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Pyrrole-based conductive polymer as the solid-phase extraction medium for the preconcentration of environmental pollutants in water samples followed by gas chromatography with flame ionization and mass spectrometry detection

Habib Bagheri*, Abdorreza Mohammadi

Department of Chemistry, Sharif University of Technology, P.O. Box 11365-9516, Tehran, Iran

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Abstract

A pyrrole-based polymer was synthesized and applied as a new sorbent for solid-phase extraction (SPE) of some environmental pollutants from water samples. Polypyrrole (PPy) was synthesized by chemical oxidation of the monomer in nonaqueous solution. SPE of selected phenols, pesticides, and polyaromatic hydrocarbons (PAHs) from aqueous samples were performed using 200 mg PPy. The determination was subsequently carried out by gas chromatography–flame ionization detection (GC–FID) and gas chromatography–mass spectrometry (GC–MS). The polymer showed much higher recoveries for aromatic compounds than aliphatics. Preconcentration of sample volumes up to 1 l led to acceptable recoveries for aromatic and other tested polar compounds. The R.S.D. for a river water sample spiked with phenols, pesticides and PAHs at sub-ppb level was lower than 10% ($n = 3$) and limits of detection for these compounds were between 15 and 120 ng l⁻¹.

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1. Introduction

Nowadays, solid-phase extraction (SPE) is a well-established technique and, due to its advantages over other sample preparation techniques, it has been used for the preconcentration and clean-up of numerous different classes of compounds in a variety of matrices. The introduction of new polymeric solid phases,

the development of new experimental configurations in order to adapt SPE to specific situations and the improvement of automatic devices will undoubtedly lead to their applications in different fields of chemical analysis [1–5]. The most commonly used material for SPE is chemically bonded silica, usually with a C₈ or C₁₈ organic group. On the other side, porous polystyrene resins could be regarded as popular organic SPE sorbents. During the last few years, a series of different packing materials either polymer-based or bonded silicas have been developed. In general, silica based materials exhibit some problems such as

* Corresponding author. Tel.: +98-21-6005718;
fax: +98-21-6012983.

E-mail address: bagheri@sharif.edu (H. Bagheri).

pH instability or inconsistent results due to the presence of free silanol groups in amounts that could not be controlled or reproduced. Different attempts have been made to develop new materials for solid-phase extraction of polar compounds; mainly using highly cross-linked copolymer sorbent by using chemically modified polymeric resins [6,7]. Fritz et al. [5] showed that lightly sulfonated resins of PS-DVB could display excellent hydrophilicity and enhanced extraction efficiencies. However, these resins were unable to extract small, polar organic molecules successfully. They introduced a molecular sieve, known as Silicalite, for SPE to complement polystyrene and bonded-phase silica adsorbents [8].

The hydrophilic character of the introduced functional groups improves the sorbent wetting property; consequently mass transfer of most polar compounds from the water solution to the sorbent is enhanced. The most common groups used for modifying polymeric sorbent are acetyl [9], hydroxy methyl [10], benzoyl [11], *o*-carboxy benzyl [12], carboxylic [13] and sulphonic acid [5,14].

The new generation of polymers such as Oasis from Water, LiChrolut EN from Merck and Absolute from Varian, is designed for extraction of variety of analytes. They are capable to extract acidic, basic, and neutral compounds, whether polar or non-polar [3]. The increase in retention of polar analytes in these sorbents is due to both the polymeric skeleton (reversed-phase mechanism and π - π interaction) and the occurrence of the functional groups. Most recently, molecularly imprinted polymers as new molecular recognition materials have been used for selective SPE of organic compounds from complex samples [15].

In recent years, intrinsic conducting polymers with conjugated double bonds have been attracted much attention as advanced materials. There has been growing interest in conducting polymers due to their multifunctional properties and potential applications, including ion exchangers, energy-storage materials, corrosion-resistant coating, catalysts, chemical sensors and material for separation [16–20]. They are versatile materials in which molecular/analyte recognition can be achieved in different ways, including: (i) the incorporation of counter ions; (ii) utilizing the inherent and unusual multifunctionality (hydrophobic, acid–base and, π - π interaction, polar functional

groups, ion exchanger, hydrogen bonding, and electroactivity) of the polymer and (iii) the introduction of functional groups to the monomers. Also, these materials have additional advantages because they can be easily synthesized in both aqueous and nonaqueous medium, chemically and electrochemically. There are varieties in type of dopant and additives during synthesis. All these conditions and varieties affect on the chemical, mechanical, morphological and electronic properties of the polymers.

