Dye-doped Nanostructure Polypyrrole Film for Electrochemically Switching Solid-phase Microextraction of Ni(II) and ICP-OES Analysis of Waste Water

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A nanostructure fiber based on conducting polypyrrole synthesized by an electrochemical method has been developed, and used for electrochemically switching solid-phase microextraction (ES-SPME). The ES-SPME was prepared by the doping of eriochrome blue in polypyrrole (PPy-ECB) and used for selectively extracting the Ni(II) cation in the presence of some transition and heavy metal ions. The cation-exchange behavior of electrochemically prepared polypyrrole on stainless-steel with and without eriochrome blue (ECB) dye was characterized using ICP-OES analysis. The effects of the scan rate for electrochemical synthesis, uptake and the release potential on the extraction behavior of the PPy-ECB conductive fiber were studied. Uptake and release time profiles show that the process of electrically switched cation exchange could be completed within 250 s. The results of the present study point concerning the possibility of developing a selective extraction process for Ni(II) from waste water was explored using such a nanostructured PPy-ECB film through an electrically switched cation exchange.

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Solid-phase microextraction (SPME) is a well-established technique, and due to its advantages over other sample-preparation techniques it is a convenient and solventless sample-preparation method that utilizes a thin polymer film coated on a silica fiber as an extraction phase. SPME has been used for the preconcentration and cleanup of numerous different classes of compounds in a variety of matrices.¹⁻⁷ It has advantages of simplicity, low cost, ease of use and rapid preconcentration and extraction of analytes that exist in low concentrations. The method successfully combines sample cleanup and preconcentration into one step. However, the neutral charge of commercially available SPME coatings results in a low coating/sample partition coefficient and poor recoveries for ionic analyte, which limited its application. Chemical modification of the sample or fiber's surface by derivatization or by the addition of complexing agents can increase the extraction efficiency. However, these reactions require expensive and toxic reagents, and sometimes produce unstable products. The most promising alternative to the extraction of ionic compounds is the use of conductive polymers as the extraction phase. The electroactivity and reversible redox properties of conductive polymers, especially polypyrrole (PPy), have attracted great interest in the development of electrochemically delivery devices. For these separation systems for charged species,⁸⁻¹⁰ electrochemical redox of the polymer is accompanied by movements of the dopants in and out of the polymer film for charge balance. The electrochemical doping/undoping features of certain conducting organic polymer electrodes could be advantageous as SPME films for the preconcentration and matrix separation of anionic,⁹⁻¹¹ cationic¹¹⁻¹³ and neutral

analytes.^{14,15} Polypyrrole and its derivatives have attracted great interest in the development of electrochemically switched solid-phase microextraction (ES-SPME) as ion-exchange material for charged species.¹⁶⁻¹⁸ The main advantage of using conducting polymers in SPME is that the charge of the coatings can be readily controlled by the oxidation and reduction of the polymers. PPy with small counter-ions, *e.g.*, Cl⁻, ClO₄⁻ and NO₃⁻, mainly exhibits an anion exchanger behavior due to the high mobility of these ions in the polymer matrix. Cation exchanger behavior can be achieved by incorporating large polyanionic counter-ions, such as polystyrene sulfonate (PSS), because of their immobility in the polymer matrix.¹⁹ An organic coating film based on overoxidized sulfonated polypyrrole (OSPPy) was also studied.²⁰ The OSPPy film is an extension of using overoxidized polypyrrole for enhancing the selectivity towards cations.²¹⁻²³ The functionalization of polypyrrole film electrodes²⁴ can be achieved by the electrostatic incorporation of multi-charged anionic complexing ligands during the electropolymerization step, or using active groups that are covalently attached to the polymeric skeleton. These complexing film materials have been synthesized, in two steps, by chemical derivatization moieties of conducting polymer films previously coated by electropolymerization onto electrodes, and then applied as a cation-exchange film that might be useful for ES-SPME. Obviously, a more straightforward and efficient route for the synthesis of chelator-modified electrodes is the electropolymerization of monomers substituted with specific complexing groups.

