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## Evaluation of highly efficient on-line yarn-in-tube solid phase extraction method for ultra-trace determination of chlorophenols in honey samples

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### ABSTRACT

In this study a novel “yarn-in-tube” configuration was introduced by packing cotton yarn inside stainless steel cartridge named packed yarn-in-tube solid phase extraction (yarn-IT-SPE) followed by high performance liquid chromatography. For the first time, cotton yarns were coated with a new polypyrrole@copper-chromium-iron ternary layered double hydroxide nanocomposite (Yarn@PPy@Cu-Cr-Fe LDH). The yarn@PPy@Cu-Cr-Fe LDH sorbent exhibited flexible substrate, high porosity, a three-dimensional, high sorbent loading, long lifetime, good mechanical stability, high anion-exchange capacity and large specific surface area as a result it is a good choice for the separation and preconcentration of acidic chlorophenols in honey samples. Several important factors affecting extraction efficiency such as extraction and desorption times, pH of solution and flow rates of the sample solution and eluent were investigated and optimized. Under the optimal conditions, the limits of detection were in the range of 0.05–0.07  $\mu\text{g L}^{-1}$ . This method showed good linearity for chlorophenols in the range of 0.10–500  $\mu\text{g L}^{-1}$ , with coefficients of determination better than 0.9989. The inter- and intra-assay precisions (RSD%,  $n=5$ ) were in the range of 3.2–4.9% and 2.1–3.6% at three concentration levels of 2, 10 and 20  $\mu\text{g L}^{-1}$ , respectively. The validated method was successfully applied for analysis of 4-chloro-, 2,4-dichloro-, and 2,4,6-trichloro phenols in honey samples.

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### 1. Introduction

The antimicrobial properties of chlorophenols (CPs) have led to their use as disinfectants, herbicides, insecticides and fungicides in agriculture, and also as wood preservatives and intermediates in many industries [1,2]. Although they are generally presented in trace levels, their carcinogenicity and toxicity may have adverse effects on human beings. They have been classified by the International Agency for Research on Cancer (IARC) as possible carcinogenic agents for humans [3]. Although the use of CPs has been restricted since 1984 [4] because of their high resistance to biodegradation, they can still be found in honey as they are transported by bees when travelling to collect nectar or even because of the treatment of wooden beehives. The negative effect of CPs for human health has led to their categorization and inclusion by the US Environmental Protection Agency (EPA) and the Commission of the European Communities (Directive 76/464/EC) in the lists of pri-

ority pollutants [4]. Although the European Union (EU) included, in the 1221/97/CE directive [5], the need to improve the treatment conditions of beehives, maximum residue limits (MRLs) for CPs in honey have never been established, and there is no doubt that their analysis is of great importance for controlling the quality of honey. Therefore, providing an appropriate method is essential in order to extract trace amounts of CPs in honey samples [6].

Recently, fabric phase sorptive extraction (FPSE) has been developed by Kabir and Furton [7]. FPSE effectively integrates most of the advantages of solid-phase microextraction (equilibrium based extraction) with solid phase extraction (exhaustive extraction). The sorbent, in FPSE, is covalently bonded to the substrate surface, and therefore offers high chemical, solvent, and thermal stability [8]. On the other hand, the high volume of fabric substrate containing easily accessible interaction sites, that is due to the chemical bonding between the sorbent and substrate and porous cellulose surface, offers a very high sample capacity and near-exhaustive extraction under the equilibrium extraction conditions. Moreover, the open geometry of FPSE media facilitates fast analyte sorption and desorption [9–11]. However, in cotton yarn based sorbents, the selection of suitable coating is necessary.

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Recently, conducting polymers have been used in sample preparation techniques. Polypyrrole (PPy) and its derivatives are a set of conducting polymers widely used for the extraction of various types of compounds because: (1) they can be easily polymerized from organic or aqueous media at neutral pH by electrochemical or chemical methods, (2) they are relatively stable in air and solution, and (3) these characteristics provide different intermolecular interactions such as acid-base,  $\pi$ - $\pi$ , dipole-dipole, hydrophobic, and hydrogen bonding, as well as exchange among the polymers and the analytes [12–16].

Layered double hydroxides (LDHs) represent a fascinating class of inorganic materials with variable chemical compositions and structures. They are also known as hydrotalcites or anionic clays [17–20]. Typically, LDHs are two-dimensional nanostructured materials consisting of positively charged layers of metal hydroxides with charge-balancing anions and some water molecules located between the layers. These materials have shown interesting properties such as high surface area, interlayers with variable sizes, two-dimensional structures, high thermal stability, and excellent anion-exchange capabilities [21,22]. To date, these materials have been mostly used in solid-phase extraction (SPE), solid-phase microextraction (SPME), and dispersive SPE (DSPE) methods [23–25].

In this work for the first time, in order to eliminate back pressure and blockage in packed sorbent in-tube SPE systems, a novel yarn-IT-SPE method was introduced by packing cotton yarn inside a stainless steel cartridge. Then, a new nanostructured PPy@Cu-Cr-Fe ternary LDH nanocomposite was synthesized on the surface of the cotton yarn by a facile chemical method. The PPy@Cu-Cr-Fe LDH nanocomposite coating on the surface of the cotton yarn was utilized for on-line yarn-IT-SPE coupled with HPLC for determining CPs in honey samples. To the best of our knowledge, this article represents the first report on (1) synthesis of a PPy@Cu-Cr-Fe ternary LDH nanocomposite coating film on cotton yarn named yarn@PPy@Cu-Cr-Fe LDH; and (2) the use of on-line yarn-IT-SPE in sample preparation methods.

