

A Comparison between Polyaniline Coated Fibers and Polyaniline-CNT Fibers for Solid Phase Microextraction of Phenols from Aqueous Sample

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Abstract

Polyaniline coated fibers and polyaniline-CNT fibers for solid phase microextraction of phenols from aqueous sample were compared. In the present work we established a method for preparation of polyaniline-CNT coated platinum wire (SPME Fiber) and investigated their capability to extract phenol from aqueous samples.

Keyword

Polyaniline; Coated; Fibers; CNT; Phenol; Conductivity

Introduction

Solid – phase Microextraction (SPME) is a rather new technique which was introduced by Pawliszyn and Lord in early 1990s. The technique is based on taking advantage of remarkable extracting ability of a solid sorbent which is coated on a fiber [1]. The adsorbed analyte is then desorbed from the fiber into a proper separation and detection system, usually a gas chromatograph.

The major advantage of SPME is its solventless nature and therefore it is considered as a green and nature-Friendly extraction technique. The first commercially fibers were introduced to the market in 1993. Extracting ability of the fibers is in direct relation with the type of coated sorbent [2]. In general, these coatings are polydimethylsiloxan (PDMS), divinylbenzene (DB), polyacrylate (PA), carboxen and Carbowax (CW, polyethylene glycol) and in fact one of the most important shortcomes of the SPME is the limited range of available stationary phases and therefore the limited range of analytes which could be extracted by these sorbents.

Fibers are available in different coating combinations, blends or copolymers, film thickness and fiber assemblies, enhancing the possible application of SPME technique. On the other hand many scientists are engaged in developing new sorbents coated on SPME fibers. Recently, The use of polyaniline- and polypyrrole-based sorbents have been Demonstrated on SPME fibers [3-7] and it appeared that these polymers are quite efficient in extracting phenolic compounds and have some advantages over some commercial sorbents [7].

In recent years, composites of polyaniline and carbon nanotubes (CNTs) have attracted enormous interest due to their unique properties. For instance, Wallace et al. have reported that these composites exhibited significant improvement in mechanical strength and conductivity [8].

In another interesting paper, Guo et al. have used a fabricated polyaniline – CNT composite for the reduction of nitrile and found out that the composite is much more efficient than merely polyaniline or

CNT modified electrodes [9]. Luo et al. developed a biosensor with improved performance by using carbon nanotube-doped polyaniline [10]. Their invention was based on the highly effective adsorbing property of CNTs.

In the present work we established a method for preparation of polyaniline-CNT coated platinum wire (SPME Fiber) and investigated their capability to extract phenol from aqueous samples.

The Platinum wires were polished with a weighing Paper, then rinsed with double- distilled water and cleaned in an ultrasonic bath and finally electrochemically treated in 0.1 M sulfuric acid by potential cycling between – 0.1 and 1.5 V versus Ag/AgCl electrode until a stable cyclic voltammogram was obtained.

Experimental

Reagents and instrumentation

Aniline, Phenol, acetonitrile, hydrochloric acid were of extra- pure grade and were purchased from Merck (Darmstadt, Germany). Aniline was vacuum distilled and stored under argon. Single walled carbon nanotubes were purchased from Iran Petroleum research center.

Electrochemical experiments were conducted on a three-electrode polarograph system with a platinum wire (i.d.=0.2 μm) as the working electrode; a platinum electrode as the counter electrode and a Ag/AgCl reference electrode. All the experiments were carried out at room temperature in pH of using a phosphate buffer solution (0.1 M)

SPME syringe was purchased from the chromatographic system used was a thermo model 2000 gas chromatograph coupled to a mass detector.

Electronic impact was used at 70 eV as ionization method. The chromatographic separation was carried out on a HP-5 capillary column 15 m × 0.33 mm i.d. with 0.5 μm film thickness.

Preparation of SPME fibers

Plane polyaniline coated fibers were prepared electrochemical oxidation of aniline on the surface of a platinum wire (0.2 μm diameter). In brief a three- electrode system with a solution of 0.2 mol/L

aniline in acetonitrile/water (70:30) was used, and a 7.5 cm long platinum wire was mounted as working electrode. A platinum electrode as the counter electrode and a Ag/AgCl electrode was used as reference electrode.

Polyaniline coating was deposited on the platinum wire by potential cycling between -0.1 and +1.1 V at scan rate of 100 mV/s after 27 cycles.

The same system was used for the preparation of SPME fibers coated by polyaniline - CNT composite. CNT was added into the solution at the amount of 20 µg CNT/1 ml.

During the polymerization process, the surface of platinum wire turned into green- black color. After coating, the SPME fiber was washed by acetonitrile and double distilled water several times to remove any remaining aniline or CNT particles. The fiber was then dried under a gentle nitrogen stream and conditioned for 24 hours at 200°C in a vacuum oven prior to their use.

