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Article

Preconcentration and Determination of Organochlorine Pesticides in Seawater Samples Using Polyaniline/Polypyrrole-Cellulose Nanocomposite-Based Solid Phase Extraction and Gas Chromatography-Electron Capture Detection

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Neste trabalho, o papel de filtro quimicamente modificado com polianilina/polipirrol (PANI/PPY), denominado de nanocompósito PANI/PPY/celulose, foi preparado e usado como sorvente para extração em fase sólida (SPE) para a pré-concentração e extração de alguns pesticidas organoclorados (OCPs) em amostras de águas naturais. O sorvente proposto também foi caracterizado por microscopia eletrônica de varredura (SEM), que mostrou que polímeros globulares poderiam ser incorporados pelas fibras de celulose da folha de papel. Vários parâmetros experimentais relacionados à pré-concentração de OCPs no papel de filtro recoberto também foram examinados. Os resultados experimentais mostraram que o papel de filtro recoberto por PANI/PPY poderia extrair OCPs com fatores de enriquecimento relativamente altos. A avaliação também exibiu um intervalo dinâmico dos OCPs de 5-250 μg L^{-1} com um coeficiente de correlação (R^2) apropriado. Os limites de detecção de heptacloro, aldrin, dieldrin, endrin e 4-diclorodifeniltricloroetano (4-DDT) foram determinados como sendo 0,39, 0,28, 0,47, 0,51 e 0,31 μg L^{-1}, respectivamente. O método proposto também foi aplicado na análise de OCPs em amostra de água do mar e as recuperações dos analitos foram na faixa de 77,4 a 102,7%.

In this work, the chemically modified filter paper with polyaniline/polypyrrole (PANI/PPY), denoted as PANI/PPY/cellulose nanocomposite, was prepared and used as the solid phase extraction (SPE) sorbent for preconcentration and extraction of some organochlorine pesticides (OCPs) in natural water samples. The proposed sorbent was also characterized with scanning electron microscopy (SEM) and exhibited that globular polymers could incorporate into the cellulose fibers of the paper sheet. Several experimental parameters related to the preconcentration of OCPs on the coated filter paper were also examined. The experimental results showed that the PANI/PPY coated filter paper could extract OCPs with relatively high enrichment factors. The evaluation also exhibited a dynamic range of 5-250 μg L^{-1} for OCPs with proper correlation coefficient (R^2). The limit of detections of heptachlor, aldrin, dieldrin, endrin and 4-dichlorodiphenyltrichloroethane (4-DDT) were found to be 0.39, 0.28, 0.47, 0.51 and 0.31 μg L^{-1}, respectively. The proposed method was also applied for analysis of OCPs in seawater sample and the recoveries of analytes were in the range of 77.4 to 102.7 %.

Keywords: polyaniline/polypyrrole, cellulose, nanocomposite, solid phase extraction, organochlorine pesticides, seawater, gas chromatography

Introduction

Conducting polymers (CPs) have been widely studied since their introduction in the 1970s due to their high conductivity, low energy optical transitions, low ionization potential and high electron affinity.[1] The suitable properties of CPs can be arisen from the conjugation of π electrons by single and double bonds along the polymer chain which allows for the efficient transfer of electrons along the polymer backbone.

The utilization of CPs has expanded to various fields such as fuel and solar cells, lightweight batteries, electrochromic devices, sensors, artificial muscles, corrosion protective coatings, field effect transistors, light emitting diodes, and separation science.[2-5]

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Among different CPs developed for valuable applications, polypyrrole (PPY) and polyaniline (PANI) are investigated intensively due to their reasonably high conductivity, good stability of the oxidized state, electrical, optical and electrochemical properties, solubility in water and ease of processing.[1,6] PPY and PANI were also applied in separation science, as packing material in solid phase extraction (SPE),[7,8] headspace SPE,[9] magnetic SPE,[10] and fiber material for solid phase micro-extraction (SPME).[11,12]

