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ABSTRACTS

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Sunday, 28 August 2022

Alfred Loomis Award Lecture

PL01
Reflections on the development of sonochemistry from the 1980's
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Introduction
There can be no doubt that when sonochemistry first came to the notice of chemists in the early 1980's it was related to either improved synthesis or enhanced reaction rates through the application of ultrasound. It is the fundamental research from the 1920's which is always referred to as the first steps in the subject [1] and there was a much broader interest in the science of ultrasound itself by the 1930's [2]. The term "sonochemistry" was first used in 1951 [3] and industrial applications of power ultrasound were well known by the 1970's [4] but the uses of ultrasound in "pure" chemistry was not widely explored until after an explosion of interest in the 1980's. With the passage of years, from that time on, it has grown into a much broader subject encompassing much more than pure chemistry. Contributors and readers of the journal Ultrasonics Sonochemistry (first published in 1994) can testify to this.

Objectives
In this presentation the evolution of sonochemistry from its origins in chemistry in the 1980's will be traced through the work of the sonochemistry group in Coventry. We broadened our interests in applications of power ultrasound during the early 1990's and the topics we became involved in spanned environmental protection, food technology, metallurgy, polymer science, therapeutic ultrasound and ultrasonically assisted extraction.

Conclusions
A study of the breadth and depth of investigations into of sonochemistry reveals its strength as a scientific discipline. It is possible to predict from this where its strengths lie and where it will find applications in the future.

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Monday, 29 August 2022

Session: Materials and nanoparticles 1

PL02
Polymer sonochemistry – Revisited
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The reduction of length in polymer chains in solution when subjected to high-intensity ultrasound is one of the earliest known sonochemical effects, having been reported as long ago as the 1930s. Over the years, a large number of publications have shown that the process applies to all types of dissolved long-chain materials; synthetic – inorganic and organic – and natural – including proteins. In the main, breakage occurs when the chains are caught in fast flow fields and shock waves around collapsing cavitation bubbles. Many of the features of ultrasonic degradation are common with extensional flows. However, other products of cavitating solvents such as reactive radicals can also play a part. More recently, comparisons with other mechanochemical processes have dominated discussion in the Literature.

Many models have been proposed to correlate the kinetics of degradation with varying degrees of sophistication – and success. However, most assume the occurrence of just a simple chain breakage. Our experiments with a wide range of polymer and solvent systems and varying experimental parameters such as temperature, concentration and sound intensity have shown that the process is often more complicated than this simple view would suggest. Secondary reactions usually occur but are often not included in models. For example, organic polymers usually undergo homolytic cleavage and the resulting radicals undergo various reactions, complicating the modelling. The products are often not the simple, shorter chains that are envisaged. The presentation will illustrate some of these effects and how they can be accounted for.

The chain breakage process occurs in parallel with any polymer synthesis reaction that might take place. The implications for the models and also for the use to ultrasound to initiate and control polymerization reactions will be discussed. Finally, an illustration of how the various effects can be used to prepare functionalised materials with known structures will be described.

OP01
Acoustically-mediated microfluidic synthesis of two-dimensional crystals
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We demonstrate the intriguing possibility of harnessing 10 MHz surface acoustic waves (SAW) for rapid and efficient synthesis of two-dimensional materials (Rezk et al, Adv Sci 8, 2001983, 2021). In particular, we show that the large surface accelerations associated with the SAW vibration—on the order of 10 million g"s, together with the high intensity electric field inherent in the electromechanical coupling of the acoustic wave during SAW microcentrifugation and nebulisation, can be exploited to rapidly exfoliate bulk three-dimensional crystalline transitional metal dichalcogenides (TMDs; e.g., MoS_2 and WS_2) and carbides/nitrides (MXenes; e.g., $Ti_3C_2T_x$) into monolayer and few-layer nanosheets and quantum dots with high yield. In the case of the TMDs, the efficacy of the exfoliation process can be attributed to their unique piezoelectric property, particularly when they exist in odd number of layers due to broken crystallographic centrosymmetry (Ahmed et al, Adv Mater 30, 1704756, 2018). For MXenes, the ease by which the Ti_3AlC_2 MAX is converted to $Ti_3C_2T_x$ MXene within milliseconds is facilitated by the production of protons when the precursor LiF solution is dissociated under the local evanescent SAW electric field, which combine with fluorine ions to selectively etch the MAX phase into MXene (El Ghazaly et al, ACS Nano 15, 4287, 2021). Given the low cost of the device (typically around US$1 each by exploiting the economies-of-scale associated with mass nanofabrication) and the rapid (millisecond) synthesis time scales, we note the potential of the setup to be scaled to achieve industrially-relevant production rates through massive parallelisation of the platform.

Fig. 1
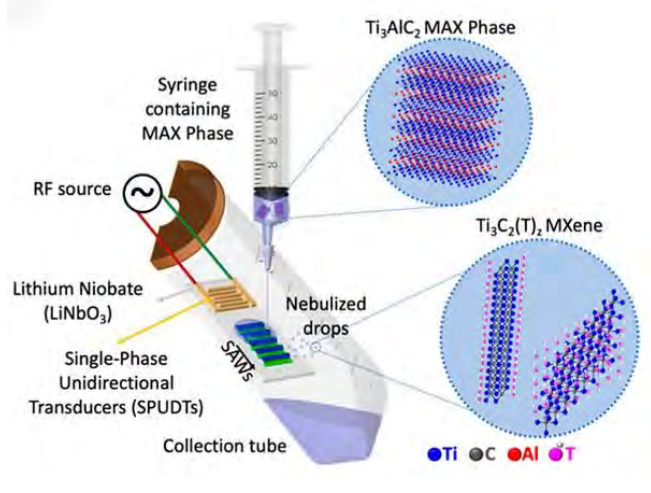
OP02

Power-Ultrasound – a sustainable way to accelerate concrete hardening

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High workability and high early strength concretes are required to maintain fast production cycles in precast concrete production. Often this is achieved by using concretes with high cement content and by applying heat treatment. Both are inducing an increased CO2 footprint of concretes. The aim is thereby to accelerate strength development of concrete by using power ultrasound (20 kHz) as activator for cement reaction. Therefore, Power-Ultrasound is applied to cement suspensions. After sonication concrete is produced by adding aggregates (sand and gravel) to the cement suspensions. The setting and early strength development (< 1 d) of sonicated concretes show a significant increase in early strength. It is shown that in sonicated concretes 30-40% of cement can be replaced by low-CO2 materials such as limestone or slag without strength reduction.

Microstructural investigations by Scanning Electron Microscopy show that Power-Ultrasound accelerates the formation of Calcium-Silicate-Hydrate phases which are the main and strength determining products of the reaction of Normal Portland cement and water (Figure 1). Reaction kinetics as measured by isothermal heat conduction calorimetry clearly show a reduction in the induction period of cement hydration. The composition of the aqueous phase of hydrating calcium silicate phase (Ca_3SiO_5, which is the main component of Portland cement) shows that sonication causes an early precipitation of Calcium-Silicate-Hydrate phases which act as seeds for further reaction. Because formation of these hydrates is an inherent process of cement hydration that is only timely shifted to an earlier stage, negative effects on concrete durability are not expected.

Based on these results it is concluded that compared to other common techniques for acceleration of concrete hardening Power-Ultrasound is an economically and ecologically sustainable technique that can be used for concrete production.
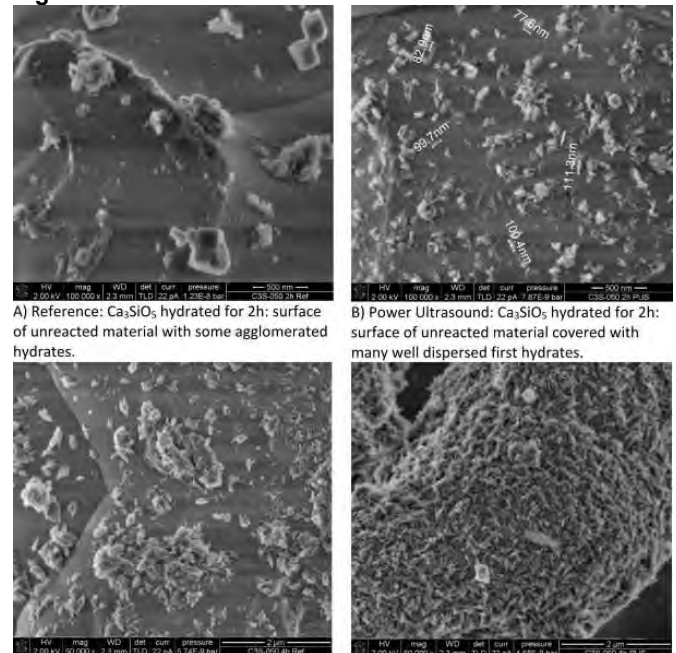
Fig. 1

A) Reference: Ca_3SiO_5 hydrated for 2h: surface of unreacted material with some agglomerated hydrates.

B) Power Ultrasound: Ca_3SiO_5 hydrated for 2h: surface of unreacted material covered with many well dispersed first hydrates.

C) Reference: Ca_3SiO_5 hydrated for 4h: surface of unreacted material with dissolution voids and some agglomerated hydrates

D) Power Ultrasound: Ca_3SiO_5 hydrated for 4h: surface of Ca_3SiO_5 covered with hydrates.

Figure 1: SEM-images (2 kV, high vacuum, secondary electron images) of Ca_3SiO_5 hydrated for 2 respectively 4h with and without ultrasound application.

OP03

Identification of the polymorphic form of paracetamol crystals produced under ultrasonic cavitation

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Bhangu *et al.* [1] have conducted anti-solvent crystallizations of paracetamol under ultrasonic cavitation, by adding cold water (the anti-solvent) in a hot solution of paracetamol and ethanol (the solvent). The authors observed crystals with different shapes in various number proportions and attributed these different shapes to the different polymorphic forms of paracetamol according to the results proposed by Sudha *et al.* [2]. Indeed, Sudha *et al.* obtained paracetamol crystals of different shapes by cooling crystallization in water and identified these different shapes as specific polymorphic forms : round crystal = form I (monoclinic) ; short stick = form II (orthorhombic); needle = form III (triclinic). The sorting of the polymorphs issued from Bhangu et al. ultrasonic crystallizations has thus been based on the length/width ratio of the crystals produced: ratio around 1 for form I, ratio slightly higher than 1 for form II and high ratios for form III. However, the limits used to discriminate between the different polymorphs were not specified. Besides, the analysis of the powder by X ray diffraction, infra-red spectroscopy or differential scanning calorimetry have missed to evidence the presence of both forms II and III ; authors indicate it is probably due to too small volume fractions of these forms. In addition, it remains a doubt, may be slight, on the presence of these forms as the solvent for crystallization differs between the both studies.

In the presented work, the polymorphic nature of the paracetamol crystals was studied with individual crystals placed in an aqueous solution of know concentration of paracetamol. For each studied crystal, its growth or dissolution was observed under an optical microscope as a function of the solution temperature and its stability domain was compared to the respective zones of stability of the three polymorphic forms given by Sudha *et al.*

First results indicate that the polymorphic forms I can exhibit a round shape, a thin plate-like shape or a short rod-like shape with triangular section. Form II is present as slightly longer rod shaped crystals. The limit value of the length/width ratio between these two polymorphs seems to be found between 3 and 5.

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Session: Fundamental aspects of cavitation

KL01
Impact of bubble coalescence in the determination of cavitation bubble sizes using a pulsed US technique

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Knowledge on cavitation bubble size distribution, ambient radius of bubbles is of interest for many applications that include therapeutic and diagnostic medicine. It however becomes a hard quest when increasing the ultrasonic frequency, when direct observation of bubble dynamics is no longer possible. A powerful experimental approach1 to measure the size distribution of bubbles active in sonoluminescence and/or sonochemistry is a technique based on pulsed ultrasound and sonoluminescence emission (Fig. 1). While it is an accepted technique, it is still lacking an understanding of the effect of various experimental parameters, including the duration of the pulse on-time, the nature of the dissolved gas, the presence of a gas flow rate, etc. The present work2, focusing on Ar-saturated water sonicated at 362 kHz, shows that increasing the pulse on-time leads to the measurement of coalesced bubbles. Reducing the on-time to a minimum and/or adding SDS to water allows to reducing coalescence so that natural active cavitation bubble sizes can be measured. A radius of 2.9-3.0 µm is obtained in Ar-saturated water at 362 kHz. The effects of acoustic power and possible formation of a standing-wave on coalescence and measured bubble sizes are discussed.

Conditions optimized with Ar are then used to derive ambient radii of cavitation bubbles in water saturated with He, Ar, Xe, O2, N2 and air: 3.0 µm for Ar, 1.2 µm for He, 3.1 µm for Xe, 2.8 µm for O2, around 1 µm for N2 and air3. If the pulse on-time is increased, bubble coalescence occurs, the extent of which is rather limited for Ar but extremely high for He or N2. As illustrated in Fig. 2 for an on-time of 4 ms.

Fig. 1: Experimental set-up used for the determination of bubble sizes.

Fig. 2: Extent of coalescence (in equivalent number of bubbles of radius R0) for different saturation gases as a function of the estimated R0, for ton = 4 ms (362 kHz, Pac = 47 W, 10°C).

1 Lee, Ashokkumar, Kentish, Grieser, *J. Am. Chem. Soc.*, 127 (2005) 16810-16811.

2 Pflieger, Bertolo, Gravier, Nikitenko, Ashokkumar, *Ultrason. Sonochem.*, 2021, 73, 105532

3 Pflieger, Audiger, Nikitenko, Ashokkumar, *Ultrason. Sonochem.*, 2021, 73, 105537
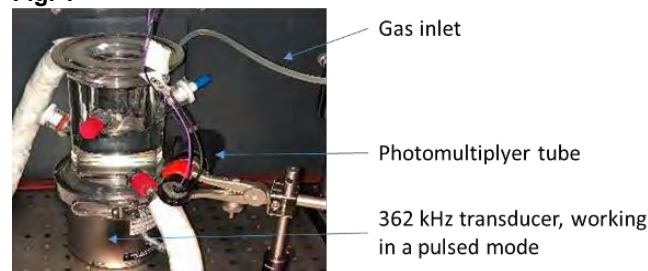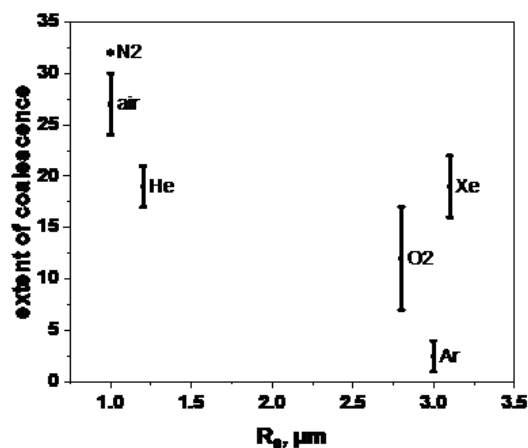
Fig. 1

Fig. 2

OP04
Ultrasonic cavitation and degassing of liquids

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Question

The degassing process of liquids by ultrasound is not well understood yet. Unclear aspects refer to the microscopic action of cavitation bubbles, and as well to macroscopic phenomena like the acoustic emission spectrum and the visual appearance of bubbles and bubble structures. In this work, we try to highlight some aspects connected with rectified diffusion and coalescence of very small, acoustically driven bubbles, and to correlate acoustic spectra, bubble field dynamics, and dissolved gas content in a laboratory scale experiment.

Method

To describe the behavior of driven bubbles in the size range of 100 nm, we use analytic approximations and simulations based on spherical single bubble models. For multi-bubble fields, the single bubble equations are coupled by pressure and secondary Bjerknes force terms. In the experiment, an 80 l ultrasonic cleaning bath is equipped with side windows and a fixed hydrophone for simultaneous observations of bubble fields and acoustic emissions. The emission spectrum is analyzed in terms of fundamental (f0=25 kHz), subharmonic, and cavitation noise levels.

Results

The microscopic considerations remain with the paradoxical situation that just for the very small bubbles, which are expected in early degassing stages, the "standard" mechanisms of ultrasonic degassing do not work well: Due to the high Laplace pressure, the volume oscillations are very weak, and dynamic diffusion effects cannot overcome gas outflow from the bubbles. For the same reason of weak oscillations, mutual attraction of bubbles is weak, and collision times of neighboring bubbles become exceedingly long. In the experiment, we see an upward progression of spectral components over about 15 minutes, until a stationary, partly degassed state is reached. This state is characterized by few visible bubbles that are concentrated in localized structures (streamers, double layers). Before, extended veils of large upwards running bubbles and large streamer structures occur, populating a large part of the bath volume. Our preliminary data of acoustic spectra indicate a kind of period doubling transition during degassing, which proceeds over many minutes.

Conclusions

The microscopic processes during the initial stages of degassing remain puzzling. On the macroscopic scale, interaction of bubble populations, bubble structures, and gas diffusion appear in evidence. Further experiments and simulations are necessary for a deeper understanding.

OP05
The suppression of cavitation in high frequency acoustic excitation: new possibilities for materials and biomaterials sonoprocessing

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[2]University of Melbourne, Parkville, Australia

We demonstrate through careful sonoluminescence and sonochemiluminescence experiments that cavitation is significantly suppressed, and, is essentially non-existent, at the typical powers at which high frequency (10 MHz order) surface acoustic wave (SAW) and its hybrid counterpart, surface reflected bulk wave (SRBW), are usually employed. Yet, it is possible to drive similar as well as distinct sonochemical and sonoelectrochemical phenomena using such high frequency excitation, albeit through altogether different fundamental physicochemical mechanisms. One example is the generation of free radicals through the dissociation of pure water. Instead of cavitation, the free radicals here are generated through the intense evanescent field associated with the intricate electromechanical coupling between the fluid phase and the underlying piezoelectric substrate on which the SAWs or SRBWs propagate. In any case, the absence of cavitation opens up new avenues for materials synthesis and processing, examples of which will be described in the talk. Given the propensity for cavitation to denature biomolecules and cells, its absence has also interesting implications for bioprocessing since considerably higher retention of biomolecular and cellular structure and function can be achieved at 10 MHz order frequencies. We show that this opens up a new field of mechanobiology for applications across intracellular delivery, endothelial barrier manipulation and stem cell differentiation, among others.

OP06
Improvement of classical nucleation theory and application to ultrasonically induced cavitation process

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Ultrasonically induced cavitation (UIC) is a promising chemical process intensification technique, which has successfully been applied to food and beverage production, drug delivery, water treatment, and processing of hydrocarbon mixtures, either fossils or bio-derived. Control and optimization of processes involving UIC require a thorough understanding of the underlying physical and chemical phenomena, and accurate and reliable mathematical models to describe them. The mechanisms behind bubble growth and collapse have been widely researched and several models proposed. Instead, the mechanisms behind bubble nucleation are still unknown, due to their stochastic nature and complexity. The classical nucleation theory (CNT) provides inconsistent results when applied to estimate the nucleation rate. The inconsistency derives from the capillary approximation.

Therefore, this work aims to overcome this limitation by accounting for the curvature dependency of surface tension. The corrected value of surface tension for a single component fluid is then compared with experimental data, to assess the validity of the approach.

The curvature-dependent surface tension can be used to compute a corrected nucleation rate, which is used to simulate the UIC process using an OpenFOAM-based CFD solver, which has been validated and presented in previous works. The simulation of the process allows the study of the cavitation phenomenon and its effect on the fluid dynamics of the system, in a variety of conditions. In particular, the effect of different amplitudes of the ultrasonic waves on the formation of bubbles can be assessed.

The accurate estimation of the nucleation rate is vital to extend and improve the applications of UIC. The approach adopted in this work can be extended to consider multicomponent fluids, which is fundamental since most of the applications involve liquid mixtures and not pure components.

OP07
GPU accelerated computation of chemically active bubble clusters

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[2]Georg August University of Göttingen, Drittes Physikalisches Institut, Göttingen, Germany
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[4]Georg August University of Göttingen, Institute for the Dynamics of Complex Systems, Göttingen, Germany

In this study, chemically active bubble clusters exposed to ultrasonic irradiation are investigated numerically. For simplicity, the positions of the spherically symmetric bubbles are fixed following a Gaussian distribution with a variance of 1 mm. The equilibrium bubble radii have a uniform distribution between 0.8 and 5 microns. From the liquid side, the governing equation is a multitude of globally coupled Keller-Miksis equations. The coupling takes place via the emitted pressure waves of the bubbles, neglecting time delay effects. To model the bubble interior, an ordinary differential equation (ODE) system for the chemical reactions is solved employing a state-of-the-art reaction mechanism for each bubble. The initial content of the bubbles is water vapour and oxygen. The mechanism takes into account the pressure dependence of the reactions (necessary due to the strong bubble collapses); the backward rates are calculated through thermodynamic equilibrium conditions; third body efficiencies are adequately taken into account; finally, duplicated

reactions are also included to describe the non-exponential temperature dependence of specific reactions. The overall chemical yield (e.g. hydroxyl radical or hydrogen peroxide) of the cluster is examined in the parameter plane of excitation frequency and pressure amplitude. The principal interest here is to determine optimal operating conditions to maximise the chemical output. By turning off the coupling between the bubbles and repeat the simulations, the possible parameter domains of enhanced overall chemical yield can be revealed. Due to the high computing power requirements, the numerical code is written in CUDA C to exploit the high processing power of professional graphics processing units (GPUs). The parallelisation strategy is simple: one thread block solves a single bubble cluster (having a specific parameter combination), and a single thread is associated with a single bubble. The main difficulty comes from the implicit nature of the coupled ODE system. That is, at every function evaluation, a system of linear equations has to be solved. The authors developed a "Physics Informed Modified Jacobi Iteration" to solve the linear system. The scheme is stable and perfectly fits to the massively parallel architecture of the GPUs. As a test case, the cluster is composed of 32 bubbles; however, the GPU code efficiently handles cluster sizes up to 1024 bubbles.

Session: Acoustic cavitation

KL02
Simulation of low-frequency sonoreactors accounting for cavitation
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The rapid expansion of ultrasonic processing and sonochemistry in the 90"s motivated a search for adequate computer simulation and prediction tools. Owing to the peculiar complexity and nonlinearity of inertial acoustic cavitation, available CFD or acoustic computer codes have proved difficult to adapt and to provide realistic predictions, at least at the scale of a whole sono-reactor [1]. Accounting rigorously for the two-way interaction between inertially oscillating bubbles and the acoustic field driving them requires very involved models and discretization methods, applicable only for limited space scales [2].

A decade ago, we proposed a simplified model for acoustics of cavitating liquids, accounting for the energy dissipation by inertially pulsating bubbles [3,4]. This feature allows to model reasonably well how acoustic energy is consumed as it travels through the liquid and the cavitation zones it creates. Its simplicity allows easy implementation under COMSOL, coupling with transducer models and vessel walls vibration, i.e. simulations of a full sonoreactor. Moreover, the realistic acoustic fields obtained allow further computation of streaming velocity fields [5].

In this lecture, we will recall the main lines of the model, show some typical results, and focus on the fact that it yields realistic estimations of the dissipated power in the liquid. Some commonly accepted results in sono-engineering will be reconsidered, especially the acoustic impedance of a cavitating liquid. We will show how the automatic frequency locking used on most US generators can also be simulated and what is exactly controlled by the amplitude level button of the latter. We will also examine how the geometry of the reactor can influence the dissipated power and examine whether beneficial effects can be expected from acoustic resonance effects. Finally, we will point out the weaknesses of the model and discuss its potential evolutions.

Fig. 1 : Left : Illustration of energy conservation in the model. Right : Simulation of a test tube immersed in an ultrasonic bath.

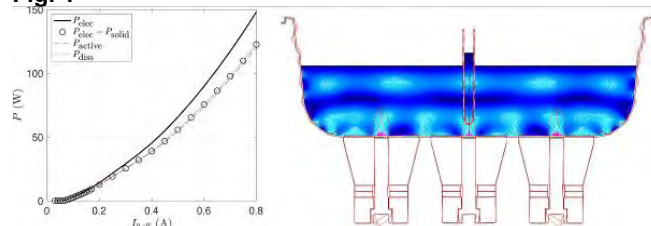[1] Tudela I. et al., Ultrason. Sonochem. *21*(3), 909-919, **2014**.

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Fig. 1

OP08
Characterising cavitation activity generated by an ultrasonic horn in a Deep Eutectic Solvent for efficient precious metal recovery from e-waste
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[2]University of Leicester, School of Chemistry, Leicester, United Kingdom
[3]National Physical Laboratory, Teddington, United Kingdom

Deep Eutectic Solvents (DESs) are a class of ionic liquid that can be used to recover metals from electronic waste. DESs are capable of selectively etching precious metals from the substrate material, over several hours[1]. This process can be significantly accelerated via application of ultrasound, to generate cavitation in the DES[2].

This work seeks to characterise acoustic cavitation activity in a DES, for the purpose of identifying optimal parameters for ultrasonically-enhanced precious metal recovery. Optimisation in terms of power consumption and processing time will be critical for upscaling to industrially relevant levels.