SPME extraction procedure

Two sets of SPME fibers were prepared as described above: plane polyaniline coated fibers and polyaniline - CNT coated fibers.

Plane polyaniline and polyaniline- CNT SPME fibers were Placed in standard phenol solutions in water (0.05, 0.1, 0.5, 1, 10, 20, 50, 100, 200 ppm) for 2 hours. During extraction the temperature was maintained at 25°C without stirring the solutions the fibers were then withdrawn and dried under a stream solute of N₂ gas for 30 minutes. A SPME syringe was used to insert the fibers onto the injection port of GC chromatograph.

GC condition

The injection port of GC chromatograph was set at 260°C. The carrier gas was helium at the flow rate of 1.0 ml/min, The initial Column temperature was 60°C which was programmed to increase at the rate of 15°C/min reaching to the final temperature of 250°C and staying at this temperature for 2 minutes. The total run time was 10 minutes.

Results and Discussion

Preparation and characterization of CNT-polyaniline coated fibers

Since CNTs have a large surface area and high surface energy, they can strongly adsorb different chemical compounds. On the other hand the ability of polyaniline coating in extracting polar and nonpolar compounds such as phenol and nitrobenzene from water has been shown by Bagheri et al. [7], Mousavi et al. [11], and Guo et al. [9] have successfully used CNT- polyaniline composites to increase the reducing property of these types of polymers and Luo et al. have shown that the doping of polyaniline film with CNTs will increase the enzyme immobilization capability of the resulting polyaniline films [10].

It is therefore expected that the doping of polyaniline with CNTs increase the extracting capability of these polymers.

Based on this rationale CNT- doped polyaniline coating was prepared on platinum wires and their performance as a SPME probe was evaluated.

Optimum coating condition

Polyaniline can be deposited on platinum wire by electropolymerization of aniline in an electrochemical cell. The quality of the polymer can be greatly influenced by reaction medium.

Sulfuric acid is the most suitable medium for electropolymerization of aniline. The optimum concentration of sulfuric acid was found to be 0.1 M in the presence of 0.1 M aniline in water.

Cyclic voltammetry was employed as a highly convenient and reproducible method. The thickness of the coated film is controlled by the number of CV cycles. The best Scan range was found to be -0.1 to +1.1 V. Electrochemical behavior of CNT-doped polyaniline composite and plane polyaniline coatings were monitored in 0.1 M H₂SO₄ through Their Voltammograms.

Figures 1A and 1B shows voltammograms obtained for the electrochemical deposition of polyaniline in sulfuric acid on the platinum wire in presence (a) and in absence (b) of CNTs. These two types of polyaniline coatings were used to extract phenol from its aqueous solutions at concentrations ranging from 0.1 ppm to 100 ppm under the same conditions. The amount of extracted phenol from these solutions was measured using GC/MS. The result showed that the amount of extracted phenol by The CNT- polyaniline coating was about two fold that of the one without CNTs, for all the concentrations within 0.1- 100 ppm range. It could be suggested that the composite material with CNTs has both an increased surface area and an elevated adsorptive capacity which leads to this overall increase in extracted phenol.

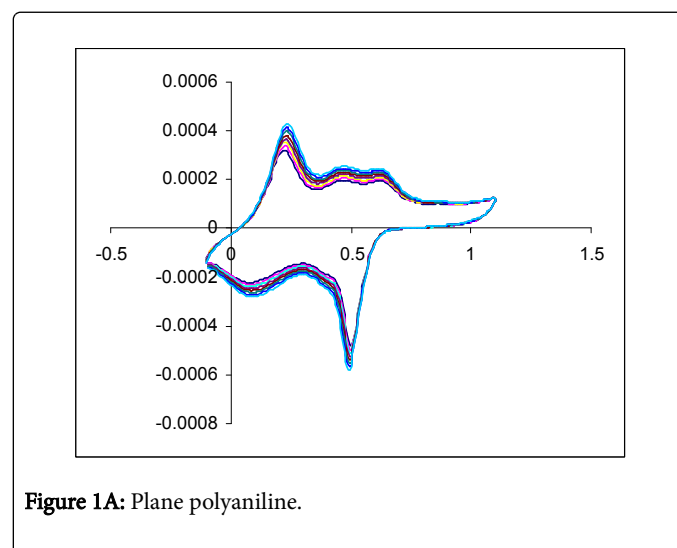


Figure 1A: Plane polyaniline.

