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Review

Enabling technologies built on a sonochemical platform: Challenges and opportunities

Pedro Cintas [a], Silvia Tagliapietra [b], Marina Caporaso [b], Silvia Tabasso [c], Giancarlo Cravotto [b,*]

[a] *Departamento de Química Orgánica e Inorgánica, Facultad de Ciencias-UEX, Avda de Elvas s/n, E-06006 Badajoz, Spain*
[b] *Dipartimento di Scienza e Tecnologia del Farmaco and NIS - Centre for Nanostructured Interfaces and Surfaces, University of Turin, Via P. Giuria 9, 10125 Turin, Italy*
[c] *Dipartimento di Chimica, University of Turin, Via P. Giuria 7, 10125 Turin, Italy*

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ABSTRACT

Scientific and technological progress now occurs at the interface between two or more scientific and technical disciplines while chemistry is intertwined with almost all scientific domains. Complementary and synergistic effects have been found in the overlay between sonochemistry and other enabling technologies such as mechanochemistry, microwave chemistry and flow-chemistry. Although their nature and effects are intrinsically different, these techniques share the ability to significantly activate most chemical processes and peculiar phenomena. These studies offer a comprehensive overview of sonochemistry, provide a better understanding of correlated phenomena (mechanochemical effects, hot spots, etc.), and pave the way for emerging applications which unite hybrid reactors.

1. Introduction

Chemical industries and laboratories are heavily involved in the development of mild, simple, environmentally friendly and inexpensive catalytic processes that adhere to the principles of green chemistry and process intensification, as well as fulfilling competitive production requirements. There is currently a huge gap between classic production processes and the new green integrated technology based protocols which aim for higher efficiency and sustainability. In spite of chemistry's multidisciplinary interactions, chemists are often extremely conservative when designing their experimental protocols. Nevertheless, the last few years have seen chemists and chemical engineers from various research fields meet under the ample umbrella of sustainability and share experiences and backgrounds. It is in this context that sonochemistry, whose effects arise from the action of ultrasound waves in liquids, has branched out into techniques like the closely related hydrodynamic cavitation (HC), microwave irradiation (MW), mechanochemical activation and flow chemistry (FC) in both meso- and microfluidic reactors. The purpose of this concise review is to draw attention to the above-mentioned combinations, their practical operational applications and reduced environmental and economical impact. The concept of synergy, i.e., the fact that the benefits of the hybrid protocol exceed those of each technique alone, has been well documented. However, the literature also deserves a more a critical assessment which highlights pros and cons alike. We believe that in doing so the discipline of non-conventional technologies will be recognised still further as a powerful ally to green chemistry and beyond.

2. Ultrasound and microwave irradiation

While popular wisdom simply associates MW with superior heating and US with efficient agitation, these techniques are capable of doing so much more and this potential provides additional impulse to their expansion in synthesis and processing [1]. Acoustic and MW fields can be coupled in a variety of forms which can provide synergy, but also harness particular properties. An overview of such opportunities is shown in Fig. 1. It may not be immediately obvious how these physical fields work together as they show different characteristics; MW is electromagnetic radiation while ultrasound lacks quantum character. Neither of them interacts with matter at a molecular level as reflected by their wavelengths and low energies. Nevertheless, both cavitation and dielectric heating account for molecular excitation by creating microzones in which local heating becomes densely concentrated.

Not all sonochemistry practitioners will be aware that acoustic waves can be generated in viscoelastic media by pulsed MW, which means that various different resonance frequencies are obtained when piezoelectric bars are excited electrically or by

* Corresponding author.

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MW irradiation [2,3]. This is a thermoelastic mechanism of acoustic wave generation that can be harnessed in the non-destructive evaluation of piezoelectric samples. As a proof of concept, a composite plate containing oriented graphite fibres was subjected to MW-excited irradiation (9.41 GHz) which gave rise to US waves with frequencies over 100 kHz [4]. It is interesting to note that as the polarisation of the MW beam is rotated (from normal to parallel to the continuous fibres), the absorbed MW energy decreases significantly, thereby decreasing concomitantly the amplitude of the resulting acoustic wave. The major portion of the MW energy is reflected back by the graphite fibres. As mentioned, non-destructive inspection may benefit from this concept, although only laminates having graphite fibres concentrated in or near a single axis will be sensitive to this effect. Applications to other carbonaceous and dielectric composites can be surmised.

Likewise and yet disconnected from chemical matters, MW and US can be coupled in a sequential fashion in therapeutic medicine (Fig. 1). MW irradiation constitutes an important ablation technique against some carcinomas along with laser ablation and high-intensity focused ultrasound (HIFU). In this therapy, a MW antenna is percutaneously inserted into the tumour under the guidance of US waves and heats the zone until coagulation occurs. The process requires *in-situ* monitoring which is usually accomplished by magnetic resonance imaging (MRI). Its high resolution is certainly an advantage; however, MRI is costly and gives poor real-time data acquisition. These limitations can be overcome by the use of ultrasonic imaging that possesses suitable human-body penetrability and enables local temperature monitoring [5].

