, bare Fe₃O₄ NPs have played a major role. However, the bare Fe₃O₄ NPs suffer from several inherent limitations as the aggregation caused by their high surface-to-volume ratio and attractive forces reduces their superparamagnetic properties. Thus, functionalization of bare Fe₃O₄ NPs has been required to protect them from aggregation and introduce desired surface properties.

Among different types of coating sorbents used for the extraction of organic analytes, conductive polymers (CPs) due to their multifunctional properties including hydrophobicity, acid–base character, π–π interaction, polar functional groups, ion exchange property, hydrogen bonding and electro-activity have attracted a great deal of attention as SPE or SPME sorbents [9–13]. Recently, research works have been focused on the copolymerization in order to prepare conducting polymers with better properties [14]. In recent years, polythiophenes have attracted much attention due to their chemical stability in air/humid environments. So, recently polythiophene have been used as solid-phase microextraction sorbent [15–18] and MSPE [19,20]. Polyindole (PIn) is another CPs that owns several advantages, especially fairly good thermal stability due to

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the incorporation of benzene rings on the polymer backbone [21–23] and high redox activity and stability [24]. It is possible to prepare a polymer that owns both the advantages of Pln and PTh.

Therefore, in this work, PTh and Pln CPs and mixture of both (copolymer) were coated on the surface of Fe_3O_4 NPs (PTh@ Fe_3O_4 , Pln@ Fe_3O_4 and Pln-co-PTh@ Fe_3O_4 , respectively) and the ability of these sorbents for extraction of aromatic amines from water samples were examined.

2. Experimental

2.1. Chemicals and reagents

The methanol, toluene, n-hexane, dichloromethane, chloroform, ferric chloride ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$), ferrous chloride ($\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$), ammonium persulfate (APS), sodium dodecyl sulfate (SDS), and sodium chloride (NaCl) were purchased from Merck (Darmstadt, Germany). Also, aromatic amines include aniline, *N,N*-dimethylaniline, *o*-toluidine, 3-chloroaniline, were purchased from Merck (Darmstadt, Germany). Thiophene (Fluka) was purified by double distillation and indole (Fluka) used without further purification. Stock solutions (100 mg L^{-1}) of aromatic amines were prepared in methanol and stored in the dark at 4°C . Working solutions were prepared by the dilution of the stocks in the deionized water.

2.2. Instrumentation

A Shimadzu gas chromatograph (Shimadzu-17A, Tokyo, Japan) equipped with a split/splitless inlet and flame ionization detector (FID) was used for the determination of aromatic amines. The injector and detector temperatures were 250 and 300°C , respectively. The carrier gas was N_2 (99.999%) with constant flow of 1 mL min^{-1} . Chromatographic separation was accomplished with a Shimadzu Hicap CBP-5-M25-025 (5% biphenyl + 95% polydimethylsiloxane) fused-silica column (25 m , length; 0.25 mm I.D.; $0.22 \mu\text{m}$, film thickness). The GC oven was programmed as follow: 100°C (1 min held), ramp to 200°C at $10^\circ\text{C min}^{-1}$ and then held for 1 min . A magnetic stirrer, model MR HCl-standard (Heidolph, Germany), with speed 0 – 1400 rpm , was employed for stirring samples during the extraction. For dispersion of NPs in the sample solution, an ultrasonic bath (Parsonic 15S, Pars Nahand Engineering Co.), was used at a frequency of 28 kHz . For sorbent collection and magnetic decantation, an Nd-Fe-B magnet ($2 \times 2 \times 1 \text{ cm}$, 1.4 T) was used. Field-emission scanning electron microscopy (FESEM) (Hitachi S-4160, Tokyo, Japan) and transmission electron microscope (TEM, Leo 912 AB, Germany) was used to characterize the morphology and size of the nanocomposites. Fourier transform infrared (FT-IR) analysis was carried out on a Bruker Tensor 27 spectrometer (Bruker, Karlsruhe, Germany). X-ray diffraction patterns were obtained at room temperature on a Rigaku $\text{CuK}\alpha$ /Max-2550 powder diffractometer (XRD, Shibuyaku, Tokyo, Japan) with a scanning rate of $5^\circ/\text{min}$, and recorded in the 2θ range of 10 – 70°C . The specific surface areas of the nanomaterials were measured using nitrogen Brunauer–Emmett–Teller (BET) adsorption instrument (BELSORP-mini II analyzer).