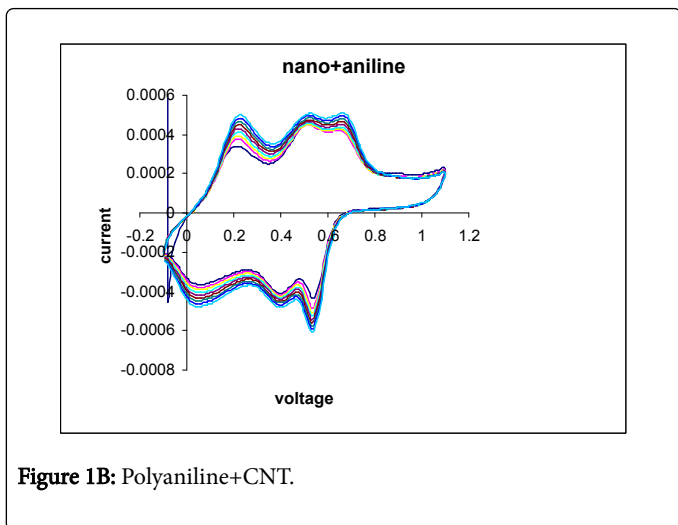


Figure 1B: Polyaniline+CNT.

This is in agreement with the Ficks first law of diffusion which has been proposed as the fundamental rule which governs the extraction process for SPME fibers with very small inner diameter of the diffusion path. The anodic Current and The cathodic current For polyaniline-CNT fibers are larger than those of polyaniline fibers.

This indicates that polyaniline- CNT fiber has a larger effective surface area Moreover, The obvious differences in the peak currents implies that the amount of polyaniline on the fibers in the presence of CNT is higher than the amount of polyaniline in the absence of CNT. The middle peak in the voltammograms could be related to the presence of a side product. There are no obvious difference in the redox peak potentials between the two types of fibers which shows that change of the substrate from aniline to aniline - CNT has no significant effect on the electrochemical behavior of polyaniline film.

The SEM images of the polyaniline films and polyaniline-CNT composites are shown in Figures 2A and 2B respectively. These images reveals that the two types of polymers have significant difference in the size and shape of polymer aggregates. The average size of aggregates in the polyaniline fibers is in micrometer scale while the average size of these aggregates in polyaniline-CNT composites is around 500 nm. This is in agreement with the larger extracting capacity of polyaniline-CNT composite fibers which has been observed for them in comparison to the plane polyaniline fibers.

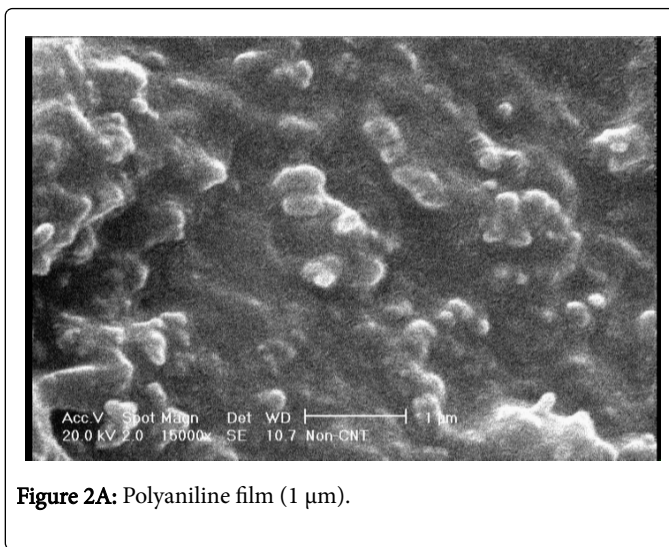


Figure 2A: Polyaniline film (1 μm).

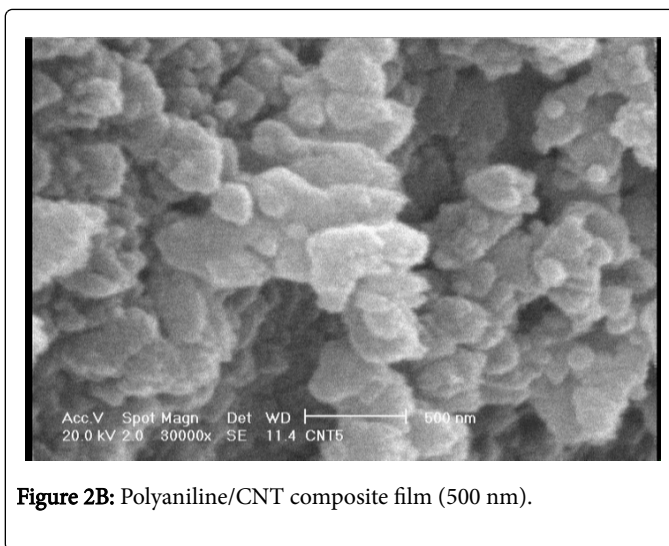


Figure 2B: Polyaniline/CNT composite film (500 nm).

Interestingly the higher peak current observed in voltammogram of polyaniline-CNT fibers also confirms the larger surface area for these fibers.