Recently, renewable materials have profited from numerous investigations. Cellulose is the most abundant and renewable biopolymer in the world that possesses properties like environmental friendliness, biocompatibility, biodegradability and low cost.[13] In this regard, filter paper is a common material which is utilized widely for separation of solid precipitates from solution and contains a matrix of cellulose fibers in a sheet that is kept together by hydrogen bonding. Nowadays, the formation of composites from compatible materials has exhibited beneficial properties and some efforts were performed for incorporating active materials into filter papers.[14] The application of cellulose fibers and their composite for the preconcentration of analytes was also reported in the literature. Zhu *et al.*[15] prepared the β-cyclodextrin modified filter paper and the obtained membrane represented the potential for screening of nitrogen heterocyclic compounds in water samples. Lanthanum hydroxide precipitate coating on cellulose fiber as sorption medium was also performed for selenium preconcentration.[16] Therefore, modified cellulose fibers can provide sufficient substrate for extraction and preconcentration of the target compounds.

Filter paper modified with CPs has some advantages than the other works that employ filter papers modified with other materials. CPs such as PANI and PPY are materials with superior extraction properties, which have been proved previously. High surface area, stability and extraction capability are some of the advantages of using CPs in the extraction process. Other advantages of using CP modified filter paper are the ease and rapidity of preparation, stability in different media with various pH values and cheapness of the prepared sorbent. The cellulose infused with CPs has been receiving significant attention recently. The development of CP composites with cellulose acquired the opportunity to develop new hybrid materials that exhibited the intrinsic proprieties of both components.[17,18]

Composite materials based on cellulose, derived from CPs, can be prepared by mixing the cellulose, conducting monomers and oxidizing agent in a one-pot process to allow *in situ* polymerization on cellulose fibrils. The polymers are fused together to fully encapsulate the individual cellulose fibers in the paper sheet. Thus, the open matrix of fibers and pore structure characteristic of the original paper sheet was retained.[18]

Chemical modification of cellulose fibers by *in situ* polymerization of CPs has been reported to be effective for the fabrication of conductive paper, which has a lot of inherent applications, such as antistatic packaging, high mechanical strength and large surface area.[19] The resulting composite can be an appropriate medium for interaction with analytes through active groups on the surface of paper sheets. Therefore, a simple and low cost sorbent for SPE by coating of CPs on paper fibers was introduced.

Organochlorine pesticides (OCPs) were used as model compounds for investigation of performance of the prepared sorbent. OCPs are persistent organic pollutants and are frequently considered so because of their stability and long term effects on living organisms.[20,21] The persistence of OCPs in aquatic systems can cause transfer ability into the food chain and accumulate in organisms like plankton. Since solubility of many pesticides is partial in water, they may percolate into surface and ground waters at ppb levels.[22]

In this study, CPs were incorporated into the sheets of filter papers for preparation of nanocomposite materials on cellulose fibers. The conventional procedures required more chemicals and times for utilization of PANI or PPY as sorbent. It can be usually applied by packing of CPs in the SPE cartridge or the electrochemical deposition for preparing SPME fibers. The simplicity, repeatability and low-cost of the resulting nanocomposite can introduce a novel sorbent. In this way, the efficiency of filter paper for extraction of organic compounds by coating with CPs was improved. Therefore, a simple filter paper was changed to an efficient SPE sorbent and developed for extraction of some OCPs.

Experimental

Chemicals and materials

Aniline (99.55%), pyrrole (98%), hydrochloric acid (HCl) 37% and iron(III) chloride hexahydrate ($FeCl_3.6H_2O$) for preparation of polymer-paper nanocomposite were obtained from Merck (Darmstadt, Germany). Pyrrole and aniline were distilled before use. Aldrin, endrin, dieldrin, heptachlor and 4-dichlorodiphenyltrichloroethane (4-DDT) were selected as OCPs and were purchased from Sigma-Aldrich (Beijing, China). Elution solvents including ethanol, acetone, *n*-hexane were obtained from Merck (Darmstadt, Germany) and dichloromethane was also obtained from Caledon (Ontario, Canada). The roll of

Whatman filter paper was cut into circle strips with 5 cm diameter by a pair of scissors for using in SPE procedure.