Materials and Methods:

Cavitation was generated in a DES (Ethaline) with a 20 kHz (*f0*) ultrasonic horn, in 1 s sonications across a range of input powers (20–100%). Shadowgraphic imaging at 8×10^4 frames per second (fps) captured cavitation activity in the vicinity of the horn-tip, including bubble-cluster collapse and shockwave generation/propagation, for the duration of each sonication. Acoustic detection of the cavitation emissions was undertaken with a broadband hollow cylindrical cavitation detector[3], for comparison to the observed bubble activity, at each input power sampled. Measurements from cavitation in DES are compared to those generated in water, at equivalent sonication parameters[4].

Results:

The high-speed imaging reveals notably different cavitation structures develop during a sonication of DES, than in water, fig. 1. Nonetheless, both the imaging and acoustic detection data confirm the generation of periodic shock waves at subharmonic frequencies of $f0/m$, with m increasing through integer values as the input power is increased. When compared to cavitation in water, during a sonication at the same power, fig. 2, it is found that $m_{DES} \approx m_{H2O}-1$. This is confirmed for the full range of input powers and is attributable to the higher viscosity of DES. Reduced shock wave content for the emissions collected at "transitional" input powers (for which m is indistinct[4]) is also confirmed, for cavitation in DES.

Conclusion:

We have characterised acoustic cavitation in DES in terms of periodic shock waves generated by cavitation-bubble collapses during sonication, and relative to the cavitation generated in water for equivalent sonications. Future work will verify that transitional input powers should be avoided for efficient delamination of precious metal from electronic waste.

References:

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[4] Yusuf et al, *Ultrason Sonochem* 2021.
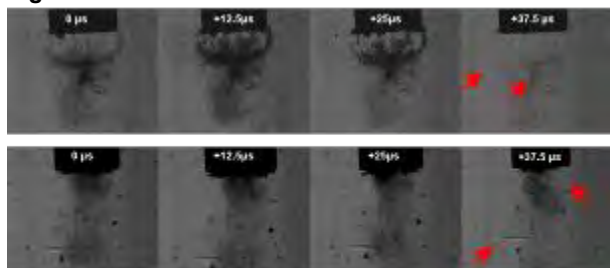
Fig. 1

Figure 1: High-speed imaging at 80 kfps in DES (top) and water (bottom), during a sonication at 70% power. Each sequence represents cavitation activity over 1 cycle of tip-vibration, several 100 ms into the sonication. Shockwaves (arrowed red) originate from the primary clusters close to the tip-surface, in water, and in DES, from larger bubbles within the structure detached from the tip.
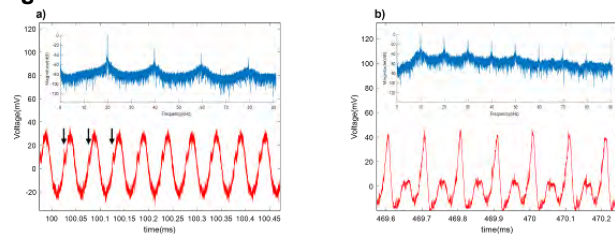
Fig. 2

Figure 2: Time-domain cavitation detector data for a 0.5 ms section of the 1 s dataset, at 20% input power in a) DES and b) water. Shockwave amplitudes are notably suppressed in DES (arrowed in black) and occur at f_0 ($m = 1$). In water, bubble collapse shockwaves are detected at $f_0/2$ ($m = 2$), with corresponding non-linear features within the spectra of the emissions from each liquid (insets).

Acoustic cavitation can be implemented in a variety of applications ranging from biological treatment to chemical reactions such as the remediation of substances. The cavitation phenomenon results in the generation of strong oxidizing agents, which ultimately provide a sustainable condition to be used for wastewater treatment. However, one of the current challenges is to develop efficient industrial scaled reactors since most of the successful studies have been on a bench scale.

Poly- and perfluoroalkyl substances (PFAS) are a widespread group of synthetic persistent chemicals. Among various emerging methods of PFAS degradation, sonochemistry is a promising non-hazardous destructive technology. In this study, the degradation efficiency of a multiple-frequency flow-through reactor (FR) was evaluated in parallel with small-scale beaker experiments.

The degradation was investigated concerning excitation frequency (20, 40, 210 kHz), ambient temperature (35, 45, 60 °C), additives (persulfate, iron), exposure time (2, 4, 6 hours), power density (60, 200 W/m3) and PFAS concentration (10, 50 nM) and flow direction (upward, downward). Both beaker and FR designs have been acoustically optimized by multiphysical numerical simulations.

The results show the importance of even distribution and generation of cavitation bubbles by stirring or turbulent flow conditions. Also, there exists an interdependency among some of the experimental parameters. The highest degradation rate of PFOA by sonication treatment in a beaker (20kHz, 30°C, 2.75g/l persulfate, 2h, and 200W/m3) was 73% in presence of a stirrer. The treatment results of PFOA and PFOS obtained through double frequency FR were 78% and 36% respectively (21 and 38 kHz, 38 °C, bottom-up flow direction, 2h, 50 W/m3). The preliminary experiment with triple frequency at 21, 38, and 209 kHz, 35 °C, upward flow direction, and 60 W/m3 achieved 23% PFOA degradation. However, the results of the triple frequency FR tests are still limited to a few trials and some problems in the experimental setup.

The comparison between the effective exposure time and power density in both beaker and FR experiments reveals a high potential for scaled-up treatment. To reach the full potential of the FR concept, multiple interactions need to be controlled in the design and optimization process.

Fig 1: Schematic setup of the triple frequency flow-through reactor

Fig 2: Experimental setup of beaker treatment

OP09
PFAS degradation by acoustic cavitation: From pilot-scale validation to future possibilities
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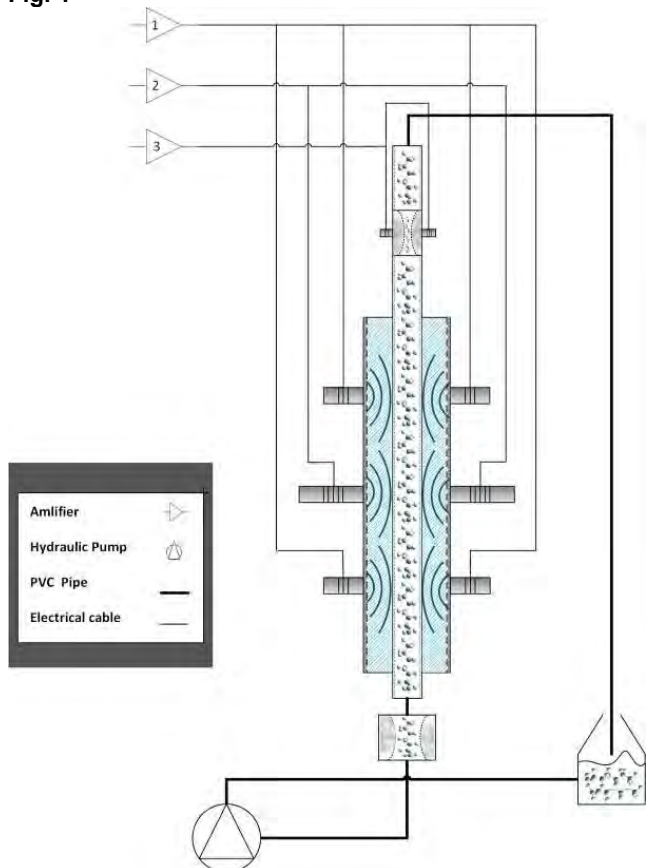[1]Luleå University of Technology, Luleå, Sweden

Fig. 1

Fig. 2

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Shock waves (SW) originating from bubble implosions have been a widely researched topic in cavitation physics. Although quite a few studies helped in understanding the SW dynamics in bubbly liquids from both fundamental and applied research perspective, majority of them have focused on water-based systems. Thus, there is a gap in knowledge with regard to SW characteristics in other liquids, which are important in a range of physical, chemical and biological applications.

This research aims at expanding the horizons of understanding the phenomenon of cavitation-induced SW by characterising their behaviour in liquids with different physical properties. The present work is a continuation of our previous work (doi:10.1017/jfm.2021.186) where we observed a strong pressure peak from the shock front formation and propagation due to the implosion of oscillating cavitation bubbles in de-ionised water (DIW). We now extended this study to other organic transparent liquids such as ethanol (EtOH), 1:1 water-ethanol (DIW:EtOH) solution and glycerol (GLC) that find uses in sono-processing systems, e.g. graphite exfoliation, sonochemical synthesis and emulsification. These liquids were acoustically characterised under ultrasonic excitation at 24 kHz using in-situ advanced high-speed imaging and a state-of-the-art fibre optic hydrophone calibrated in the MHz broadband frequency range.

The obtained pressure-frequency spectra revealed that the prominent SW pressure peak was barely observed in the cases of EtOH and GLC, specifically at low input powers, however was consistently visible for the DIW:EtOH solution, similar to DIW but with a slight frequency shift. Based on the spectral analysis of the prominent frequency peak, we discovered that SW propagating within the sonicated environment seemed to project a universal wavelength that labelled them with a unique acoustic identity for the substances tested. We further found that for DIW, EtOH and DIW:EtOH, the bubble growth and collapse dynamics was dictated by the surface tension forces that led to the increase in the cavitation shielding efficiency with input power. Whereas in GLC, the cavitation dynamics was predominantly governed by the viscous forces resulting in a lower or almost negligible shielding efficiency with rapid dissipation of SW intensity. Acoustic pressure mapping of the cavitation activity indicated an overall higher shock pressure amplitude for DIW:EtOH compared to other liquids.

OP10
Effect of liquid physical properties on the formation and propagation of cavitation-induced shock waves

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OP11
Differences in the desorption of N2, O2 and Ar from supersaturated water during sonication with low-frequency, high-power ultrasound

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The release of air-supersaturated water into the natural environment can be the source of several problems. Originating mostly from artificial installations such as

hydropower plants, total dissolved gas (TDG) supersaturation above tolerance limits causes significant damage to wildlife and especially fish[1]. A technical solution is developed to remove excess dissolved air from the water body prior to the release into the environment. Ultrasonic degassing, already used in several industrial applications fields[2], is considered as a possible solution.

To help with the design of a technical solution, tests are conducted in a laboratory reactor. The degassing behavior of the main gases present in air-supersaturated water, which are nitrogen, oxygen and argon, during ultrasonication with 20 kHz and 40 kHz is investigated. The gases are dissolved in pressurized water by injection of microbubbles beforehand, creating a targeted saturation value between 100 % and 200 % TDG. Once supersaturated, the water is continuously sonicated with low-frequency, high-intensity ultrasound, resulting in desorption of the gas due to acoustic cavitation and rectified diffusion[3]. Three different ultrasonic amplitudes are used, and the resulting desorption efficiencies are compared to the naturally occurring desorption. The liquid gas mass transfer coefficient[4],[5] is determined using a steady state method and shows a linear trend with the TDG level. The desorption behavior is dependent on the solubility of the respective gas in water.

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Tuesday, 30 August 2022

Session: Environmental remediation 1

PL03
Sonocatalysis and sonophotocatalysis
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This conference plenary will debate recent advances in the employment of sonolysis to design tailored materials and the power of sonocatalytic and sonophotocatalytic processes for water remediation.

In a polluted and energy-hungry world, photocatalysis play a key role in pollution remediation and energy conversion. In this context, ultrasou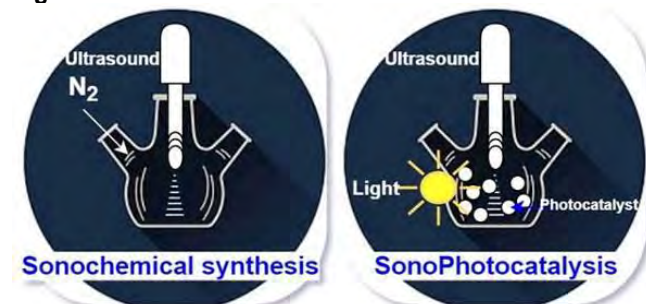nd is an invaluable tool to tailor the synthesis of photocatalysts and to boost catalytic efficiencies by process intensification.

Today, exploration of the ultrasonic power in the catalytic synthesis of innovative (nano)-materials and chemical products at the lab and large scale has become a research hotspot. Many research studies reported that ultrasonic synthesis was the key factor in controlling some specific properties of materials, such as the size of nanoparticles, structure, interface interactions, porosity, and so on. On the other hand, sonolysis can induce the breakage of water molecules in different reactive oxygen species (ROSs) in liquid bulk by applying higher frequency values. Sonolysis has been widely applied to oxidize a huge range of organic pollutants and microorganisms. Recently, ultrasonic technology has been combined with several technologies for enhanced water remediation, and one of the most successful approaches was the sono-photocatalysis which showed several advantages such as synergetic generation of ROSs upon simultaneous utilization of <u>ultrasound</u> and light, enhanced mineralization of toxic by-products, and continuous cleaning of the photocatalyst surface preventing the fast deactivation. Intensive research studies have been reported on optimizing operating factors and engineering sono-photocatalytic reactors.

In this presentation, our laboratory"s progress in the development of better (sono)photocatalytic materials and processes will be discussed. Specifically, this talk will focus on the role of ultrasound in tuning the physico-chemical features of oxide-based photocatalysts and their efficiency in hybrid advanced oxidation processes for emerging pollutant degradation. The key role of the (sono)photocatalyst morphological features will be discussed, also with respect to piezo-enhanced photocatalytic strategies.

Overall, it is shown that ultrasound technology can offer promise for more efficient photocatalytic materials and hybrid processes with potential applications extending also to energy conversion.

Fig. 1

OP12
Machine learning in wastewater treatment - prediction of degradability of micropollutants by sonolysis in water with QSPR
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The increasing quantity and variety of organic contaminants discharged into surface and groundwater increase the necessity of additional and suitable water treatment

methods, which can be incorporated into existing wastewater treatment plants. The huge variety of micropollutants and local variability of the composition of the organic load or matrix effects paired with multiple possible degradation processes lead to the requirement of a recommendation tool for the best possible water treatment method under given local conditions. Due to the diversity of physicochemical properties of micropollutants, such predictions are challenging, as the accumulation of extensive experimental data to characterize the activity and behaviour of all relevant substances in every possible degradation method is highly cost and time consuming. As an alternative, predictive Quantitative Structure-Property Relationship (QSPR) can be used to correlate different biological, chemical or physical properties of a compound with its physicochemical characteristics. Applied to ultrasound-assisted degradation, the tool of QSPR modelling can contribute to a broader understanding of reaction pathways by identifying important molecular properties and sites, which are the most relevant for the degradation. Within my studies, QSPR modelling is executed using a combination of the software PaDEL for descriptor calculation and QSARINS for the modelling process respecting all five OECD-requirements for applicable QSAR/QSPR-models. The final models are selected using a multi-criteria decision-making tool to evaluate the model quality based on all calculated statistical quality parameters. Interesting structural influences could be identified during that process so far, which helped to connect the modelling results with experimental observations on the degradability of aromatic compounds. Based on the experimental data of phenol derivates for example, the final QSPR model showed an influence of the molecular polarity and the occurrence of hydrogen bonds on the reaction rate constants in accordance with observations of previous experimental studies.[1]

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Fig. 1
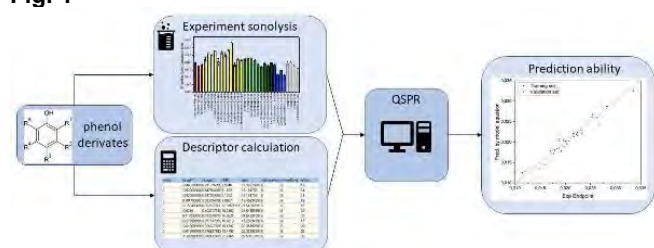
OP13
Synergistic and kinetics effects of frequency in the combination of ultrasound with different additives for the removal of pharmaceuticals in water

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Ultrasound (US) is an advanced oxidation process based on the HO· action. It is widely used for degrading contaminants of emerging concern (e.g., pharmaceuticals) in water. Recently, approaches such as the combination with oxidants, Fenton-based systems, and hybridization with carbonaceous materials have been used to improve the efficiency of US.

This work reports the effect of ultrasonic frequency (40, 375, and 1135 kHz) on both kinetics and synergy for the degradation of a representative pharmaceutical (acetaminophen, ACE) by US in presence of various additives. US was combined with peroxymonosulfate (US/PMS), iron sulfate (US/Fe2+/PMS), and a carbonaceous material synthesized from agro-industrial residues and activated with iron chloride (US/Fe-AC/PMS). In all these systems, 40 μM ACE and 0.1 mM PMS were used. Fe2+ at 3 mg L–1 was used in the US/Fe2+/PMS system, while Fe-AC at 50 mg L–1 was utilized in the US/Fe-AC/PMS system. The US experiments were performed in a Meinhardt reactor and it was adjusted to the desired frequencies through different transducers. During treatments, aliquots were taken to determine the evolution of oxidants (iodometric method) and the ACE removal (by HPLC). For the US/PMS system (Fig. 1a), the kinetics are higher at the intermediate frequency (375 kHz), where the US led to the greatest HO· formation. Contrastingly, at 40 kHz and 1135 kHz, the synergistic effects were more favored. The addition of Fe2+ and PMS to US (Fig. 1b) intensified the ACE removal due to the activation of added PMS and sonogenerated H2O2, producing extra hydroxyl and sulfate radicals. Interestingly, the US/Fe-AC/PMS became more efficient kinetically than the other two combined systems, removing higher ACE percentages in only 10 min of treatment (Fig. 1c). In this case, both the kinetics and the synergy were more favored at 40 kHz due to a greater dispersion of the activated carbon and mass transfer enhancement (increasing the surface area and activity of Fe-AC) caused by the high mechanical effects of the low frequency US that disaggregates particles. Finally, the replacement of PMS in the US/Fe-AC/PMS system at 40 kHz by peroxydisulfate (PDS) or H2O2 (Fig. 1d) resulted in high synergy values, also both PMS and PDS favored the kinetics. In conclusion, a synergistic system does not always imply that it is the most favorable kinetically.

Fig. 1
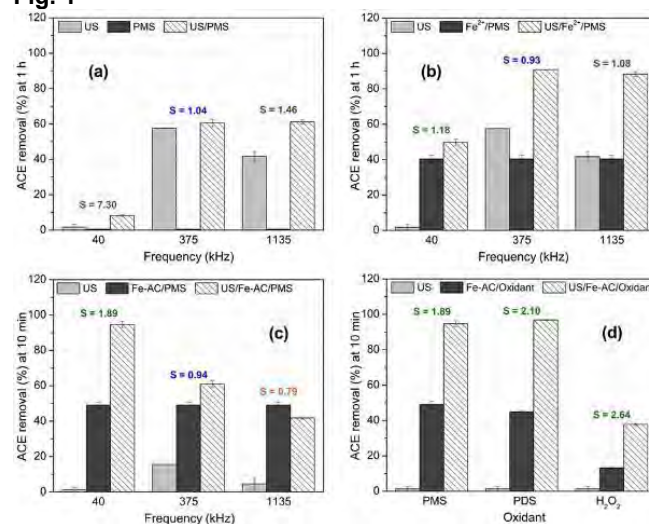
OP14
Wandering between ultrasonic cavitation and hydrodynamic cavitation – Sonochemical story in Jena and in Turin

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Dedicated to Professor Bernd Ondruscka on the occasion of his 75th birthday.

The occurrence and removal of organic micropollutants have received wide attention due to their health and environmental effects. Both ultrasonic cavitation and hydrodynamic cavitation are magical and versatile tools for removing organic pollutants from water. This work reviews our studies on the degradation of hazardous pollutants by using sonication, hydrodynamic cavitation, as well as cavitation-enhanced oxidation processes.

In the individual sonication, halogenated pollutants (chlorobenzene and chlorophenol), oxygenated fuel additives – methyl tertiary butyl ether, cyclic C6Hx hydrocarbons - benzene, thiophene and its derivatives, thioethers and fumaric acid were efficiently removed. The mechanism and effects of critical factors, such as physicochemical properties of pollutants, ultrasonic frequency and power, initial concentrations and temperature, on the organic degradation are discussed in detail. In the individual process of hydrodynamic cavitation, the volatile organics, such as chlorocarbons (chloroform and carbon tetrachloride), halogenated aromatic hydrocarbons (α-chlorotoluene, chlorobenzene, bromobenzene, α-bromotoluene) and BETX (benzene, ethylbenzene, toluene and xylene) were eliminated. The effects of upstream or downstream pressure, fluid velocity, cavitation number, and β0 on the removal efficiency were studied. Moreover, the cavitation-based hybrid processes, such as ultrasound/microwaves, ultrasound/hydrodynamic cavitation, sonoeletrochemistry, cavitation/ozonation, cavitation/Fenton, etc., were investigated. Attractively, the synergetic effects on the degradation kinetics or removal efficiency of organic pollutants, such as phenol, chloroform, carbamazepine, triclosan, endocrine disruptor bisphenol A, succinic acid, blue-green algae, as well as cork wastewater, were observed and discussed, respectively.

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Session: Materials and nanoparticles 2

PL04
Hydrogen sonocatalysis – Sonochemical production of fuel cell and electrolyser catalytic materials

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It is well accepted in the ultrasonic and sono(electro)chemistry (the application of ultrasound in (electro)chemistry) communities that ultrasonic waves propagating in liquids lead to acoustic cavitation, sonolysis (*in-situ* radical generation), areas of extreme mixing close to the ultrasonic source (transducer) and electrode, degassing, electrode surface cleaning (and erosion), and rises in bulk temperature and pressure. The publications of "The use of ultrasound for the fabrication of fuel cell materials" (2010) and the "Sonochemical and sonoelectrochemical production of hydrogen" (2019) triggered an international interest in the use of ultrasound, sonochemistry and sonoelectrochemistry for the synthesis of energy materials and useful gases. This is due to the fact that these methods are efficient and do not require intensive labour as well as the use of large amounts of toxic and environmentally hazardous solvents.

This presentation highlights the development of novel electrolyser and fuel cell catalysts and electrodes as well as the production of hydrogen by utilising power ultrasound (20kHz–1MHz). It also highlights that care should be taken when ultrasonicating (in the form of a laboratory-grade ultrasonic bath, or an ultrasonic probe, sonifier) catalyst ink slurries prior to deposition for the fabrication of fuel cell and electrolyser electrodes as it has been shown that ultrasound leads to catalyst dissolution and ionomer degradation induced by acoustic cavitation.

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Fig. 1
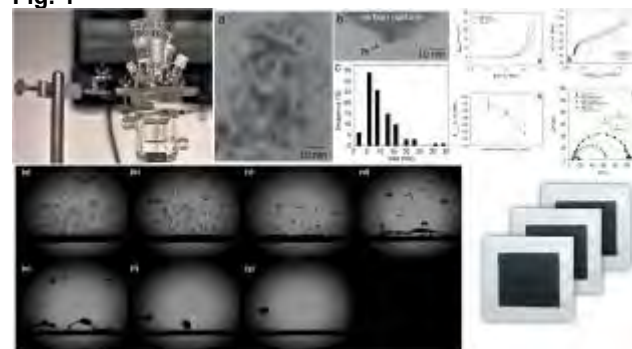
OP15
Miniemulsion polymerization in an ultrasonic microreactor

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Polymeric dispersions have broad applications in adhesives, coatings, catalyst support, encapsulation, and drug and gene delivery 1. One approach is the generation of miniemulsions (50 nm < d < 1000 nm) and subsequent polymerization to

synthesize polymer nanoparticles that can achieve the desired size and morphology for targeting a specific application. Ultrasonic microreactors have proven to be effective in the generation of miniemulsions, although with a high polydispersity (PDI > 0.3) 2,3.

To address this issue, an ultrasonic microreactor was developed, which enables the generation of a monodisperse miniemulsion (PDI < 0.3) to synthesize polymer nanoparticles. This ultrasonic microreactor consists of serpentine channels with a square cross-section of 1.2 mm in borosilicate glass with a piezoelectric plate transducer attached to one side. The miniemulsion created by the cavitation activity in the ultrasonic microreactor is then fed into a temperature controlled (75°C) coiled loop reactor for the continuous polymerization of monomer droplets.

Specifically, we study the cross-linking polymerization of butyl methacrylate, for which the continuous phase is water with a surfactant (Lutensol AT50), and the dispersed phase consists of the monomer butyl methacrylate, the cross-linking agent ethyl glycol dimethacrylate, the costabilizer hexadecane and the thermal initiator AIBN. The obtained polymer nanoparticle size is measured by DLS, and in addition the particles are centrifuged, washed, and dried for SEM to analyze their size and morphology.

We will discuss the influence of the operating parameters (load power, frequency, surfactant concentration, flow rate ratio and residence time) on the size of the miniemulsion droplets and the resulting nanoparticles. Preliminary results highlight the performance of the developed system. For a dispersed to continuous volumetric flow rate ratio of 1:4, residence time of 4 min at US frequency and power of 47kHz and 15W, particles with a mean hydrodynamic diameter of 94 nm and PDI of 0.15 were obtained.

In conclusion, we will present an ultrasonic microreactor coupled to a coiled loop reactor to synthesize monodisperse polymer nanoparticles and control the final particle size.

