



Editorial overview: A closer look on sustainable solvents and processes

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João A. P. Coutinho is a full professor at the Chemistry Department of the University of Aveiro, Portugal, where he is the vice-director of CICECO, one of the leading European laboratories in Materials Science. He leads a multidisciplinary research team that focuses on the development of green solvents and novel separation processes for biorefinery and circular economy. Currently, he strives to apply bio-based solvents, deep eutectic solvents, and ionic liquids to these processes and attempts to better understand their physical–chemical behavior.

In 2015, 17 Sustainable Development Goals were outlined by the United Nations (“Transforming our World: the 2030 Agenda for Sustainable Development”), representing a plan of action for people, the planet, and prosperity [1]. Several of these goals highlight the need for sustainable chemistry and engineering, where green and sustainable solvents play a pivotal role. High quantities of organic solvents in respect to the products obtained are essential for chemical reactions to proceed. Furthermore, separation processes depend on the use of high amounts of solvents to accomplish high purity levels of the target compounds. As a result, the annual industrial-scale production of organic solvents has been estimated at ca. 20 million metric tons [2]. Although the current society cannot proceed without solvents, a growing awareness of the impact of solvents on human health and the environment has been faced in the past decades. To overcome these drawbacks, while keeping our society standards, a range of greener and sustainable solvents has been proposed, and the sustainability of some industrial processes has been improved.

The understanding of solvent properties is a core part of sustainable development; in this line, several guides of solvents (mainly published by pharmaceutical companies) have been proposed to rank solvents according to their environmental, safety, and health (ESH) characteristics [3]. These guides can be used to help researchers and companies to identify solvents with low ESH impacts, while discouraging the use of nonrenewable and toxic solvents. Among some well-known and currently used solvents with low ESH impact, such as water, ethanol, ethylacetate, and anisole, among others, examples of neoteric solvents that have been studied in a sustainable perspective include solvents derived from biomass, ionic liquids (ILs), deep eutectic solvents (DESs), liquid polymers, supercritical carbon dioxide, gas-expanded solvents, and switchable solvents. Nevertheless, if a common volatile solvent can be replaced by a neoteric solvent, it does not mean that it should be. There are several barriers that need to be addressed before such neoteric solvents can be adopted at a large scale, namely, cost, availability, purity, safety regulations, disposal procedures, and recycling procedures, among others. Furthermore, the entire life cycle of the solvents used and proposed processes are critical issues that must be considered. Ideally, to improve process sustainability, the following strategies should be considered: processes should be carried out without any solvents (e.g. mechanochemistry), water should be considered as a primordial solvent, and solvents should be selected based on their ESH impact and able to

display a multiple role (e.g. as a solvent and reagent, as a solvent and for product separation, and so on). Given the critical need of improving sustainability of both solvents and processes, this issue covers state-of-the-art reviews on neoteric and greener solvents and their application in several fields.

Jimenez-Gonzalez (<https://www.sciencedirect.com/science/article/pii/S2452223618301147>) provides an overview on life cycle considerations of solvents. The author clearly highlights that ‘the most sustainable solvent is the solvent that is not used.’ However, when this approach is not possible, efforts are critically needed to minimize the solvent footprint, both by minimizing the amount of solvents used and their health and environmental impact. Their impact could be addressed by the solvent’s life cycle analysis, which considers raw material extraction and production, manufacturing, transportation, use, recycling, and final disposal. This review describes key aspects to be taken into account when evaluating and selecting solvents by a life cycle assessment approach.

Li and co-workers (<https://www.sciencedirect.com/science/article/pii/S2452223619300215>) give an overview on the greenest solvent overall: water. In this review, the advantages and disadvantages of several neoteric solvents are described and compared with the features offered by water, including supercritical or subcritical water. The combination of solvent strategies and separation technologies is also overviewed. The authors conclude that there is no perfect solvent for all chemical applications. However, the use of water as a solvent, if no other solvent can be applied, should be always considered. Within the field of green solvents, **Marrucho and co-workers** (<https://www.sciencedirect.com/science/article/pii/S2452223618301135>) disclose an overview of the potential of DESs as promising solvents in clean water, clean energy, and biotechnology fields. The remarkable properties of these solvents, namely, their chemical versatility, which allows their tailoring for target applications, easy preparation, and no need for purification steps, are highlighted. Current challenges and opportunities arising from the use of DESs aligned with the scope of today’s major concerns are described. **Giner and co-workers** (<https://www.sciencedirect.com/science/article/pii/S2452223618301342>) outline solvents derived from biomass and their potential as green solvents. Their environmental impact and other key physicochemical properties, such as vapor pressure or solubility, are described and compared with those displayed by conventional volatile organic solvents. The toxicity of these chemicals in several organisms is compiled, described, and analyzed according to the type of end point studied. Although solvents from biomass have some green credentials, genotoxicity is a crucial property that still needs to be considered. In addition to ILs as neoteric solvents, mixtures of two ILs have been gaining

momentum to tailor their properties. **Dhakar and Shah** (<https://www.sciencedirect.com/science/article/pii/S2452223618301159>) overview the knowledge gathered using molecular simulations applied to IL–IL mixtures. With the continuous rise in the computational power and accessibility of software packages supporting the implementation of polarizable models, future accurately modeling is expected aiming at tailoring the properties of ILs and other green solvents for target applications.