Preparation of PANI/PPY-cellulose nanocomposite

The conducting polymer-cellulose nanocomposite was prepared by polymerization of the monomer solution, which included aniline (0.1 mol L^{-1}) and pyrrole (0.1 mol L^{-1}) in acidified media (1 mol L^{-1} HCl) on the filter paper sheet using $FeCl_3$ (0.67 mol L^{-1}) as oxidizing agent. The black paper was obtained by coating of polymers on the surface of filter paper. Following polymerization and the ensuing encapsulation of the cellulose fibers by PPY and PANI, the paper was subjected to sonication to remove excess and unbonded polymers. For this purpose, the modified filter paper was placed in a beaker containing 10 mL ultrapure water and sonicated for 10 min. Then, the polymers bonded with the surface of the filter paper were exposed to the target analytes for interaction.

Apparatus

An Agilent 6890 N gas chromatograph (Wilmington, DE, USA) equipped with split/splitless inlet and electron capture detector (ECD) was used in the measurements. Chromatographic separation was accomplished with a HP-5 column (30 m × 0.32 mm × 0.25 μm). The injector and detector temperatures were set at 280 and 300 °C, respectively. Nitrogen (99.999%) was used as a carrier gas and the flow rate of carrier gas was adjusted at 1 mL min^{-1}. The oven temperature program was isothermal for 2 min at 50 °C, raised to 200 °C at a rate of 20 °C min^{-1} and then raised to 300 °C at a rate of 10 °C min^{-1} and held for 5 min at this temperature. The sorbent was also characterized by scanning electron microscopy (SEM, Hitachi S-4160, Tokyo, Japan).

SPE procedure

The OCP stock solution was prepared in ethanol and the working standard solutions were prepared daily in Milli-Q water. The paper composite was firstly placed on a Buchner funnel. The OCP samples (100 mL) were gradually loaded onto the polymerized paper and then eluted with 10 mL of dichloromethane. The extract was evaporated and re-solved in 1 mL of dichloromethane and finally injected in the gas chromatograph (GC). For comparison, the non-polymerized paper was also examined under the same conditions.

Results and Discussion

Composite materials containing cellulose have been attracting attention owing to their compatibility with the environment and high specific strength.[14] On the other hand, the CPs were investigated widely because of their physical and chemical properties. The combination of CPs and paper sheets generates a beneficial composite and can also introduce a new sorbent for SPE procedure. The modified filter paper can adsorb the target analytes by π-π interactions and hydrogen bonds. Thus, the qualified sorbent was simply prepared and it can be applied for extraction of the target analytes.

Characterization of PANI/PPY-cellulose nanocomposite

The morphology of the prepared nanocomposite was investigated by SEM images. The comparison of SEM images of polymerized nanocomposite paper and the origin paper is exhibited in Figure 1. As can be seen, the PANI and PPY spheres with particle size below 100 nm formed an integral film with encapsulation of individual cellulose fibers of the paper sheet. Therefore, the large available surface area of paper nanocomposite was provided.