A substantial body of research into the combined use of MW and US has been devoted to enhancing chemical reactivity as well as to improving chemical processing and separation. Although pioneering works in the field threw up various technical and safety considerations in combining US and MW irradiation, the last decade has seen their coupling efficiently performed on lab and pilot scales [6–10]. MW and US can be employed in simultaneous and sequential modes (Fig. 2), which can either involve the use of loop reactors with two separate compartments or typical two-step treatments (pre-sonication and MW-assisted reaction).

Loop reactors and flow systems are particularly attractive for selective activations and show promise as automation may cause batch MW- or US-based chemistries to develop into cleaner and more efficient continuous processes (*vide infra*). As mentioned above, enhanced chemical effects have been observed when dielectric heating is associated with the large amount of energy released in cavitational collapse, causing particle fragmentation (especially in heterogeneous transformations) and molecular excitation.

The use of hybrid US/MW irradiation in plant molecule extraction is truly remarkable. Plants are an invaluable source of bioactive substances for the pharmaceutical and nutraceutical industries as well as being important in the preparation of perfumes and cosmetics. This combination is often superior to ultrasound- and MW-only assisted extractions (UAE and MAE, respectively) and leads to higher yields in shorter reaction times [8,11]. Prolonged sonication can become detrimental and decomposition is a potential, undesirable side effect, particularly with sensitive molecules.

Most synthetic uses of the US/MW marriage are found in classical organic reactions and in metal-assisted catalytic reactions, in particular. Applicability has so far been limited to a few venerable reactions such as the Suzuki, Heck or click reactions and has proven to be indispensable in modern organic synthesis. This field would clearly benefit from further exploration into the use of combined irradiation, but will also require precise reaction set-up design which would be able to convert the aforementioned physical effects into solid results in terms of reactivity and thereby provide satisfactory rationales. Early studies, such as the hydrazinolysis of esters in solventless conditions for example [12], were conducted in simple, home-made devices by inserting a detachable horn into a modified domestic oven. Despite this same procedure furnishing both reaction acceleration and high-yielding syntheses [7,8], it can no longer be employed as the use of domestic ovens is strongly discouraged in contemporary studies because of its lack of reproducibility and inaccuracies in power and temperature measurements. Moreover, horn material was not always specified, which may have misled many readers (as hazards may occur when metallic materials are irradiated by MW).

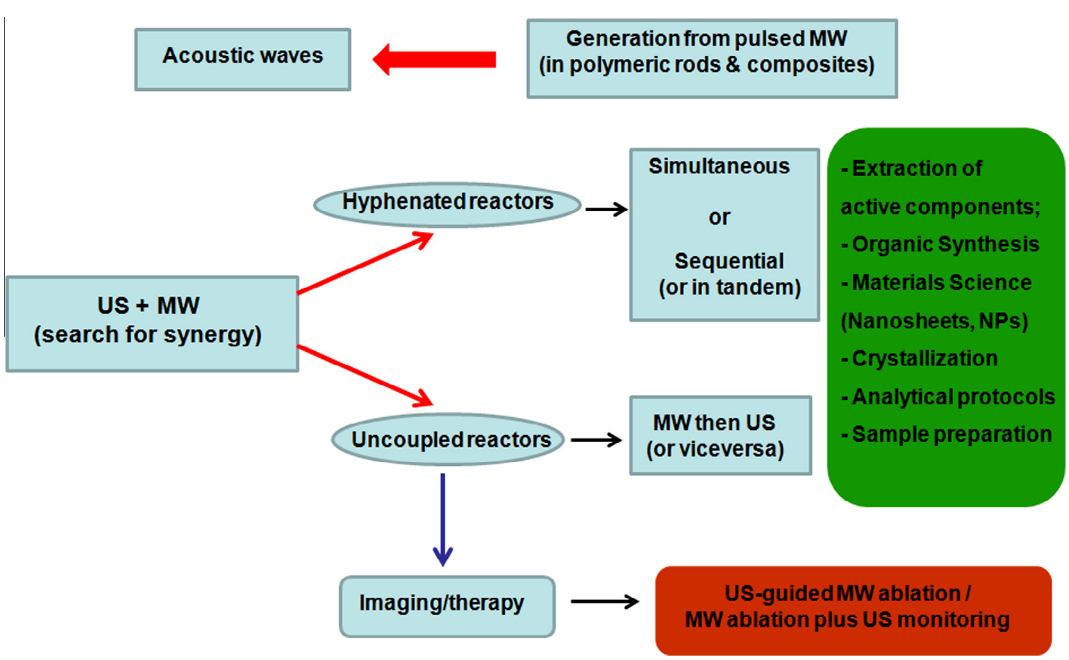

Fig. 1. Ultrasound (US) and microwaves (MW) interplay.