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OP16
Ultrasound-assisted conversion of UO$_2$ into U(VI) peroxides in aqueous solution saturated with Ar/O$_2$

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In the French nuclear industry, uranium is used as nuclear fuel in the oxide form U(IV)O$_2$. After being used in the reactor, spent nuclear fuel is very damaging for organisms and must be safely contained for thousands of years. During storage, the potential intrusion of groundwaters through containment failures could result in the production of radiolytic species such as H$_2$O$_2$ that can contribute in the corrosion of UO$_2$-based matrices and promote the dissolution and release of radionuclides into the surroundings. Sonochemistry provides an original route to slowly accumulate H$_2$O$_2$ in solution through the acoustic cavitation phenomenon. **[1-3]**

After the formation of well-characterized UO$_2$ powder with different refractory characters using the oxalate route, the powder behavior was studied in aqueous solution as a function of the sonochemical parameters (acoustic frequency, solution composition, gas). This revealed the possible complete conversion of U(IV)O$_2$ into (meta-)studtite [(UO$_2$(O$_2$)(H$_2$O)$_2$)xH$_2$O] with optimized conditions. **[4]**

The evolution of the reaction media was followed by ICP/AES and UV-Visible absorption spectroscopy while the solids taken during the experiments were characterized by SEM, XRD and AFM.

The formation of studtite crystal structures was observed on the surface of UO$_2$ platelets with a preserved morphology of the initial oxide (Figure 1.b). This behavior suggest a complex formation mechanism of uranyl peroxide. Interestingly, specific sonochemical conditions allowed the observation of unexpected structures illustrated in Figure 1.c.

Figure 1: a) SEM image of UO$_2$ platelets synthetized from oxalate route b) and c) SEM image of the uranyl peroxide observed after sonication of UO$_2$ in H$_2$SO$_4$ 5.10^{-4} M at 346 kHz (20 W.mL^{-1}, 20°C, Ar/O$_2$, and 6h)

The evolution of H$_2$O$_2$ accumulation rate under these conditions suggests that H$_2$O$_2$ contributes in oxidizing U(IV)O$_2$ into U(VI) and complexing the latter in solution. This work describes an original alternative to study the behaviour of actinides in solution in the presence of H$_2$O$_2$.
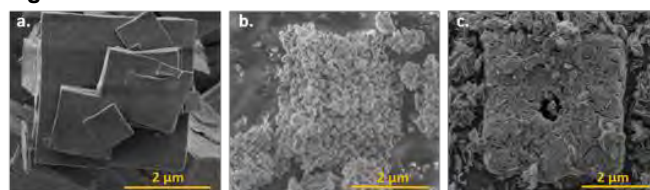
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Fig. 1

OP17
Low-frequency acoustic radiation (38 kHz) aided photocatalysis of Congo Red using LaNi0.5Co0.5O3/g-C3N4 nanocomposite

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Sonophotocatalysis is a contemporary energy transfer approach employed for wastewater remediation. In this study, we describe the fabrication of a sequence of LaNi0.5Co0.5O3/g-C3N4 Z-scheme catalysts with varying amounts of g-C3N4 via a facile impregnation procedure. To comprehend the crystallite structure, microscopic surface, element composition, and chemical oxidation state of the

LaNi0.5Co0.5O3/g-C3N4, several characterization methodologies were performed. The findings demonstrate that the heterojunctions formed between the rhombohedral perovskite-type LaNi0.5Co0.5O3 crystal and g-C3N4 nanosheets boost visible light absorption, aid in the separation of photogenerated electron-hole pairs, and play a critical role in suppressing their recombination thereby substantially improving catalytic activity. Furthermore, the sonophotocatalytic efficacy of these nanohybrids was examined against the removal of Congo Red (CR) dye employing ultrasonic-assisted UV photon stimulation. Consequently, LaNi0.5Co0.5O3/g-C3N4-25 wt.% displayed the optimum degradation, with approximately 83% of CR degraded after 120 min with a first-order kinetic rate of 0.01545 min-1, which was about 3.1 and 5.9 times greater than pristine LaNi0.5Co0.5O3 and g-C3N4, respectively advocating a Z-scheme charge carrier mechanism for the degradation process. The synergistic effect of sonolysis and photolysis has been discussed, and a suitable mechanism was proposed which validates LaNi0.5Co0.5O3/g-C3N4 composite as an affordable and efficient catalyst for environmental remediation.

Session: Hydrodynamic cavitation

KL03
Process intensification of chemical processing applications using cavitational reactors: design, scale up and applications

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The present talk aims at presenting an overview of design and operation of cavitational reactors also focusing on the different areas of application illustrating some typical case studies. The initial part of the talk will be devoted to basic concepts of cavitation phenomena and mechanism of observed intensification in different chemical/physical systems. Different designs of cavitational reactors including sonochemical and hydrodynamic cavitation reactors will be discussed and recommendations given for selection of optimum design and operating parameters. For the sonochemical reactors, ultrasonic power dissipation, frequency and duty cycle are the important parameters whereas for hydrodynamic cavitation reactors, inlet pressure/speed, geometry of the cavitating device and the flow rate govern the cavitational effects. In addition, the operating parameters like temperature, pH, presence of gases or solid particles and catalyst loading also govern the extent of intensification obtained due to the use of cavitation.

Comparison of different reactor configurations will be presented using two criteria of energy efficiency and cavitational yield estimations for different reactions. The talk will also present some experimental case studies using industrially important operations, highlighting the degree of intensification achieved as compared to the conventional approaches. The specific case studies will focus in the area of crystallization and wastewater treatment. The specific advantages obtained using cavitation in crystallization include ease of nucleation, tailoring the size distribution, obtaining particles with lower mean size and higher crystallinity as well as speeding up the crystallization process. The application in wastewater treatment basically includes enhancing the efficacy of commonly applied biological oxidation. Developing combined treatment schemes is the need of the hour to tackle the highly loaded effluents often seen in speciality chemical industries. The effective application of hydrodynamic cavitation in combination with other oxidation processes yielding the

desired COD reduction (about 98% with final COD ≤ 250 mg/L meeting the discharge water compliance). Overall it appears that considerable economic savings is possible by means of harnessing the spectacular effects of cavitation in chemical and physical processing.
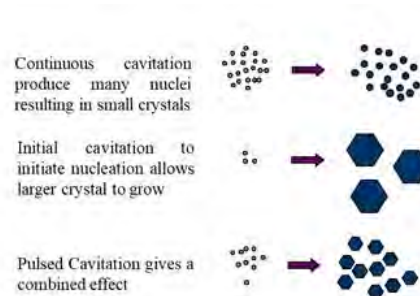
Fig. 1

Illustration 1: Controlling size distribution in crystallization using cavitation

Fig. 2

Illustration 2: Combined oxidation processes applied to real industrial effluent

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OP18
Synergistic effect of hydrodynamic cavitation and cold plasma discharge for water treatment and pollutants removal

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Introduction

Micropollutants (pharmaceuticals, hormones, pesticides, etc.) in water, albeit in nanoconcentrations, become a topical problem. Different approaches and their combinations were devised to eliminate micropollutants in the last stage of wastewater treatment. So-called quarternary treatment like active coal sorption, nanofiltration, or advanced oxidation processes (AOP) is employed. Application of non-thermal plasma discharge forms one of AOP techniques. However current plasma treatment methods of water are confined to very low volumes and employ rather inefficient mechanisms of plasma discharge like diaphragm discharge, or discharge in clouds of gas bubbles, all of them requiring high breakdown voltage.

Objectives

Creating a gaseous and low-pressure environment creates very favorable conditions for cold plasma discharge with very low breakdown voltage on the order of 1 kV/cm. Our new device called CaviPlasma is made up of a nozzle to induce developed hydrodynamic cavitation. High-voltage electrodes placed in the cavitation region ignite plasma discharge with a stream of ions, free electrons, and neutral molecules. Resulting effect of hydrodynamic cavitation, electrical field and plasma stream induce plasma chemical reactions with strong production of OH radicals and hydrogen peroxide, which have powerful oxidizing effects.

Materials and methods

CaviPlasma unit was developed with a flow rate of 1,3 m3/hour and energy consumption of 1 kWh/m3. Another unit operates with an even larger flow rate of 15 m3/hour.

Results

CaviPlasma device was successfully tested for the elimination of biological pollutants (cyanobacteria, gram-positive and negative bacteria) and for the removal of pharmaceutical residuals and estrogens in wastewater. Elimination efficiency reaches almost 100% for biological pollutants and 85-100% for different types of pharmaceutical residuals.

Conclusion

A new device employing a novel principle based on a combination of hydrodynamic cavitation and non-thermal plasma discharge was developed and successfully tested. The striking feature, compared to other plasma technologies for water treatment, is the large treated volume. Peroxide production enables high-level oxidation of both pathogenic microorganisms and organic chemical compounds.

Ref:

Rudolf, P.; Pochylý, F.; Sťahel, P.; Ráheľ, J.; Maršálek, B.; Čech, J.: Device for treatment of liquids and the method of treatment of liquids with use of this device, PCT/CZ2020/000054

Fig. 1

OP19
Hybrid hydrodynamic cavitation and AOPs based on O₃, UV and H₂O₂ – selected implications on oxidation of NOM in drinking water

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INTRODUCTION Practically all sources of fresh water contain Natural Organic matter (NOM). Among others, NOM presents a challenge due to formation of oxidation and disinfection by-products (DBPs). There is practically no equal occurrence, constitution, characterisation and quantity of NOM and no accurate and correct prediction is possible. The quest of sufficient NOM treatment is therefore almost always present, especially when untreated water TOC exceeds 2 mg L^{-1}. Application of hydrodynamic cavitation HC in combination with various chemical and/or photochemical AOPs can potentially be synergistic.

METHODS The experimental set-up was constructed as a semi-batch scale-up system with the reaction volumes of 50–83 L. Humic acid (HA) was added in concentrations of 1.1 to 3.4 mg L–1. Ozonation and processes combining ozone with H_2O_2 (H_2O_2/O_3) or UV (O_3/UV) as well as H_2O_2/UV Each set of oxidation experiments was upgraded with an application of hybrid HC. To measure the formation potentials (-FPs) of the AOX, THM and HAA, the samples were at first treated with 20 mg L–1 of free chlorine (from 11% NaOCl solution), were then placed into lab shaker for 48 hours at 20 °C, terminated at the end by $Na_2S_2O_3$.

RESULTS In terms of DOC removal efficiency, the beneficial effects of hybrid HC application are emphasized for shortest observed reaction time (20 min) that is herein synonymous to relatively low doses of applied (photo). The potential benefits of the HC application as a hybrid process to the applied AOPs were emphasized in the conditions of relatively high UV absorbance (at λ = 254 nm) and colourization of the matrix, high pollutant concentrations, low dosages of oxidants and UV and low ratio of (photo-) oxidants dosages to pollutant concentration. Nevertheless, in herein described experiments, application of hybrid HC generally increased the formation potentials of AOXs, THMs and HAAs.

CONCLUSIONS It has been confirmed that ozone-based AOPs lowered the formation potentials of the investigated by-products in comparison to the untreated samples, while the combination of hydrogen peroxide and UV resulted in general increase of the concentrations of by-products. HC was beneficial in terms of TOC/DOC removal efficiency at relatively low dosages. Combinations with HC produced noticeably higher concentrations of the investigated DBPs of post-chlorination, suggesting non-predictable reaction pathways, thus implicating experimental assessment on case-by-case basis.

Fig. 1

Process	DOC removal (%)			UVA₂₅₄ reduction (%)		
	t = 20 min	t = 40 min	t = 60 min	t = 20 min	t = 40 min	t = 60 min
H₂O₂ / O₃	8.9	26.7	43.6	37.7	60.9	73.7
H₂O₂ / O₃ + HC	13.5	24.3	40.5	39.2	64.3	77.5
H₂O₂ / UV	15.4	20.0	23.1	5.4	24.3	44.9
H₂O₂ / UV + HC	23.1	26.2	30.8	7.4	24.3	45.3
O₃ / UV	25.7	35.7	45.7	44.0	70.1	82.6
O₃ / UV + HC	9.8	11.8	23.5	38.1	64.2	78.0
O₃	3.8	15.4	19.2	40.6	58.3	71.6
O₃ / HC	8.8	9.1	11.7	42.1	63.9	76.6

Fig. 2
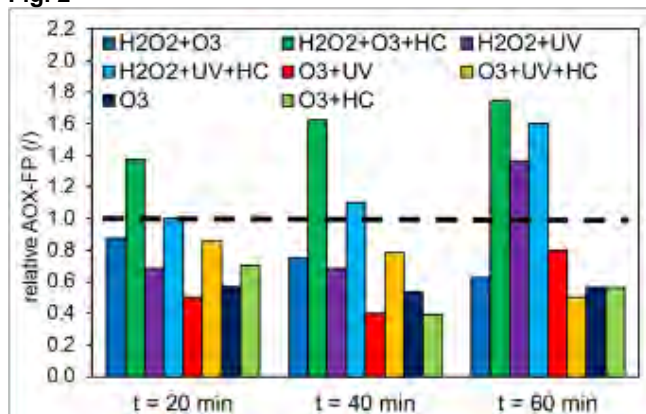
OP20
Sustainable refining of cellulose fibers by hydrodynamic and acoustic cavitation

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Introduction

Cellulose material is one of Sweden's most important export products. To reduce the electric energy consumption for refining, a combination of hydrodynamic and acoustic cavitation (HAC) may provide an alternative to the traditional disc refiners. The gentler refining provided by HAC can also extend the lifespan of the cellulose fibers. High power ultrasonic excitation of a multi-phase fluid with a periodic signal creates collapse of cavitation bubbles near the cellulose fibers. This results in very high micro-level pressures and temperatures that alters the flexibility of the fibers due to internal fibrillation of the fiber wall. The transient cavitation also gives rise to swelling, deformation/delamination of the fiber wall and outer fibrillation.

Objective

To develop a HAC-refiner concept by multi-physical simulation to optimize a chain of components and non-linear aspects to each other. The goal is to define the most energy efficient combination of hydrodynamic and acoustic cavitation effects in relation to the properties of the cellulose material.

Materials & methods

Three types of cellulose material has been treated in the developed HAC-refiner. Two types of CTMP fibers soft wood from spruce and hard wood from birch, and secondary fibers from liner material. The developed HAC-refiner is a double tube flow-through reactor concept chosen on basis of energy efficiency, robustness, and up-scaling. The multi-phase suspension flows through the inner tube where the cavitation intensity is maximized by hydrodynamic initiation, superposition of different resonant modes and a geometrical focusing effect. The hydrodynamic cavitation was enabled by flow through a Venturi shaped nozzle.

Results

Figure 1 shows the simulated and verified response of acoustic and hydrodynamic cavitation in the developed HAC-refiner. Figure 2 shows the improvement in tensile strength

index for two types of CTMP fibers and secondary fibers. However, strength properties were not improved in proportion to the effects on fiber properties and morphology. Still, the best process conditions related to temperature, concentration and cavitation intensity are yet to be defined.
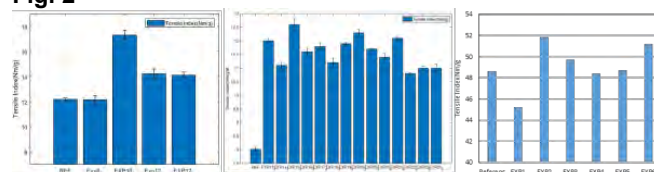
Conclusion

Specific HAC-refining condition gave an energy efficient improvement of the fiber bonding and paper strength properties for all tested fiber types. HAC-refining of secondary fibers are of special interest since traditional disc refiners cannot be used due to maintenance costs.

Fig. 1
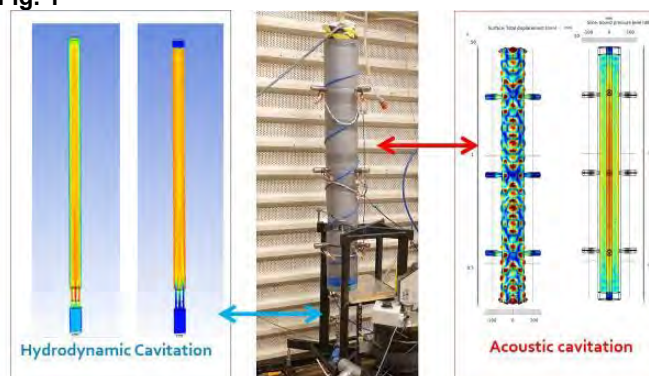
Fig. 2

OP21
Impact of hydrodynamic induced cavitation & supercavitation on water pollutant

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Introduction

Hydrodynamic induced cavitation generate imploding cavities, which can lead to degradation or even mineralisation of water constituents without addition of any chemicals. In the presented paper hydrodynamic cavitation can be stabilized and extended inside a pipe downstream a nozzle depending on the ambient pressure conditions (imploding cavities as well as supercavitation). The presented study shows an easy technology to modify water by cavitation exposure to form radicals, which are capable to increase elimination rates and change chemical structures of different trace pollutants.

Method

The system was run with a commercial centrifugal pump, generating a pressure of app. 3.5 bar at a flow rate of app. 5 l/s, feeding a nozzle to generate cavitation (see figure 1).

Figure 1: pilot-scale plant

Results

During the pilot tests MTBE and ETBE were degraded and complete mineralisation started at a time delay of app. 20 minutes. Expanding the experiments to ethan-1,2-diol (deicing agent), the biological degradation characteristics changes significantly depending on cavitation exposure time. A significant difference on chemical effects was observed between imploding cavitation bubbles and supercavitation. Supercavitation can mobilize chemical stable compounds for further treatment.

The unknown intermediates originated from industrial deicing agents can be degraded under aerobic conditions, leading to a 15% additional oxygen requirement after supercavitation exposure of app. 1.5 minutes. After 1 minute COD increases, indicating that stable chemical compounds are transferred toward reactive compounds (see figure 2).

Figure 2: COD-release of deicing agent by supercavitation

Conclusions

The chemical modifications are strongly dependent on the form of cavitation - imploding cavitation bubbles or supercavitation. Supercavitation can obviously mobilize chemically stable compounds, which might be treated in a downstream biological reactor. This technology is not restricted to the investigated chemicals only; it is very likely, that this technology can be applied to other interfering water constituents, too. Main focus should concentrate on changes on biodegradability for final elimination inside biological reactors to reduce energy consumption, instead of complete mineralisation.
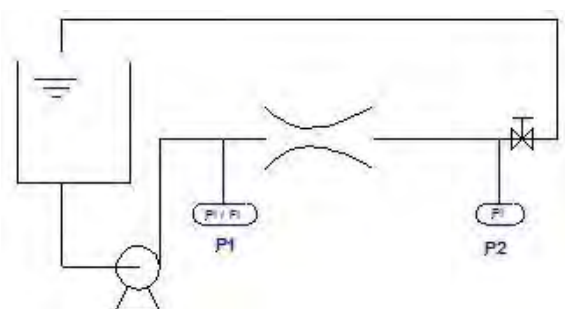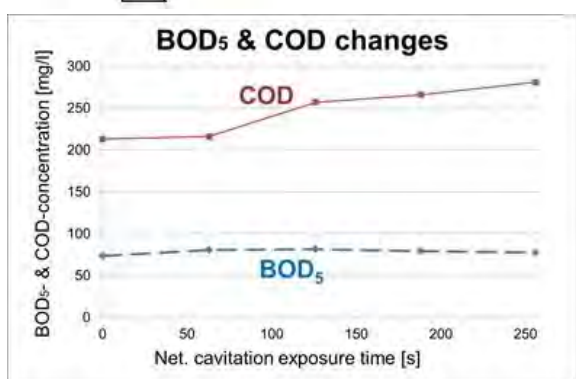

Fig. 1

Fig. 2

Wednesday, 31 August 2022

Session: Engineering

PL05
The way from the laboratory to the market
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Three sonochemical products developed in my laboratory have been commercialized and are sold globally. They are based on different sonochemical processes.

The first product is an antibacterial cream that contains nanoparticles (NPs) of hyaluronic acid. We have discovered a few years back that when you sonicate a solution you form NPs of the solute. In other word an aqueous solution of NaCl will form NPs of NaCl. The same is true for organic molecules such as enzymes. Leaving the NPs in the solution for 24-48 hours would lead to the dissolution of the molecules. It is therefore suggested to avoid it by one of the two procedures 1) mixing it with a natural cream, and 2) introducing a solid surface during the sonication, two stages take place first, the NPs are being formed, second they are embedded in the solid surface. This enables us to measure their sizes and shapes.

The second and the third products are related to the Sonochemical Coating technique that was developed in my laboratory and was recently announced by IUPAC as ONE of the TEN best chemical technologies developed in 2021. See https://iupac.org/iupac-announces-the-2021-top-ten-emerging-technologies-in-chemistry/

The products are 1) The SONOMASK a mask that is coated sonochemically with ZnO NPs and protects you against bacteria and COVID-19, 2) an antibacterial and antiviral air-filter that is part of the air-conditioning system of vehicles, that provides clean and safe air to passengers sitting inside the vehicle. The air-filter is coated sonochemically with CuO NPs.

The Sonomask is sold in the US for about 100 $, because the mask can be washed 100 times and reveal the same antiviral activity. In Figure 1 we demonstrate the roll-to-roll system at work coating the air-filter. All Red Cross ambulances in Israel are equipped with these air-filters, and the sales of this product is continuously increasing.

Figure 1. Roll-to-roll pilot installation.

Fig. 1

OP22
Semi-empirical models: The next step in sonoreactor simulations?
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Introduction

In power ultrasound, scaling-up and replicating laboratory successes at commercial settings remains difficult due to complexities of large-scale sonoreactor design. Digital prototyping is a promising solution for a cheaper and more practical design process. Recently, bubbly-liquid models

became a promising tool for predicting sonoreactor acoustic behavior. However, an accurate bubble field specification is difficult due to current technological limitations. Tuning the bubble field parameters against an empirical benchmark may serve as a promising tool to circumvent this problem.

Objectives

This study provides an in-depth discussion on the application of bubbly-liquid models for sonoreactor simulations, notably on the current limitations. A possible workaround is suggested in the form of a semi-empirical Commander and Prosperetti (CP) model, which was demonstrated using a sonoreactor operating at a near-linear regime.

Materials and Methods

The monodisperse CP model was selected for this study. The equilibrium bubble radius was kept constant while the bubble density was used as a tuning parameter. A hexagonal sonoreactor was used to demonstrate and validate some assumptions for the proposed method. The frequencies that were investigated are 40 and 70 kHz at design power of 300 W. Sonochemiluminescence (SCL) was used as the proxy measurement to characterize the bubble field. Figure 1 graphically describes the methodology involved in applying the model.

Results

Extensive research had shown that a full bubble field characterization remains impractical for large systems in the near future. Therefore, alternatives such as the proposed method can serve as a temporary workaround until better methods are discovered. As long as the system satisfies certain conditions (weakly-cavitating, uniform bubble field etc.), the proposed method can be used to address the uncertainties related to the bubble field. Figure 2 shows the validated acoustic pressure simulation and summarizes the findings of this study.

Conclusion

This study serves as a proof of concept for the proposed semi-empirical implementation of the Commander and Prosperetti model. Promising results were observed when validated against a medium-scale sonoreactor operating at a weakly-cavitating regime (40 kHz and 70 kHz). It is believed that this method will be useful in providing a reliable way to circumvent limitations in bubble field measurements.
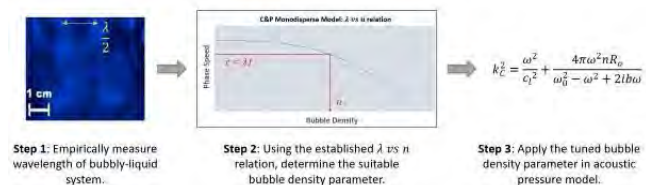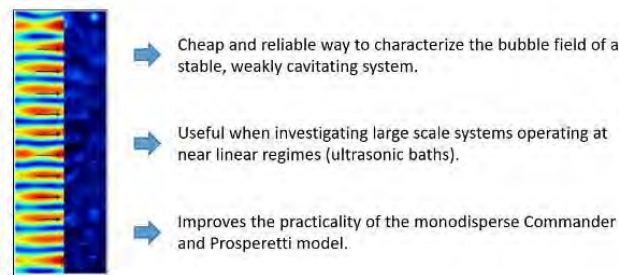
Fig. 1

Step 1: Empirically measure wavelength of bubbly-liquid system.

Step 2: Using the established λ vs n relation, determine the suitable bubble density parameter.

Step 3: Apply the tuned bubble density parameter in acoustic pressure model.

Fig. 2

Cheap and reliable way to characterize the bubble field of a stable, weakly cavitating system.

Useful when investigating large scale systems operating at near linear regimes (ultrasonic baths).

Improves the practicality of the monodisperse Commander and Prosperetti model.

OP23
20 Years of ultrasonically assisted biodiesel synthesis
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Introduction

The move away from fossil-based fuels has led the world to consider a range of non-polluting alternatives. For national power generation these include nuclear, wind, solar and tidal sources. However, for motor vehicles electric power, hydrogen fuel or fuel cells seem to be the popular choices but a potential world shortage of some of the chemical elements required suggests a problem in the future for these technologies. A realistic green alternative is biodiesel, especially after the discovery by a group of Romanian and Japanese scientists (the true pioneers in the field) of an improved synthetic methodologies using ultrasound [1].