## 2. Experimental

### 2.1. Chemicals and reagents

All of chemicals were of analytical reagent grade. Standards of 2-chlorophenol (2-CP), 4-chlorophenol (4-CP), 2,4-dichlorophenol (2,4-DCP), and 2,4,6-trichlorophenol (2,4,6-TCP) were obtained from Sigma-Aldrich (Milwaukee, WI, USA). The stock solutions of the chlorophenols ( $1000 \text{ mg L}^{-1}$ ) were prepared by dissolving 10 mg of the compounds in 10 mL methanol. Lower concentrations were prepared by diluting the stock solution with methanol. Cotton yarn substrates for solid phase extraction media, spinning essentials of unbleached 100% cotton, was obtained from spinning Nabris (Tehran, Iran). Synthetic pyrrole (98% pure) was obtained from Aldrich (Milwaukee, WI, USA).  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  was purchased from Merck (Darmstadt, Germany). Purified  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  (99%),  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  (99%) and  $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  (99%) were purchased from Merck. Sodium hydroxide and hydrochloric acid (95% pure) were obtained from Merck. Ultra-pure water was produced using a Youngling ultrapure water purification system model Aqua MaxTM-ultra (Seoul, South Korea). Other chemicals used were of analytical reagent grade or of the highest purity available.

### 2.2. Apparatus

Particle size and morphology of the synthesized nanoparticles were determined by a scanning electron microscope (SEM) model EM3200 from KYKY Zhongguancun (Beijing, China). A GPFA1-380

peristaltic pump from Ultra-Voltammetry Company (Tehran, Iran) was applied to pass the solutions through the stainless steel packed column. The chromatographic analysis was performed with a HPLC instrument including a Varian 9012 HPLC pump (Walnut Creek, CA, USA), a six-port Cheminert HPLC valve from Valco (Houston, TX, USA) with a 500- $\mu\text{L}$  sample loop, and equipped with a Varian 9050 UV-vis detector. The chromatographic data were recorded and analyzed using Chromana software (version 3.6.4). The separations were run under isocratic elution conditions on an ODS-3 column (250 mm  $\times$  4.6 mm, with a 5- $\mu\text{m}$  particle size) from HECTOR Company (Daejeon, Korea). The chromatographic separation was performed using a mobile phase consisting of 20 mmol  $\text{L}^{-1}$  phosphate buffer (pH = 4.0) and acetonitrile (40:60) at a flow rate of 1.0 mL  $\text{min}^{-1}$ . The detection of the analytes was achieved at 210 nm.

### 2.3. Preparation of cotton yarn@PPy@Cu-Cr-Fe layered double hydroxide nanocomposite coating

The synthesis procedure involved (1) preparation of cotton yarn for the synthesis of the coating; (2) preparation of cotton yarn@PPy; and (3) the growth of LDH nanoplatelets on the surface of cotton yarn@PPy by co-precipitation method [26]. The whole process is shown in Fig. 1. The details of synthesis are as follows:

- Preparation of cotton yarn for the synthesis of coating: A 100 mg of yarn fragmented from cellulose yarn (cotton yarn) was first rinsed with deionized water for 15 min to remove water soluble particulates and treatment chemicals. The cotton yarn was then soaked in a 1 mol  $\text{L}^{-1}$  NaOH solution for 1 h under sonication. The base treated cotton yarn was then washed several times with a profuse amount of deionized water, followed by treatment with 0.1 mol  $\text{L}^{-1}$  HCl solution for 1 h under sonication. The treated cotton yarn was subsequently washed with a copious amount of deionized water and finally dried in an inert atmosphere overnight. The dried cotton yarn was stored in clean, airtight glass containers until they were coated with the polymerization PPy sorbent.
- Preparation of cotton yarn@PPy: For coating PPy on the cotton yarn, 50 mL distilled water was first degassed by bubbling of nitrogen for 30 min. Then, 100 mg cotton yarn was introduced in to the water and the solution was stirred for 15 min. In the next step, 0.5 mL pyrrole was added and stirred for 1 h till the pyrrole dispersed entirely and was absorbed on cellulose surface. Polymerization started when the  $\text{FeCl}_3$  solution (0.28 g dissolved in 5.0 mL distilled water) was added dropwise, and the mixture was stirred for 12 h at room temperature. Finally, the synthesized cotton yarn @PPy was washed with water and ethanol in sequence, and dried at 50 °C in vacuum for 24 h.
- Preparation of cotton yarn@PPy@Cu-Cr-Fe LDH nanocomposite: The cotton yarn@PPy@Cu-Cr-Fe LDH was synthesized using a co-precipitation method. Briefly, metallic nitrates of Cu / Cr / Fe with a molar ratio of 1:3 ( $\text{Cu}^{2+}$  0.25 M,  $\text{Cr}^{3+}$  0.375 M and  $\text{Fe}^{3+}$  0.375 M) were dissolved in 80 mL of water. 100 mg cotton yarn@PPy was mixed with the above solution and the pH of the medium was adjusted to  $10.0 \pm 0.1$  using 2 mol  $\text{L}^{-1}$  NaOH with continuous stirring for 2 h. The cotton yarn together with the gel-like slurry was aged at 65 °C for 24 h. The resulting cotton yarn after crystallization of the LDH was separated, washed twice with ultrapure water, and the cotton yarn product was dried. The entire synthesis process was performed in a nitrogen atmosphere to avoid contamination by  $\text{CO}_2$  from the atmosphere. The synthesized material is referred here to as cotton yarn@PPy@Cu-Cr-Fe LDH.

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