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Deacidification of palm oil using betaine monohydrate-based natural deep eutectic solvents

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ABSTRACT

In the palm oil industry, the deacidification process is performed by steam stripping which causes the loss of most of palm oil's natural antioxidants due to high temperature. The liquid–liquid extraction process which is carried out at low temperature is preferable in order to preserve these compounds. The use of hydrated ethanol can reduce the losses of antioxidants, but the ability of this solvent to extract free fatty acids also decreases. Betaine monohydrate-based natural deep eutectic solvents (NADES) have extensive potential for this process. The selectivity of these NADES was determined to select a preferable solvent. The betaine monohydrate-glycerol NADES in a molar ratio of 1:8 was determined to be the preferred solvent with the highest selectivity. This solvent has an efficiency of palmitic acid extraction of 34.14%, and the amount of antioxidants can be preserved in the refined palm oil up to 99%. The compounds are stable during extraction.

1. Introduction

Crude palm oil is very rich in natural antioxidant compounds, such as carotenes and tocopherols which are beneficial to human health; therefore, most palm oil products are used as edible products (Chuang & Brunner, 2006). On the industrial scale, the deacidification process is performed by steam stripping at high temperature (Zulkurnain et al., 2012) at which carotenes are thermally degraded, and significant amounts of tocopherols and tocotrienols are evaporated (da Silva et al., 2011).

In order to preserve the antioxidant compounds originally present in crude palm oil and to maintain the nutritional value of the refined palm oil product, deacidification by liquid–liquid extraction is preferred. This process can be performed at room temperature, thereby reducing energy consumption and minimizing the losses of antioxidant compounds (Gonçalves & Meirelles, 2004; Rodrigues, Peixoto, & Meirelles, 2007). Previous studies have concluded that deacidification of palm oils using hydrated ethanol as a solvent can reduce the losses of natural antioxidants, but the amount of free fatty acids that can be extracted also decreases (Gonçalves, Filho, & Meirelles, 2007). Therefore, the possibility of using an alternative solvent for the palm oil deacidification process should be explored in order to obtain solvent with high selectivity.

Natural deep eutectic solvents (NADES) are recently developed by eutectic mixture of a non-toxic quaternary ammonium salt (such as choline chloride or betaine) and a hydrogen bond donor (HBD) (such as sugars, polyols, and organic acids) (Abbot et al., 2011; Choi et al., 2011; Dai, van Spronsen, Witkamp, Verpoorte, & Choi, 2013; Maugeri & de Maria, 2012; Ribeiro, Coelho, & Marrucho, 2013; Shahbaz, Baroutian, Mjalli, Hashim, & AlNashef, 2012).

NADES are attractive because of their non-toxicity, low vapor pressure, low flammability (Wu, Caparanga, Leron, & Li, 2012), and easily recycled (Maugeri, Leitner, & de María, 2012). Additionally, the poorly water soluble compounds, such as bioactive and macromolecules are highly soluble in sugar or polyalcohol based-NADES that have least polarity (Choi et al., 2011; Dai et al., 2013). NADES are also described as designer solvents due to their physicochemical properties that can be controlled by properly combining various salts with different HBDs (Abbot et al., 2011; Hayyan et al., 2012, 2013).

Recently, NADES have been widely applied as solvents for extraction (Bubalo, Curko, Tomasevic, Ganic, & Redovnikovic, 2016; Cui et al., 2015; Dai, Rozema, Verpoorte, & Choi, 2016; Das, Sharma, Mondal, & Prasad, 2016; Garcia, Rodriguez-Juan, Rodriguez-Gutierrez, Rios, & Fernandez-Bolanos, 2016; Karimi, Dadfarnia, Shabani, Tamaddon, & Azadi, 2015; Li et al., 2016; Peng et al., 2016; Wei et al., 2015). Peng et al. (2016) studied a range of DES with different alcohol/choline chloride mole ratios to select the best DES for extraction of phenolic acids, and they concluded that DES of 1,3-butanediol and choline chloride mixture in a mole ratio of 6:1 possessed higher extraction efficiency. Also, the extraction yields of bioactive compounds

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(genistin, genistein, and apigenin) were found to increase with increasing 1,6-hexanediol/choline chloride from 1:1 to 7:1 mol ratio (Cui et al., 2015). Manic, Najdanovic-Visak, da Ponte, and Visak (2011) reported that ionic liquids (1-butyl-3-methylimidazolium dicyanamide, and Cocos alkyl pentaethoxi methyl ammonium methyl sulfate) were successfully applied as the solvents for the deacidification of soybean oil with a high distribution coefficient of linoleic acid and low distribution coefficient of oil.

Betaine monohydrate is a quaternary ammonium salt that is made as an additional product during the separation process of sucrose from sugar beet (Makela, 2004). Betaine monohydrate is a cheap, natural, sustainable, biodegradable and non-toxic resource; therefore, it also has potential for application as a salt in addition to choline chloride and betaine. Additionally, betaine monohydrate has strong hydrogen bonding behavior for itself due to the carbonyl group acts as a hydrogen bond acceptor and the hydrogen from water acts as a hydrogen bond donor (Hertel, Bommarius, Realff, & Kang, 2012). In the extraction process, target compounds can be extracted due to the presence of hydrogen bonding interaction between these compounds with NADES molecules (Dai et al., 2013). The presence of water molecules in NADES induces the solutes to interact with salt and HBD molecules of NADES and also to interact with the H atoms of water via hydrogen bonding.

