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Review

Natural deep eutectic solvents-mediated extractions: The way forward for sustainable analytical developments

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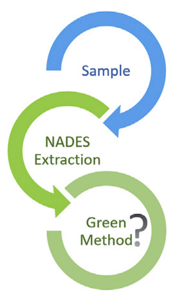
HIGHLIGHTS

- Contributions regarding NADES as extraction media are analyzed in terms of energy, time, sample and solvent consumption.
- Strategies to make NADES-mediated approaches even greener are presented.
- The review underlines the relevance of developing sustainable analytical methodologies.

GRAPHICAL ABSTRACT



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ABSTRACT

The concept of sustainable development has impacted in analytical chemistry changing the way of thinking processes and methods. It is important for analytical chemists to consider how sample preparation can integrate the basic concepts of Green Chemistry. In this sense, the replacement of traditional organic solvents is of utmost importance. Natural Deep Eutectic Solvents (NADES) have come to light as a green alternative. In the last few years, a growing number of contributions have applied these natural solvents proving their efficiency in terms of extraction ability, analyte stabilization capacity and detection compatibility. However, the arising question that has to be answered is: the use of NADES is enough to green an extraction process? This review presents an overview of knowledge regarding sustainability of NADES-based extraction procedures, focused on reported literature within the timeframe spanning from 2011 up to date. The contributions were analyzed from a green perspective in terms of energy, time, sample and solvent consumption. Moreover, we include a critical analysis to clarify whether the use of NADES as extraction media is enough for greening an analytical methodology; strategies to make them even greener are also presented. Finally, recent trends and future perspectives on how NADES-based extraction approaches in combination with computational methodologies can contribute are discussed.

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Contents

1. Introduction

Nowadays, global sustainability challenges are intimately interconnected being human health and environmental impact the main concerns. In this context, it is not possible to deal with analytical chemistry in isolation [1]. Bearing in mind that analytical chemistry methods are used to solve problems, only holistic and disruptive approaches integrating research, development, and innovation in interdisciplinary and transdisciplinary studies will make revolutionary advances. Over the last few years, scientific chemistry community has been mobilized on the development of green practises. Concerning the contemporary goals of analytical chemists, the great challenge is to align the principles of Green Analytical Chemistry (GAC) with the twelve principles of Green Chemistry [1–3].

Despite unquestioned advances in analytical instrumentation, sample prep is the bottleneck of every analytical procedure. The adverse environmental impact of analytical procedures can be overcome applying the following strategies: miniaturizing the analytical scale and/or replacing hazardous solvents by safer alternatives. Although the ideal situation is the development of “solvent-free” extraction schemes [4], this concept is still rather utopic. Therefore, the search for alternative solvents is of utmost important [5].

Over the past two decades, ionic liquids (ILs) gained great attention as green media. Nevertheless, their “greenness” is often argued, due to their poor biodegradability, biocompatibility, and sustainability [6]. Later, a new kind of solvents based on the eutectic behaviour of their counterparts, emerged as an alternative to ILs. Deep eutectic solvents (DES) were introduced by Abbott et al. [7], showing a wide liquid range and interesting properties to be used as a solvent. Eutectic system, from the Greek "ευ" (eu = easy) and "Τήξις" (teksis = melting) is denoting a mixture of substances forming a joint super-lattice that melts and freezes at a single temperature that is lower than the melting points of the separate constituents. The application of DES has been focused to organic reactions, organic extractions, electrochemistry, and enzyme reactions carried out at 60 °C [8]. Nevertheless, the synthetic components of DESs can be toxic, reducing their possible use for applications in food and pharmacology industries [9].

In 2011, Verpoorte and co-workers [10] coined the term “Natural Deep Eutectic Solvents” (NADES), for the mixtures formed by cellular constituents such as sugars, alcohols, amino acids, organic acids and choline derivates. NADES fully represent the Green Chemistry principles. They are considered as the third solvent in living cells, which explains their high solubilizing capacity for natural products. The different compositions of NADES result in a broad range of physical properties.

NADES are typically obtained by mixing a hydrogen-bond acceptor (HBA), with a hydrogen bond donor (HBD) molecule, leading to a significant depression of the melting point. Hydrogen bonding and Van der Walls interactions are the main driving force of this phenomenon. Alcohol, amine, aldehyde, ketone and carboxylic groups behave both as hydrogen-bond donor and acceptors. Taking into account the chemical nature of their components, NADES can be classified as follows: 1) Derivatives from organic acids, 2) Derivate from choline chloride, 3) Mixtures of sugars, 4) Others combinations [6].

Readily available components, simple preparation, biodegradability, safety, reusability and low cost are major advantages that are encouraging research on their analytical applications. Indeed, they show excellent physicochemical properties: negligible volatility, a wide range of liquid state, adjustable viscosity and polarity and a high solubilisation capacity [11,12]. Three methods are most commonly used for preparing NADES: a) heating and stirring: the mixture is placed in a bottle with a stirring bar and cap and heated with agitation till a clear liquid is formed (about 30–90 min) [8,13,14]; b) evaporating method: components are dissolved in water and evaporated with a rotatory evaporator. The liquid obtained is put in a desiccator with silica gel till they reach a constant weight [8]; c) freeze drying method: aqueous solutions of the individual counterparts are freezzed-dried [15].

When analyzing the publications concerning NADES applications (Fig. 1), Europe and Asia are the leading territories of this subject, while contributions from America (North and South) are beginning to walk. Taken together, NADES are designer solvents due to the numerous structural possibilities and the potential for tuning their physico-chemical properties for different purposes [13]. Unique interactions between the NADES with target analytes make it possible to selectively separate trace compounds from complex matrices.

Several interesting review reports concerning the features and applications of DES have been published recently. Bubalo et al. [16] presented an overview of different green approaches for the extraction of plant biologically active compounds, including supercritical fluid, subcritical water and NADES extractions. Their

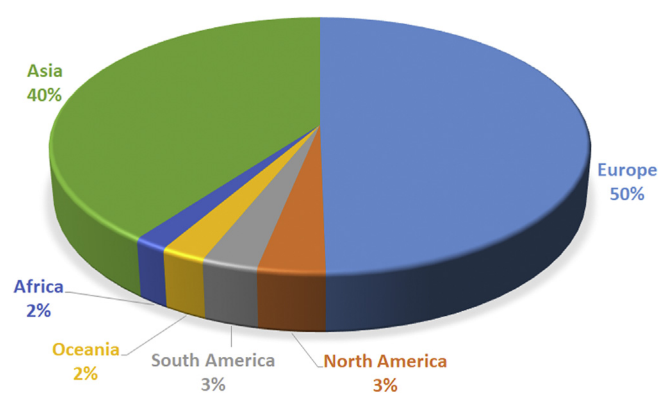

Fig. 1. World-wide geographical origin of the publications concerning NADES applications using the keywords natural deep eutectic solvents (source www.scopus.com; date of search: 07.19.18).