In electrochemically controlled ion exchange and solid phase microextraction devices, the ion-exchange capacity of conductive film was generally controlled by the thickness of the film. To improve the ion-exchange capacity of conductive film, materials with very large surface areas should be used. Increasing the

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Table 1 Instrumentation of ICP-OES and used conditions

ICP-OES condition (radial torch)	
Plasma gas	Argon
Power/kW	1.5
Plasma flow rate/L min ⁻¹	15
Auxiliary flow rate/L min ⁻¹	1.5
Nebulizer pressure/kPa	160
Viewing height/mm	8
Replicates	3
Replicate read time/s	1
Wavelength/nm	
Ni(II)	231.604
Cr(III)	267.716
Co(II)	228.615
Cu(II)	324.754
Cd(II)	228.802
Zn(II)	213.857
Pb(II)	220.353

surface area of the electrode, while keeping the film thickness constant, is consequently an obvious alternative way to improve the ion-exchange capacity of the electrode. A high specific surface area conductive PPy cellulose composite material potentially useful in various electrochemically controlled ion-exchange and separation processes was described by Mihranyan *et al.*²⁵

The present study describes the electrosynthesis of a dye-doped PPy containing eriochrome blue (ECB) as a multi-charged anion, and its ion-exchange properties in aqueous solution.

This combination features both fast electrochemical synthesis with cation exclusion properties and electrostatic interaction of cations enhanced by the presence of the negatively charged sulfonate group. Moreover, in this ES-SPME, the accumulation in dye-doped PPy of cations with more interacting with dye molecule should be largely enhanced due to concurrent effects of ion-exchange at the sulfate moieties, and complex formation with the chelating sites of the dye. We report herein study of different parameters, such as the effect of the scan rate of electropolymerization films on the extracted amounts of ions, the uptake/release potential, the uptake/release time of the analyte, percent recovery, interferences and figures of merits for the selective extraction and ICP-OES analysis of Ni(II) in the presence of other cations in aqueous samples.

Experimental

Chemicals and reagents

Pyrrole (99%) was obtained from Merck (Darmstadt, Germany) and distilled before use. Eriochrome blue (SE), sodium dodecylbenzenesulfonate (SDBS), nitrate salts of the cations and NaCl were obtained from Sigma-Aldrich (Deisenhofen, Germany), and used without further purification. All solutions were prepared by appropriate dilution from stock solutions (1000 mg L⁻¹).

Apparatus

The electrochemical polymerization of pyrrole was carried out using Behpajuh (BHP 2061-C Model) potentiostat (Isfahan, Iran). An electrochemical cell including a stainless-steel rod working electrode (2 cm × 1 mm o.d.), a Pt counter electrode and an Ag/AgCl electrode, as a reference electrode was used for preparation of the polymer. Prior to each electrochemical

Fig. 1 Cyclic voltammogram of a 0.1 mol L⁻¹ pyrrole solution containing 2.5 × 10⁻³ mol L⁻¹ ECB on bare stainless-steel (a) and modified stainless-steel electrode (b) at a scan rate of 50 mV s⁻¹.

polymerization, all solutions were deoxygenated by purging, and them with nitrogen for 10 min; the working electrode was cleaned in methanol by using an ultrasonic bath for 15 min, and was subsequently washed with distilled water before electropolymerization. All pH measurements were performed at 25 ± 0.1 °C by using a pH/ion-meter Metrohm 713 with a standard uncertainty of 0.1 mV (Metrohm, Switzerland). The IR spectra (4000 – 500 cm⁻¹) were recorded on an IR100 Model FT-IR spectrometer (Nicolet, USA). Scanning electron micrographs (SEM) of the fiber surface were obtained using a Philips XL30 scanning electron microscopy (Holland). A radial-view Varian Vista-Pro simultaneous ICP-OES (Spring-vale, Australia) coupled to a V-groove nebulizer and equipped with a charge-coupled device (CCD) was applied for the determination of metal ions. The operational conditions and selected wavelengths for ions are summarized in Table 1.