2.3. Synthesis of Pln@ Fe_3O_4 , PTh@ Fe_3O_4 and Pln-co-PTh@ Fe_3O_4 nanocomposites

2.3.1. Synthesis of Fe_3O_4 magnetic nanoparticles

Fe_3O_4 nanoparticles were prepared by co-precipitation method from a mixture solution of Fe (II) and Fe (III) salts according to the already reported method with a slight modification [12]. Briefly, 1 g $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ and 3.68 g of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ were dissolved in 50 mL deionized water at room temperature under nitrogen gas. The mixture was stirred at 80°C and then 10 mL of $25\% \text{ NH}_4\text{OH}$ was added to the solution dropwise during 30 min under nitrogen gas stream. The mixture was stirring at 80°C for 1 h . After the reaction, the black precipitate was separated by magnetic decantation and washed several times with deionized water

and twice with ethanol. Finally, Fe_3O_4 magnetic nanoparticles were dried at 80°C under vacuum for 6 h .

2.3.2. Synthesis of Pln@ Fe_3O_4 nanocomposites

The Pln@ Fe_3O_4 nanocomposites were prepared by emulsion polymerization according to the already reported method with some modification [25]. Briefly, 0.5 g Fe_3O_4 nanoparticles and 0.1 g SDS were dissolved in 30 mL deionized water under sonication for 10 min . Subsequently, indole solution (3 g indole in 10 mL ethanol) was gradually added to the mixture solution under the N_2 gas. Afterwards, APS solution (1 g of APS in 20 mL of deionized water) was added dropwise to the mixture under stirring at the room temperature. After that, the reaction was continuously stirred for 24 h . Finally, Pln@ Fe_3O_4 nanoparticles product was rinsed by deionized water and ethanol several times and dried at 70°C for 5 h under vacuum.

2.3.3. Synthesis of PTh@ Fe_3O_4 nanocomposites

The Fe_3O_4 nanoparticles were modified by polythiophene using emulsion polymerization of the thiophene monomers. For this purpose, 0.5 g of Fe_3O_4 nanoparticles and 0.1 g SDS were dissolved in 30 mL deionized water under sonication for 10 min . Then, 4 mL thiophene solution was added to the mixture and stirred for 15 min by mechanical stirrer. Afterwards, 1 g of APS was dissolved in 20 mL of deionized water and added dropwise to solution within 30 min . Then, the mixture was stirred for 12 h at 50°C under nitrogen atmosphere. To terminate the reaction, acetone was added to the reaction mixture. The obtained PTh@ Fe_3O_4 nanocomposites were filtrated and washed by deionized water and ethanol several times and dried at 50°C for 24 h under vacuum.

2.3.4. Synthesis of Pln-co-PTh@ Fe_3O_4 nanocomposites

Pln-co-PTh@ Fe_3O_4 nanoparticles were synthesized by emulsion polymerization according to the literature with some modifications [26]. Briefly, Fe_3O_4 nanoparticles (1.0 g), SDS (0.15 g) and 20 mL chloroform were added into 30 mL of deionized water. Then the resulting mixture dispersed with ultrasonic bath at room temperature for 1 h . Then the solution of thiophene monomer (1.5 g) and indole (2.0 g) were added into the solution. Thereafter, the APS solution (2.0 g in 20 mL deionized water) was gradually added into the emulsion and the polymerization was carried out for 24 h at room temperature under nitrogen atmosphere. To terminate the reaction, acetone was added to the reaction mixture and the formed precipitate was filtered and washed several times with deionized water and once with methanol. Finally, Pln-co-PTh@ Fe_3O_4 nanoparticles product was dried at 50°C for 24 h under vacuum. Fig. 1 shows the schematic diagram of preparation procedure of Pln-co-PTh@ Fe_3O_4 sorbent.

2.4. Magnetic SPE procedure

An amount of 30 mg of sorbent was added to 20 mL of spiked sample solution adjusted at pH 6 in a 25 mL sample vial. The solution was sonicated for 10 s to form a dispersive solution and then stirred for 2 min . After performing the extraction, the magnetic sorbent was collected using an external magnet and supernatant water was decanted. Then, the adsorbed analytes on the sorbent were eluted with $150 \mu\text{L}$ desorption solvent (dichloromethane) by stirring for 3 min . Finally, the magnet was again attached to the vial and the supernatant was collected into an Eppendorf tube. Finally, $1 \mu\text{L}$ of the desorption solution was injected into GC–FID instrument for analysis.

3. Results and discussions

3.1. Characterization of materials

The FT-IR spectra of (a) Pln@ Fe_3O_4 , (b) PTh@ Fe_3O_4 and (c) Pln-co-PTh@ Fe_3O_4 are shown in Fig. 2. The spectrum of Pln@ Fe_3O_4 (Fig. 2a) appears to have some absorbance peaks at 3365 , 1594 , 1486 and 741 cm^{-1} , which are characteristics of pristine Pln [25,27]. A sharp

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