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Environmentally friendly and non-polluting solvent pretreatment of palm samples for polyphenol analysis using choline chloride deep eutectic solvents

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ABSTRACT

In this work, choline chloride (ChCl) deep eutectic solvents (DESs) were evaluated for the pretreatment of palm samples in the analysis of polyphenols, such as protocatechuic acid, catechins, epicatechin, and caffeic acid. During the enrichment step of the pretreatment, eight DESs comprising ChCl with ethylene glycol (EG), glycerol (Gly), xylitol (Xyl), phenol (Ph), formic acid (FA), citric acid (CiA), oxalic acid (OA), or malonic acid (MA), were prepared and applied to the reflux extraction of polyphenols from palm samples. All the DESs exhibited higher polyphenol extraction efficiency than methanol, and the highest extraction efficiency was obtained using ChCl-FA (1:1, mole ratio). For the purification step of the pretreatment, eight ChCl DES-modified adsorbents were prepared by hydrothermal polymerization and packed into solid-phase extraction (SPE) cartridges, and ChCl-Urea, ChCl-Gly, ChCl-FA, and water, were used as eluents. The ChCl DES-modified adsorbents were characterized by Fourier transform infrared spectroscopy, thermal gravimetric analysis, scanning electron microscopy, and Brunauer–Emmett–Teller surface analysis, and the polyphenols were analyzed by mass spectrometry and high-performance liquid chromatograph-ultraviolet detection. The highest purification efficiency was obtained using the ChCl-Ph DES-modified adsorbent as the SPE packing material and ChCl-Urea-H_2O (1:1:5, mole ratio), ChCl-Gly (1:1, mole ratio), ChCl-FA-H_2O (1:1:5, mole ratio), and H_2O as the eluents. Compared to conventional purification processes that employ commercial C_{18} or C_8 SPE columns with organic solvents as eluents, the ChCl DES-based SPE purification process successfully avoided the use of expensive commercial SPE columns and organic solvents. Furthermore, it isolated a larger amount of the target compounds under the same experimental conditions, and could be applied over five cycles with good reversibility. This work indicates that DESs as green solvents have great potential for the totally green pretreatment of samples during the enrichment and purification processes.

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1. INTRODUCTION

In recent years, the application of green chemistry has become increasingly important in many research areas such as organic synthesis, inorganic materials preparation, biotechnology, and analytical methods [1–3]. An aspect of green chemistry that much research has focused on is mitigating the use of traditional organic solvents such as methanol, dichloromethane, acetonitrile, hexane, and acetone because of their negative effects on the environment. Thus, the exploration and application of green solvents has been receiving increasing attention. In recent decades, ionic liquids (ILs) have emerged as potential green solvents owing to their special physical and chemical properties [4–6]. Traditional ILs comprises an organic salt liquid based on an organic cation paired with an organic or an inorganic anion. They are widely recognized as ecofriendly solvents with low vapor pressure, low combustibility,

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and excellent thermal stability [7–9]. However, there are several disadvantages with traditional ILs, including their complex preparation, high cost, and poor biodegradability [10–12]. To overcome these disadvantages, deep eutectic solvents (DESs) as a new type of ILs or pseudo ILs have been developed.

The first DES was introduced by Abbot et al. in 2003, and is a eutectic mixture of a hydrogen bond acceptor (HBA) and a hydrogen bond donor (HBD) that has a lower melting point than either of the individual components [13–16]. DESs have similar characteristics to ILs, such as low vapor pressure, thermal stability, availability, but also have several advantages over traditional ILs, including biodegradability, simple preparation, and low cost. Consequently, DESs have been studied for application in many fields of chemistry, including electrochemistry, organic chemistry, inorganic chemistry, biochemistry, and analytical chemistry [17–19]. The exploration and application of DESs in the key pretreatment step of sample analysis has received particular attention.

Sample pretreatment is a key process for many analytical methods, especially for the analysis of bioactive compounds in plants. Pretreatment of a plant sample usually includes enrichment and purification steps, and then the purified target compounds are analyzed using the appropriate instruments. In conventional enrichment processes, common solvents such as alcohols, short alkanes, ketones, and aromatic hydrocarbon are applied in the extraction of targets compounds from plants [20–22]. However, these solvents make environmental pollution a problem for common processes. In addition, for purification processes, solid-phase extraction (SPE) is a popular and simple method, and many different adsorbents are used in SPE with traditional organic solvents as eluents to purify analytes from complex samples [23–25]. However, the adsorbents are generally expensive and the organic eluents cause pollution, which are common drawbacks of SPE. In comparison, DESs and DES-modified adsorbents show obvious advantages, such as environmental benignity and lower cost, but have not been applied and studied for SPE. Therefore, in this study, DESs and DES-modified adsorbents are proposed as alternatives to traditional adsorbents and eluents in SPE for the purification of targets compounds.