Preparation and characterization of the PPy-ECB cation exchanger electrodes

Polypyrrole film was prepared electrochemically using a three-electrode system using a cyclic voltammetry (CV) technique from -0.4 to +0.7 V vs. Ag/AgCl. The PPy-ECB film was not directly electrodeposited on the surface of the working electrode (stainless-steel rod) in an aqueous solution containing pyrrole (0.1 mol L⁻¹) and ECB (2.5 × 10⁻³ mol L⁻¹) as an anion dopant. The electropolymerization of pyrrole is inefficient in a dye solution. For example, cyclic voltammetry experiment has shown that the pyrrole oxidation peak is abnormally weak for ECB under these experimental conditions, and the oxidation current is low (Fig. 1). Stable dye-doped fibers have been synthesized in two steps; in the first step, an electrode coated by pre-electropolymerization with the presence of 0.1 mol L⁻¹ pyrrole and 0.01 mol L⁻¹ DBS⁻ as a hydrophobic anion dopant with a scan rate of 50 mV s⁻¹ at potential range of -0.4 to +0.7 V vs. Ag/AgCl and the number of scans was set at 10 cycles. After the pre-electropolymerization step, the modified

Fig. 2 Fourier-transform infrared spectra of PPy, ECB, and PPy-ECB.

electrode was transferred into a mixture of 0.1 mol L^{-1} pyrrole and $2.5 \times 10^{-3} \text{ mol L}^{-1}$ ECB aqueous solution, in which the dye-doped polypyrrole was coated on the surface of the modified electrode under the same electrochemical conditions as in the first step. In contrast, a well-developed pyrrole oxidation wave is observed after pre-electropolymerization, and was then applied to the ES-SPME and an analysis of the metal ions. The formation of a conducting PPy film was evidenced by an increase of the oxidation current. For achieving good physical stability of the synthesized polymer, the second step was performed in a mixture of 0.1 mol L^{-1} pyrrole, $2.5 \times 10^{-3} \text{ mol L}^{-1}$ ECB and $2.0 \times 10^{-4} \text{ mol L}^{-1}$ DBS⁻ aqueous solution. For comparison, a conducting non-dye-doped PPy was prepared in a similar manner as described above, with concentrations of 0.01 mol L^{-1} DBS⁻ as the non-chelating anion dopant (in the absence of ECB) to investigate the extraction ability of PPy-ECB film.

The FT-IR spectra of a PPy-ECB film synthesized on a stainless-steel sheet under the same conditions are shown in Fig. 2, and were compared with the ECB and PPy spectra. The absorption band at around 1455.9 cm^{-1} , which is a characteristic band related to -N=N- stretching in the azo group, as shown in Fig. 2, suggests that ECB is doped in the PPy film.

ES-SPME of cations

Before the experiments the PPy-ECB fibers were washed with water to remove excess pyrrole and electrolyte. It was then transferred to a 12-mL sample of aqueous target solutions (300 ng mL^{-1}) for extraction, by applying a negative potential under stirred conditions. After extraction, the PPy-ECB fiber was washed with water, and then transferred to a cell containing $1.2 \text{ mL } 0.01 \text{ mol L}^{-1}$ NaCl solutions, where the analyte was released at a positive potential. The uptake potential was -1.2 V , and the released potential was $+1.0 \text{ V}$ for all cations vs. reference electrode. All data points reported in this work represent the average of three replicates.

Results and Discussion

Properties of the extraction phase (effect of ECB)

ECB is a sulfonated dihydroxyazo dye and is a sensitive reagent as an indicator in the complexometric determination of heavy and transition metal ions.²⁶ The chelating property of ECB and its application for the separation of heavy and transition-metal ions were also reported in the literature.²⁷ The structure of ECB

Scheme 1 Structure of eriochrome blue SE (ECB).

Fig. 3 Extraction ability (accumulation and release amounts per fiber) of PPy-ECB fibers prepared under different scan rates. pH of uptake solutions, 6; concentration for all cations, 300 ng mL^{-1} .

is shown in Scheme 1. The doping of negatively charged groups (*i.e.*, sulfonates) of ECB to the PPy induces the cation exchange properties of the PPy-ECB film; the ionic exchangeability feature of the PPy-ECB film plays a key role in the uptake and release processes. However, these processes and electrical properties of the polymer are also influenced by the surface morphology. The morphology of polymeric films is one of the determining features in their ability to serve as an SPME device, since the porosity of the film surface and the size of the inclusion sites differ under differing polymerization conditions.²³ Since it is essential for the polymer to adhere well to the electrode after synthesis, the electrochemical method was employed. The effect of the presence of ECB as a chelating anion dopant in the PPy is also clearly seen in the extraction of ions. This can be seen in Fig. 3 from a comparison of the dye-doped PPy and non-dye-doped PPy (column 7). The result of Fig. 3, indicating that chelating ability of dye (ECB) in addition to the exchange property of the sulfonate group enhanced the extraction property of fiber in comparison to the DBS⁻ as the non-chelating anion dopant (sulfonate and OH groups that are able to capture cations in the solution phase).