Objectives

In towns and cities electrically, powered vehicles are an obvious clean replacement for fossil fuel driven transport. However, this is not the case in rural or third world communities, where electricity and charging infrastructure is not easily available. A simple alternative is biodiesel, obtained from vegetal sources and able to power trucks, public buses and farm vehicles [2].

Materials and methods

A biodiesel refinery was built in the USA 40 years ago and conventional technology was used until 2003 when the first paper dealing with ultrasonically assisted biodiesel synthesis (UABS) was published [1]. The improvements achieved using ultrasound and some later developments suggested that UABS could be produced in rural locations to support farm vehicles and become part of "self-sustaining" agricultural communities [3].

Conclusions

In the presentation an overview of evolution of UABS will be discussed, from its beginning in 2003 until today, aiming the aspects that could be translated towards industrial application [3].

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OP24
Acoustic resonance effects in sonochemical reactors
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1. Introduction

Sono-reactors are closed vessel and should normally exhibit acoustic resonances for some discrete frequencies/geometries, as far as linear acoustics is involved. However, the presence of cavitation bubbles makes acoustics nonlinear, and the remanence of such linear effects is questionable, despite some experimental evidence exists [1].

2. Objectives

The three objectives of this study are to check, experimentally and numerically: 1- whether such resonances can be observed 2- if frequency self-adjustment, commonly used in ultrasound generators, can hide these effects 3- if global sonochemical yields can benefit from such effects.

3. Materials & methods

A cylindrical reactor H:30 cm x D:18 cm is insonified by a specially designed 20 kHz SinapTec transducer. The water level can be slowly varied and measured. Luminol was used to image the chemically active cavitation zones. The generator continuously monitors electrical data (voltage, phase, active power) and automatic frequency control can be disabled.

The acoustic field in the liquid is computed with COMSOL by a nonlinear model accounting for the energy dissipation by inertially pulsating bubbles [2], coupled to a full transducer model. The unique inputs of the model are the current amplitude and frequency feeding the transducer. The power dissipated can be easily computed.

4. Results

Active power can vary in a wide range as the water level is varied (Fig. 1 and Fig. 2), which suggests acoustic resonance. Our model captures such variations but with different maxima locations, and acoustic power is underestimated.

Fig. 1: Electrical power versus liquid height (pink: experimental, blue: simulation). Fig. 2: acoustic field (bar) at = 22.8 cm. Yellow lines are energy streamlines.

5. Conclusion

Ongoing work aims at examining more geometrical configurations, performing sonochemistry experiment near resonances, predicting resonances locations in the parameter space, and clarifying the discrepancy between our model and experimental results.

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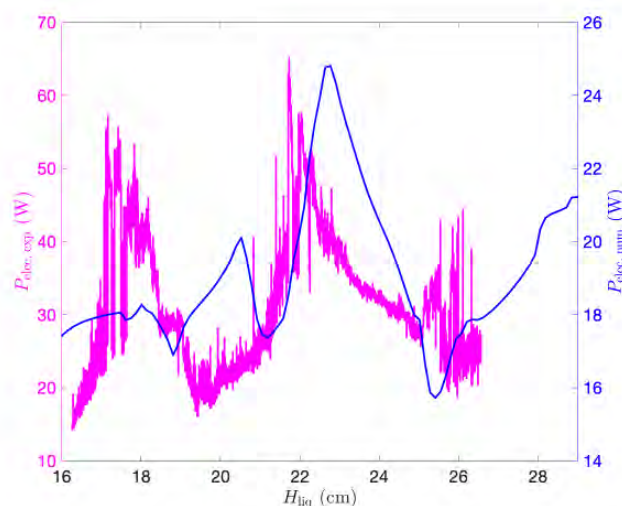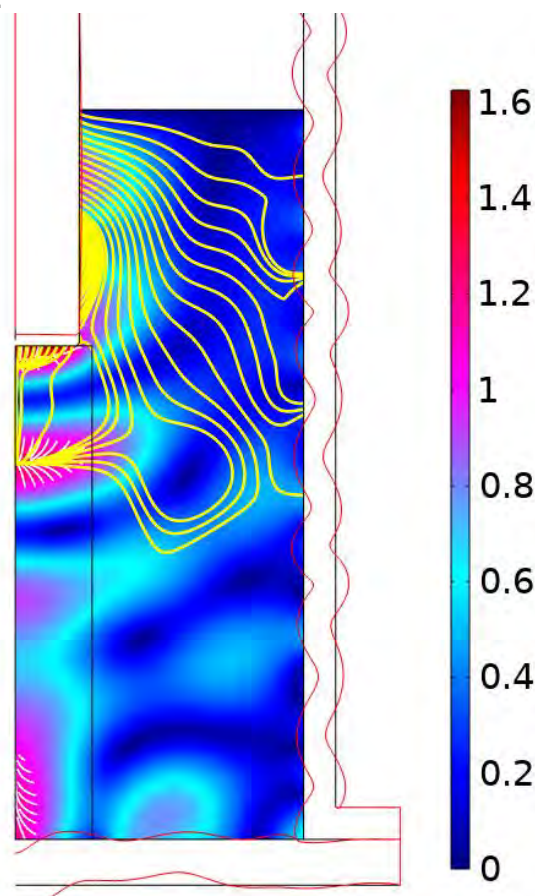
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Fig. 1

Fig. 2

KL04
Investigations into the interaction of a single cavitation bubble with bacteria

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Introduction

Despite significant progress we are still not able to answer the fundamental question: What are the mechanisms how bubbles can clean, disinfect, kill bacteria? To address this we are investigating the physical background of cavitation from physical, biological and engineering perspectives.

Objectives

A single cavitation bubble interaction with bacterial cell has not been reported yet. In this study we aimed to develop an experimental method which allows direct observation of this interaction. Additionally, we pursue a numerical strategy, which would enable an even more detailed look into the process.

Methods

Positioning of a single bubble by optical tweezers and controlled triggering of bubble cavitation was observed by a high-speed camera. The setup was equipped with fluorescence microscopy, which enables the study bacterial physiology during the event. In addition, we numerically addressed interaction between a collapsing bubble and a nearby structure, that mechanically and structurally resembles a bacterial cell. A fluid-structure interaction was employed, where compressible flow is considered and cell wall is modeled as a multi-layered shell structure.

Figure 1: Optical tweezer system. High speed and fluorescent cameras are used to observe the bubble evolution and the response of the bacteria.

Results

The results show that bubble collapse results in shear loads that create a crater of detached bacterial cells, surrounded by an annulus of attached but severely damaged bacterial cells. The extent of damage of bacteria surrounded the microjet decayed exponentially from the center of the microjet. The experimental data were complemented by mechanical and numerical models, which allowed us to propose a mechanistic model of bacterial inactivation and the estimate of the maximal shear load that bacteria can survive during the single cavitation event.

Figure 2: (a) Cell detachment and cell staining probability and (b) cell staining probability of non-detached cells in relation to the non-dimensional bubble-cell distance.

Conclusion

Finally, the results are also discussed in the scope of bacteria eradication by cavitation treatment on a macro scale, where processes of hydrodynamic and ultrasonic cavitation are being employed. The understanding of the interaction between can be considered a steppingstone on the path towards efficient, reliable, and chemically free water treatment by cavitation in the future.
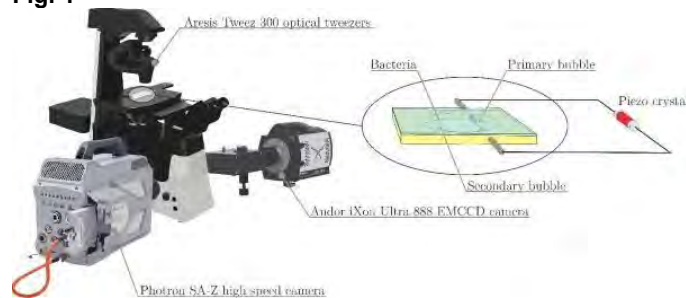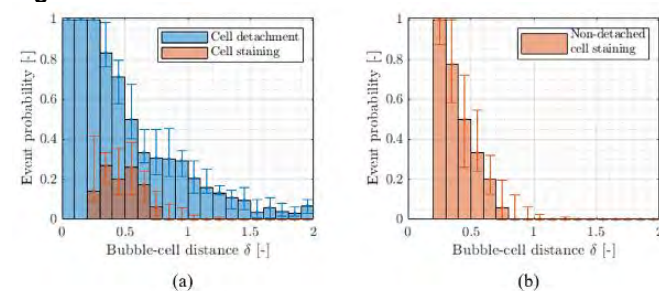
Fig. 1

Fig. 2

OP25
Control of cell destruction and proteins green-extraction of *Tetraselmis suecica* by ultrasound: correlation of process parameters to cell lysis

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Introduction

Microalgae are single-celled organisms of interest for a wide range of applications: biofuels, human food or animal feed. *Tetraselmis suecica* is a green marine microalgae covered by a cell wall relatively resistant containing 35-38% DW (w/w) protein [1]. To produce these proteins and other molecules of interest on an industrial scale, a biorefinery process must be designed. This usually includes a step of cell destruction and mechanical methods, such as ultrasound, are particularly interesting to avoid the use of harmful organic solvents [2].

Objectives

The main objective of this study is to evaluate the effect of sonication parameters and how they affect the cell destruction of a fresh *Tetraselmis suecica* cells suspension.

Materials & methods

Sonication tests were performed in a glass reactor of 2 L capacity, stirred at 900 rpm and equipped with a double jacket. The suspension was irradiated under different ultrasonic frequencies (12, 20 and 100 kHz) at different powers (50, 100 and 200 W) in continuous or pulsed mode. The cell disruption level and proteins recovery were studied by combining four evaluation methods: elemental analysis, laser diffraction granulometry, optical and scanning electron microscopy. Ultrasound were also compared to two other

mechanical cell destruction methods: high-pressure homogenization and stirred bead milling.

Results

Increasing the ultrasonication time causes cell disaggregation and increases cell destruction leading to the formation of cellular debris (1 µm) (Fig 1 : Particle size distribution of Tetraselmis suecica cells versus sonication time (20 kHz at 100W)). SEM images show that cells do not fragment in the same way depending on the method used. The high-pressure homogenizer and the stirred bead mill appeared to generate rapidly cell debris around 1 µm in size, whereas a milder ultrasonic treatment can permeabilize the cells without necessarily damaging them completely. The three processes were also compared in terms of protein extraction yield, selectivity and energy efficiency.

Conclusion

This study revealed the possibility of combining the processes with multiple levels of cell destruction, allowing for better control for subsequent downstream processing steps. Further research is underway to ensure the sustainability and feasibility of the process on an industrial scale.

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Fig. 1
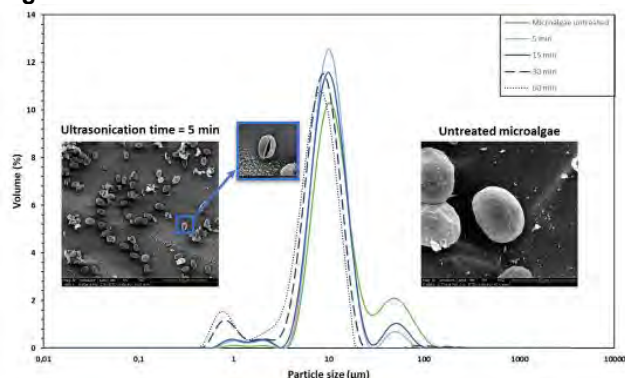
OP26
Study of ceramic coatings resistant against cavitation erosion

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Cavitation erosion dramatically impacts the efficiency and lifetime of materials and results in an extra-cost for maintenance and parts replacement [1]. Knowing materials resistance against cavitation impact is mandatory to avoid or predict cavitation damage. For this reason, cavitation erosion has been the focus of numerous studies aimed at discovering the best materials or coatings with erosion-resistant properties[2]. This work focuses on investigating cavitation effect on metallic surfaces coated with a protective layer of ceramic coatings (YSZ, Cr2O3, Cr2O3/Al2O3, Cr2O3/SiO2) applied by thermal spraying. A 20 kHz vibratory apparatus with an amplitude control system is used to set in oscillation interchangeable horn tips coated with candidate ceramics. This is an accelerated test (a few hours) which is

adapted from ASTM-G32 standards used for solid materials. The results were normalized using nickel 200. Thus, three types of substrates have been studied: stainless steel 316 L, bronze alloy NAB and titanium TA6V which are irradiated following a specific test procedure and defined time intervals. To evaluate and track the impact of cavitation erosion, a set of characterization methods is performed such as cumulative erosion curves and erosion rate as a function of irradiation time driven by material mass loss. Surface morphology and topography changes are observed by SEM images, surface profilometry, optic digital microscopy. XRD and SEM/EDS analysis were used to elaborate the modification of the composition and internal stresses of the coating. Consequently, results of Ni200 at different vibrating amplitude (20, 50 and 140 µm) show that the vibration amplitude does not change the erosion patterns but only the kinetics. Also, the initial surface state is of great importance as cavitation highlighted even exacerbate the former defects. Furthermore, additional information are gathered, including event latency and the study of the correlation between cavitation and erosion.

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OP27
Magnesium dissolution by 3.6 MHz HIFU

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High Intensity Focused Ultrasound (HIFU) transducers are possibly used in sonochemistry to generate very intense acoustic intensities at very high frequencies (>1 MHz)[1]. UTINAM institute has elaborate a technique allowing the control of cavitation activity by controlling HIFU excitation signal. Sweeping the initial frequency in reverse (negative sweep) enhance tremendously the cavitation activity while it"s quenched under positive sweep [2] The present work tend to investigate the real reason behind these changes in the cavitation activity, by studying bubbles conditions generated by 3.6 MHz HIFU under different sweeping parameter. To this end, sonochemiluminescence of luminol SCL, cavitation noise spectra and sonoluminescence emission spectra measurements were recorded in order to reveal the impact of sweeping parameters on bubbles. For the first time, molecular emissions have been detected at such a high frequency. Despite the low intensity of most molecular emissions, the CN emission chosen as a spectroscopic probe is intense and was used to simulate rovibronic temperatures inside HIFU bubbles. The resulting sweeping parameters exhibiting the most severe cavitation activity were investigated on magnesium surfaces (pure and alloy AZ31). Sonication was stopped at regular intervals to follow the evolution of the sample with a systematic set of characterization (mass loss, images, optic microscopy, interferometer). Also, surface impact is measured using profilometer, SEM/EDS, AFM. Solution quantitve analysis ICP confirms the obtain mass loss values for each frequency sweep condition. The highest mean dissolution rates reached for a pure magnesium sample correspond to negative sweeping condition with an increase of about 30 % of the kinetics compared to fixed frequency. Under all conditions the surface roughness has increase with an

appearance of different patterns. Although, the surface ripples are directly dependent of the corresponding acoustic sweeping parameters. These promesing results open a vast range of possible applications in the magnesium alloys field.

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OP28
Development of integrated flow emulsion electrosynthetic system

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In this work, we developed a continuous flow emulsion electrosynthetic system. This new flow system involves 20 kHz ultrasonication for acoustic emulsification of water-insoluble *n*-octylamine in an aqueous electrolyte without the use of a surfactant, followed by emulsion electrolysis in the flow microreactor and separation of the emulsion into aqueous and oil product (octanitrile) phases using a liquid–liquid separator (Figs. 1 and 2). The 20 kHz ultrasonication provided a stable emulsified solution containing n-octylamine droplets with a relatively narrow size distribution in the micrometer range. The subsequent emulsion electrolysis in the microreactor yielded the desired nitrile product very effectively. In addition, in a continuous flow operation, the emulsion after the electrolysis was efficiently separated into an aqueous electrolyte and oil product using a liquid–liquid separator. The system is applicable across various hydrophobic amines, which were successfully oxidized to provide the corresponding nitriles with good current efficiencies under continuous flow. The proposed system is robust, and the desired product was successfully synthesized at the gram scale.
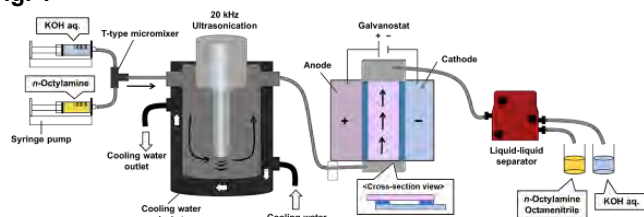
Fig.1 Schematic of the integrated flow emulsion electrosynthetic system for the oxidation of *n*-octylamine.

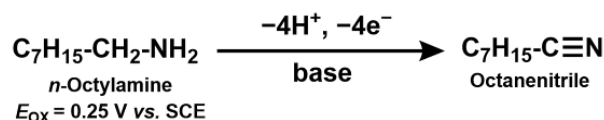**Fig. 2** Electrochemical oxidation of *n*-octylamine.

Reference

R. Mikami, N Shida, M. Atobe, *Org. Process Res. Dev.*, accepted (doi.org/ 10.1021/acs.oprd.2c00004).

Fig. 1

Fig. 2

$$C_7H_{15}\text{-}CH_2\text{-}NH_2 \xrightarrow[\text{base}]{-4H^+,\ -4e^-} C_7H_{15}\text{-}C\equiv N$$

n-Octylamine
$E_{OX} = 0.25\ V\ vs.\ SCE$

Octanenitrile

Session: Ultrasonic processing 1

KL05
Biorefineries & ultrasound: perspective symbiosis

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Introduction:

Current shift towards renewable fuels, chemicals and materials, has lead to the rise of the biorefinery concept. They utilize the inherent potential residing in biomass by converting wood, grasses or other feedstocks into multiple product streams. While cellulose and hemicellulose are comprised of monosaccharides, lignin, the third major component, consists of aromatic subunits. Biorefineries aim to maximize conversion of all three biopolymers to monomeric compounds, macromolecules or other materials. Ultrasound (US) can be an universal tool for forest biorefineries in order to achieve these goals.

Objectives:

In literature, several beneficial US treatments for biomass have been described, whereas we aim to create a modular approach for multiple steps throughout the whole production process. Our partner, a biorefinery in Estonia, is using forestry hardwood leftovers as raw material. The recalcitrant woodchips are converted by thermo-chemo-mechanical means into a mixture of lignocellulose from which the main components can be separated. All of the next steps (Fig. 1) can involve US to yield different outcomes: improved efficiency of cellulose hydrolysis or lignin dissolution (pre- or continuous treatment), creation of novel nanocrystalline cellulose-lignin mixtures, etc. Separated lignin can be further valorized by US assistance to increase lignin reactivity through structural, molecular weight or particle size changes. This in turn could lead to novel biomaterials.

Materials & methods:

In this study raw materials produced by a pilot scale plant were used. The US system is based on Sonopuls HD 4200 (20 kHz). Characterization of lignin is based on NMR methods (31P and HSQC), with Bruker Avance-III 700 MHz spectrometer. Other methods include FT-IR, HPLC/SEC, TGA, DSC, particle size distribution analysis.
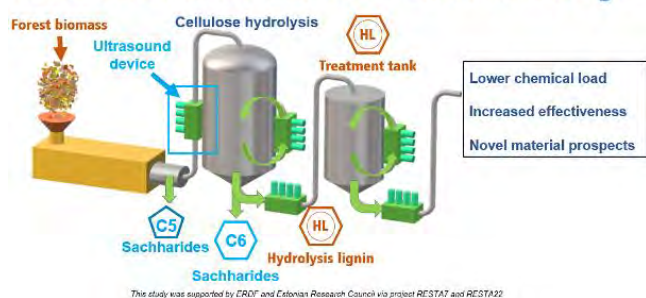
Results:

We have promising results of US treatment in the multiple processes, which include maximal solubility of lignin under mild alkaline conditions, higher efficiency of cellulases in

lignocellulose mixtures, production of novel microcrystalline cellulose-lignin materials, etc. More detailed results will be presented.

Conclusion:

Forest biorefinery success is based on their efficient performance and the full valorization of different product streams. US can increase the efficiency and sustainability in multiple steps. Moreover, US can act as an amplifier of biorefineries, creating a new wave of potential.
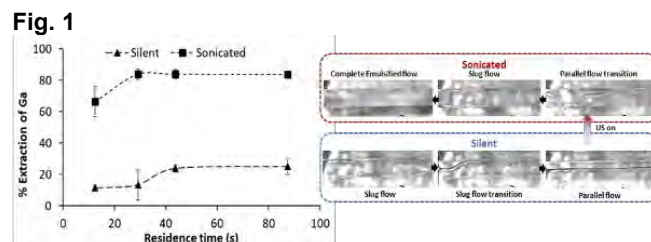
Fig. 1

OP29
Feasibility study on solvent extraction of gallium in flow using ultrasound

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[2]KU Leuven, Chemistry, Heverlee, Belgium

Introduction: Gallium (Ga) is a critical metal with increasing demand for its use in wireless communication and optoelectronics. There are no gallium deposits and it occurs as minor element in ores of other elements. The main source of gallium is the aluminum (Al) ore bauxite and it is extracted from the liquor of the Bayer process for alumina refining. Solvent extraction with Kelex 100 is an effective method for Ga/Al separation, but the process is suffering from slow kinetics due to mass transfer limitation and it has never been explored in flow reactors yet[1]. Ultrasound has been proven to be effective for faster extraction in batch[2].

Objective: This work explores the feasibility of carrying out the extraction of gallium with Kelex 100 in milli-flow using ultrasound (US).

Materials & methods: A mill-flow contactor with intermittent US contact and temperature control was used[3]. The effects of flow, solvent type, Kelex concentration, Al concentration, and US were assessed. The effects in a synthetic Bayer solution were also explored.

Results: The initial experiments with a mono-metal gallium feed solution showed 83% extraction in 30 s using kerosene as the diluent with 6 times improvement with US (Figure 1 - Left). This drastic change is a result of almost complete emulsion flow instead of interchanging parallel and slug flow (Figure 1 - Right). US worked more efficiently than using a chemical emulsifier and the combined effect of both led to third phase formation, hence the modifier was deemed to be not appropriate with US. The effect of frequency coincided with the reactor performance with no additional effects. Equimolar experiments with Ga and Al showed 80% extraction but with a decreased improvement of 2.5 times with US owing to better results in silent condition and

minimal effect on the extraction of Al. The synthetic solution showed similar improvements as the pure gallium system but with a lower absolute concentration of 73% due to the very large comparative amounts of Al being present.

Conclusion: The use of ultrasound was found to be critical and effective for gallium solvent extraction with the extractant Kelex 100 in a mill-flow contactor.

References: 1. Cote, G. *Radiochim. Acta* 91, 639–643 (2003), **2.** Pesic, B. et al. *JOM* 41, 42–45 (1989), **3.** John, J. J. et al. *Chem. Eng. Res. Des.* 125, 146–155 (2017)

Fig. 1

Figure 1: (Left) Extraction of gallium in flow (0.8 mm PFA tube) with and without ultrasound (40 kHz, 590 m.V, 20 W). (Right) two phase flow behavior with and without ultrasound. **Aqueous phase** (Slug & bottom phase in parallel) is 200 ppm Ga in 2M NaOH, **Organic Phase** (Continuous in slug flow & top phase in parallel flow) is 5% Kelex 100 in kerosene.

OP30
Application of sonolytically formed nanometal catalyst for the new energy production utilizing by-product glycerin from the production process of Sustainable Aviation Fuel

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Introduction: The use of Sustainable Aviation Fuel (SAF) made from renewable biomass as aviation fuel is proposed to prevent global warming. In this study, we investigated the co-solvent method for SAF production from coconut oil, which contains short-chain fatty acid, and found that it produces very high quality glycerin. Therefore, we investigated (1) microwave purification of glycerin, (2) its use as a suitable fuel for fuel cells, and (3) the acceleration effect of glycerin on the generation of hydrogen from water on a Pt-TiO2 photocatalyst conditioned by ultrasound.

Experimental: Pt-TiO2 photocatalyst was prepared by adding TiO2 to aqueous platinum chloride acid solution then synthesis for 30 minutes using a 200 kHz ultrasonic irradiation device (Kaijo Electric Co., Ltd). Microwave purification of glycerin was by a household microwave oven. The fuel cell used a Nafion membrane with Pt as the electrode.

Results and discussion: Glycerin contains three OH groups in the molecule, it was easily heated to boiling point by microwaves at 1.45 GHz, obtained glycerin with a purity of 99.5%. Compared to an ordinary microwave oven that consumes the same 500 W of power, the power to heat to boiling point was about 1/7. Glycerin prepared by this method was substituted glycerin for methanol in the methanol fuel cell, the results showed that there is more electric current was generated than with methanol and ethanol. (Figure 1) The oxidation reaction of these alcohols occurred at the same voltage, and when the same moles of

alcohol were added to the fuel, according to the carbon number, methanol:ethanol:glycerin = 1:2:3 current values were obtained. The generation of hydrogen from water by sunlight was further investigated using a Pt-TiO2 photocatalyst conditioned by ultrasound. More hydrogen was produced when glycerin was added than when other alcohols were added. (Figure 2) The addition of glycerin generated 100 times more hydrogen than the addition of no glycerin. The mechanism of hydrogen generation was examined using deuterated glycerin, and about 80% of the hydrogen generated was hydrogen in the water molecules, and about 20% in the glycerin molecules.

