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Marine-based green chemistry

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Sustainability is the color of cyan: from the terrestrial green to the marine blue, our planet's finite resources must be not only preserved, but utilized in a sustainable way. We live on a blue planet with over two thirds of the surface covered in water. The oceans have the potential to provide resources, such as food, biopolymers to replace plastics, and minerals to replace mining, but this environment is also under threat from plastic, pollution, and increasing carbon dioxide levels.

This themed issue of *Green Chemistry* is dedicated to the sustainable development of ocean resources at the interface of green technology and the blue economy. Chemistry has a major role to play in both utilizing and protecting the oceans and thus, this themed issue explores how green chemistry is tackling the dual challenges the oceans represent with a few examples from an extensive and growing list.

The blue biorefinery: general routes to chemicals from marine organisms. Just as biorefineries using feedstocks produced on land have been developed during the past two decades, blue biorefineries are being researched where ocean resources (algae or seafood by-products) are separated into fractions according to their chemical properties. Marine organisms, due to their habitats, produce significantly different metabolites to those made by land-based organisms and so the suite of chemicals accessed is quite different: calcium carbonate, agar, alginates, carrageenan, chitin, collagen, fucoidan, lipids, astaxanthin and other pigments, *etc*. Some of these have been widely used for hundreds of years. Irish moss, a species of red algae *Chondrus crispus*, contains carrageenan and has been used as a thickener and gelling agent in foods domestically and industrially. In some cases, methods to isolate the desired product from biomass are relatively mild (*e.g.*, extraction in water) but in other cases they are harsh and need re-evaluation in light of new green technologies. Green chemistry can play an important role across all parts of the marine-derived product life cycle from its birth (extraction and processing) through to its use and end-of-life or re-use.

Sustainable extraction and processing of marine biomass. Sustainable extraction and processing methods are needed in blue biorefineries. Conventional methods to obtain chitin from waste crustacean shells involve treatment with concentrated hydrochloric acid (to demineralize) and sodium hydroxide (to remove protein). Further heating and treatment with concentrated sodium hydroxide is needed to obtain chitosan. These hazardous processing methods produce significant quantities of waste that need neutralizing and degrade the biopolymer (*e.g.*, molecular weight reduction). Therefore, many researchers have developed greener methods of biopolymer isolation and processing. These often use alternative solvents such as deep eutectic solvents and ionic liquids, or mechanochemical methods (*e.g.*, cryo-milling). Catalysts, especially enzymes and more sustainable reagents are also being widely explored in ocean biomass processing. These approaches directly align with the twelve principles of green chemistry. However, it is wrong to assume that green methods employed in processing land-derived biomass will directly translate to a blue biorefinery, as often the matrices are more complex in ocean biomass feedstocks and the bioproducts themselves have different structures, solubilities, and properties.

Marine biopolymers to materials. Marine biopolymers have been used across a range of applications either alone or more recently in combination with each other to optimize desirable properties. For example, they can afford sustainable formulations for use in the biomedical sector including as scaffolds for cell growth or for slow, controlled release of pharmaceuticals. Many of these materials are inherently biocompatible and biodegradable but processing or modification may impact these parameters, and scientists should not assume that the bio-derived materials are a perfect green solution. Indeed, there is a significant need for more research into marine-degradable materials, especially as degradation in the oceans is highly dependent on regional conditions (*e.g.*, temperature, currents, organisms).

The use of green chemistry tools to manufacture marine-based products pro-

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vides a sustainable route to a range of products including minerals, fuels, polymers, and nutritional supplements. In many cases, the blue biorefinery uses waste from aquaculture and fisheries as its primary feedstock, which decreases the environmental footprint of these industries while increasing economic value and rural employment opportunities. Also, invasive species such as *Sargassum muticum* (a brown macroalgae) in Spain and green crab (*Carcinus maenas*) in Canada are being explored as feedstocks. However, care must be taken not to incentivize the harvest of invasive species, as some might further distribute the species more widely for economic gain.

This field is growing as more become aware of the bountiful opportunities that the oceans present and the need to protect ocean habitats. Further, with population growth, the United Nations has highlighted aquaculture as an important sustainable food production method, which will lead to more seafood waste being produced. This should be seen as an exciting opportunity to build environmentally sustainability into the system from the beginning. However, the language used by ocean scientists and food chemists is different to that of green chemistry, which can lead to misunderstandings. We need to be careful not to put up barriers between science and engineering sub-disciplines and try to understand how marine-based research both can be influenced by and influence, green chemistry. These barriers are artificial and great success can be achieved when they are broken down. For example, chemists, engineers, and physicists have made great impact in materials for energy applications despite their different perspectives. Interdisciplinary research will be critical to advancements in the blue biorefinery just as in other fields addressing environmental sustainability.

As guest editors of this themed issue, we would like to thank all the authors for their excellent contributions, the reviewers for their valuable time and energy, and the editorial staff of *Green Chemistry* for their guidance and support throughout the production of this issue. We hope that researchers in chemistry, biochemistry, materials science and beyond will enjoy reading the articles, and get inspired to delve into the waters of the blue biorefinery.