Effect of the scan rate on the extracted amounts of ions

The morphology of fiber film can be controlled by the electrochemical conditions. Thus, the effect of the scan rate of film synthesis on the extracted amounts of ions by PPy-ECB fiber was also investigated. The extraction ability of PPy-ECB fibers prepared by the CV technique at various scan rates is shown in Fig. 3. Good extraction ability was observed for PPy-ECB films prepared under scan rates of $5 - 30 \text{ mV s}^{-1}$. The scan rate for the synthesis of polymer film influences the

Fig. 4 Scanning electron micrograph of the dye-doped polypyrrole fiber PPy-ECB at different scan rates: (a) 10 mV S⁻¹, (b) 50 mV S⁻¹ with 30000-fold magnification.

extraction efficiency due to the increased surface area. The film structure is highly effective on the surface area up to a certain value due to the porous nanostructure. However, the extraction ability diminished at higher scan rates.

The surface characteristics of the polymer films were investigated by scanning electron microscopy. Figure 4 shows micrographs of the PPy-ECB fiber at different scan rates of 10 and 50 mV s⁻¹ with 30000-fold magnification. As can be seen from Fig. 4, the electrochemical coating possesses a porous nanostructure with a “cauliflower” morphology, and the surface of the polymer films is very-well distributed (50 – 100 nm, Fig. 4a). The scan rates for the synthesis of the dye-doped coatings used in this study were 10 mV s⁻¹. The physical adhesion of the film to the bare stainless-steel wire surface was also affected by the electrodeposition process. Different metallic wires, such as platinum and steel, can be used as ES-SPME fibers. The process of electrodeposition of dye-doped PPy on steel fiber is very simple and not expensive. The coating also showed good adhesion onto the steel surface. The average film thickness was calculated to be 72 ± 5 μm by comparing the coated and bare wire images. The film lifetime is important for practical applications. We used the PPy-ECB fiber for the extraction of different cations from aqueous solutions 3 times. The extraction efficiency results showed that it had no obvious decline after a PPy-ECB fiber was used for 3 times; it was still both stable and reusable. However, the film lifetime and stability were dominated by the potential ranges.

The fiber-to-fiber reproducibility was also investigated. To evaluate the reproducibility of the electrochemical coating procedure, three different fibers were coated under the same

Fig. 5 Effect of varying uptake potential (release potential, +1.0 V) and release potential (uptake potential, -1.2 V) of PPy-ECB film on the accumulation (a) and release amounts (b) of different cations per fiber. Uptake and release time, 250 s; pH of the uptake solutions, 6; concentration for all cations, 300 ng mL⁻¹.

synthetic conditions. After performing microextractions of different cations under similar experimental conditions, the results of ICP-OES analysis were found to be almost identical within the precision of the method (RSD = 3.3 – 8.4%). The electrochemical switching uptake and release of different cations by the PPy-ECB fiber was examined both under the open circuit and controlled potential conditions. The cation uptake at open circuit was very slow, even for times longer than 20 min, and was not released to any measurable extent at open circuit during a period of 30 min (data are not shown).

Effect of the uptake and release potential

The effect of the uptake and release potential on the accumulation and release of different cations was achieved by applying different positive and negative potentials, respectively. The PPy-ECB fiber was immersed in 300 ng mL⁻¹ of different cations into deionized water during a period of 300 s. The negative charges of PPy-ECB films were responsible for the accumulation of cations during the applied negative potentials in the extraction step. To determine the effect of the release potential on the cation release capacity of the polymer film, after the extraction step PPy-ECB fiber was washed with water, and then transferred to a 1.2-mL cell containing 0.01 mol L⁻¹ NaCl solution and applied released potential vs. Ag/AgCl reference electrode for 300 s. Figure 5 shows the effect of the uptake and release potentials on the extraction behavior of PPy-ECB for different cations. The uptake of the ions to the film was found to increase with increasing cathodic potential up to -1.2 V vs. Ag/AgCl. The optimum uptake and release potentials were found to be -1.2 and +1.0 V with the highest responses for all cations, respectively.