Figure 1. oxidation of alcohol with Pt electrode

Figure 2. Effect of Glycerin on the formation of hydrogen by Pt-TiO2 photocatalyst
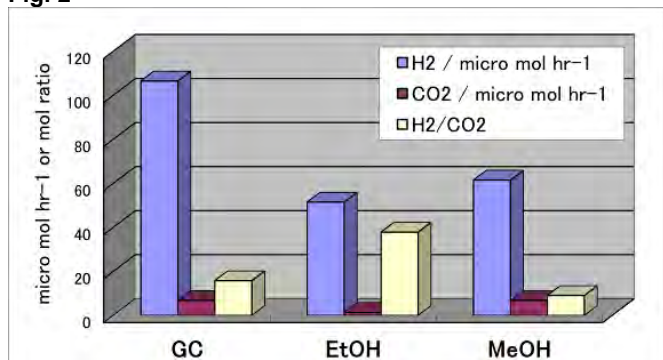
Fig. 1
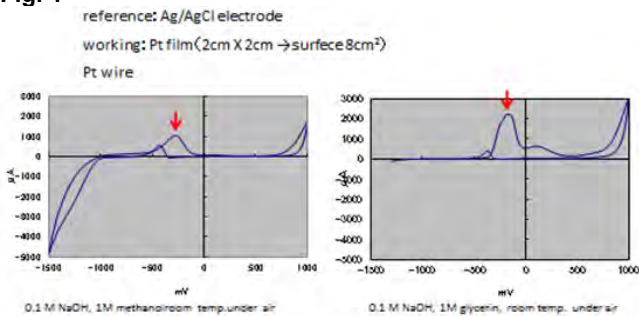
Fig. 2

OP31

Insight into the formation of Fe3O4-Mn-rGO core-shell nanocomposites through sonoelectrochemical approach and its electrochemical studies for lithium-ion battery

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[2]National Institute of Technology Tiruchirappalli, Tiruchirappalli, India

Among versatile utilization of iron oxide (Fe3O4) nanomaterials, prominent advantages have been identified in electrochemical application as it possesses high gravimetric capacity (Fe3O4 - 926 mAhg-1), moderate working potential, large availability, non-polluting nature, etc. In this work, spherical Fe3O4 (SEF) nanoparticles was synthesized using a facile sonoelectrochemical method under optimized ultrasonic parameters. The shell formation of manganese oxide over Fe3O4 (SEFM) was done to mitigate volume expansion nature; and further, it has been doped with carbon matrix (SEFMGO) to utilize it as an anode material for Li-ion battery. The functional groups of prepared nanocomposite were confirmed by FTIR and it was amorphous nature in 10-50 nm size range through XRD. The thermal stability was increased after core/shell formation and further doping with

carbon matrix which was confirmed with TGA results. The spherical shape of SEF, core/shell structure of SEFM and its distribution with carbon matrix of SEFMGO were evident by FE-SEM and HR-TEM as shown in Fig.1.

The cyclic voltammetry studies (Fig.2) exhibits two clear peaks at 0.98V and 0.51V (versus Li+/Li) in the first scan, are attributed to the formation of SEI during lithiation and delithiation process. The reducing peak intensity indicates the irreversible redox reactions of SEF and SEFMGO, and the curve overlapping consecutive scans confirms the stable SEI film formation. Hence, the carbon matrix can enhance the structural integrity of SEF during subsequent charge/discharge cycles, thus leading to high columbic efficiency, superior and stable reversibility of the nanocomposites.

By coupling electrochemical reaction with ultrasound, the kinetics and mass transport of the redox reactions had enhanced through simultaneous nucleation (at the electrode surface) and cavitation (in the solution mixture). As a result, Fe3O4 nanomaterials synthesized through sonoelectrochemical method and its core shell nanocomposites would yield high capacity anode material for lithium ion battery with reduced cost, energy and synthesis time with higher stability.

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L. Cabrera, S. Gutiérrez, P. Herrasti, D. Reyman, Sonoelectrochemical synthesis of magnetite, Physics Procedia 3 (2010) 89-94.
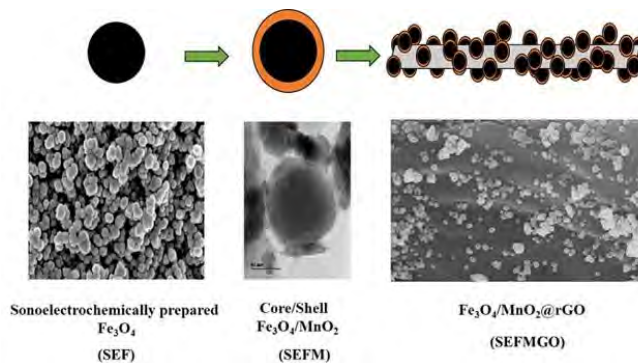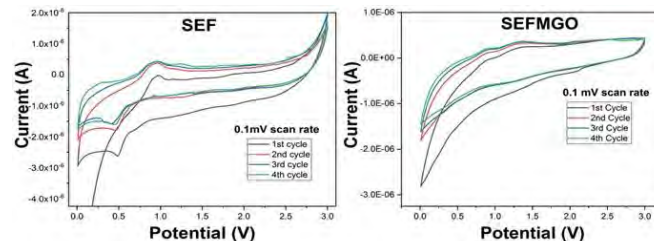
Fig. 1

Sonoelectrochemically prepared Fe3O4 (SEF) | Core/Shell Fe3O4/MnO2 (SEFM) | Fe3O4/MnO2@rGO (SEFMGO)

Fig. 2

OP32

A flexible hybrid reactor for simultaneous application of ultrasound and microwave radiation

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Introduction

Ultrasound (US) and Microwaves (MW) are effective methods for processes intensification [1]. The rationale behind merging US and MW as an energy source stems from the differences between them. Although MW provide rapid heating of a reaction mixture, mass transfer is a limiting factor in the overall rate of the process. US provides good mass transfer but with limited heating. Thus a hybrid reactor combining US and MW may overcome limitations of mass transfer and heating [2].

Objectives

A new type of hybrid reactor has been developed with more flexible input than previous types employing adjustable US frequencies and power together with different MW powers. Full control of temperature allows high power densities to be applied continuously.

Materials and methods

The reactor can receive at the same time, or separately, MW and US excitation. US power is provided through a multifrequency transducer via a MW transparent coupling fluid. MW energy is supplied from a solid-state MW generator via a single mode applicator. The coupling fluid is cooled by a jacket of circulating liquid in which the reactor is partially immersed to control the reaction temperature [3].

Conclusions

A new combined (hybrid) ultrasonic and microwave installation was built and characterized. This new system maintains a low temperature in the reaction medium even when using high-power densities which has proved extremely important for the:

- extraction of valuable active principles from plants;
- transesterification of vegetal oil with ethanol, under heterogenous acidic catalysis

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[3] I. Călinescu, M. Vinatoru, D. Ghimpețeanu, V. Lavric, T.J. Mason, A new reactor for process intensification involving the simultaneous application of adjustable ultrasound and microwave radiation, Ultrasonics Sonochemistry, 77 (2021) 105701 10.1016/j.ultsonch.2021.105701

Fig. 1
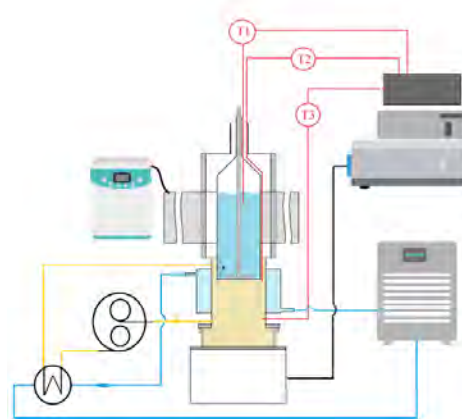
Session: Environmental remediation 2

KL06

Sono-assisted hybrid methods for micropollutant removal from water

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The aim of the scientific work is the development and qualification of combination processes for the degradation of micropollutants in water.

The global water industry faces the enormous challenge of so-called micropollutants [[i]]. These are highly diluted human- or ecotoxicologically active substances, such as pharmaceutical residues, endocrine disruptors or production residues. Classic sewage treatment plant technology is not capable for removing or destroying these micropollutants [[ii]]. One the other hand, new treatment methods, have to be efficient and effective across a broad spectrum, cost-effective and ideally, be able to be operated with renewable energies.

Micropollutants can be completely removed by oxidation processes [[iii]]. In the present work, the oxidizing agents are generated "in situ" by means of cavitation (ultrasound) and photocatalysis. In addition, sorbents (e.g., graphene species) are used, which create and exploit synergetic effects (Fig. 1).

The work focused on the analytical evaluation of the planned hybrid processes. Various dosimeters were used to determine the cavitation intensity. These include, for example, salicylic acid dosimetry or the Fricke dosimeter. Optical and acoustic analysis methods were also used. By combining chemical and physical measurement methods, statements can be made about the efficiency and mode of action of the processes and these can be used for future reactor design. Furthermore, various dyes and trace substances and their degradation behavior were examined and evaluated. The results and findings obtained allow conclusions to be drawn about future reactor concepts and operating parameters.

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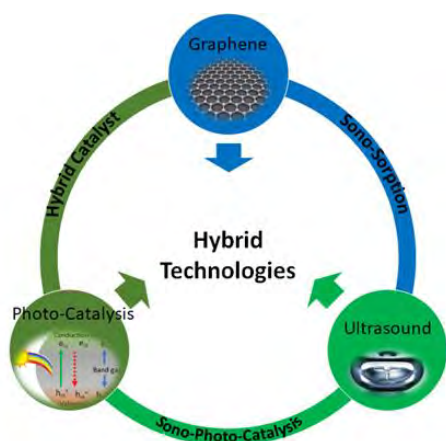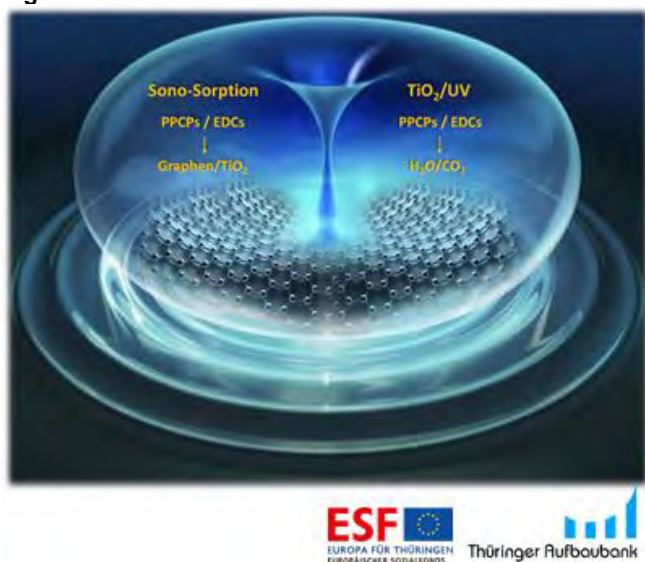
Fig. 1

Fig. 2

OP33
Sonocatalytic activity of ZnO nanoparticles for Methylene blue degradation at different ultrasound frequencies

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Sono-catalysis has emerged in these last years as a tool for enhancing the radicals production by ultrasonic irradiation of aqueous solutions. Despite the generation of radicals in water exposed to high intensity ultrasound is well know, the reactions mechanism as function of ultrasonic frequency, gas dissolved and, more recently, the presence of micro-nano particles is currently under investigation for environmental[1], biomedical [1] and lastly also for energetic applications[3]. Here we report the effect of ZnO nanoparticles on degradation of Methylene blue aqueous solutions exposed to different ultrasonic frequencies and as function of dissolved gas. Monitoring of OH• and H• radical generation through ESR technique have been also performed. As expected high frequency, 858 kHz, is more efficient than typical 20 kHz horn transducer, however the enhancing effect of ZnO nanoparticles was clearly observed and the result obtained with different gas suggest that

dissolved oxygen plays a key role in presence of ZnO nanoparticles. Other studies have reported similar results under the topic of "piezocatalysys " using different oxides nanoparticles and plastic microparticles [4], although the proposed mechanism is not fully clear[5]. In this study some insight on this phenomenon relatively to different ultrasonic frequencies ad gas dissolved are presented.

Fig 1 Degradation of **Methylene blue** *in presence of ZnO nanoparticles using 20 kHz transducer*

[1] X. Ning et al. *Effective promoting piezocatalytic property of zinc oxide for degradationof organic pollutants and insight into piezocatalytic mechanism* **Journal of Colloid and Interface Science 577 (2020) 290–299**

[2] Piao Zhu et al. *Piezocatalytic Tumor Therapy by Ultrasound-Triggered and BaTiO 3 -Mediated Piezoelectricity* **Adv. Mater. 2020, 32, 2001976**

[3] Dengkui Shao et al. *Oxygen Reduction Reaction for Generating H 2 O 2 through a Piezo-Catalytic Process over Bismuth Oxychloride* **ChemSusChem 2018, 11, 527 – 531**

[4] Yanfeng Wang et al*. Ultrasonic activation of inert poly(tetrafluoroethylene) enables piezocatalytic generation of reactive oxygen species* **NATURE COMMUNICATIONS | (2021) 12:3508**

[5] Franziska Bößl and Ignacio Tudela *Piezocatalysis: Can catalysts really dance?* **Current Opinion in Green and Sustainable Chemistry 2021, 32:100537**

Fig. 1
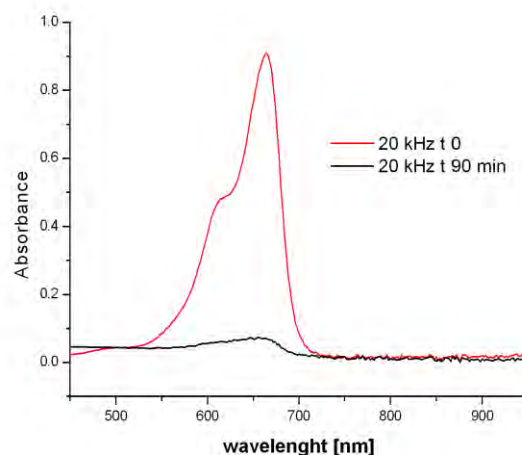
OP34
Kinetics analysis of sonochemical degradation of phenol

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Water pollution caused by factory effluent and domestic wastewater is one of the environmental problems. Organic materials are often difficult to degrade, and there is a need to develop methods for their degradation. Several oxidation processes using photocatalysis and ozone have been investigated as degradation process for organic compounds, but the separation process of photocatalytic particles after degradation process and the complexity of the equipment,

such as fine bubbles for efficient ozone dissolution, have become issues. On the other hand, advanced oxidation processes of hazardous organic materials such as phenol using ultrasound has been proposed. Ultrasonic technology is being considered for use in a wide range of chemical processes other than degradation reactions. The reaction rate and product characteristics are strongly dependent on the ultrasonic frequency, so it is very important to select the optimal frequency for the system of interest. The authors investigated the effects of operating conditions such as frequency, power, and initial concentration of methylene blue on the degradation reaction rate, and proposed a model for estimating the degradation reaction rate constant, which quantitatively expresses the effect of frequency by sonochemical efficiency value. In this study, we perform an ultrasonic degradation of phenol and investigate the application feasibility of the proposed model.

The degradation of organic compounds using ultrasound often proceeds in a pseudo-first-order reaction, and phenol degradation proceeded in a pseudo-first-order reaction in this study as well. The highest degradation rate constant was observed at 490 kHz. The frequency dependence of the degradation rate constant of phenol revealed the same trend as sonochemical efficiency value, suggesting that the established kinetic model can be applied. On the other hand, the threshold power value was about 1.3 W, not dependent on frequency. The cavitation threshold increased with increasing frequency, but was constant in this study. From the above, it is considered that the degradation reaction does not proceed unless a sufficient amount of OH radicals are generated.

OP35
Combination of sono-sorption and photocatalysis for the degradation of organic dye over Ag/SrTiO3 under visible light

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[2]Polytechnique Montréal, Department of Chemical Engineering, Québec, Canada

Strontium titanium (SrTiO3) as a cubic structured perovskite has excellent chemical stability, low cost, large surface area, low toxicity, and high photocatalyst activity under UV light. For the photocatalyst effect in the visible light spectrum, strontium titanate semiconductors can be modified by doping with metals., among which, Ag. Ultrasonic irradiation has been widely used to assist the synthesis and modification of inorganic materials, possibly leading to increased inactivity. This is due to the fact that the ultrasonic irradiation can activate the particles by removing the oxide layer and inducing the particle fragmentation, which can increase the BET surface area of the particles.

In this work, ultrasonic irradiation was used for the synthesis of Ag/SrTiO3 nanophotocatalysis. The photocatalytic activity of as-synthesized Ag/SrTiO3 nanophotocatalyst was studied by photocatalytic degradation of reactive blue as the pollutant model. Although ultrasound irradiation for wastewater treatment has been used, applying this method alone for the degradation of persistent organic pollutants is time-consuming. Hence, to overcome this problem, ultrasound has been coupled with sorption (sono-sorption). This combination increases the adsorptive removal efficiency and photocatalytic degradation, which may result in reducing the process cost.

Fig. 1
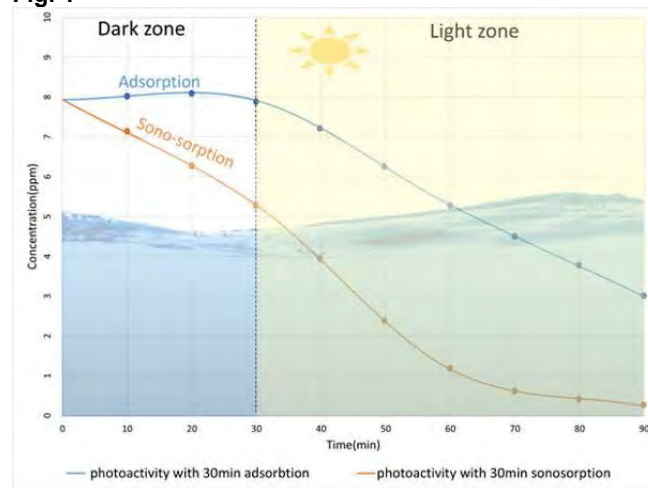
OP36
High frequencysonolysis of Per- and Polyfluoroalkyl Substances (PFAS)

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[2]Arcadis, Manchester, United Kingdom

For more than 50 years, Per- and poly-fluorinated substances (PFASs) have been used to manufacture surfactants, aqueous film forming foams (AFFFs), and plastics such as polytetrafluoroethylene (PTFE)[1]. PFAS contain a fluorinated carbon chain and hydrophilic head group(s) giving them desirable hydrophobic, lipophobic and fluorophillic properties which also makes them difficult to degrade. PFAS are ubiquitous in global environments [2], and bioaccumulate in plants and animals. In the European Economic Area alone, estimated medical costs from PFAS exposure are of €52 - €84 bn annually [3]. Many PFAS are now banned or heavily regulated and the introduction of fluorine-free AFFFs means that legacy foams, stockpiled worldwide, await destruction.

Many processes have been adapted for PFAS removal, such as nano-filtration, ozofractionation and adsorption. However, these generate concentrated PFAS streams which require further treatment, usually incineration at 1,000oC+ that emits HF and organofluorine compounds, which necessitate scrubbing [4]. High frequency ultrasound mineralizes aqueous PFASs into less harmful and easily treatable species, such as CO2 and F- ions [5]. Building on past work, this work discusses the upscale of PFAS sonolysis with respect to treatment of landfill leachate and AFFFs. Multiple reactors/transducers in a flow through configuration is shown to optimise cost effectiveness and treatment time. Power density and intensity are dominant parameters for rapid treatment, while liquid flow rate and temperature have limited, but sonochemically interesting, effects. Common and prevalent PFAS in both leachate and AFFFs are well degraded, while more novel and sparser PFAS structures appear recalcitrant. Thus, sonolysis could soon be utilised for industrial scale treatment of contaminated water, leachate and defunct AFFFs.

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Thursday, 01 September 2022

Session: Ultrasonic processing 2

PL06
Applications of ultrasound for food processing and chemical process intensification

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Introduction: Nowadays, ultrasound (US) has been successfully used for many applications in food processing and chemical conversions. It has been shown that the particular characteristics of the action of ultrasound waves and their effects bring many benefits to various applications. The improvement and acceleration of various chemical processes have been demonstrated, especially in the field of food processing, biomass treatment and conversion, solid waste treatment and even in the petroleum industry. In this presentation, the recent advances using ultrasound for meat processing, chemical conversions and for improving extraction procedures will be shown. Applications for the treatment of solid residues and the potential of the US for crude oil treatment and demulsification processes will be also presented.

Methods: In this work, meat and meat products as sausages were treated in ultrasound baths (frequency ranging from 20 to 130 kHz) or probes (20 kHz) were evaluated. The US systems were also used for demulsification of crude oil and for the removal of chromium from tanned leather.

Results: Post-packaging pasteurization of sausages using ultrasound was demonstrated to be feasible, by saving time and extending the shelf life of products. Demulsification of heavy and extra-heavy crude oil (efficiency over 70% for real crude oil emulsions) was achieved by using low frequency ultrasound (20 to 45 kHz). Ultrasound was also feasible for Cr removal from tanned leather, increasing more than 20% the removal efficiency when compared to the systems without using US.

Conclusion: Ultrasound was demonstrated to be a suitable option to improve the processing of meat and meat products and also to help in the demulsification of crude oils. Ultrasound was also successful for helping the removal of Cr from solid tanned leather residues.

OP37
Ultrasound-assisted photochemistry in flow

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Photochemistry has significant potential in advancing sustainable chemical synthesis, providing a means of synthesizing chemicals with improved reaction efficiency that requires fewer intermediate reagents. These reactions perform exceptionally well at microfluidic length scales [1]. At this scale phase distribution is of consequential importance for gas-liquid reactions in flow, affecting both conversion and photon efficiency [2]. In conventional microfluidic systems, a large fraction of light and effective reaction volume is lost due to the presence of the gas phase, leading to lower throughput. With ultrasound, it is possible to redistribute both the gas and liquid phases [3], improving photon efficiency and throughput, see Fig.1.

Fig.1. a) Phase distribution for gas-liquid Taylor flow leading to a high loss of light. b) Acoustically altered phase distribution for improved light absorption.

In this work, photon transport is studied and quantified for a microfluidic system with and without ultrasound using an established actinometrical method [2]. For a gas fraction of 0.75, actinometer conversion is improved by a factor of 1.8 with ultrasound, see Fig.2, demonstrating the capability of ultrasound to improve photon efficiency. Secondly, the liquid residence time and phase distributions will be investigated using tracer-pulse experiments and high-speed image analysis respectively to characterize the system. With this information, it will be possible to determine and model photon transport for this system which, in turn, can be used to optimize the system for relevant photochemical reactions.

Ultrasound offers a facile and noninvasive method to alter the phase distribution in microfluidic reactors, enhancing throughput and making it possible to study and predict the role it plays in various photochemical reactions in flow. Additionally, allowing an extra degree of freedom to optimize different reaction systems without having to redesign and replace the microfluidic reactor itself. We will demonstrate this by characterizing photon transport with and without ultrasound for our system, and use these results to improve and optimize a benchmark photochemical reaction involving singlet oxygen.
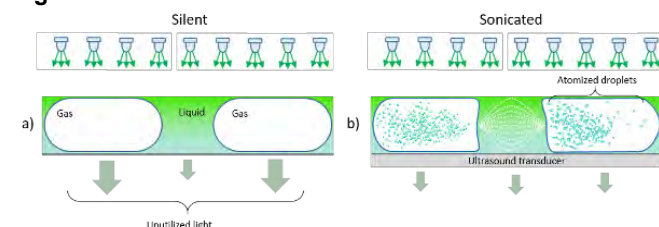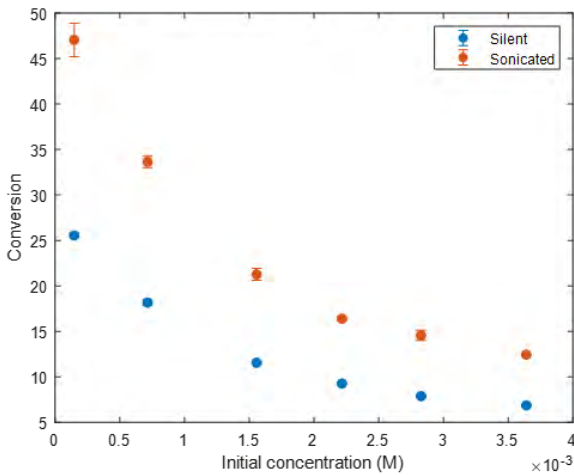
Fig.2. Actinometer conversion with and without ultrasound at varying initial concentrations of the actinometer.

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Fig. 1

Fig. 2

OP38
Intensification of convective heat transfer by means of ultrasound: evidence of a close relationship with the thermal boundary layer
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Introduction

Several studies have shown that ultrasonic waves can disturb the hydrodynamics of a liquid flow and thereby increases its turbulent intensity [1]. These perturbations depend on the effects induced by ultrasound, such as acoustic cavitation or acoustic streaming. By generating turbulence within the fluid flow, ultrasound may thus reduce the thermal boundary layer and consequently enhance heat transfer [2]. However, no study has been conducted on heat transfer enhancement in relation to the thermal boundary layer in the presence of ultrasound, which is the aim of this work.