Among those conducting polymers, polypyrrole (PPy) is especially promising for commercial applications because of its good environmental stability, facile synthesis and higher conductivity than many other conductive polymers. Recently, aniline-based polymers were used as sorbents for solid-phase extraction of chlorophenols from water samples [21,22]. Also, Pawliszyn and co-workers have applied PPy and poly-*N*-phenyl pyrrole as a coating material for solid phase microextraction of some inorganic anions and organic compounds [23–25].

Following our previous works on aniline-based polymers [21,22], the use of PPy as a solid phase sorbent for SPE of some selected pollutants from aquatic media has been investigated. Different conditions were applied to obtain higher retaining capacity for adsorbed pollutants. The efficiency of the new sorbent was compared with those obtained from commercial C₁₈, and LiChrolut EN.

2. Experimental

2.1. Reagents

Pyrrole (Merck, Darmstadt, Germany) was distilled before the use. Phenolic compounds studied include phenol (Ph), 2-chlorophenol (2CP), 4-chlorophenol (4CP), 2,4-dichlorophenol (24DCP), and 2,4,6-trichlorophenol (246TCP) were obtained from Merck (Darmstadt, Germany). Standard solutions (1 mg ml⁻¹) from each individual compound were prepared in methanol. The polyaromatic hydrocarbons (PAHs) including naphthalene, anthracene, fluorene, acenaphthylene and acenaphthene were obtained from Merck (Darmstadt, Germany). The stock solution of these compounds was prepared in benzene:methylene chloride (50:50) at concentration

of 1.5 mg ml⁻¹. The pesticides including simazine, atrazine, diazinon and fenthion were purchased from Riedel-de-Haen (Seelze, Germany). A stock solution of pesticides was prepared in methanol at a concentration of 1 mg ml⁻¹. The working solution of above compounds was prepared weekly by diluting the stock solution with methanol and benzene:methylene chloride (50:50), and more diluted working solutions were prepared daily by diluting these solutions with triple distilled water or river water. The pH of water samples was adjusted with sulfuric acid (Fluka, Switzerland). Anhydrous sodium sulfite was obtained from Riedel-de-Haen (Seelze, Germany). All solvents used in this study were of analytical reagent grade or HPLC grade. Acetic anhydride and other reagents were of maximum purity available and obtained from Merck (Darmstadt, Germany).

2.2. Apparatus

A Surva HPLC Eluent supply pump (Germany) together with an Ismatec (ISM 444) peristaltic pump (Switzerland) were used for loading of the sample and eluting the SPE precolumn, respectively. SPE was carried out on a polypropylene cartridge packed with 200 mg PPy. A Perkin-Elmer liquid chromatograph model 601 equipped with two reservoirs was modified for elution of PAHs from the SPE precolumn.

A gas chromatograph model Chrompack CP 9001 (The Netherlands) equipped with flame ionization detector and a split/splitless injector was used. Separation of phenols were carried out using a capillary column CP-Sil 5 CB low bleed MS, (25 m, 0.25 mm I.D.) with 0.25 μm film thickness. The injector and detector temperatures were set at 250 and 280 °C, respectively.

A Hewlett-Packard (HP, Palo Alta, USA) HP 6890 series gas chromatograph equipped with a split/splitless injector and a HP 5973 mass-selective detector was also used. The analytical column was a HP-5 MS 0.25 μm of 30 m × 250 μm I.D. Chromatographic data were recorded using an HP Chemsation, which was controlled by Windows NT (Microsoft) and equipped with Wiley mass spectral library. Helium and nitrogen (99.999%) were used as carrier and make-up gas, respectively. The flow rate of carrier gas was adjusted at 1 ml min⁻¹.

