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(Article begins on next page)

Sustainable by design approaches[#]

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[#]This Virtual Special Issue is dedicated to the memory of Professor Pietro Tundo.

Recently, an increasing amount of interest from academia, industry and policy makers has been devoted to the application of the 12 Principles of the Green Chemistry and Green Engineering to pursue Sustainable Development Goals (SDGs) and favor a New Green Deal worldwide. These important actions, driven by chemistry & engineering, are based on the fundamental idea of guiding political decisions toward more environmentally friendly choices. In this framework, the evaluation of nexus solutions which include not only the performance of a molecule but also its sustainability through a careful assessment of the intrinsic properties and transformations is crucial. With this virtual special issue, we aim to favor the development of an innovative conceptual construct about products/feedstocks/processes including sustainability considerations in addition to the reductionist evaluation of performance (Cespi et al., 2020). Herein, several applications in the field of sustainable by design approaches are discussed.

Licursi and coworkers (Licursi et al., 2023) proposed a cascade synthesis for the preparation of carbon-based precursor, followed by its sulfonation to increase the pristine acidity combining hydrothermal carbonization and pyrolysis. A chemometric approach was employed to optimize the hydrochar synthesis, using microcrystalline cellulose as starting feedstock and the identified optimal reaction conditions were applied to the hydrothermal carbonization of hazelnut shells, using a biobased feedstock. The most promising chars were sulfonated and

tested as heterogeneous acid catalysts in the aqueous conversion of fructose to 5-(hydroxymethyl)furfural obtaining maximum yields of about 40 mol%. These promising results pave the way for the use of such wastes as efficient acid catalysts for the synthesis of 5-(hydroxymethyl)furfural, contributing to ensure the biomass circular exploitation.

In their work, Guravaiah (Guravaiah et al., 2023) reported a novel one-pot construction of *N*-acyl α -cyanoamines from α -amino amides and acids *via* propanephosphonic acid anhydride (T3P®)-assisted cascade strategy. The products are formed in 81–94% in 12 h at room temperature. The developed protocol has also been successfully utilized for the construction of two biologically important molecules such as DPP-4 (Dipeptidyl peptidase-4) inhibition agent and a clinical agent of COVID-19. Moreover, the products with multiple functional groups including chiral centers were transformed conveniently into desired complex molecules.

Das and coworkers (Das et al., 2023) investigated the use of Draksha Beeja supplements (Grape Seed Extract, INLIFE) loaded edible gelatin and potato starch-based mat in prospective tissue engineering applications. The fabricated mats were characterized physicochemically in detail and were also examined in-vitro and in-vivo for cytocompatibility and biocompatibility assessment. The hemocompatibility assay indicated no blood toxicity while the in-vivo testing showed high biocompatibility and no toxic reactions for the prepared materials.

To overcome the limitation due to sluggish kinetics of cathodic oxygen reduction reaction (ORR) in fuel cells, Hsu and coworkers (Hsu et al., 2023) reported the improvement of polymer electrolyte membrane by using Mn-doped vacancy boron nitride nanosheet as a noble-metal-free and efficient electrocatalyst for ORR process employing DFT (Density-functional theory) computation. Results show that boron has a greater desire to replace in vacancy-BN than nitrogen to capture Mn atoms. In addition, computations of electronic features indicated that the active site for the ORR process is the top site of Mn. In addition, the authors have shown that the Mn atom has a high activity to adsorb oxygen-containing intermediates, which is due to the remarkable charge difference between nitrogen and manganese on catalysts surface. They reported that for oxygen-contained intermediates, Eads values are reduced in order of: O > OH > OOH > O₂ > H₂O₂ > H₂O. Moreover, higher Eads of value O₂ suggests greater Eads of oxygen-contained intermediates.

Finally, Rizki and coworkers (Rizki et al., 2023) reviewed the utilization of marine organisms for the green synthesis of silver and gold nanoparticles. In fact, nanobiotechnology has tremendous potential to support eco-friendly systems and industrial sustainability through the production of metal nanoparticles using biological sources. The review extensively discussed the use of different types of marine organisms, including bacteria, fungi, vertebrates, invertebrates, and diverse algae, able to withstand environmental pressure and the capability to grow in the presence of high metal concentrations to synthesize metal nanoparticles. Furthermore, marine organisms are a source of active compounds as reducing and stabilizing agents present in the biological extract. The adoption of these procedures is reviewed in the light of green chemistry principles.