Materials and Methods

This study has been performed in a rectangular channel, with a heating wall and an ultrasonic transducer facing it. Different flow regimes (from Re = 900 to Re = 15000) and for 3 distances between the ultrasonic emitter and the heating wall, noted *d* has been studied (33, 63 and 107.5 mm). The experiments were carried out for 2 distinct ultrasonic frequencies (25 kHz or 2 MHz), at a given ultrasonic power (Pus = 110 W).

Results

Figure 1 given here below shows the evolution of the HTEF as a function of the thermal resistance of the initial thermal boundary layer, given by *1/h*, and of the equivalent thickness of the thermal boundary layer, δ_{th} for both investigated ultrasonic frequencies:

Figure 1. Evolution of the Heat Transfer Enhancement Factor as a function of the 1/h ratio for 3 distances d and for the 2 frequencies tested: f = 25 kHz (a) and f = 2 MHz (b), Pus= 110 W.

Conclusion

As shown by experimental data reported in this paper, heat transfer enhancement by means of ultrasonic waves can be linked to the thickness of the initial thermal boundary layer, (*i.e.*, same hydrodynamic conditions but under silent conditions). At high frequency, the main convective effect induced by the presence of ultrasound is attenuated for thin boundary layers that is to say for high Reynolds numbers. At low frequency, effects due to acoustic cavitation remain effective whatever the flow regime since it occurs at the surface of the heating wall.

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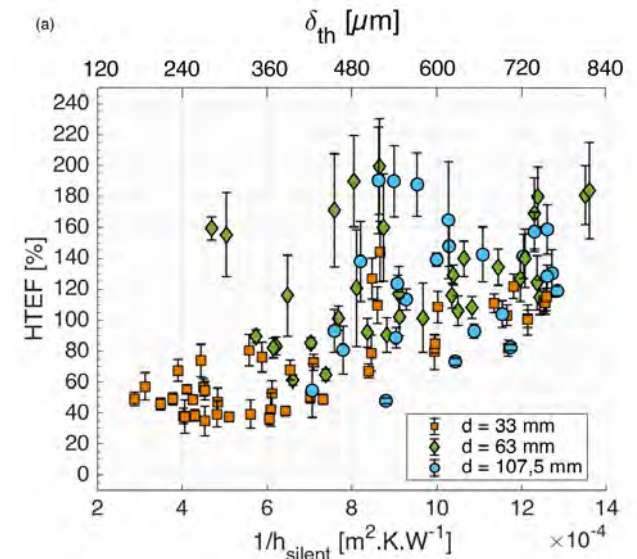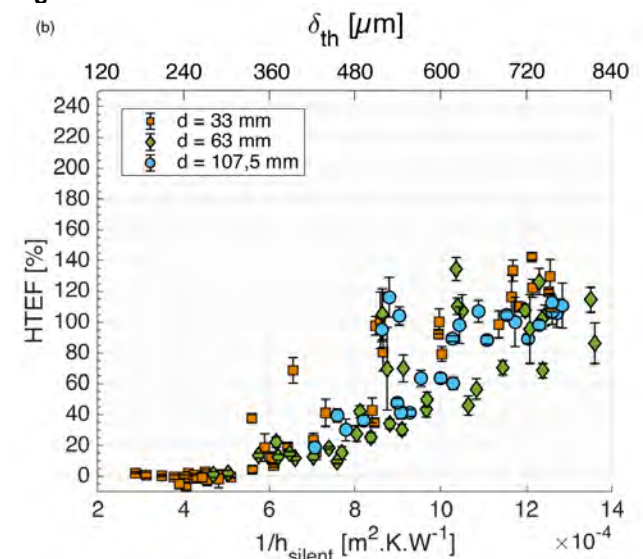
Fig. 1

Fig. 2

OP39

Characterization of an ultrasonic milli-fluidic continuous reactor for zeolite synthesis

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Introduction: Zeolites are crystalline solid materials industrially synthesized in batch reactors. Transition towards continuous synthesis would improve crystallization performance, although solid handling still remains a challenge[1]. Application of low frequency ultrasound limits solid deposition whilst enhancing mass transfer and mixing. The formation of •OH radicals might also play a role by decreasing the activation energy required for nucleation[2]. The effect of ultrasound parameters in a milli-fluidic continuous reactor is in this work quantified, to establish the optimal conditions for zeolite synthesis[3].

Objectives: The objective of the research is twofold: first, to define the optimal frequency and power which deliver the highest concentration of •OH for zeolite synthesis. Second, to characterize macro- and micro-mixing effects provided by ultrasound in comparison to silent conditions.

Materials & methods: The ultrasonic continuous reactor consists of a coiled PFA tubing (ID 2 mm, V 12 mL) enclosed in an aluminum box with oil recirculation (Figure 1) [**Figure 1** Reactor assembly]. It is surrounded by six Langevin-type transducers, which work at three resonance frequencies (40-80-120 kHz). The cavitation activity in the system is quantified via measurement of the concentration of •OH by performing terephthalic acid (TA) dosimetry in flow. Tested conditions starting with 20 W applied power per transducer are listed in Table 1 [**Table 1** Tested conditions during TA dosimetry experiments]. Macro-mixing is characterized via residence time distribution measurement with a conductive KCl solution. Deviations from the ideal plug flow in the system are quantified via calculation of the Bodenstein number. The extent of micro-mixing is quantified via the Villermaux-Dushman protocol[4].

Results: A quantitative characterization of the reactor will reveal the optimal frequency at which the highest concentration of •OH is obtained, as well as the best mixing condition to enhance mass transfer for zeolite synthesis.

Conclusion: This research contributes to the transition from batch to continuous zeolite manufacturing, by developing and optimizing a novel synthesis methodology that exploits the added value of ultrasound.

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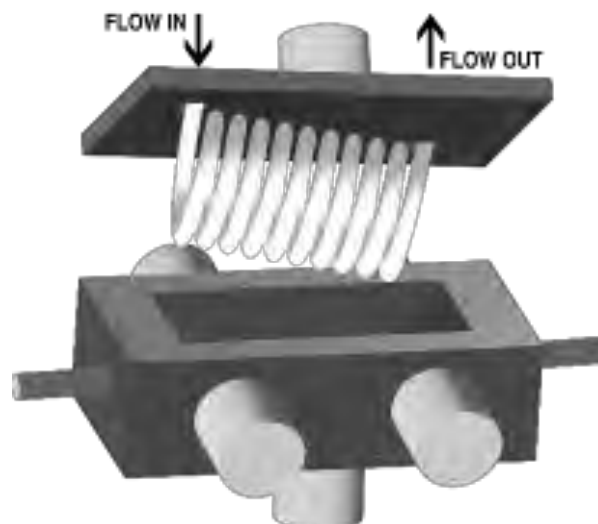**4** Jordens, J. *et al. Ultrason. Sonochem.* 32, 68–78 (2016)

Fig. 1

FLOW IN   FLOW OUT

Fig. 2

Frequency [kHz]	Pressure [bar]	Residence time [min]
40	1	10
80	3	20
120	5	30
	7	45

Session: Ultrasonic processing and Environmental remediation

KL07

Polymorph control and high yield in flow crystallization with ultrasound

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Introduction

Polymorphism i.e. multiple crystal forms of the same substance, can affect performance of medicines [1]. Anti-solvent crystallization allows fast supersaturation development for which ultrasound (US) fits as a credible mixing technique. US generated cavitation further triggers fast nucleation [2]. Assisting polymorph control can make US a promising technique for flow crystallization.

Objectives

Non-seeded and seeded flow crystallization of *o*-ABA (*Ortho*-aminobenzoic acid, form-I stable, form-II, III meta-stable) was carried out with and without US for high yield with polymorph control. A high speed camera was used for deeper understanding of nucleation. To the best of authors" knowledge, this is the first time, for *o*-ABA, polymorph-controlled flow sonocrystallization has been conducted.

Methodology

o-ABA was dissolved in ethanol at 1.08 and 1.2 mol/L. Water was used as anti-solvent. A flow crystallizer with 4 mm ID tubes, coupled to US was used (20.4 kHz, 10W). Product crystals were analyzed with ATR-FTIR to determine the polymorph. Induction time, yield, particle sizes were also measured.

Results

In silent, non-seeded experiments, the solution and anti-solvent flow rate was 10 mL/min. The product form was mainly form-II. Even with US, the product form still remained form-II. Seeding without US at 4%, was also ineffective as the product was again form-II. An exceptional result was achieved in seeded experiments with US where pure form-I was successfully produced (Fig. 1). Producing form-I continuously with a yield of 85% was possible by combining seeding and US. High-speed videos showed that US improved dispersion which led to better interaction of the seeds with the supersaturated solution and thus making them more effective.

Fig. 1 (left) FTIR results (right) High speed camera pics.

Conclusion

Without US, even seeding was ineffective in producing the stable form-I. Seeding worked only with US and pure form-I with a yield of 85% was produced. High speed videos showed US made seeds effective by improved dispersion and reduced wall nucleation.
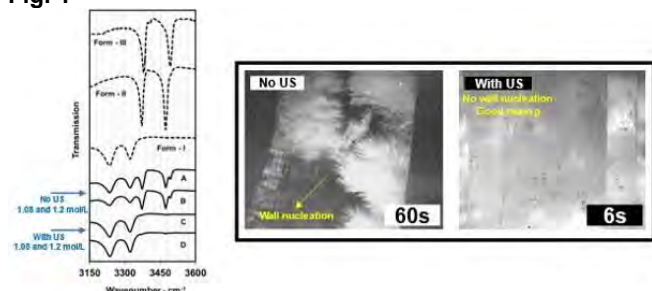
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Fig. 1

OP40
Use of sodium chlorate's enantiomeric properties to assess primary and secondary nucleation during sonocrystallisation

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Ultrasound is known to promote crystal nucleation, but there remains uncertainty about the mechanisms behind the observed effects. Despite the proposal of various primary nucleation theories, most studies do not quantify or observe the extent to which primary nucleation is taking place, leaving open the possibility that sonocrystallisation is occurring by a secondary nucleation-driven mechanism. In this study we have used the widely reported enantiomeric

properties of sodium chlorate to probe the extent to which ultrasound can induce primary nucleation. During seeded cooling crystallisation, it was observed that when stirring was applied the seed similarity was 99.3% on average, indicating secondary nucleation had almost exclusively taken place. When ultrasound was applied, the seed similarity decreased to 85.8% and 92.4% for 98kHz and 200kHz, respectively. This clearly suggests that primary nucleation had been induced and is frequency dependent. This frequency dependency is indicative a link between crystal nucleation and high intensity cavitation collisions and collapses, and the potential existence of a collapse/collision intensity threshold required to induce primary nucleation. In addition, secondary nucleation rate was investigated using anti-solvent crystallisation and was observed to increase with the application of ultrasound, though it appeared frequency independent (between 98kHz & 200kHz), suggesting that higher energy cavitational events are less important in inducing secondary nucleation or that a lower cavitation intensity threshold exists compared to primary nucleation.

OP41
Experimental and numerical investigation of the ultrasound field in a lab scale batch reactor: focusing on the liquid viscosity

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Introduction: Ultrasound (US) as an energy source has been reported for various applications. The main effects of US are coupled with cavitation. However, predicting cavitational activity in a reactor is challenging and becomes the bottleneck for scaling up even the most promising cases[1]. Both linear and non-linear models can be used to predict acoustic pressure in a bubbly medium[1–3] with the Commander and Prosperetti equation being the most common linear approach[2].

Objectives: To understand the US field in a batch reactor containing liquids of increasing viscosity, both numerically and experimentally. To our knowledge no experimentally validated models are available that account for both cavitational and thermoviscous attenuation.

Materials & methods: The numerical model uses the Pressure Acoustics module from COMSOL Multiphysics in the frequency domain with a user defined wave number. For the validation experiments, various water/ethylene glycol mixtures will be utilized. Sonochemiluminescence (SCL) and aluminum foil erosion (AFE) techniques are used to map cavitation zones[1]. The experimental set up allows for temperature and pressure recordings in combination with making SCL photos.

Results: The simulation provides correlatable results of acoustic pressure distribution for the initial case of water. Zones of high acoustic pressure sufficient to generate cavitation were clearly identified in the reactor by SCL and AFE (Figure 1). Higher viscosity mixtures are currently explored and show potential.

Conclusions: At this stage, the water model corresponds well with experimental data. The model's further development could become a dependable tool for understanding and predicting cavitation behavior in advanced, higher viscosity applications.

Future work: Further validation and refinement of the numerical model to more viscous mixtures, followed by experimental measurement of the acoustic pressure.

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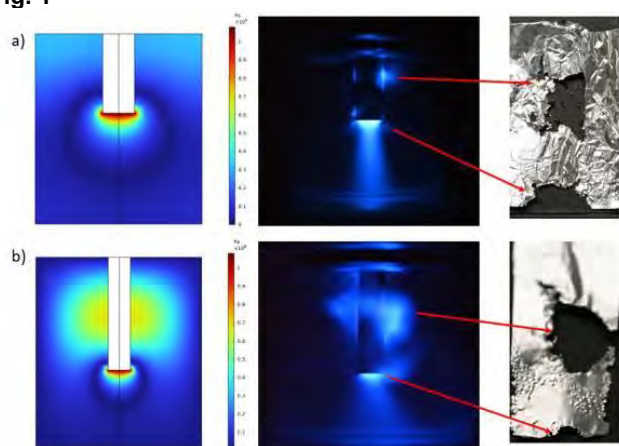
Fig. 1

Figure 1. Simulation results compared to SCL and AFE for (a) horn 1 (20 kHz, max 200 W, tip diameter 10 mm), insertion depth = 2.5 cm and (b) horn 2 (30 kHz, max 50 W, tip diameter 7 mm), insertion depth = 3.5 cm. Both cases were tested in a reactor with diameter 5.3 cm and liquid height 6 cm.

Poster presentations

PP01
Low-frequency piezoelectric-based ultrasound transducer for cavitation yield on biomaterial surfaces

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Introduction: Low-frequency ultrasound waves around 100 kHz have been utilized in transdermal drug delivery; mechanical and thermal stimuli arising from ultrasound cavitation bubbles enhances the skin permeability of drug molecules.

Langevin transducers are widely used to generate low-frequency ultrasound because of their simple and tough structure. However, the total length of the transducers is likely to be greater than the diameter. This is because the thickness of piezoelectric disks increases when the resonance frequencies are tuned to the low-frequency. Moreover, Langevin transducers have a half-wavelength horn structure to amplify the vibration amplitude at the transducer tip. Therefore, high-power ultrasound devices with a short total length operated at low resonance frequencies have yet to be developed.

Objectives: This study aims to develop a handy and lightweight piezoelectric-based ultrasound transducer which is much thinner in the total length than the Langevin transducers and yields ultrasound cavitation on biomaterial surfaces. In that novel design, radial compressive vibration of a thin piezoelectric disk is used to realize low resonance frequencies of the device with a short total length.

Materials & methods: The transducer consists of a PZT disk and a cup-shaped acoustic radiator made from silica glass (Fig. 1). The PZT disk and the radiator are bonded by epoxy adhesion. The total axial length is 10 mm. We measured the impedance of the transducer by an LCR meter to find the resonance frequency. Cavitation yields were observed by a high-speed video camera (FASTCAM NOVA S12, Photron).

Results: By measuring the impedance minima, we found that the fundamental resonance frequency of the transducer was 124 kHz, which is between the fundamental resonance frequency of the PZT disk (105 kHz) and the natural frequency of the second bending mode of the acoustic radiator (127 kHz). Furthermore, the total length is 10 mm, which is more than seven times shorter than that of our reference Langevin transducer (74 mm). At the resonance frequency, we observed cavitation yields on a urethane gel surface.

Conclusion: An ultrasound transducer of 10 mm in length with a resonance frequency of 124 kHz has been developed, which is shorter in length than one-seventh of our reference transducer. The transducer has the potential to generate ultrasound cavitation in a small liquid volume for needle-less treatments in transdermal drug delivery.

Fig. 1
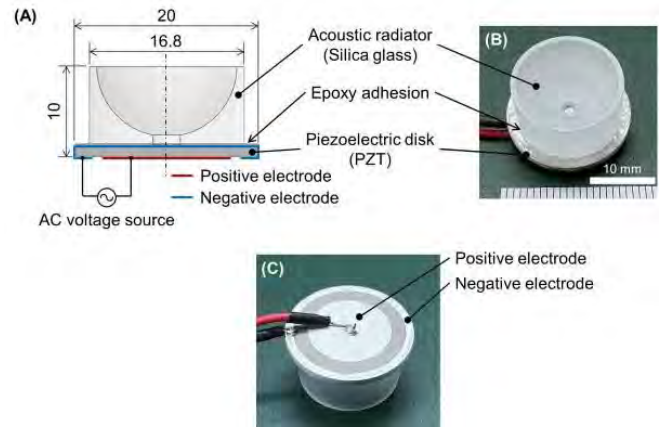
PP02
Investigation of the dual-frequency excitation impact on the inertial cavitation in different viscoelastic mediums

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Question

The inertial cavitation threshold depends on various parameters (initial bubble size, ultrasound properties, viscoelastic medium properties, etc.), however, the inertial cavitation under dual-frequency ultrasound signal is poorly understood. Thus, we decided to carry out a detailed parametric study of the inertial cavitation process under dual-frequency ultrasonic excitation in various viscoelastic mediums for a deeper understanding of the inertial cavitation.

Methods

Inertial cavitation thresholds under dual-frequency ultrasonic signals are studied numerically in various soft tissues. The Gilmore-Akulichev-Zener model is used to simulate the bubble dynamics. Westervelt equation is used to model nonlinear wave propagation.

Results

Using the optimal dual-frequency signal is able not only to significantly reduce the threshold pressure but keep the same threshold pressure for different initial bubble sizes. For optimal frequencies, the influence of elasticity prevails over the influence of viscosity. For a dual-frequency excitation with low viscosity, the analysis showed that the predicted optimal frequencies differed from each other. However, for high viscosities, the optimal frequencies had almost equal low values. Besides the all investigated parameters, the choice of the inertial cavitation threshold criterion can also strongly impact the behavior of the threshold pressures and optimal frequency combinations. The influence of different parameters on the temperature and radiated power during bubble collapse were also investigated and analyzed during bubble collapse.

Conclusions

The current study demonstrates detailed analysis of the inertial cavitation process in soft tissues under dual-frequency ultrasonic excitation. This study can be helpful for

the further development of different applications of biomedical ultrasound.

PP03
Reducing total dissolved gas levels of flowing water by using low-frequency, high-power ultrasoun

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Total dissolved gas (TDG) supersaturation is an emerging problem in specific hydropower plants with regard to increasing flood seasons expected to appear due to climate change. In Norway, a recent project identified several hydropower plants being in risk of producing air-supersaturated water. Multiple events of TDG supersaturation with values of up to 180 % TDG have been monitored[1]. Above certain thresholds, TDG values have negative effects on fish and other aquatic lifeforms in the waterways downstream the hydropower plant. Natural desorption of dissolved air occurs very slow, and dangerous TDG levels are monitored over several kilometers of river. Therefore, degassing mechanisms are studied in order to invent a technical solution for reduction of TDG levels in the power plant prior to releasing the water at the outlet.

The use of 20 kHz power ultrasound to remove excess air from flowing water is investigated. Low-frequency, high-power ultrasound is known to increase the gas-liquid mass transfer in liquids[2],[3], and is used in several applications in different fields[4]. A large scale test rig has been designed and build to observe the change in TDG levels in dependence on the positioning and orientation of the ultrasonic transducer. The degassing efficiency is tested for five ultrasonic amplitudes and two different volumetric flow rates. The experiments show that degassing air-supersaturated water with power ultrasound is feasible. The TDG level is reduced efficiently and fast. Microbubbles introduced to the flow by acoustic cavitation and rectified diffusion increase the desorption of dissolved gases during their flotation downstream and upwards the water column.

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PP04
Ultrasonically-induced cavitation in biological media

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Ultrasonically induced cavitation (UIC) has been studied as an effective way to produce cavitation in biological tissues. One of the main applications of this process is improved drug targeting. Cavitation can activate nanoparticles in a given location, thus reducing the dose of a drug required for successful treatment and the overall treatment side effects associated with drug toxicity and non-targeted delivery. This study aims to understand how ultrasounds propagate in a biological medium and estimate eventual bubbles formation in blood vessels. The methodology adopted to understand the problem involves a computational fluid dynamics (CFD) simulation performed with in-house software based on the OpenFOAM framework. The fluid is described as multi-phase and single-component. The solver is based on the volume-of-fluid method (VoF), which transports a variable representing the volume fraction of liquid in the computational domain. The occurrence of cavitation is characterised by a secondary routine that triggers bubble formation if the nucleation threshold is overcome in that specific location. The coupling between gas a liquid is performed by converting the change in bubble size into a source term in the volume fraction advection equation. Bubbles' nucleation is based on a modified classical nucleation theory (CNT) version. In particular, the Tolman length was used to evaluate the surface tension and a realistic equation of state to evaluate the thermodynamic properties of the liquid. Bubbles oscillations are modelled using the Rayleigh-Plesset (RP) equation accounting for surface tension and viscosity contributions. The simulation performed consists of a blood vessel to which UIC is applied. An oscillating boundary propagates the sound waves through the blood vessel. The simulation outcome consists of estimating the occurrence of localised cavitation in the blood vessel and the consequent eventual increase in temperature.

PP05
Bubble dynamics and sonoluminescence in higher viscous liquids

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Question

While most studies of cavitation and sonoluminescence (SL) are concerned with aqueous systems, other liquids than water are as well found in applications of intense ultrasound. Of present interest are liquids of higher viscosity, and previous results have shown that bubble dynamics, bubble structures, and SL in such liquids can be quite distinct to the aqueous case. A particular feature seen in some higher viscous acids is the ultra-bright SL, which allowed to image individual emitting bubbles in multi-bubble fields [1]. While the low vapour pressure in the acids should be an important factor for this phenomenon, the peculiar bubble dynamics at higher viscosity might be important as well. This study tries to obtain further knowledge on acoustic cavitation and SL in the higher viscous regime, with a particular focus on mechanical stirring of the liquid.

Methods

Multi-bubble systems in sonotrode and resonator setups are investigated. The methods employed comprise imaging by sensitive high-speed cameras, spectroscopy, hydrophone measurements, and numerical simulations.

Results

Generally, larger stable bubbles seem to appear at higher viscosity. This might be one more factor for ultra-bright SL in some acids, but also for structural changes, since Bjerknes forces grow with bubble size. For instance, in sonotrode systems, bubbles evolve with increasing viscosity to a pronounced half-sphere structure, apparently driven by larger repulsive Bjerknes forces. Stirring of phosphoric acid results in a further bubble growth and an increase of SL emissions, and extremely bright bubbles could be imaged together with their volume oscillations, jetting, and collision with neighbor bubbles. Further, many very small bubbles with retarded dissolution are seen, e.g. as traces behind larger bubbles.

Conclusions

Acoustic cavitation in liquids of higher viscosity can significantly differ from cavitation in water. Investigation of the peculiar phenomena might lead to further interesting findings and to a better understanding and optimization of applications.

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PP06
Experimental and computational methods to track acoustic cavitation in a bubbly liquid

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The implosion of ultrasound-generated bubbles of void in a liquid medium elicits chemical effects mostly amenable to the radical species generation in the processing medium. These effects are widely explored in various sonoreactors. However, the relationship between the bubble dynamics and their chemical activity in different cavitation zones of horn-type sonoreactors, filled with either inorganic or organic slurry solutions, remains poorly understood. Here, we applied Luminol (Sonochemiluminescence), KI dosimetry under different ultrasound power (40 % to 100 %), probe immersion depths (1.5 cm and 3.5 cm) and liquid heights (4 cm and 4.8 cm) in a 20 kHz sonoreactor to characterize the cavitation activity. An immersion depth of 3.5 cm (close to the vessel bottom) and moderate power density, approximately 388 W/L, provided the highest cavitation yield and enhanced the radical formation by up to 92.4 % by creating an active region around the probe neck. However, enhanced sonochemical activity at the active region around the probe neck was associated with adverse effects at the tip and below the tip. We identified and quantified the ultrasonically generated radicals in an organic solvent and in the presence of solid particles. We used ultrasound to sonicate polyalcohols and SiO_2 with different sizes (5-15 nm,

0.2-0.3 µm, 12-26 µm) and amounts (0.5 wt% and 3 wt%). The generated radicals were hydroxyalkyls identified by electron paramagnetic resonance spectroscopy. In the presence of solids, acoustic cavitation increased the radical species production. A solution containing SiO_2 of size 12-26 µm generated 1.5 times more radicals than a solution without particles (29 µM versus 19 µM after 1 h sonication). However, a high concentration of solid particles (3 wt%) reduced the effects of acoustic activity and thereby the number of the generated radicals. The catalyst size effect analysis demonstrated that the radical concentration in the medium increases with the particle size. For particles in the 12-26 µm size range, the amount of radicals produced was twice that of 5-15 nm particles. High-speed videos revealed that cavitation bubbles' number and size are linked with the acoustic pressure and active zone"s location within the ultrasound field. A numerical model, considering the bubbles formation, predicts the location and size of the cavitation zones. The model identifies the optimal combination of probe immersion depth and power to maximize the chemical activity.