The separation of phenolic compounds on gas chromatography–flame ionization detection (GC–FID) and gas chromatography–mass spectrometry (GC–MS) was performed by a temperature program as follows: 60 °C during 5 min, at 10 °C min⁻¹ to 230 °C, 5 min hold at 230 °C. The temperature program used for PAHs was: 60 °C during 1 min, at 10 °C min⁻¹ to 220 °C, 5 min hold at 220 °C. For pesticides analysis, the program was: 140 °C during 7 min, at 20 °C min⁻¹ to 260 °C, 5 min hold at 260 °C. An aliquot of 1–2 μl from each sample was introduced into the chromatographic columns using splitless mode injection.

The scanning electron micrographs (SEM) of the polymer particles were obtained using a JXA-840 Jeol scanning electron microscopy (Japan).

2.3. Polymer preparation

PPy particles could be prepared chemically according to the following method [26]. An amount of 3.35 g (0.05 mol) of pyrrole was added slowly to 24.3 g (0.15 mol) of ferric chloride dissolved in 200 ml of acetonitrile with good stirring. A black precipitate was formed immediately; the addition was completed in 15 min. The reaction mixture was then stirred for an additional hour at room temperature. The solid was filtered and washed well with acetonitrile and methanol. The polymer was dried under the vacuum. The product was subsequently extracted in a Soxhlet with THF, methanol and acetone until the extracted solvent was colorless. After extraction, the synthesized polymer was washed with methanol and water and dried under vacuum and following grinding. The structure of the synthetic polymer is shown in Fig. 1. The easy-handling black solid particles sized 53–75 μm were collected and stored in a vial. The specific surface area was determined according to the B.E.T. method using a Quantasorb surface area analyzer (Quantachrome Inc., Boynton Beach FL, USA) and found to be 40 m² g⁻¹.

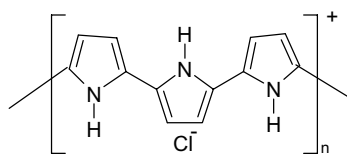


Fig. 1. Simple chemical structure of synthesized PPy.

2.4. Sample preparation and derivatization of phenolic compounds

A known volume of distilled or river water, buffered at pH 2, was spiked with phenol standards and was subsequently passed through a preconditioned SPE column at a flow rate of 6 ml min^{-1} . When the sample had passed through, the cartridge was eluted with 2 ml of methanol at the flow rate of 0.8 ml min^{-1} . The cartridge was preconditioned by washing with 3 ml of methanol and activated with 5 ml of distilled water.

The derivatization procedure used was based on previous report by Rodríguez et al. [27]. A volume of 2 ml of a methanol solution containing phenols was mixed with 1 ml of 5% K_2CO_3 and 2 ml of *n*-hexane containing 200 ml of acetic anhydride and internal standard. The mixture was shaken for 1 min and the organic phase was allowed to be separate. The aqueous phase was then extracted with a further 1 ml of *n*-hexane containing only internal standard. The two *n*-hexane portions were collected, mixed and dried over anhydrous sodium sulfate and injected into the GC. To access lower detection limit in the sample solution at sub-ppb concentration, final extract was concentrated to 0.5 ml under a gentle stream of nitrogen.

2.5. SPE of pesticides

To evaluate the capability of polypyrrole for the preconcentration of pesticides from water sample, simazine, atrazine, diazinon and fenthion were used as model compounds. A known volume of distilled or river water was spiked with these compounds and was subsequently passed through a preconditioned SPE column at flow rate of 6 ml min^{-1} . The cartridge was, then, eluted with 2 ml of methanol at the flow rate of 0.8 ml min^{-1} . The extracted volume was concentrated to 0.5 ml under a gentle stream of nitrogen and analyzed by GC–FID.

2.6. SPE of PAHs

A known volume of distilled or river water containing 7% acetonitrile was spiked with PAHs standards including naphthalene, anthracene, fluorene, acenaphthylene and acenaphthene and was subsequently passed through a preconditioned SPE column at a

flow rate of 6 ml min^{-1} . When the sample had passed through, the cartridge was eluted with 3 ml of acetone at the flow rate of 0.8 ml min^{-1} . The extracted volume was concentrated to 0.5 ml under a gentle stream of nitrogen and analyzed by GC–FID. The cartridge was preconditioned by washing with 3 ml of methanol and activated with 5 ml of distilled water.