Fig. 6 Effect of the uptake (a) and release (b) time of PPy-ECB film on the accumulation and release amounts of different cations per fiber. Applied potential for uptake, -1.2 V; release potential, $+1.0$ V; pH of the uptake solutions, 6; concentration for all cations, 300 ng mL^{-1} .

Effect of the uptake and release times

The uptake and release times are equivalent to the time needed to reach equilibrium at the coating/solution interface for a given PPy-ECB film for the extraction and desorption steps. It should be noted, however, that the PPy-ECB film used as ES-SPME coatings in this study showed remarkably short equilibration times for the analytes (*ca.* 150 – 250 s). The uptake and release time profiles of 300 ng mL^{-1} of Pb(II), Cd(II), Cr(III), Co(II), Ni(II), Cu(II) and Zn(II) at PPy-ECB film are given in Fig. 6. From the data depicted in Fig. 6, the optimum time used for uptake and release was 250 s. To determine the linearity behavior of PPy-ECB fiber for the extraction of Pb(II), Cd(II), Cr(III), Co(II), Ni(II), Cu(II) and Zn(II) ions by using ES-SPME method, a series of mixed standard solutions of these ions in the concentration range of 20 to 1000 ng mL^{-1} were tested under the optimum conditions. Calibration curves were observed by simultaneously measuring the ICP-OES peak intensity *versus* the concentration of each cation. The theoretical limits of detection (LODs), calculated as the amount, gives a reading equal to three-times the standard deviation of a series of the procedural blank signals. It can be estimated as

$$\text{LOD} = 3\sigma_b/(\text{calibration sensitivity}). \quad (1)$$

The LODs were in the range of 4 – 20 ng mL^{-1} . Their corresponding figures of merit are listed in Table 2. From these results we concluded that PPy-ECB fiber could reliably be used as an ES-SPME element for cations such as Pb(II), Cd(II), Cr(III), Co(II), Ni(II), Cu(II) and Zn(II). The data clearly show that based on the extracted amounts of Ni(II) relative to other ions in the same concentration and conditions, PPy-ECB fiber

Table 2 Figures of merit for calibration curves of EC-SPME-ICP-OES measurements and exchange capacity of fiber for different ions

Ion	Linear range ^a / ng mL^{-1}	Selectivity ^b	Exchange capacity/ $\mu\text{g g}^{-1}$	R^2	RSD, % ^c	Limit of detection ^d / ng mL^{-1}
Ni(II)	1000 – 20	6.1	811.7	0.989	4.9	4.3
Cr(III)	1000 – 50	3.7	492.5	0.982	4.4	5.8
Co(II)	300 – 100	1.6	213.0	0.993	5.0	10.0
Zn(II)	1000 – 30	1.8	239.6	0.992	5.8	8.7
Pb(II)	800 – 100	2.7	359.4	0.976	7.4	17.3
Cu(II)	1000 – 50	1.0	133.1	0.983	6.3	6.2
Cd(II)	1000 – 50	2.5	332.8	0.991	4.6	8.6

EC-SPME condition: E_{uptake} , -1.2 V; E_{release} , $+1.0$ V; t_a , 250 s; t_d , 200 s.

a. All data points represent the average of three replicates.

b. Based on the extracted amounts of ions relative to Cu(II) ion in the same concentration (300 ng mL^{-1}) by PPy-ECB fiber.

c. RSD% calculated from three separate experiments for 100 ng mL^{-1} concentration of analyte.

d. Three times of the standard deviation of blank measurements.

has a unique selectivity property towards Ni(II) in the presence of other cations and confirms that the complexation/decomplexation process of PPy-ECB film is an effective sample cleanup.