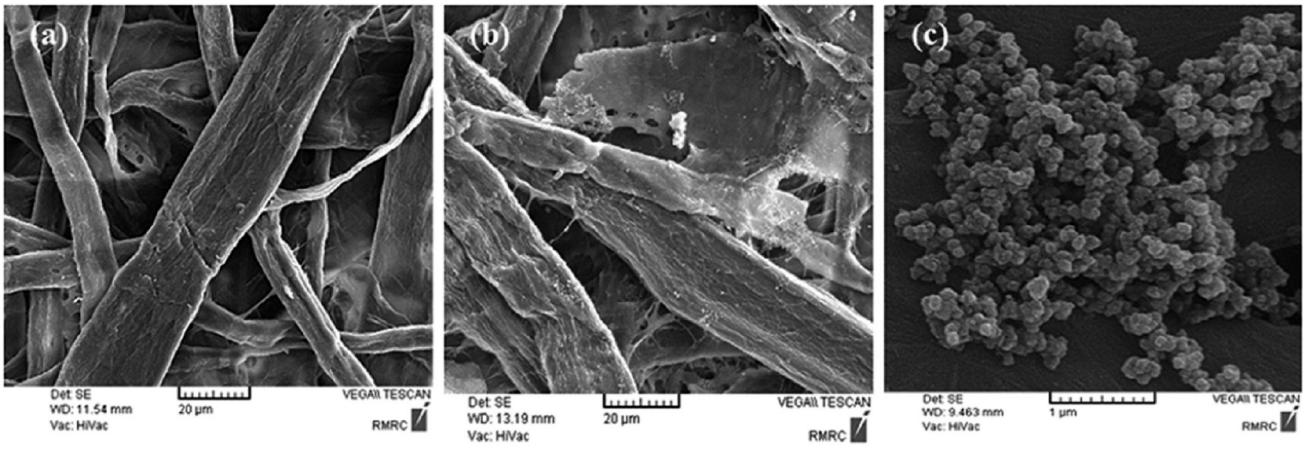

Figure 1. SEM images of the filter paper before polymerization (a) and PANI/PPY-cellulose nanocomposite with low (b) and high (c) magnifications.

Optimization of molar ratio of monomers

In order to provide a high efficiency sorbent for extraction of OCPs, the molar ratio of aniline (ANI) and pyrrole (PY) was optimized. As shown in Figure 2, different molar ratios of PY to ANI, including 1:0, 0:1, 1:1, 1:2 and 2:1, were examined. The results expressed that the highest peak area was obtained for 1:2 molar ratio of PY to ANI. In addition, it can be seen that the amount of extracted OCPs enhanced when the molar ratio of ANI was increased. It can be related to this fact that PANI has more delocalized electrons than PPY in its structure and then, with increasing the molar ratio of ANI to PY, the π-π interactions of the composite with the OCPs can increase, resulting in higher extraction efficiency.

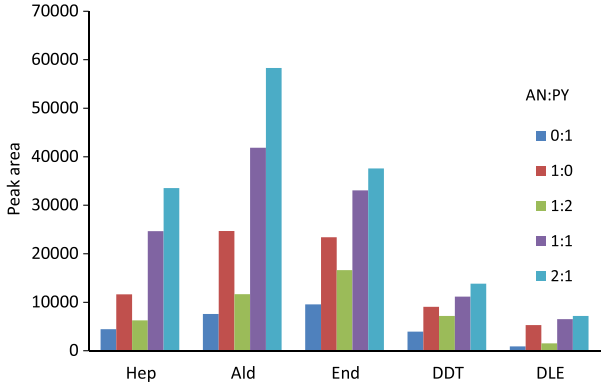

Figure 2. Optimization diagram of PANI/PPY paper composites with various molar ratio of PANI to PPY. Hep: heptachlor; Ald: aldrin; End: endrin; DDT: 4-DDT; DLE: dieldrin.

Investigation of type and volume of elution solvent

Four types of solvents, including ethanol, acetone, *n*-hexane and dichloromethane, were utilized for extraction of the OCPs (1 mL with concentration of 100 μg L^{-1}) in the elution step of SPE. From Figure 3, we can conclude that dichloromethane can be considered a suitable solvent for elution of analytes. It was also required to use the suitable volume of elution solvent for extraction of OCPs. The various volumes of dichloromethane of 1, 2, 5 and 10 mL were considered and according to Figure 4, extraction efficiency increased with increasing elution solvent volume. However, 10 mL was selected as enough elution volume for extraction of OCPs.