3. Results and discussion

3.1. Preparation of PPy

Pyrrole can be polymerized conveniently with oxidation reactions electrochemically or chemically. The quality of the polymer can be greatly influenced by parameters such as the counter ions, reaction medium, and temperature. The counter ions allow specific effects to be introduced in to the PPy. If the counter ions such as ClO_4^- or BF_4^- with hydrophilic character are employed, the synthesized PPy will have a hydrophilic property. It can thus be understood that it is precisely the anion (e.g. its size, geometry, charge, etc.) that governs the properties of the polymers. The reaction medium has a great influence on the synthesized polymer. The polymer chain and conductivity increase when it is produced in nonaqueous medium [26]. By changing the conditions, it is possible to obtain polymers with different surface morphology. In the present work, PPy was synthesized using different oxidants such as ferric sulfate, ammonium persulphate, ferric chloride, and peroxide hydrogen in nonaqueous medium. The best polymer for SPE was synthesized by ferric chloride as oxidant in acetonitrile. In this chemical polymerization, ferric chloride acts as the initiator (oxidant) and also performs as the dopant. The synthesized polymer using this initiator-dopant in the absence of any stabilizers contains about one chlorine unit per three pyrrole units. The ideal structure of doped PPy should have the empirical formula $\text{C}_4\text{H}_3\text{NCl}_x$, where x is 0.3. Fig. 1 shows the structure of the synthesized PPy. The SEM studies on the PPy particles revealed that the polymer has a porous and relatively homogeneous structure, which is shown in Fig. 2.

Since the polymer has been synthesized chemically, the obtained porous and homogenous structure is rather acceptable.

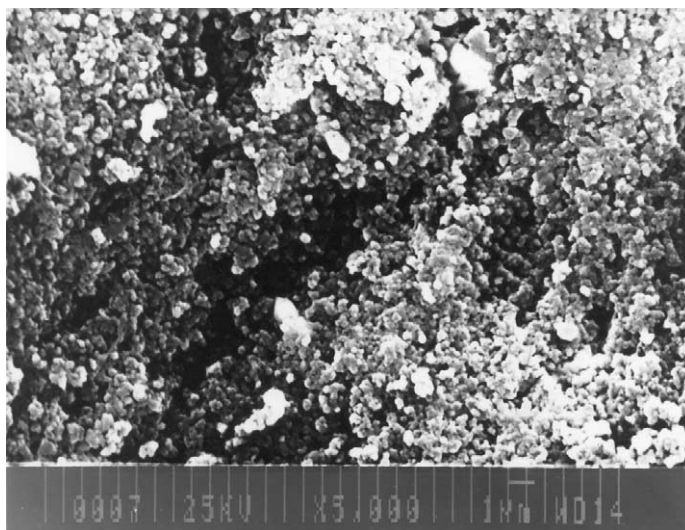


Fig. 2. The scanning electron micrographs of the PPy particles.

3.2. Evaluation of sorbent

Since PPy contains a conjugated π structure, it is expected that it efficiently extract the aromatic compounds easily through π – π and hydrophobic interactions. Moreover, it should extract polar aromatic analytes via additional interactions between the polar components of the polymer and analytes. PAHs, phenol, chlorophenols and some pesticides were, therefore, used to examine the capability of PPy for the preconcentration of variety of compounds with different polarities from water sample.

3.2.1. Phenolic compounds

To evaluate the ability of PPy for the extraction of phenolic compounds from water samples, a mixture of five phenolic compounds including Ph, 2CP, 4CP, 24DCP, and 246TCP were used as model compounds. In general, phenols are amenable to GC without derivatization [27–30]. But at lower concentration, peak tailing and discrimination in the injector of capillary column might occur [30,31], especially when environmental samples are analyzed. To overcome these problems, phenols could be derivatized with a suitable derivatizing reagent [32–35]. Among the wide variety of derivatizing reagents used for this purpose, acetylating agents have been employed to the greatest extent [27,36,37].

Effects of different parameters such as the sample pH, the sample volume, the volume of eluting solvent, the capacity of sorbent and the linearity of recovery were evaluated using this new polymeric sorbent.

