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A green solvent holder in electro-mediated microextraction for the extraction of phenols in water

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ABSTRACT

Electro-mediated microextraction (EMM) combined with micro-high performance liquid chromatography-ultraviolet detection was successfully developed for the determination of selected phenols, namely 4-chlorophenol (4CP), 2-nitrophenol (2NP) and 2,4-dichlorophenols (2,4 DCP) in water. A solvent-impregnated agarose gel disc was utilized as a solvent holder in this study. Under optimum extraction conditions, the method showed good linearity in the range of 0.1–250 μg L^{-1}, 0.3–250 μg L^{-1} and 0.2–500 μg L^{-1} for 4CP, 2NP and 2,4 DCP, respectively with correlation coefficients of ≥ 0.9975, ultra-trace LODs (0.03–0.1 μg L^{-1}) and satisfactory relative recovery average (85.0–114.1%) for the analysis of selected phenols. The proposed method was rapid and eco-friendly as the solvent holder was constructed using minute amounts of extraction solvent immobilized within the biodegradable agarose gel disc. A comparative microextraction technique termed solvent-impregnated agarose gel liquid phase microextraction (AG-LPME) was re-optimized and validated for the extraction of phenols in water. The method offered good linearity, ultra-trace LODs ranging 0.1–0.5 μg L^{-1} and satisfactory average of relative recovery (86.1–114.1%). The EMM was superior in terms of sensitivity and time-effectiveness compared to AG-LPME. Both techniques combine extraction and pre-concentration in mini-scaled approaches using an eco-friendly solvent holder that fulfil the green chemistry concept.

1. Introduction

Many analytical methods require sample pretreatment for the selective extraction and preconcentration of the analytes, as well as exclusion of matrix effect. Traditionally, this is performed using liquid-liquid extraction (LLE) that requires high consumption of organic solvents. Since 1996, the eco-friendly extraction techniques, solvent microextraction and solvent extraction in a microdrop have emerged as the alternatives to LLE [1,2]. However, the dissolution of the extraction solvent into the sample solution is always reported as a result of long extraction time and high agitation speed. Therefore, the development of membrane that could hold the extraction solvent firmly is important to improve the solvent microextraction and solvent extraction in a microdrop techniques. To-date, much effort has been focused on developing simple, rapid, in-expensive, minimized and eco-friendly sample preparation methods to provide good and effective extraction.

Phenols are among the most important contaminants present in the environment. The phenols are applied in formulating pesticides, explosive, drugs and dyes in various industries. The hydroxyl group of phenol is reactive to the disinfection by-products formed during oxidative water treatment to form chlorination products such as 2-chloro, 4-chloro and higher chlorophenols [3,4]. Besides, the discharge from herbicide manufacturing plant is also the main source for the chlorophenol. The toxic nitrophenol is formed when the nitrite ion contacts with the phenol in the environmental water [5]. Chloro and nitrophenols are more toxic than hydrocarbon-based phenols. The nitrophenols readily undergo bio-degradation via reduction to form amines. However, chlorophenols are more persistent and the persistency increases human exposure to chlorophenols [4]. Due to the properties of phenols owing the high toxicity and persistence in the environment, they have been listed as priority pollutants by the United States Environmental Protection Agency [6].

A number of analytical methods have been demonstrated to determine phenols in the aquatic environment, including drinking water, sea water, river water and wastewater [7–11]. The conventional methods employed to extract the phenols mainly involved the derivatization or solvent-exchange steps that were tedious, consuming large amounts of solvents and time-consuming [6,12,13]. These conventional extraction methods were also not user and environmental friendly as they were hazardous to the humans and damaging the environment. These shortcomings have been overcome by alternatives mini-scaled techniques termed as solid-phase microextraction (SPME)

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and liquid-phase microextraction (LPME).

Peng and co-researchers developed a hollow fiber-liquid phase microextraction (HF-LPME) for the determination of chlorophenols in environmental water [14]. This micro-scale LLE has significantly enhanced the analytes enrichment, minimized the consumption of organic solvent, avoided time consuming clean up and eliminated evaporation steps. However, the technique required a long extraction time (60 min) and this may attribute to the loss of the extraction solvent especially when high agitation speed was applied. Lopez-Darias et al. compared both dispersive liquid-liquid microextraction (DLLME) and single drop microextraction (SDME) for the determination of phenols in seawater [11]. The authors concluded that both techniques were environmental-friendly due to the low consumption of organic solvents. However, DLLME was superior to SDME as the former provided lower detection limits, better recoveries and rapid extraction. The extraction solvent was dispersed homogeneously in the sample solution to enhance the mass transfer of phenols into the dispersed solvent when DLLME was applied. A new liquid microextraction approach, termed stir membrane liquid-liquid microextraction (SM-LLME), was proposed by Alcudia-Leon et al. for the determination of phenols in water [15]. The extraction technique involved the advantages of LPME and stirring in the same unit allowing the extraction of the analytes in a simple and efficient way. The simplified procedures however still required 45 min of extraction to achieve the equilibrium time and were not beneficial for on-site application. Since 2008, the electromembrane extraction (EME) that combines both electroextraction and technical setup of HF-LPME has emerged as the latest alternative technique to extract the charged analytes. The sample preparation technique offers selective, superior enrichment and shorter analysis time. However, most of the EME set-up still utilized HF as a membrane and agitation method to enhance the diffusion of analytes. Therefore, this technique is not beneficial for on-site extraction [16–18].