In the optimal condition, the preconcentration factor was also investigated for polymerized paper and it was obtained as 95.64, 90.83, 80.33, 83.50 and 99.12 for heptachlor, aldrin, dieldrin, endrin, and 4-DDT respectively. Therefore, the presence of aromatic and some functional groups, e.g., –NH, on the surface of the paper presented

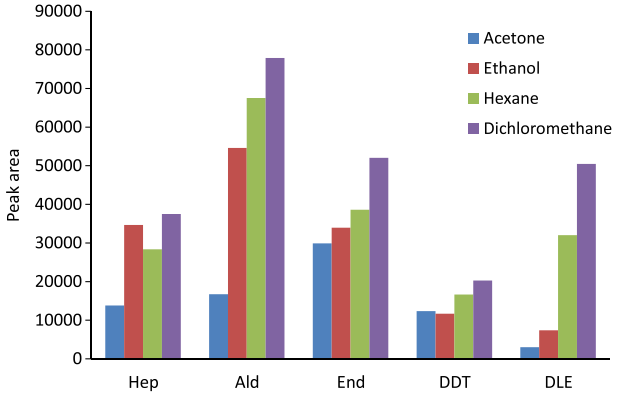

Figure 3. Effect of different elution solvents on the extraction efficiency of OCPs. Hep: heptachlor; Ald: aldrin; End: endrin; DDT: 4-DDT; DLE: dieldrin.

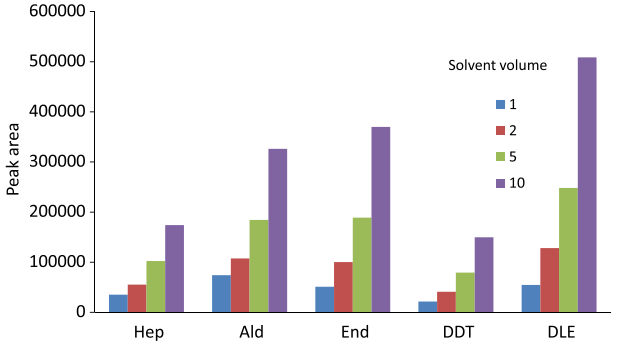

Figure 4. Effect of volume of eluting solvent on the extraction efficiencies of OCPs. Hep: heptachlor; Ald: aldrin; End: endrin; DDT: 4-DDT; DLE: dieldrin.

appropriate performance for preconcentration of OCPs as model compounds.

It was also demonstrated in Figure 5 by comparing the resulted chromatograms of extracted OCPs with non-polymerized paper and the paper composite at the optimized condition.

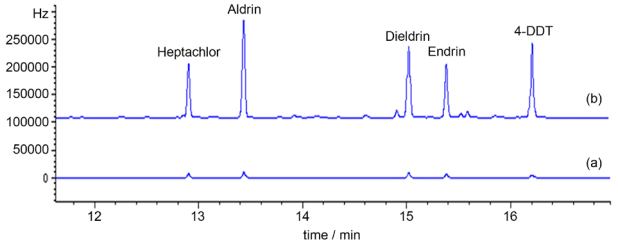

Figure 5. Chromatograms of extracted OCPs by paper (a) and paper composite (b) at the optimized condition.

Validation data

The analytical methodology was also evaluated by description of linearity and limit of detection for the present procedure in the determination of OCPs. The capability of

Table 1. Comparison of the prepared sorbent with the previous sorbents used for determination of OCPs

Type of sorbent	Extraction technique	Matrix	Pesticide	Linear range / (μg L^{-1})	LOD / (μg L^{-1})	RSD / %	Reference
PPY	SPME	Water	Heptachlor Aldrin	0.78-100	0.14 0.23	3.8 1.6	12
PDMS	SPME	Human fluid	Heptachlor Aldrin Endrin 4-DDT	–	10 10 2 10	7.0 9.0 11.0 9.0	23
PS-DVB	SPE	Water	Heptachlor Aldrin Dieldrin Endrin 4-DDT	0.05-100	0.01 0.03 0.01 0.05 0.05	3.7 4.2 2.7 3.5 4.7	24
C-18	SPE	Water	Heptachlor Aldrin Dieldrin Endrin 4-DDT	1-25	0.1 0.36 0.06 0.17 0.05	9.8 5.1 6.3 9.1 6.3	25
PANI/PPY-cellulose	SPE	Water	Heptachlor Aldrin Dieldrin Endrin 4-DDT	5-250	0.39 0.28 0.47 0.51 0.31	5.1 3.8 4.9 4.8 4.0	This work