The sample pH is an important factor, which may affect on the recovery of phenols from water. To increase the extraction recovery of chlorophenols by non-polar sorbents, it is necessary to acidify the sample [28]. At low pH, the acid–base equilibrium for the chlorophenols shifts significantly toward the neutral forms, which have greater affinities toward the sorbent, and the extraction efficiencies are, therefore, increased. To study the effect of sample pH on the recovery of phenols from water samples, 125 ml samples with same concentration in the 200–300 $\mu\text{g l}^{-1}$ levels at different pH values (2, 4, 7) were preconcentrated using PPy as a sorbent. Table 1 shows the recovery obtained at each pH and clearly, the maximum recovery is obtained at pH 2. Higher recovery results at low pH could indicate that the ion exchange interactions have little contribution in retaining mechanisms. The pronounced recovery decrease for chlorophenols in comparison with phenol at higher pH, justifies the non-ion-exchange interactions.

In order to determine the volume of the sample that can be concentrated with acceptable recoveries for all the compounds studied, it was necessary to obtain the

Table 1

The extraction recoveries obtained for the studied phenols at different sample pH^a

Compound	Recovery (%)		
	pH 2	pH 4	pH 7
Ph	99	98	94
2CP	101	97	78
4CP	101	98	76
24DCP	102	95	68
246TCP	100	89	62

^a Values are means of three determinations.

breakthrough volumes. Different volumes (100, 125, 150, 200, 300, 500, 1000 ml) of distilled water, at pH 2, were spiked with a solution containing five phenolic compounds at the 200–300 $\mu\text{g l}^{-1}$ levels. Following the preconcentration step, the trapped analytes on the percolumn were eluted with 2 ml of methanol. After derivatization and extraction with a total of 3 ml of *n*-hexane, an aliquot of 2 μl was injected into the GC system. The recovery of phenolic compounds and the repeatability for the different volumes are given in Table 2. Good recoveries were obtained for all compounds studied using 250 ml sample volumes. Of course, when samples of 500 ml were preconcentrated, the recoveries were, still, acceptable, except for phenol. Further experiments revealed that, for less polar

Table 2

The extraction recoveries obtained for the studied selected pesticides and PAHs at different volumes (in ml) of sample solutions^a

Compound	Recovery (%)			
	200	300	500	1000
Ph	69	42	19	n.d.
2CP	96	88	69	49
4CP	98	93	72	52
24DCP	99	98	96	78
246TCP	99	98	97	87
Naphthalene	101	99	101	69
Acenaphthylene	98	101	103	98
Acenaphthene	104	102	99	101
Flourene	98	103	103	96
Anthracene	102	100	96	98
Atrazine	104	98	94	78
Simazin	100	96	91	72
Diazinon	101	99	97	89
Fenthion	97	102	98	86

n.d.: not detected.

^a Values are mean of three determinations.

compounds, i.e. 24DCP, 246TCP, breakthrough volumes higher than 600 ml were obtainable. It was also found that flow rates up to 7 ml min^{-1} for water samples loading on the percolumn had no effect on the recovery percentage.

To find the required volume of methanol to elute all phenols from the cartridge, elution volumes up to 4 ml were examined. It was found that a volume of 1 ml was sufficient to desorb the trapped pollutants from the SPE percolumn. This relatively low volume of methanol eluted all compounds from the cartridge easily and other solvents were, therefore, excluded from any further examination. The low consumption of desorbing solvent is a clear advantage of this sorbent, which would be far more useful in on-line applications.

In order to study the capacity of the new sorbent and the linearity of recovery, each compound was determined using a river water sample spiked at much higher levels, i.e. 0.2–1 $\mu\text{g ml}^{-1}$, by GC–FID. No significant differences were obtained, indicating that its capacity is sufficiently high. It also demonstrates that even the preconcentration of water samples spiked with such levels of concentrations has no negative influence on the recovery results.

Lately, in an extensive comparison study we have shown that another conductive polymer, poly-*N*-methylaniline (PNMA) has a clear advantage, over C₁₈, on the recoveries of phenols under similar circumstances [22]. Also, the results obtained from PNMA were comparable with those obtained from Oasis HLB and LiChrolut EN. In the mean time, the use of PPy has led to the results, which are comparable with the well-known commercial LiChrolut EN. Both sorbents were evaluated for the extraction of phenols in real samples. This is especially true when PPy is compared with PNMA, both producing similar results.