The use of green solvents has been a hot topic in the development of sustainable processes. In this line, **Sheldon** (<https://www.sciencedirect.com/science/article/pii/S2452223618301172>) provides an overview on the ‘greening of solvents’ focused on the development of sustainable organic synthesis. Recent developments on the use of sustainable solvents in organic synthesis are critically reviewed, where the commonly used organic solvents and less common bio-based examples are assessed and ranked according to their waste disposal and environmental impact, health, and safety parameters. The use of water as a solvent, including the use of aqueous biphasic catalysis, micelle-enabled catalysis, and biocatalysis, is finally outlined as a more sustainable alternative to reactions in organic solvents. In quest of shifting to a sustainable bio-based economy, lignocellulose is becoming an increasingly important feedstock. However, its valorization demands for the effective and sustainable deconstruction of the lignocellulosic matrix and fractionation of its constituents. **Hummel and co-workers** (<https://www.sciencedirect.com/science/article/pii/S2452223618301354>) describe the use of ILs and gamma-valerolactone as alternative solvents in the deconstruction and refining of biomass. The latest progresses in this field are described, as well as their feasibility in terms of costs and recyclability. Recent demands for the decrease, reutilization, and valorization of waste have motivated research within a biorefinery and circular economy perspective. **Meireles and co-workers** (<https://www.sciencedirect.com/science/article/pii/S2452223618301202>) disclose the perspectives on biorefining of plant matrices into marketable products using supercritical CO₂. A wide variety of products can be obtained from vegetable biomass, including extracts with relevant biological activities and biopolymers, which are overviewed. **Prasad and Sharma** (<https://www.sciencedirect.com/science/article/pii/S2452223618301366>) describe and analyze the use of green solvents, such as ILs, DESs, and bio-derived solvents, for the extraction, dissolution, and processing of biopolymers. Biopolymers such as guar gum, tamarind gum, cellulose, agarose, κ-carrageenan, chitin, and DNA are a target of this overview. Although neoteric solvents such as ILs and DESs are suitable for the processing of various biopolymers and functional material preparation, additional efforts are still needed to scale up the described processes, while turning them cost-effective and environmentally friendly.

Within a circular economy perspective, **Billard** (<https://www.sciencedirect.com/science/article/pii/S2452223618301123>) overviews the use of green solvents in urban mining, namely, by the use of green solvents in recycling processes and metal recovery from technological objects. Significant advances have been achieved in the recovery of metals from phosphor lamps, multilayer flexible packaging, permanent magnets, and used tires. **Pacheco-Fernández and Pino** (<https://www.sciencedirect.com/science/article/pii/S2452223618301391>) report on the use of green solvents in analytical chemistry. Among the neoteric solvents investigated, amphiphilic solvents, ILs, and DESs received significant attention. These have been investigated in liquid-phase microextraction methods (within sample preparation) and as additives or pseudo-stationary phases in liquid chromatography (within analytical separation methods). Given their potential, an increase in the number of analytical applications of green solvents is expected in the following years. **Nematollahi and Carvalho** (<https://www.sciencedirect.com/science/article/pii/S2452223618301160>) provide a critical analysis on the use of alternative solvents (ILs and related mixtures and DESs) for CO₂ capture. The limitations that have been hampering the development of separation units and processes capable of fulfilling industrial demands are described, as well as the steps needed to turn the carbon capture, utilization, and storage by neoteric solvents a reality. Within the application of green solvents to develop sustainable processes, **Schuur and co-workers** (<https://www.sciencedirect.com/science/article/pii/S2452223618300919>) provide an overview on solvent-based separation processes. These processes can reduce the energy input for separation, for example, when compared with distillation, and improve biocompatibility. The authors conclude that for all solvent systems not only

the primary separation operation should be considered but also all the entire process should be taken into account, including solvent recovery, where most of the energetic input takes place.

In this issue, the green credentials of neoteric solvents are described, as well as their performance and potential in several applications, ranging from catalysis, biomass processing, and urban mining to CO₂ capture. A range of technical, economic, and environmental factors are summarized, giving a more complete picture of the current status of sustainable solvents and process development. Although it is still a long path to take, owing to the remarkable characteristics and performance of neoteric solvents, their use in industrial processes is becoming a reality, as appraised by some recent created companies.

Conflict of interest statement

Nothing declared.

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