LOD: limit of detection; RSD: relative standard deviation; PPY: polypyrrole; PDMS: polydimethylsiloxane; PS-DVB: polystyrene divinylbenzene; C-18: octadecylsilane; SPME: solid phase micro-extraction; SPE: solid phase extraction.

the proposed sorbent for extraction of OCPs is compared with the results obtained from literature data in Table 1. The linearity was investigated in the range of 1-1000 μg L^{-1} but suitable linearity was obtained in the range of 5-250 μg L^{-1} with correlation coefficients (R^2) of 0.992, 0.997, 0.999, 0.996 and 0.998 for heptachlor, aldrin, dieldrin, endrin, and 4-DDT, respectively. The limit of detection (LOD) of the method was in the range of 0.28-0.51 μg L^{-1}. The relative standard deviations (RSDs) for the target analytes varied from 3.8 to 5.1%. Comparable performance data including linearity and RSD were obtained for the proposed sorbent than for the other sorbents used for extraction of OCPs Although the LODs in the present work were greater than in the other studies, according to the World Health Organization (WHO) guidelines for drinking water quality, and fish and shellfish tissue[26] (Table 2) the proposed method was suitable for monitoring the studied pesticides in water and fish tissue samples. However, the present study developed a facile and inexpensive sorbent preparation procedure for determination of OCPs compared with the other adsorbents.

The reusability of the prepared sorbent was investigated several times by the extraction process and it was found that the extraction efficiency of the sorbent is not decreased up to 50 times.

Table 2. Permissible values for OCPs in drinking water, fish and shellfish tissue

Pesticide	Drinking water level / (μg L^{-1})	Fish and shellfish tissue / (ng g^{-1})
Heptachlor	30	300
Aldrin	30	300
Dieldrin	–	–
Endrin	2000	300
4-DDT	2000	5000

Real sample analysis

For the accuracy test, natural water samples were spiked with 50 μg L^{-1} of the OCPs and then the samples were analyzed for determination of OCP concentrations. By dividing the difference of the concentration of OCPs after and before spiking by the spiked value (50 μg L^{-1}), the recovery values were obtained. The recovery is representative of the accuracy of a method.

Caspian seawater was chosen for the analysis of a real sample and the obtained recovery was also higher than 77.4% for the analytes. The results of recovery are listed in Table 3. It demonstrated that the prepared sorbent has good

Table 3. Determination of OCPs in seawater sample by the prepared paper composite

Analyte	Added / (μg L^{-1})	Found / (μg L^{-1})	Recovery / %
Heptachlor	–	11.72	–
	50	63.07	102.7
Aldrin	–	13.85	–
	50	59.42	91.1
Dieldrin	–	9.94	–
	50	48.64	77.4
Endrin	–	6.27	–
	50	47.56	82.6
4-DDT	–	17.22	–
	50	67.93	101.4

applicability for the preconcentration and determination of OCPs in aqueous media.

Conclusions

In the present study, a simple and low-cost SPE sorbent for extracting organic compounds was developed. The PANI/PPY-cellulose nanocomposite was fabricated using a simple approach. The retention of the open paper matrix provided the high specific surface area to increase the chemical and physical properties of the used polymers. The presence of aromatic and NH groups in the surface of paper sheet is the appropriate substrate for π-π systems and hydrogen bonding. The resulting nanocomposite can be utilized as a new SPE sorbent for extraction of OCPs. Good recovery and linearity were also observed for determination of the analytes in natural water samples.

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