PP07
Effect of ultrasound bubble acceleration on NaCl crystallisation in a microchannel

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Anti-solvent crystallisation is commonly used for purification or separation. However, the induction time of this process shows a high degree of variation due to the stochastic nature of crystallisation. It is widely reported that acoustic cavitation promotes nucleation, induction time and size of the crystals [1, 2]. However, the exact mechanism is still disputed. This is largely due to crystallisation and acoustic cavitation being two complex dynamic systems, and when coupled, this complexity becomes compounded. Therefore, this study aims to gain an insight into the sonocrystallisation mechanism by restricting sonocrystallisation within a narrow microchannel and observing the sonocrystallisation process under high-speed imaging.

Sodium chloride was chosen as the model solute because it is a widely studied salt that has no polymorphs, and its solubility exhibits low temperature and pressure dependence [3]. A low supersaturation ratio was established inside the microchannel, and acoustic cavitation was generated using 22 kHz. It was observed that crystallisation readily occurred at the microchannel wall as well as in the path of a moving cluster of cavitation bubbles. However, not all moving clusters of cavitation bubbles led to crystallisation. The speed and acceleration of the moving bubble cluster were calculated and correlated with crystallisation events. No visible link between bubble speed and crystal nucleation was observed. However, it was seen that cavitation bubbles would only induce crystallisation if they were accelerating faster than 750 mm/s2. To the best of the authors" knowledge, this is the first time such an acceleration threshold for sonocrystallisation has been reported. It is hypothesised that bubbles cavitating near the microchannel wall are collapsing asymmetrically, forming jets with acceleration above this threshold and leading to the observed crystallisation.

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Fig. 1

Figure 1. Removal of Reactive Black 5 by US/PS processes (US frequency=575 kHz, US power=60W, P680W=6.66W, RB 5 conc.= 0.05mM)

Fig. 2

Figure 2. Reaction kinetics of RB 5 removal by US/PS process at 1:1000 dye: PS molar ratio and under various pH conditions (US frequency=575 kHz, US power=60W, P680W=6.66W, RB 5 conc. = 0.05mM)

PP08

Degradation of Reactive Black 5 by Ultrasound-activated Persulfate Process

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Sulfate radicals proposed to have high redox potential (2.5 – 3.1 V) and longer life time than hydroxyl radical [1, 3-5]. In literature, the performance of US and PS combination with or without solid catalysts were tested under low frequency conditions such as 20, 40, 60, 130 kHz [2-15]. In this study, Reactive Black 5 (RB 5) was selected as a recalcitrant pollutant where few studies [16-17] exist to reveal US performance for its removal. This study aims to investigate the removal and mineralization of RB 5 under high frequency ultrasonic irradiation (575-861-1141kHz) and at various molar ratios of dye:persulfate (1:100, 1:500 and 1:1000) and three different pH conditions (3, 7, 10). Reactive Black 5 (Dye content 50%) and Potassium persulfate (ACS reagent ≥99%) was purchased from Sigma Aldrich. Potassium hydrogen phthalate (Reag. Ph Eur) was supplied from Merck Milipore. Pure water was obtained from Sartorius 61316 system. Ultrasound was generated from plate type of generator which was supplied from Meinhardt Ultraschalltechnik. The concentration of the dye was measured with Shimadzu UV-2450 UV-visible spectrophotometer at 597 nm. Mineralization was calculated by Shimadzu TOC-VCPN analyzer with Non-Purgeable Organic Carbon (NPOC) method. Concentration of PS was monitored using spectrophotometric method [18]. The highest removal (25%) achieved when 575 kHz frequency was applied. The combination of US with PS increased the removal percentage to 88, 64 and 37% after 90 minutes of treatment at 1:1000, 1:500 and 1:100 dye:PS molar ratios (Figure 1) at pH 7 condition. The decrease in PS concentration after 90 minutes irradiation was 10mM at 1:500 ratio dose which can be attributed to the possible generation of sulfate radicals. The RB 5 removal was faster under acidic conditions compare to neutral and alkaline conditions (Figure 1). Almost complete removal (94%) was achieved after 90 minutes when pH is adjusted to 3. The molecule becomes more hydrophobic due to the protonation of negatively charged -SO3- group under acidic conditions [16] and the increased hydrophobicity might cause faster degradation of the molecule when exposed to high frequency ultrasound. Degradation curves of RB 5 were best fitted to the first order kinetics (Figure 2). Mineralization was only observed at the highest dose (1:1000) after 90 minutes and it was found 10%. Future studies should be conducted to find ways for achieving complete mineralization such as addition of catalyst.

PP09

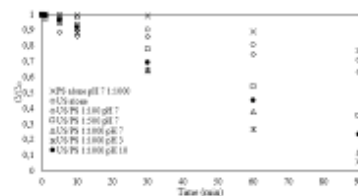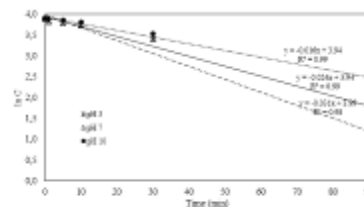**Sonophotocatalytic degradation of bisphenol A with a low-frequency tip-sonotrode in a suspended batch-system**

*D. Paustian[1], M. Franke[1], M. Stelter[1], P. Bräutigam[1]
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Introduction

Advanced Oxidation Processes are promising techniques for water remediation and for degradation of micropollutants in aqueous systems. Since single processes like sonolysis and photocatalysis exhibit limitations, combined AOP-systems can enhance the degradation efficiency.

Objectives

The present work addresses the synergistic intensification potential of an ultrasound-assisted photocatalysis for bisphenol A degradation with a low-frequency tip-sonotrode in a batch-system. The effect of energy-input and suspended catalyst dosage were investigated. Furthermore, the connection of resulting synergy values and the overall optimal proceeding conditions is discussed. In addition, the sonication characteristics were clarified to understand the mainly synergistic effects.

Material and methods

The sonication characteristics were clarified by bubble-field analysis, hydrophonic measurements and in addition by chemiluminescence of luminol to determine oxidizing cavitation areas due to the generation of hydroxyl radicals. The degradation experiments were carried out in a batch-system with a low-frequency tip-sonotrode (f_{US} = 20 kHz) and suspended TiO_2-nanoparticles (0-0.5 g/l). The irradiation was carried out with an UVB-LED-system (300 nm, 52 mW/cm²).

Results

Comparing the sonophotocatalysis with the sonolysis and the photocatalysis (incl. mechanical stirring), synergies up to 295% and degradation rates up to 1.35 min^{-1} were achieved. It was found out that the cavitation effects can be primarily

utilized in low-suspended systems due to the highest observed synergies. However, despite this observation, the optimal proceeding conditions were found in the higher suspended reaction systems. It could also be demonstrated that the cavitation lost his effectiveness with increasing catalyst-dosage and that the oxidizing cavitation zones can be neglected in the sonophotocatalytic process. Beside the proof of synergistic intensification, the investigation of energy-efficiency for a degradation degree of 80% had shown, that there can be realized a process optimization, but there is no proportionality between energy-input, synergy and degradation.

Conclusion

The synergistic intensification via ultrasound was proved for certain proceeding conditions depending on catalyst dosage and it could be shown that there is an effective limit of energy-input.


PP10
Elimination of organic micropollutants in water by cavitation and cavitation-assisted methods

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In recent years, micropollutants have become an emerging issue in natural water bodies, especially in industrialized countries. To treat those micropollutants, different advanced oxidation processes were developed and optimized. Some of the advanced oxidation processes need additional chemicals (catalysts, oxidation agents, pH control), which have to be separated, (re)activated or degraded after the treatment process often followed by a neutralization step accompanied with high salt loads. Cavitation processes belongs to the group of advanced oxidation processes, due to the formation of highly reactive hydroxyl radicals by the homolytic cleavage of water molecules in the cavitation bubbles. Cavitation processes do not need any additional chemicals and do not rely on the salt content or turbidity. Moreover, the formation of hydroxyl radicals takes place in the whole volume of the treated water and is not restricted to a specific surface. However, the energy demand of cavitation processes is higher compared to other advanced oxidation processes. Therefore, new cavitation-based processes have to be developed, to overcome the disadvantages.

Fig. 1
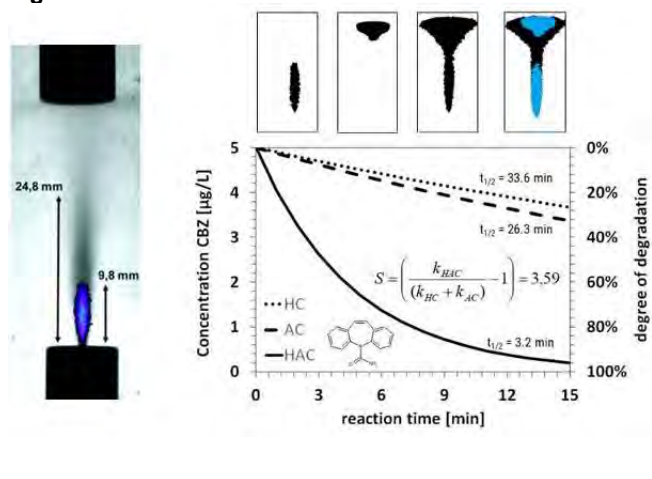
PP11
Ultrasound-assisted soil washing process for the removal of heavy metals from clays

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The proportion of soils contaminated by a wide range of pollutants (heavy metals, PCBs, pesticides, etc.) of anthropogenic origin is constantly increasing. Conventional remediation methods rely on physical, chemical, or biological approaches, or a combination of these. Among remediation methods, soil washing is an effective, relatively fast and widely used process and this study assesses its coupling with ultrasound.

The removal of Ni(II) and Zn(II) from vermiculite clay by solid-liquid extraction has been studied under 20/362 kHz ultrasound or silent conditions. A phyllosilicate clay was used to simulate a soil given the importance of this fraction in the soil and its role in the adsorption of metals. Hydrochloric and citric acids were tested and the effects of solid/liquid ratio and particle size were investigated. Metal repartition in the clay was followed by Tessier sequential extraction procedure1.

Fig 1 shows the Zn2+/Ni2+ desorption yields with HCl as a function of time for different conditions used. The results showed that after 30 min of 20 kHz sonolysis, Zn2+ desorption yields decreased and reached lower values than under silent conditions. This can be attributed to particle size diminution and creation of new adsorption sites where freshly desorbed metal ions could re-adsorb. At high US frequency (362 kHz) on the contrary, fragmentation of the vermiculite particles is limited, while positive effects of US in the decontamination are kept as shown by the higher Zn2+ desorption rates than in silent conditions.

Figure 1: Desorption kinetics in 0.1 M HCl. Initial metal concentration of 30 mgNi2+/g and 36 mgZn2+/g. Initial particle size <100 µm. Ratio of 50 g of vermiculite for 1 L of solution.

For nickel, there is little difference between the three processes and overall the obtained yields are much lower than for Zn2+, which is related to their different affinity towards the clay.

Results of Tessier sequential extraction procedure indicated that more metal elements bound to the challenging residual phase were desorbed with ultrasound than in silent conditions, for both frequencies. This supports the promising application of ultrasound for heavy metal desorption in difficult conditions.

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Fig. 1
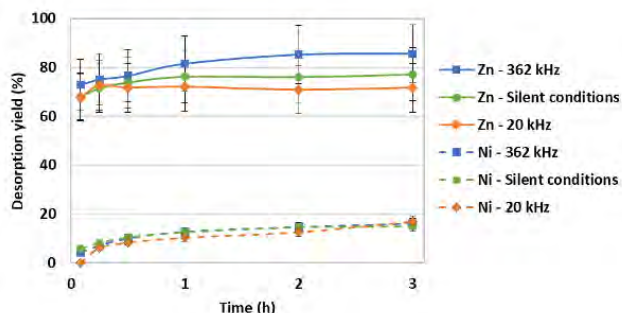
PP12

Impact of frequency and power on the sonochemical activity and degradation of paracetamol under single- and dual-frequency ultrasound

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In this study, the effects of the sonication frequency and calorimetric power on the degradation of paracetamol as well as the sonochemical activity were studied and compared between single (plate transducers with frequencies of 22, 98, 200, 300, 400, 500, 760, 850, 1000 and 2000 kHz) and dual-frequency (the plate transducers paired with 20 kHz ultrasonic horn) ultrasound. For this purpose, the yields of both HO· and H_2O_2 were measured separately via dosimetry. Also, the collapse intensity and spatial distribution of the cavitation bubbles were determined by measuring sonoluminescence (SL) intensity. The sono-degradation of paracetamol was analysed using UV-VIS and LC/MS. Based on the UV-Vis results, the comparison of the degradation rates of both single (SFUS) and dual-frequency (DFUS) sonication systems with the dosimetry and SL intensity measurements revealed the dependency of degradation rates on the yield of HO· to some extent. This suggests the chemical oxidation on or near the cavitation bubbles" surface as the main degradation mechanism. However, when the HO· yield exceeded a certain threshold, the observed decrease in the degradation rate was attributed to the reaction between HO· with the formed H_2O_2. This implies the shortage of the paracetamol molecules on the bubbles" surface due to the resistance against the transfer of the hydrophilic paracetamol molecules from the solution bulk to the surface of the bubbles. The results also revealed considerably higher degradation rates for all frequencies under DFUS. However, increasing the power of the 20 kHz ultrasound horn had a minimal effect on the yield of HO·, suggesting that the degradation rate improvement under the DFUS is due to the enhanced mass transfer by introducing the low frequency (20 kHz) horn to the acoustic field of the plate transducers [1, 2]. Additionally, the comparison of the UV-Vis and the LC/MS results showed that the dual-frequency ultrasound also plays a more significant role in the degradation of the intermediates.

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PP14

Possibilities and limitations of degrading organic pollutants using sono-Fenton process at high-frequency ultrasound

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High-frequency ultrasound (100-1000 kHz) degrades pollutants in water by HO* formed *in situ*. In addition to eliminating pollutants, this process can produce H_2O_2 as a byproduct. To take advantage of accumulated H_2O_2, an iron source is added to generate a sono-Fenton process (sF). Herein, the possibilities and limitations of sF to degrade organic pollutants are presented. The process was carried out in a Meinhardt® ultrasound reactor. The accumulation of H_2O_2 was determined using the iodometry method. The evolution of pollutants was followed by UV-vis spectrophotometry and/or liquid chromatography. Diverse iron sources, heterogeneous (a natural mineral and a zeolite Y) and homogeneous (Fe^{2+} and Fe^{3+} ions), were considered. Acetaminophen, ciprofloxacin and methyl orange were the model pollutants. The H_2O_2 production was favored at 375 kHz, and this sonochemical system alone induced the degradation of the three model compounds but the natural mineral or zeolite Y (0.02-0.20 g/L) had no significant effects on the elimination of pollutants. These solid iron sources may have a dual competing role, providing additional nuclei for cavitation bubbles and ultrasound waves attenuation. Furthermore, high-frequency ultrasound has softer mechanical effects compared with low-frequency ultrasound, which could limit the iron ions leaching from the solids to the solution, limiting the development of sF process. In contrast, both Fe^{2+} and Fe^{3+} ions enhanced the pollutants degradation via sF. Fe^{2+} led to a better enhancement due to its higher reactivity toward H_2O_2. However, the benefits decreased at very high Fe^{2+} concentrations (e.g., 5 mg/L) because of scavenger effects. Additionally, in the particular case of ciprofloxacin, the Fe^{2+} addition accelerated the elimination at short treatment times but it was stopped by complexation of the pollutant with Fe^{3+} (from the Fenton reaction). Such a complex showed a slow degradation by the action of ultrasound and even under UVC light. We remark on the degrading action of ultrasound despite the presence of solid iron sources that can quench the cavitation activity. There is a strong dependence of the sF performance on both oxidation state and concentration of iron ions. Finally, it must be considered the interaction of the pollutants with the iron species that can alter the degrading action of the sF system.

PP15

Simulation of hydrodynamic cavitation in nozzles and comparison with optic experiments
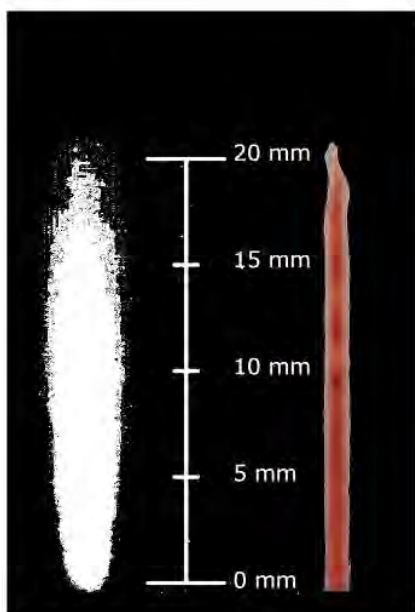
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As the world's population grows and global water consumption increases, the pollution of water available to mankind continues to rise. At the same time, more and more so-called micropollutants are being discharged into water bodies. These micropollutants cannot be removed by existing wastewater treatment processes. Therefore, new processes for the removal of micropollutants have to be developed. The focus here is particularly on advanced oxidation processes. Hydrodynamic cavitation is a process which is able to remove micropollutants without the addition of oxidants. Therefore, it is necessary to develop suitable nozzles to achieve the best possible effect. In order to keep the costs and the effort for practical experiments low and to specifically research critical nozzle parameters, computer-aided simulation is used. Different nozzle diameters are investigated and compared with each other regarding various parameters such as pressure, velocity and bubble formation.

The simulation software OpenFOAM was used for this purpose. To verify the accuracy of the simulation results, they are compared with optical experiments. For this purpose, luminol and shadowgraphy experiments are performed. The experiments have shown that the simulation results can be used as a tool to predict cavitation.

Figure 1: Comparison of simulation and Luminol experiment.

Fig. 1

PP16
Hydrodynamic cavitation: a technique for effective PVOH degradation during conventional WWT

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Microplastic pollution is one of the world's most pressing environmental problems. Scientists focus on all forms of solid microplastics, but the same considerations should also apply to water-soluble synthetic polymers. Their solubility makes them invisible, nontheless they can remain in the environment and have undesirable effects. One of the most extensively used water-soluble polymers, polyvinyl alcohol (PVOH), is a major cause for such concern. Widely used in the textile and paper industries and in households in the form of detergent pods, PVOH presents a new environmental threat alongside traditional microplastics. It is usually flushed unnoticed and unimpeded down the drain and enters the aquatic environment through wastewater treatment plants (WWTPs).

The present study aims to address the chemical and mechanical degradation of PVOH at laboratory scale using hydrodynamic cavitation (HC).

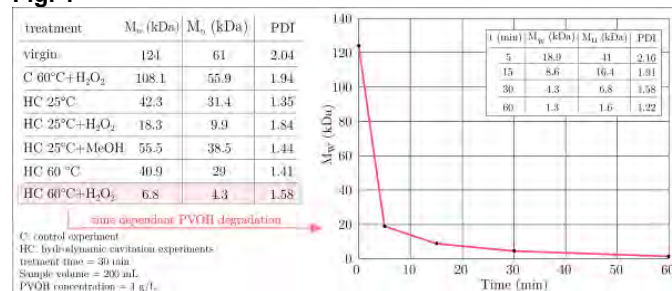The experimental setup consisted of a HC generator installed in a closed loop and equipped with a cooling coil to maintain a constant temperature. A special rotor-stator design allowed exploitation of cavitation generation and pumping performance simultaneoulsy in the same device. The effects of temperature, addition of external oxidant (H_2O_2), and addition of methanol (MeOH) as a hydroxyl radical ($^{\bullet}OH$) scavenger to 1 g/L of virgin PVOH sample were systematically studied. A set of experiments was performed with 200 mL samples and a treatment time of 30 min. Then, time-dependent experiments were performed under optimized operating conditions (60 °C and H_2O_2 addition). The molar mass averages of the treated PVOH samples were determined using SEC /UV- MALS-RI.

The results show that HC reduces the molar mass of PVOH under all experimental conditions (Figure 1). Raising the temperature (up to 60 °C) does not play an important role in the degradation. The highest reduction in molar mass (99 %) was achieved after 60 min of treatment at elevated temperature and addition of H_2O_2. The results obtained with the addition of MeOH indicate that chemical effects ($^{\bullet}OH$) resulting from HC contribute to the reduction of PVOH molar mass.

This study shows that HC is a promising technique for the degradation of PVOH that can be easily integrated into current WWT schemes and acts as a last barrier between WWTPs and the aquatic environment. These encouraging results could guide future studies on the degradation of other problematic polymers with fully-carbon backbones.

Fig. 1: Results.

Fig. 1

PP18
Sonochemical coating of textiles with metal oxides and their subsequent functionalization

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Textiles with functional properties have received enormous attention in recent years. In addition to their use in the textile industry, as high-tech materials they fulfill technical or protective functions.

Depending on their field of application, they offer protection against moisture, UV radiation, heat and flames, mechanical effects, chemical substances and substances and microorganisms. By coating textile fibers in industrial processes, properties such as hydrophobicity are achieved. Modifying surface properties of materials such as textiles in a targeted manner results by a change in the surface structure, by physical or mechanical processes (change in roughness), application of other material layers (e.g. waxes, polymers, nanoparticles), or by chemical modification of the surface (change in bonding). In recent years, nanometals and nanometal oxides have been widely used in this regard. Compared to conventional powders in bulk form,

nanoparticles (NPs) have a higher activity due to their larger surface to volume ratio.

The modification or functionalization of NPs in industry is mainly carried out via toxic, environmentally harmful and expensive functionalization reagents.

Today, modern research is focused on the development of novel, environmentally friendly and energy-saving techniques such as ultrasound-assisted application methods. In the following, an efficient, resource-saving and innovative method for the application of metal oxide particles on textile surfaces and its functionalization via alternative modifier compounds is described.

Fig. 1

Fig. 2

PP19
Sonochemical preparation of nanostructured calcium carbonate in a cup-horn reactor

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Micro- and nanostructured calcium carbonate has been widely used in pigments, rubber, cosmetics, biomaterials, etc.[1] The microparticles of $CaCO_3$ were conventionally obtained by the reaction of calcium chloride and sodium carbonate with stirring and the particle size of $CaCO_3$ reached in the range of 3-15 μm.[2,3] In this study, a home-made cup-horn reactor was used to prepare nanoparticles of $CaCO_3$ by sonication at 19.5 kHz, aiming to reduce particles size and reaction time. The reaction mixture (10 mL of 0.5 M calcium chloride and 10 mL of 0.5 M sodium carbonate), was sonicated at 20℃ for 3 min a shorter time if compared with conventional stirring (≥30 min).4 The effects of ultrasonic power, time, and reaction volume on the particle size were investigated. As shown in Figure 1, under the optimum reaction conditions, the smaller particle sizes (ca 35 nm), measured with Quasi Elastic Light Scattering, are much less than those of conventional magnetic stirring.

Figure 1. The particle size distribution of $CaCO_3$ with magnetic stirring (A) and cup-horn apparatus (B).

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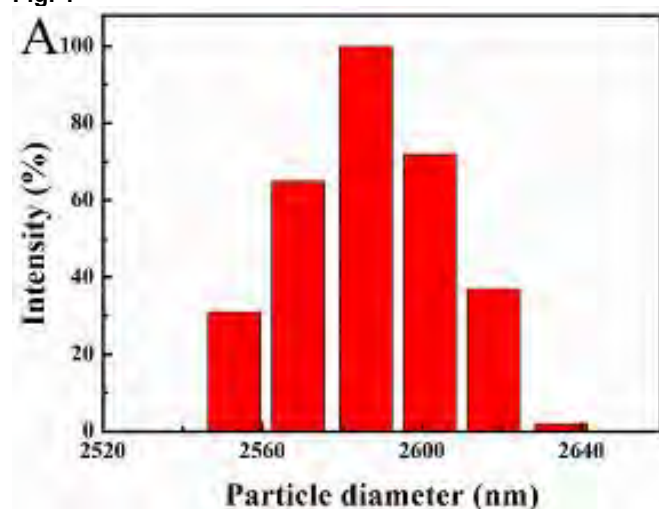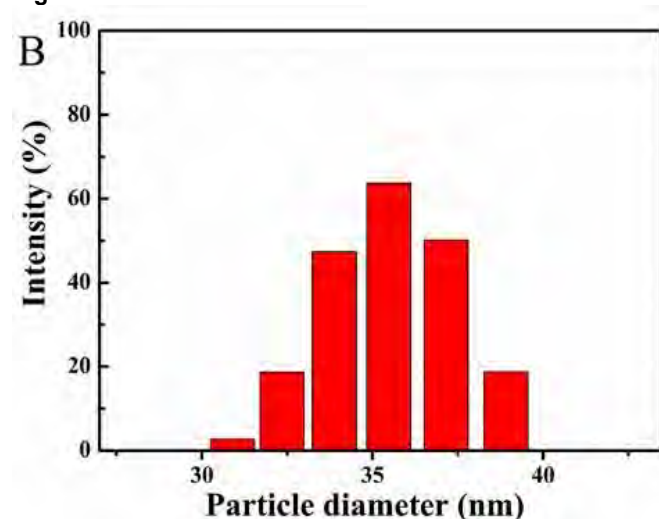
Fig. 1

Fig. 2

PP21
Effect of ultrasonic processing on structural and functional properties of whey protein isolate
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Introduction: Whey proteins are a widely used ingredient in food industry owing to their high nutritional quality, being a rich source of essential amino acids, and excellent functional properties. However, their sensitivity to environmental and process conditions, such as heat, pH and ionic strength, which may limit their applications has led to a tremendous effort to improve their functional properties through different chemical, physical and biological approaches. Ultrasonication is an innovative safe and promising method that can be used for modification of proteins structure and thus their functional properties.