Di Prima et al. (Di Prima et al.,2022) investigated the isolation from grapefruit of IntegroPectin, a new family of pectins of exceptionally high and broad biological activity obtained via hydrodynamic cavitation of citrus biowaste carried out in water only. The study compared grapefruit IntegroPectin powders obtained via spray drying and via freeze drying in terms of phenolic content, quantification of the most representative flavonoids, radical scavenging activity, total protein content, and pH of the aqueous solutions. The optimization of the spray drying parameters allowed to maximize the yield of isolated pectin that nearly approached (>95%) the quantitative yield obtained via freeze drying, while preserving its phenolic content. The usage of tools like Life Cycle Assessment (LCA) and Material Flow Analysis (MFA) was also part of the special issue. The first is a technical methodology applied to understand how materials or energy are metabolized in natural- anthropogenic systems at different scales (e.g., processes, isolated populations, regions, countries, groups of countries to the entire world), providing quantifiable information to support decision-making processes in the fields of resource management, waste management, and environmental management. Based on the principle of mass conservation, MFA detects how and where a given resource is transported, stored, or metabolized through different processes and sinks.

Mejia Duque Torres et al. (Mejia Duque Torres et al., 2023) applied MFA to address the issue of phosphorus (P), element rank as nearly critical by the United States and labeled as critical raw material (together with the phosphate rocks) by the European Union. In the study. The authors characterized the 2020 P cycle in the Province of Rimini (Italy) and the State of San Marino, which are served by a wastewater treatment plant of Santa Giustina (RN) with a 560,000 person-equivalent capacity. The model shows that among the total amount of P entered the system (about 236 ± 23 t) only the 65% (155 ± 14 t) left it, resulting in a net accumulation of 81 ± 21 t P. This is mainly located in soil for crop production, water bodies, and sedimentation due to dissipative flows. Therefore, the greatest potential for phosphorous recovery is embedded into the digested sludge from the wastewater treatment plant, which would ideally meet 96% of the annual local demand of mineral fertilizers. However, this flow is currently disposed of by landfilling.

The LCA, on the other hand, is a standardized methodology (ISO 14040 and ISO 14044) able to address the potential environmental impacts of product, processes and services along the entire life cycle or part of it. Two studies were proposed on such issue.

In the first, Piazzzi et al. (Piazzzi et al., 2023) the LCA methodology was combined with experimental analysis and software engineering simulation to study the production of biobutanol from bioethanol (Guerbet reaction) toward an organo-metallic homogeneous catalytic system based on Ruthenium. After a first optimization at laboratory scale, a conceptual design of a process at industrial scale has been carried out to simulate a plant able to produce 340 kg of biobutanol. Finally, the LCA analysis was performed to assess the potentialities in terms of environmental burdens by considering a multi-impact approach (18 impact categories through ReCiPe 2016). For the first time the catalyst synthesis was simulated from the roots, by including all the mass flows and taking into account its recyclability for 3 or 5 times (sensitivity scenarios). Results depict the impact of the Ru-based homogeneous catalyst is not negligible on the whole, therefore a higher recyclability is preferable to mitigate the impacts. A further comparison with the traditional fossil-based route (oxo synthesis) was also

carried out, underlining the biobutanol is more competitive in terms of resources consumption (fossil), climate change and fine particulate matter.

The LCA was also adopted by Ruini and co-workers (Ruini et al., 2023) to address the potential impacts of three glucosyl genistein derivatives (1 g) by adopting a cradle to synthesis perspective. The use phase of glucosyl derivatives was separately considered in order to determine the potential human health advantages occurring during the administration of these derivatives. The chemical synthesis over the extraction of genistein from soybean was considered. The preparation of genistin was experimentally conducted by exploiting a two-step synthetic protocol. During the work-up procedure, two further derivatives were isolated. The LCA analysis showed the intermediate 7-O-(β -Dglucosyl)genistein (AcG-7-GEN) has the greater contribution on the majority of the 18 impact categories analyzed at midpoint level (ReCiPe 2016). A further analysis revealed that the most of the contributions is associated to pharmaceutical quality genistein, but also to the use of silver carbonate and ethyl acetate. In order to also comprise the potential human health benefits of the synthesized compounds, this work also proposed for the first time a potential damage assessment factor for genistein and its derivatives. This allowed also to consider the potential benefits on human health occurring during the administration (i.e., the use phase) of the three synthesized genistein derivatives.

We hope that the advances presented in this special issue will be of interest to the readers. We thank all the authors, reviewers, and Editorial Board members of Sustainable Chemistry and Pharmacy, whose contributions and support were vital to the publication of this special issue.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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