3.2.2. Pesticides

The capability of the new sorbent for the extraction of some polar compounds has been examined and four different pesticides including simazine, atrazine, diazinon and fenthion were, therefore, selected as model compounds. It has been shown that the acidic property of PPy is stronger than its basic property [38]. It is, therefore, expected that PPy could extract the basic compounds more efficiently than the acidic ones.

Different volumes (150, 200, 300, 500, 800, 1000 ml) of distilled water at pH 7 were spiked with a solution containing four pesticides at the 300–400 $\mu\text{g l}^{-1}$ levels. As shown in Table 2, PPy showed high breakthrough volume for selected pesticides. These results are quite comparable with those obtained using commercial sorbents such as C₁₈ and ENV⁺ [39,40]. The high extraction ability of PPy to these compounds might be due to the increased interactions such as base–acid, dipole–dipole interactions and hydrogen bonding between the polymer and analytes, and also to the π – π and hydrophobic interaction.

3.2.3. PAHs

In order to extend the application of PPy-sorbent, a mixture of five PAHs, including naphthalene, anthracene, fluorene, acenaphthylene and acenaphthene was tested. According to Table 2, PPy shows high breakthrough volumes for the PAHs studied. The data obtained by other researchers using commercial sorbents are in agreement with these results [41,42]. In addition, the enhanced extraction efficiency might be due to the increase of molecule size and to the increased π – π and hydrophobic interactions. The high extraction ability of PPy, allows the PAHs to be analyzed at sub ng l^{-1} level.

3.3. Real samples

In order to study the effects of sample matrix on the performance of the sorbent, the recovery results were examined using real-life sample spiked with the phenolic compounds at two different concentration levels. A water sample from Zayandeh-rood River (Esfahan, Iran) was spiked with the selected phenols at 2–3 $\mu\text{g l}^{-1}$ levels. After the SPE and derivatization step, an aliquot of final extraction was injected into the GC–MS system. The TIC traces obtained from SPE of 250 ml of river water spiked with a standard solution of phenols when PPy and LiChrolut EN were used revealed that, in the case of PPy, the clean up process was more efficient. The capacity of PPy for retaining chlorophenols were 50–125 mg g^{-1} , while for phenol was 30 mg g^{-1} .

The limits of detection using 250 ml of water were calculated based on a signal-to-noise ratio of 3 and were in the range of 15–120 ng l^{-1} , using TIC mode (Table 3).

Table 3

The extraction recoveries obtained for the studied phenols at 250 ml volume of sample solution spiked in the range between 2–3 $\mu\text{g l}^{-1}$ using PPy and LiChrolut EN^a

Compound	PPy		LiChrolut EN	
	LOD (ng l^{-1})	Recovery (%)	LOD (ng l^{-1})	Recovery (%)
Ph	118	54	92	88
2CP	75	89	69	94
4CP	64	97	59	98
24DCP	34	99	25	99
246TCP	15	102	18	99

^a The relative standard deviations (R.S.D.) are between 2 and 10% ($n = 3$).

4. Conclusions

A synthesized sorbent, originally classified as a conductive polymer, has been introduced and evaluated for extraction of organic pollutants from water samples. The capability of this sorbent to extract phenols, PAHs and pesticides has been compared with the results obtained for commercial LiChrolut EN and this laboratory-made polymer, with a relatively small specific surface area, showed comparable breakthrough volumes for the studied compounds. Using PPy as a SPE sorbent, led to quantitative results for preconcentration of chlorophenols, PAHs and the selected polar pesticides from 1 l water sample, except for phenol.

The low consumption of desorbing solvent, more efficient clean-up and the stability against pH are clear advantages of this sorbent in comparison with C₁₈ and highly cross-linked commercial LiChrolut EN, which would be far more beneficial for on-line sample enrichment.

Our observations indicate that this laboratory-made polymer, similar to those already reported for aniline-based polymers [21,22], can be used frequently even after being dried out. It can be added that conductive polymers have shown to have the potential to be employed as packing material for the SPE purposes.

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