This project aims to provide a simple and efficient approach by improving the existing LPME techniques for the determination of a group of phenols in water samples with shorter extraction time and incorporation of green material for selective extraction. This study proposes to complement and augment the latest requirements in sample preparation trends: miniaturization, simplification, economization, and environmental-friendly alternatives.

2. Experimental

2.1. Chemicals and materials

2-Nitrophenol (2NP), 4-chlorophenol (4CP) and 2,4-dichlorophenol (2,4 DCP) were purchased from Sigma-Aldrich (St. Louis, MO, USA). Individual stock solutions (500 mg L^{-1} for each analyte) were prepared in methanol. Serial mixture working standard solutions were prepared by dilution of stock solutions with methanol. All standard solutions were stored in dark at 0 °C when not in use. The 1-octanol (analytical grade), methanol (HPLC grade) and acetonitrile (HPLC grade) were purchased from Merck (Darmstadt, Germany). The analytical grade sodium chloride, hydrochloric acid, phosphoric acid and absolute ethanol were obtained from BDH (London, United Kingdom). The double-distilled deionized water was purified by Nano ultra pure water system (Barnstead, USA). Agarose (analytical grade) was obtained from Promega (Madison, USA).

A hot plate stirrer (Corning, USA) and a stirring bar (10 × 4.5 mm) were used to agitate the samples during extraction. A custom-made tiny glass tube (50 mm × 2 mm I.D., 1 mm wall thickness) was used as the agarose gel mould. The OmniPAC Mini 300 V power supply unit was obtained from Cleaver Scientific (Warwickshire, United Kingdom). The annealed platinum wire with diameter 0.5 mm was purchased from Goodfellow Cambridge (England, United Kingdom) and applied as electrodes.

2.2. Chromatographic conditions

The quantitation was carried out with a micro-high performance liquid chromatography (Agilent Technologies, Milan, Italy) coupled with ultraviolet detection (Agilent Technologies). The chromatographic separation of phenols was performed on a ZORBAX Eclipse XDB-C_{18} column (2.1 × 100 mm, 3.5 μm) purchased from Agilent. The separation was performed using isocratic mobile phase acetonitrile-water at pH3 (50:50) (v/v) at column temperature of 30 °C. The flow rate, injection volume and detection wavelength were fixed at 0.2 mL min^{-1}, 2 μL and 220 nm, respectively. The chromatographic data were processed using Agilent Chemstation software.

2.3. Preparation of solvent-impregnated agarose gel

The agarose gel disc (2 mm × 2 mm I.D.) was prepared according to the procedure adopted from Loh et al. [19] without any further modification. In this study, 1-octanol was applied as acceptor phase.

2.4. Electro-mediated microextraction

The water sample (10 mL, pre-modified to pH9) was pipetted into a glass petri dish (15 mm × 50 mm I.D.). In this study, 1-octanol was used as acceptor phase. The platinum wires were attached to the power supply unit. The wire that connected to the anode was poked into an agarose gel disc to function as a positive or acceptor electrode. Both electrodes were then dipped into the sample solution for extraction. The electrical potential (25 V) was immediately applied for 20 min. After the extraction, the disc was removed using forceps and centrifuged at 12,000 rpm for 5 min to destroy the agarose gel framework, and release the 1-octanol. The supernatant was then withdrawn and injected into the micro-high performance liquid chromatography-ultraviolet detection (μHPLC-UV) system.

2.5. Solvent-impregnated agarose gel liquid phase microextraction

The solvent-impregnated agarose gel liquid phase microextraction (AG-LPME) technique [19] was re-optimized and performed for the extraction of phenols in water. Minor modification was made from the original work [19] where the solvent-impregnated agarose gel disc was fixed at one position using a disposable syringe. This was to ensure the apparatus set-ups for both AG-LPME and electro-mediated microextraction (EMM) were kept minimal.

The water sample (10 mL, pre-modified to pH3) was pipetted into a glass petri dish (15 mm × 50 mm I.D.). The disposable syringe was poked into an agarose gel disc to function as the acceptor phase. The disposable syringe was clamped to a retort stand. The disposable syringe was then dipped into the sample solution for extraction. The sample solution was agitated at 800 rpm and extracted for 40 min. After the extraction, the disc was removed using forceps and centrifuged at 12,000 rpm for 5 min to destroy the agarose gel framework, and release the extraction solvent. The supernatant was then withdrawn and injected into the μHPLC-UV system. The schematics of both EMM and AG-LPME are shown in Fig. 1.

2.6. Validation of analytical method

Minimal validation was performed which included linearity, relative recovery, repeatability, limit of detection (LOD) and limit of quantification (LOQ).

3. Results and discussion

3.1. Optimization of electro-mediated microextraction technique

Agarose concentration, sample pH, salting out effect, agitation