To solve the above problems of the pretreatment process, DESs as green solvents without organic solvents are applied to avoid environment pollution. Based on related research into DESs, choline chloride (ChCl), which is a member of the vitamin B family that is biodegradable and non-toxic, has been widely studied as a HBA [26]. Polyphenols are derived from a wide range of plants, and have good antioxidant activity, thus removing free radicals that are harmful to human health [27]. Consequently, a totally green pretreatment of palm samples for polyphenol analysis using ChCl DESs was explored in this work, and it shows enormous potential for the development of green sample pretreatment methods as shown in Fig. 1.

2. EXPERIMENTAL

2.1. Reagents and Materials

The polyphenol standards protocatechuic acid (PA, ≥ 97%), catechins (Cat, ≥ 97%), 1,3,5-trimethylbenzene (97%), formic acid (FA, 99%), and anhydrous citric acid (CiA, 99.5%), were purchased from Aladdin Industrial Corporation (Shanghai, China). Epicatechin (Epi, ≥ 98%), caffeic acid (CA, ≥ 98%) polyethylene-polypropylene-polyglycol (P123) triblock copolymer, and xylitol (Xyl), were purchased from Shanghai Macklin Biochemical Co., Ltd. (Shanghai, China). Teraethoxysilane (98%), malonic acid (MA, 99%), hydrochloric acid (37%), anhydrous ethanol, ethylene glycol (EG), glycerol (Gly), ChCl (98%), oxalic acid (OA, 99.5%), and phenol (Ph) were supplied by Tianjin Reagent Factory (Tianjin, China). Distilled water was filtered using a vacuum pump and filter (HA, 0.45) prior to use. Palm (*Trachycarpus fortunei* (Hook.) H. Wendl.) samples were collected from Qinling, China in June, 2016.

2.2. Pretreatment of Palm Samples: Enrichment

2.2.1. Preparation of DESs

DESs were prepared following the method described by Abbott et al. [14]. Eight DESs were prepared by mixing ChCl and each of the HBDs EG, Gly, Xyl, Ph, FA, CiA, OA, and MA at a set molar ratio at 40–90 °C for 60 min with constant stirring until a homogeneous liquid formed. Then, the eutectic mixture was cooled to room temperature and was applied in the following processes (Table 1).

2.2.2. Extraction by DESs

In each extraction process, a sample of dry palm bark was crushed to a fine powder, and 0.5 g of the palm powder was soaked in 7.5 g of the DES and 2.5 g of H_2O in a 50 mL round-bottom flask. The mixture was refluxed at 40 °C for 6 h in a water bath for extraction. After the reflux extraction, the extraction mixture comprised two phases, i.e., solution and residue. Therefore, the extraction mixture was centrifuged at 4000 rpm for 10 min and then at 12,000 rpm for 5 min, and the extraction solution was obtained as the supernatant. For comparison to the above DES-based extraction, 0.5 g of palm powder was soaked and refluxed in 10 g of methanol as the extraction solvent, and all other operations were the same.

2.3. Pretreatment of Palm Samples: Purification

2.3.1. Preparation and Characterization of DES-Modified Adsorbents

In this work, the adsorbents used for SPE were DES-modified materials prepared by hydrothermal polymerization in the following steps: P123 (4.0 g) was dissolved in 65.0 mL of H_2O and 10.0 mL of HCl in a round-bottom flask. Then, 4.0 g of 1,3,5-trimethylbenzene was slowly added to the mixture with stirring at 40 °C for 2 h. Subsequently, 9.2 mL of ethyl silicate was added, and the mixture was transferred to a 250 mL reaction kettle and heated at 40 °C for 20 h, and then the DES was added to the kettle and heated at 100 °C for 24 h. After aging, the resulting mixture was filtered, washed sequentially with water and anhydrous ethanol, and dried at 65 °C. The resulting white powder was calcined at 900 °C for 6 h. After cooling, the desired DES-modified adsorbents were obtained.

Fourier transform infrared spectroscopy (FT-IR, Bruker, Germany) analysis of the DES-modified adsorbents between 500 and 4000 cm^{-1} was performed using KBr pellets. Thermogravimetric analysis (TG), derivative thermogravimetric (DTG) analysis, and differential thermal analysis (DTA) data were obtained using an S-1000 thermal gravimeter (Bruker, Germany) under air atmosphere over the temperature range 40–800 °C at a heating rate of 10 °C min^{-1}. Scanning electron microscopy (SEM) images were obtained using a JSM-7500 field-emission scanning electron microscope (Japanese Electronics, Japan). The Brunauer–Emmett–Teller (BET) surface areas were measured under N_2 using an Autosorb-iQ-MP surface area and porosimetry analyzer (Quantachrome Instruments, USA).

2.3.2. Purification by DES-Based SPE

To select a suitable adsorbent for SPE, evaluation of the adsorption ability of an adsorbent is key [28]. Consequently, each of the ChCl DES-modified adsorbents was added to 1.0 mL aliquots of the sample extraction solutions prepared in section 2.2.2. for 3.5 h to adsorb the target compounds, by which the adsorption ability of

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