The effect of uptake pH solutions on the extraction of Ni(II) by PPy-ECB fiber was also studied (Fig. 7). The accumulation pH of 5 – 8 was found to give the highest responses for the Ni(II) ion (increases the uptake capacity of the film), while at more acidic and basic pH values there was a considerable decrease in the uptake capacity of the PPy-ECB fiber both below and above these pH values. Because of protonation of the anionic groups of the ECB, the extraction yield decreased in a highly acidic medium (monoprotic dissociation constant, $\text{pK} = 7.3$).²⁸ This effect increased with decreasing pH value of the uptake solution. In high basic solutions the solubility of the cation decreases, and then the extraction yield decreases in a highly basic medium. The accumulated cation to the PPy-ECB fiber surface desorbs into the extraction solution in a lightly acidic medium. Therefore, the optimum pH of the uptake solution was found to be 5 – 6.5. For this reason, the pH of the medium in which the extraction occurred with the PPy-ECB fiber was adjusted to 5.5 (this means that the metal ions are present as free metal ions in the uptake solution).

The ion-exchange capacity of PPy-ECB fiber can be obtained approximately based on the thickness ($72 \mu\text{m}$) and density of the polymer. If we assume the density of the film to be 1.5 g cm^{-3} ,²⁹ then the ion-exchange capacity of PPy-ECB fiber for Ni(II) ion is estimated to be $811.7 \mu\text{g g}^{-1}$ (0.03 meq g^{-1}) under the optimal conditions (Table 2). It is, hence, clear that only a small portion of the polymer layer is active for uptake and ion exchanging.²⁵ The extraction of Ni(II) ion by sulfonated overoxidized PPy with a film thickness of $300 \mu\text{m}$ and an exchange capacity of $0.86 - 1.46 \text{ meq g}^{-1}$ was reported by Tamer *et al.*²⁰

Application of ES-SPME-ICP for the analysis of Ni(II) in real samples

To evaluate the reliability of the proposed method, three real water samples, Zayaneh Rood River (Isfahan, Iran), waste water and tap water (Tehran, Iran) were collected in amber glass bottles (1000 mL). The bottles were rinsed several times with the water to be analyzed. No Ni(II) was found in any tap-water

Fig. 7 Effect of the uptake pH solutions on the extraction of 300 ng mL⁻¹ of Ni(II) by PPY-ECB fiber. Applied potential for uptake, -1.2 V; release potential, +1.0 V; uptake and release time, 250 s.

Table 3 ES-SPME by PPY-ECB and ICP-OES analysis of Ni(II) in real water samples

Sample	Added	Found	Recovery, %
Tap water (<i>n</i> = 6)	0	ND ^a	
Tap water (<i>n</i> = 6)	50	52 ± 3.2 ^b	104 ± 6
Zayandeh Rood river (<i>n</i> = 3)	0	358 ± 6.1	
Waste water (<i>n</i> = 3)	0	98 ± 8.6	

a. Not detected.

b. Mean ± SD (ng L⁻¹).

sample under ES-SPME-ICP-OES analysis. Thus, the tap-water sample was spiked with 50 ng mL⁻¹ of Ni(II). The other water samples were filtered before analysis. Finally, the water samples were analyzed for Ni(II) by the ES-SPME-ICP-OES method under the optimal conditions. The analytical results are summarized in Table 3. These results show that ES-SPME, using the PPY-ECB fiber, is an effective sample cleanup method, and allows selective monitoring of Ni(II).

Conclusions

The electrochemical synthesis nanostructure dye-doped PPY offers a simple and convenient technique for the preparation of ES-SPME fibers. The porous structure, inexpensive and easy preparation, selective interaction and reproducible preparation are among the clear advantages of the proposed method. The selectivity of the polymer film can be controlled by the type of dye-doped based on the electrochemical conditions. Dye-doped polypyrrole (PPY-ECB) as a fiber was introduced and evaluated for the extraction of Ni(II) from water samples. The combination of ES-SPME by dye-doped PPY fiber with ICP-OES can achieve a rate enhancement of the cation uptake and release due to potential switching, an effective sample cleanup, low LODs, and reproducible applied for the extraction and determination of cations in real samples. However, the preconcentration factor of PPY-ECB fiber (2.5) is not very impressive.

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