Figure 3A shows the SEM of plane polyaniline and Figure 3B shows the SEM of polyaniline-CNT composite and Figure 3C shows the SEM image of carbon nanotubes before being used in polymerization process.

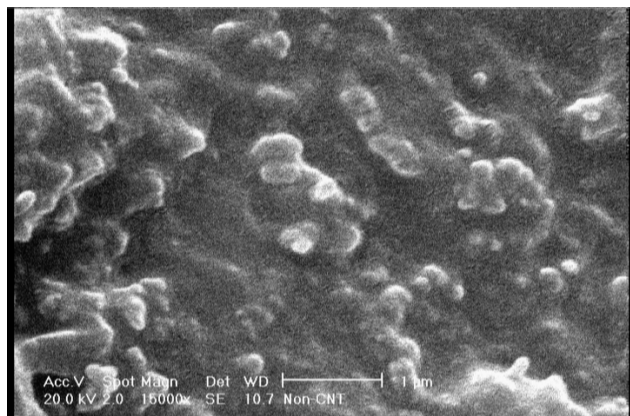


Figure 3A: Polyaniline(PANI film) the scanning electron micrographs of PANI fiber.

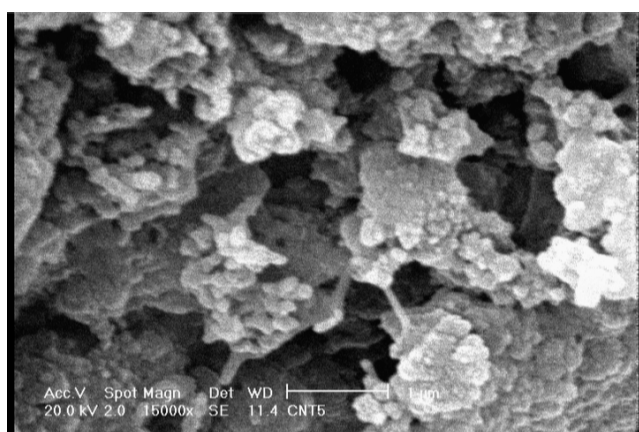


Figure 3B: PANI/CNT composite film coated on a platinum wire (7.5 cm, 0.2 μm i.d.).

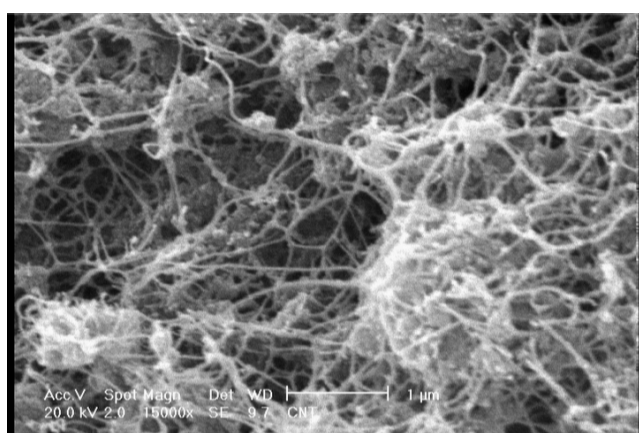


Figure 3C: CNT coated on a platinum wire (7.5 cm, 0.2 μm i.d.).

As can be seen, Carbonnanotubes are wrapped with polyaniline aggregates and it could be speculated that in the presence of CNTs, polyaniline grows around the CNTs and encapsulate them.

This could be the reason for the greater capacity of polyaniline-CNT composites for extracting phenol from aqueous solutions.

In fact CNTs provide a scaffold for the deposition of polyaniline and apparently this leads to the formation of smaller aggregates and thus larger effective surface area for the adsorption.

Conclusion

In conclusion the present research revealed that CNTs could be used successfully in the preparation of SPME fibers and they can greatly enhance the performance of these fibers. Electrochemical evidence as well as SEM images indicate that the presence of CNTs in the electrochemical cell while the process of polymerization is in progress causes the formation of polymers with larger surface area and thus more extracting capability.

In a more general sense it could be concluded that the doping of electrochemically produced polymers for SPME with CNTs will enhance the adsorbing capacity of the resulted films. This could open a new horizon in the application of Nanoparticles and Nanotechnology in the Field of Solid Phase Microextraction (SPME) and analytical Chemistry.

Further studies about the preparation of Other SPME coatings in the presence of CNTs are being conducted.

In the meanwhile the Stability of these type of polymers are being studied under different conditions in order to find out whether they are capable of being used for several times. Apart from being easy and inexpensive, electrochemical preparation of CNT-doped coatings of CNT-doped coatings for SPME purposes is also quite flexible and the thickness of the fibers can be controlled by the number of CV cycles.

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