NADES that are formed by mixing of the betaine monohydrate and different HBDs (polyol and mixed polyol/organic acid) can be utilized as highly selective solvents for the deacidification of palm oil by liquid–liquid extraction. The polyol-based NADES are least polarity (Dai et al., 2013). It is hypothesized that the palmitic acid with least polarity is soluble in betaine monohydrate-polyol based NADES, and contrarily with non-polar long-chain compounds (α-tocopherol and β-carotene).

The distribution coefficients of solutes (palmitic acid, β-carotene, α-tocopherol) and selectivity of betaine monohydrate-based NADES at a different mole ratio of betaine monohydrate to HBD should be determined in order to screen a preferential solvent for the palm oil deacidification process. The relationship between the physicochemical properties of NADES and the distribution coefficients of solutes was studied. The interaction between NADES and palmitic acid molecules was also investigated. In this work, palmitic acid was chosen as a model free fatty acid. Palmitic acid is major compound acid that highest concentration in palm oil (Lin, 2002).

2. Experimental

2.1. Material

The HBD compounds: glycerol (purity 99.5%), propylene glycol (purity 99%) and propionic acid (purity 99%) were purchased from Merck. Betaine monohydrate (purity greater than 99%) and Nile red (dye) were purchased from Sigma Aldrich. Commercial palmitic acid (purity 99%), β-carotene (purity 98.5%) and α-tocopherol (purity 99%) were purchased from Sigma Aldrich. Analytical standard palm oil, β-carotene (99% purity), and α-tocopherol (99.9% purity) were purchased from Sigma Aldrich. HPLC grade tetrahydrofuran (purity greater than 99.9%), acetonitrile (99.9% purity), acetic acid (glacial), and methanol (99.9% purity) were purchased from Merck. Analytical grade diethyl ether, ethanol, methanol, chloroform and phenolphthalein indicator were also purchased from Merck. Potassium dichromate and sulfuric acid were purchased from Merck for Jones' reagent preparation.

2.2. NADES preparation

NADES samples were prepared according to the procedure described by previous works (Dai et al., 2013; Hayyan et al., 2012). Because of its hygroscopic nature, betaine monohydrate was treated by drying in a vacuum dryer at 80 °C for 6 h before utilization. The betaine monohydrate and the HBD (glycerol or propylene glycol) were mixed in molar ratios of 1:2, 1:3, 1:4, 1:6, and 1:8. Additionally, mixtures of betaine monohydrate and mixed HBDs were prepared in this work. Table 1 lists the abbreviations of NADES. The components were weighed on an analytical balance with accuracy of 0.0001 g (Sartorius TE214S). The mixture was placed in a bottle with a screw cap and a stirring bar. Further, the mixture was heated on a hotplate with a stirrer (IKA C-MAG HS7) at a temperature of 50 ± 1 °C, with agitation at 150 rpm for a period of 90 min. A thermocouple (Lutron TM-914 C) was used to monitor the temperature of the mixture in the bottle. After reaching the liquid state, the mixture was cooled. Triplicate runs were performed for each NADES. The NADES were kept in well-sealed vials after preparation.

Table 1
List of abbreviation of betaine monohydrate-based NADES.

Salt	HBD type	Mole ratios salt:HBD	Abbreviation
Betaine monohydrate	Glycerol	1:2	DES 1
		1:3	DES 2
		1:4	DES 3
		1:6	DES 4
		1:8	DES 5
	Propylene glycol	1:3	DES 6
		1:4	DES 7
		1:6	DES 8
		1:8	DES 9
	Propylene glycol + Glycerol	1:1:1	DES 10
	Propylene glycol + Glycerol	1:2:2	DES 11
	Propylene glycol + Propionic acid	1:2:2	DES 12
	Glycerol + Propionic acid	1:1:1	DES 13

2.3. Liquid-liquid extraction process

The model palm oil feed containing palmitic acid (5%-mass), β-carotene (700 ppm), α-tocopherol (1000 ppm), as well as other compounds that generally compose crude palm oil. The time taken to reach equilibrium was estimated by sampling the phases every 10 min until a few consecutive samples produced essentially the same result of the analysis. It was determined that 120 min were sufficient to reach equilibrium (Fig. S1 in Supporting Information).

The palm oil and NADES at a volume ratio of 1:2 were mixed for 2 h at a temperature of 40 °C with agitation at 250 rpm on a hotplate with a stirrer (IKA C-MAG HS7). A thermocouple (Lutron TM-914 C) with a resolution of 0.1 °C was used for monitoring the temperature of the mixture during the mixing process. After stirring, phase separation of the mixtures was conducted by centrifugation, and the mixtures were then left still for at least 60 min (Centrifuge Nesco 80-2A). Using a Hamilton syringe, the NADES-rich phase (lower layer) was separated from the oil-rich phase and further prepared for analysis of the palmitic acid, β-carotene and α-tocopherol contents.

2.4. Determination of palmitic acid, β-carotene, and α-tocopherol content in NADES-rich phase

The quantity of palmitic acid was determined according to the official titration method 2201 by the IUPAC (Manic et al., 2011). The oil-rich phase was washed with warm water until all traces of NADES were removed, which was tested by qualitative analysis with Jones' reagent. The sample was later dried over Na_2SO_4. Two milliliters of the sample was accurately measured using a micropipette (Brand) and then mixed with 25 mL of the mixture (ethyl ether and ethanol at a volume ratio of 2:1) to which two drops of phenolphthalein solution were added. These mixtures were titrated with a 0.05 M ethanolic solution of KOH until