Objectives: The present work was aimed to investigate the influence of high-intensity ultrasound on the physicochemical, structural and rheological characteristics of WPI which were subsequently linked to its functional properties**.**

Materials & methods: WPI solution of constant concentration was sonicated at 20 kHz and 100% amplitude for 20 min at 25 °C and changes in particle size, zeta-potential, surface hydrophobicity, free sulfhydryl and amino groups, turbidity, surface tension, emulsifying activity index, solubility, secondary structure and rheological properties were studied.

Results: It was revealed that sonication significantly decreased the size of WPI particles which was associated with a sharp drop in turbidity, whilst solubility showed only a slight increase. Secondary structure also exhibited a rise in the percentage of α-helix and random coil elements at the expense of β-sheet and β-turn components. This was accompanied by a growth in surface hydrophobicity leading to a decline in surface tension. Furthermore, ultrasound-induced conformational transitions raised free amino and thiol groups, as well as the zeta potential. These structural changes enhanced the surface activity of WPI resulting in a higher emulsifying activity index with almost no effect on the flow behavior of the solution remaining Newtonian.

Conclusion: The findings of this study demonstrated that ultrasonically-modified WPI possesses superior interfacial activity compared to the native protein which can be attributed to the increased surface hydrophobicity and higher proportion of random coil element which promotes its tendency towards the oil phase and makes it structurally more flexible to more readily adsorb and rearrange at the interface.

Keywords: high power ultrasound, whey protein isolate, functional property, secondary structure, emulsifying activity.

PP22
Production and characterization of electroless nickel-boron coatings from stabilizer-free bath with ultrasound agitation
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Introduction

Electroless nickel-boron coatings present unique properties such as high hardness, superior wear resistance, thickness uniformity, and shape compliance and are thus used in numerous industries such as automotive, aerospace, medical, and petrochemical. The plating solution is agitated in order to increase transportation of reactants to the surface of the plated part. Ultrasonically-agitated electroless nickel process has many advantages such as a higher plating rate and improved properties: higher hardness and better corrosion resistance [1,2].

Objectives

In this study, ultrasonic agitation was used in a stabilizer-free electroless nickel-boron process. The coatings produced from this process were characterized and compared with those produced from the mechanically agitated baths.

Material and methods

The study was carried out on St-37 mild steel with standard surface preparation (degreasing and HCl activation). The plating solution was agitated using ultrasound with a frequency of 35 kHz.

The morphology of the coating was investigated by SEM and optical microscopy (OM). Knoop and Vickers microindentation and Instrumented Indentation Test (IIT) were employed to determine the hardness of the coating. Coating thickness was determined via the Calo test and OM. Tribological and corrosion properties of the coating were investigated by pin-on-disk and potentiodynamic polarization, respectively.

Results

An increase of 20% in thickness (14 μm to 17 μm for 1 hour) was when ultrasound was employed instead of mechanical agitation but the morphology of the coating was left unchanged..

Conclusion

Ultrasonic-based process is shown to reduce the production time by increasing the plating rate without degradation of mechanical and morphological properties of coatings.

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PP23
Ultrasonic treatment of polymer surfaces to enhance biodegradation
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Plastics are artificial synthetic organic polymers that have found use in every facet of daily life as well as in industries. Microplastics are plastic pieces that enter natural ecosystems from a number of sources. Plastic pollution is currently one of the most serious issues. However, the majority of the procedures used to date are inadequate. As a result, in recent years, the interest has switched to innovative, alternative ways of managing plastic garbage. The samples should be treated since enzymatic or bacterial attachment is not feasible if the plastic surface environment is not optimal. We focuse on the use of new technologies in order to modify the surfaces of various polymeric materials for their further biodegradation by subsequently attaching bacteria on the pre-treated surface. We achieve the surface activation using Sonochemistry, High-Frequency Ultrasounds (US) at 860 KHz and Low-Frequency US at 20 KHz. Experiments were performed on plastic foils of Polylactic Acid (PLA), Polyurethane (PU) and Polycaprolactone (PCL). Following the treatments, in order to see how they affect the surface of plastics, the samples were analyzed by various characterization methods, such as Infrared Spectroscopy (IR), Drop Contact Angle (DCA), Confocal Laser Scanning Microscopy (CLSM) and X-ray Photoelectron Spectroscopy (XPS). Combining the results of each characterization method we scrutinize how each pre-treatment method affects the surface of treated samples, both chemically and morphologically. Based on the CLSM results, it is estimated that the high ultrasonic frequency of 860 kHz impacts the surface of the samples more, whilst the low frequency appears to generate just a modest change when compared to the non-treated sample. According to the XPS results, the surface of the treated samples is less oxidized than the reference sample, so either the US energy input is insufficient to significantly rearrange the surface or the radicals created in the US are insufficiently reactive to further oxidize the surface. The DCA results indicate whether the polymer surface is hydrophilic or hydrophobic. All treatments appear to increase the hydrophobicity of the polymer surface. When compared to the reference sample, the CLSM findings reveal a flat surface with slightly increased root mean squared roughness. Treatment with US at 20 kHz appears to result in somewhat reduced surface activation compared to the other techniques, based on surface roughness.

PP25
Sonochemical synthesis of Alkaline Earth (Mg, Ca, Sr) Metal-Organic Frameworks (MOFs) based on 2,5-Dihydroxy Terephthalic Acid

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Metal-Organic Frameworks (MOFs) are a new class of porous crystalline materials, consisting of inorganic metal ions/clusters and organic linkers that have been very attractive, granted their high surface areas and chemical versatility. They possess unique morphologies and varying pore sizes, depending on chemical nature, synthesis method and conditions. MOFs have been traditionally synthesized via solvothermal approaches at high temperatures. Over the last few years, more methods have appeared, including microwaves, electrochemistry, mechanochemistry and ultrasounds [1]. The sonochemical approach provides shorter reaction times, smaller particle sizes and phase-selectivity [2, 3].

2,5-dihydroxyterephthalic acid (H_4dhtp) has been a popular linker for the preparation of MOF-74 (Mg, Mn, Co, Ni, Cu, Zn). However, more structures can be obtained by varying the synthesis conditions or utilizing different metals. Alkaline earth metals, albeit not as preferred as transition ones due to formation and crystallization difficulties, have the potential to construct MOFs with unique physicochemical properties [4]. Additionally, their stability, nontoxicity and low cost could make them very promising for larger scale development.

In this work, MOFs based on Mg, Ca and Sr metal ions and 2,5-dihydroxyterephthalate linker are prepared via both solvothermal and sonochemical methods, while the possibility of utilizing a generic MOF-74 synthetic procedure for their preparation has been investigated. Ultrasounds have managed to yield highly crystalline structures, with good thermal stability and smaller particle size in only 60 minutes, instead of the high reaction time requirement (24 h) of the solvothermal synthesis.

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PP26
Ultrasound-assisted method for the synthesis of alkaline earth perovskites (Ba, Sr) based on ZrO_2 and ZrO_2-TiO_2 composites

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Perovskite oxides are a class of materials with crystal structure formula of ABO_3, which is a subcategory of the perovskites ABX_3 structure. Their structure consists of 12 large size coordinated cations at the A site and 6 small sized coordinated cations at the B site, where A possess a lower charge (e.g Sr^{2+}, Ba^{2+}) and B a higher charge (e.g. Ti^{4+}, Zr^{4+}) [1].

Structurally, a perovskite compound displays a crystalline cubic unit cell where the large A cations are located at each of the corners of the unit cell. The small B cation and the X anion reside at the center and on every face of the cubic cell [2]. Titanate-based perovskites show excellent photocatalytic properties under UV radiation due to their large band gap > 3.0 eV, though doping has been widely used to alter their band gap for the adsorption of visible light. Some popular

perovskites in the literature include $CaTiO_3$, $SrTiO_3$, $SrZrO_3$ and $BaZrO_3$ [3,4].

In this work, we have explored the synthesis of two crystalline solid-state materials, barium and strontium zirconate ($BaZrO_3$ and $SrZrO_3$) along with TiO_2 composites via a sonochemical method. Additionally, synthesis parameters, such as reaction time, ultrasound amplitude, solution pH and calcination duration/temperature were thoroughly investigated.

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PP27
The rate constant of microorganisms destruction after gas/ultrasound treatment of the water
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Nowadays more importance is attracted to physical factors of influence on a water system, including the use of cavitation water treatment which is marked by numerous positive reviews in the processes of water disinfection.

Materials & methods. Oxygen, carbon dioxide and argon were used to bubble the aquatic medium. For the cavitation source used an ultrasonic generator UZDN-2T with a frequency of 22 kHz and a power of 35 W. The experimental conditions were as follows: T = 298 ± 1 K, P = 0.1 MPa, t=2 hours. Deaerated distilled water was used to create microbial water by boiling it in an open container to remove dissolved gases, followed by cooling without air.

Results. The working NM_0 in the microbial waters created by us were $8 \cdot 10^2$; $2 \cdot 10^4$; $7 \cdot 10^5$; $1,5 \cdot 10^6$ and $3 \cdot 10^6$ CFU/cm^3, thus approaching the actual level of microbiological contamination of both natural and wastewater, which we previously found during the identification of aquatic micro-objects. After an investigation the NM change of time duration for all studied modes it is possible to evaluate the cavitation efficiency of bacillary cell destruction, depending on the nature of the bubbled gas. The largest kd values are calculated for the argon action, and the smallest - for carbon dioxide. For each gas the region of close k_d values for a relatively wide range of NM_0 values is clearly distinguished. Even with an increase in the value of the NM_0 by almost four

orders of magnitude (from $8 \cdot 10^2$ to $3 \cdot 10^6$ CFU/cm^3 - for Ar/US and O$_2$/US) and almost by two orders of magnitude (from $2.2 \cdot 10^3$ to $8.5 \cdot 10^4$ CFU/cm^3 - for CO$_2$/US), the k_d values for each gas vary within close values, but differ in value depending on its nature: $k_d(Ar/US) = (9.46 \pm 0.64) \cdot 10^{-4}$ s^{-1}; $k_d(O_2/US) = (8.54 \pm 1.22) \cdot 10^{-4}$ s^{-1}; $k_d(CO_2/US) = (7.84 \pm 0.85) \cdot 10^{-4}$ s^{-1}. This indicates that the kd value does not depend on the NM0, but is determined by the nature of the bubble gas. On the basis of the presented researches the regular number of effective rate constants of bacteria destruction depending on the nature of bubbled gas in the ultrasonic cavitation conditions is established: $k_d(Ar/US) > k_d(O_2/US) > k_d(CO_2/US)$.

Conclusions. It has been experimentally established that kd value depends on the gas nature under cavitation conditions, but does not depend on the initial number of microorganisms per unit volume of water. During the Ar/US treatment mode, the highest efficiency of bacterial destruction was found, and the lowest - during CO$_2$/US action.

PP28
Numerical and experimental flow characterization of a sonicated continuous oscillatory baffled reactor
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Introduction:

Over the last years, industry has shown interest in more efficient production techniques and intensified resource management[1,2]. Specific for the chemical industry, the strive for efficiency and sustainability is heavily associated with process intensification[3,4]. Amongst the technologies available to achieve this, continuous oscillatory baffled reactors (COBRs) augmented with alternative energy sources such as ultrasound (US) have been identified as a novel compelling solution.

Objective:

This work investigates the effect of sonication on the hydrodynamic performance of COBRs using numerical and experimental techniques.

Materials & methods:

An elaborate and integrated numerical model was constructed using COMSOL Multiphysics (Figure 1). To verify the simulation results, planar laser induced fluorescence experiments (PLIF) and sonochemiluminescence (SCL) were conducted using a 3D-printed reactor.

Results:

The constructed numerical model successfully incorporates aspects of solid mechanics, electrostatics, pressure acoustics and fluid dynamics to simulate the effects of low-frequency ultrasound on the hydrodynamic performance of a COBR (Figure 2). The level of complexity is low, yet the model is able to capture important events including acoustic streaming. The model is versatile and easily adaptable to different geometries or boundary conditions. It is feasible to combine it with additional physics to simulate for example chemical reactions. Initial qualitative experimental verification of the model through PLIF and SCL shows promising results and confirms US as an additional mechanism of introducing

(micro)mixing. Further quantitative validation through for example particle image velocimetry is advisable.

Conclusion:

This study has shown numerically and experimentally that US contributes to the overall mixing performance of COBRs. Qualitative correspondence of the numerical model with experimental data was obtained, with further suggestions on how to improve the model and validation being provided.

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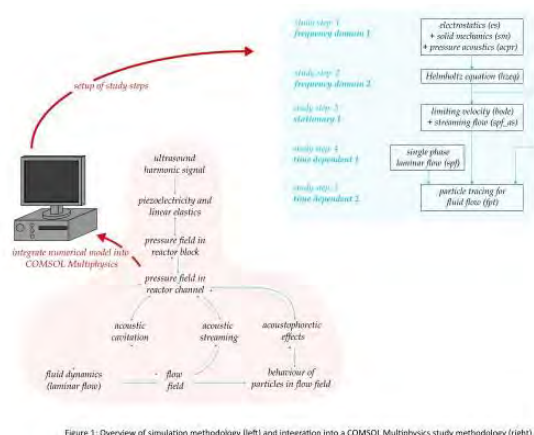
Acknowledgement:

Fig. 1

Figure 1: Overview of simulation methodology (left) and integration into a COMSOL Multiphysics study methodology (right).
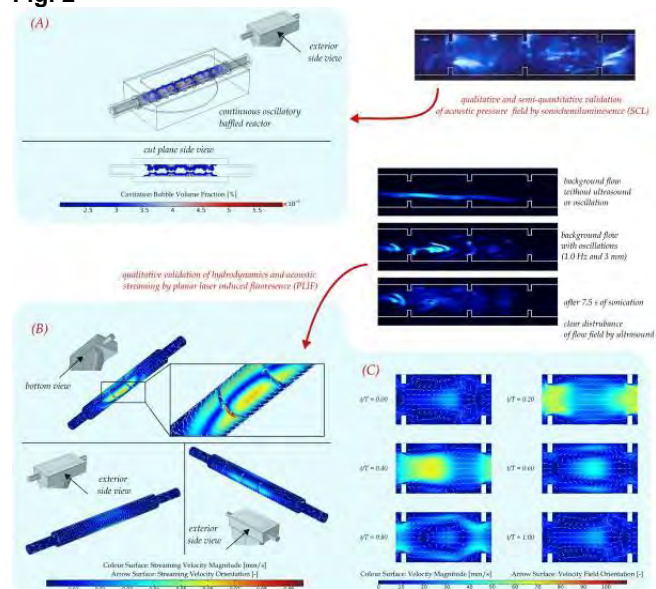
Fig. 2

Figure 2: Overview of simulation results including the acoustic pressure field (a), the acoustic streaming velocity field (b) and the laminar background velocity field (c). Figure constructed using the cavitation bubble attenuation model with an equivalent acoustic power input of 50 W and acoustic frequency of 46.25 kHz. Experimental data for qualitative and semi-quantitative comparison obtained using identical conditions.

PP29
Experimental study of ultrasound power on mixing enhancement within an ultrasonic flow reactor

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Introduction

Chemical reactors in industry are mostly batch reactors. In order to improve the process's chemical yield, safety and effluent processing, some manufacturers wish to switch to continuous operation in millimetric or micrometric reactors. At this scale, a homogeneous ultrasound field can prevent clogging and allow for turbulent flows with high mixing properties even for low Reynolds numbers flows.

Objectives

This work studies the behaviour of mixing within an ultrasonic vibrating wall duct, used as flow reactor, with respect to flow rate and electrical power injected into an ultrasound transducer in order to determine the lowest energy consumption for the best mixing.

Materials & methods

The flow reactor is made of an ultrasonic fork used as vibrating channel walls (30 kHz) and two PMMA viewing windows used as fixed walls of the reactor channel. Two fluids (distilled water and distilled water + E133 dye) are mixed in a volume of 1.715 ml. A monochrome camera picks up images from the mixed zone. The grey scale value of each pixel is used to calculate the mixing coefficient η, which represents the contribution of the ultrasounds to obtain a homogeneous mixture ($\eta = 1$) and the normalized concentration C_n is calculated. C_n varies between 0 and 1 with a homogeneous mixture at $C_n = 0.5$ with an uncertainty of about 5% on each concentration value. We define

therefore an acceptable mixing range as a normalized concentration between 0.45 and 0.55.

Results

When the ultrasounds are activated, the acoustic streaming generates dye jets and vortices that pass through the entire channel. This causes colour variations observable as vortices (Fig. 1a). The movement and appearance of cavitation bubbles generates low grey scale values on the image processing of the mixing zone (Fig. 1b). Figure 2 shows a rapid increase in mixing coefficient values ($0 < \eta < 0.87$) for volumetric electrical energy e_v values between 0 J/ml and 150 J/ml until reaching a plateau with η values between 0.79 and 0.95.

Conclusion

The asymptotical behaviour of this mixing coefficient with respect to volumetric electrical energy injected within the system, highlight an optimum in terms of energy consumed needed to reach acceptable mixing. This optimum is an interesting comparison tool to find the channel design that gives the best energy efficiency.
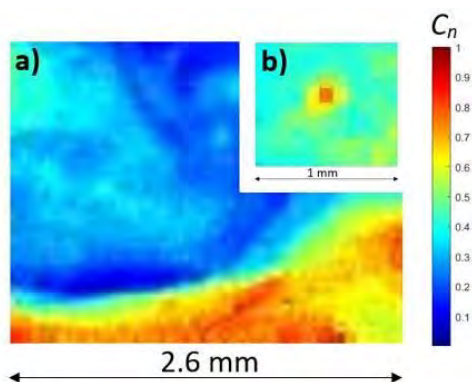
Fig. 1

Figure 1: a) Acoustic flow in the channel generated by ultrasound. b) An acoustic cavitation bubble in the channel generated by ultrasound.
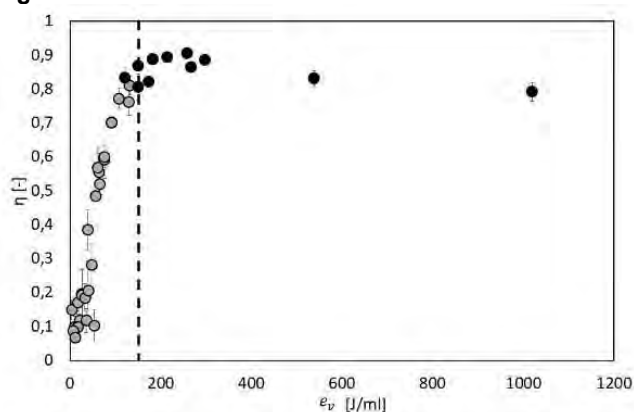
Fig. 2

Figure 2: Evolution of the mixing coefficient η as a function of the volumetric electrical energy e_v. Black dots indicate acceptable mixing achieved.

PP30
A continuous flow crystallization system for miconazole with ultrasound

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Introduction

Continuous crystallization is a fast growing method which provides multiple benefits over batch crystallization like less product variability, steady state operation, less wastage etc. However there are challenges like clogging which are still restricting it from being implemented in the large scales. Ultrasound is a technique that provides improvements like better mixing and less clogging and can help in making flow systems viable [1].

Objectives

Only very few works in literature on flow sonocrystallization actually focus on long operation of the system [2]. This work aims to bridge this lack of investigation. Specifically, anti-solvent crystallization of miconazole nitrate has been carried out with an aim to demonstrate a flow crystallization system that runs for long times and produces stable particle sizes.

Methodology

Miconazole nitrate was dissolved in methanol at 13 g/l. DI water was used as anti-solvent. A flow crystallizer with 4 mm ID tubes, coupled to US was used at different frequencies and powers. The experiment was continuously monitored for noticing induction times and clogging behavior. Product crystals sizes were analyzed with a laser diffractometer.

Results

It was noticed that although there is clogging behavior the flow never gets completely blocked. For quantitative understanding of this behavior the back pressure in the system was monitored which could go as high as 27 bars during severe clogging. By changing residence times, ultrasonic frequency and power, clogging behavior and back pressures could be reduced significantly. A crystallization system that runs for 4 hours at least without significant clogging is possible. Particle size distributions also stay consistent (6 (D10) – 25 (D90) mm) in tested experiments. Fig. 1 shows some results.

Fig. 1 (top) Crystallization setup (bottom) Particle sizes.

Conclusion

A continuous flow sonocrystallization system for miconazole nitrate was developed and optimized by analyzing quantitative clogging behavior. By changing ultrasound and flow parameters a system working for nearly 4 hours without significant clogging was so far possible.
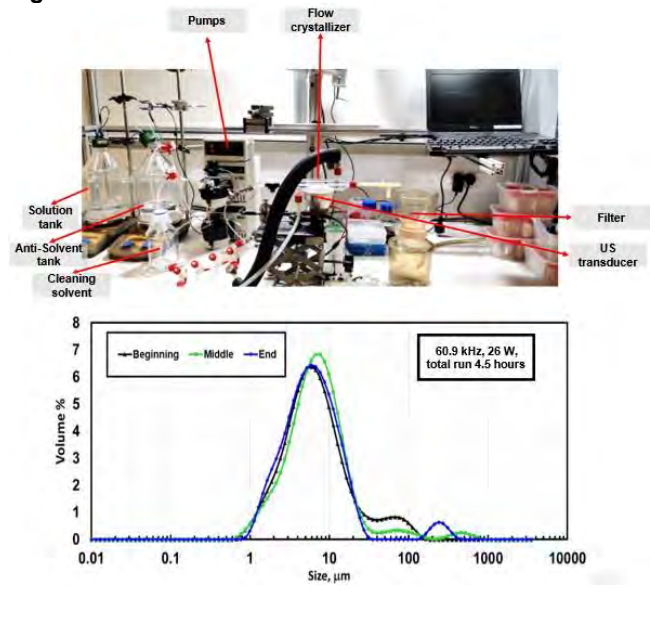
Acknowledgments

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Fig. 1

PP31
Improvement of oxidation stabilities of vegetable oil and biodiesel fuel by adding ultrafine bubbles of hydrogen

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Introduction: The consumption of carbon-neutral renewable fuels is recommended to reduce CO2 in the atmosphere for global warming protection. However, those Biomass fuels contain unsaturated alkyl groups and are very rapidly oxidized and change their fuel activities. In this study, we found that the ultrafine bubbles (UFB) of hydrogen can make extremely long-lasting oxidation stability of oil and biodiesel fuel (BDF) by dispersing UFB into them.

Experimental: UFB of H2, CO2 and argon (Ar) to oil and BDF with a bubble diameter of about 100 nm were added to rapeseed oil and BDF using a UFB mixer (model GS-3A73 PD51-FA-2109-001) and the number of UFBs in the liquid was measured using the light scattering UFB measurement device (model 75 NBM-L-2020-002). Oxidative stabilities of oil and BDF were studied by Rancimat method.

Results and Discussions: UFBs with a bubble diameter of about 100 nm in liquid is stable for more than 3 months. They have the surface charge and remain small without union of two. Because of their small diameter of approximately 100 nm, they exhibit Brownian motion, and they remain in water for a long time without rising and escaping into the gas phase or atmosphere. Numbers of UFB dispersed in water was almost the same as that of the conventional ultrasonic UFB dispersion. On the other hand, when UFBs of hydrogen and oxygen were introduced into rapeseed oil and BDF, as much as 1013 –1014 UFBs/mL could be dispersed. Once the UFB is dispersed in the liquid, it is extremely difficult to remove them from the liquid. The oxidation stability of oil and BDF containing various UFBs measured by the Rancimat method is shown in Fig 1 and Photo 1, where the oxidation stability of rapeseed oil and BDF with dispersed hydrogen UFBs increased more than 5 times. It is also strange that the oxidation stability does not change at all when Ar is dissolved in the UFB.

Figure:

Figure 1. Variations of electrical conductivity of BDF measured by Rancimat method.

Photo 2. Photograph of difference in color of the BDF and plant oil after Rancimat oxidation stability Test (for 6 hours)
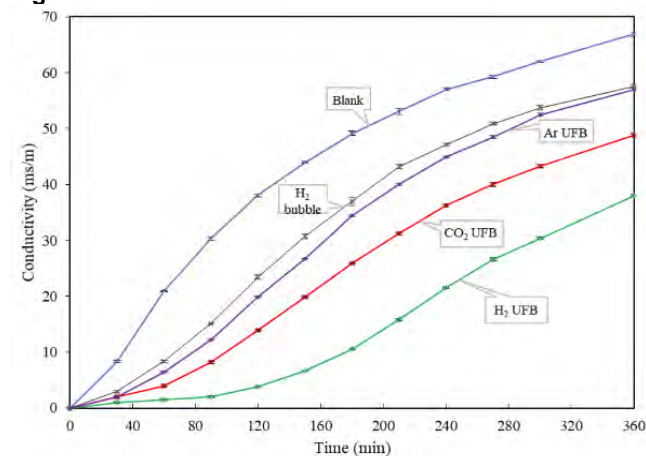
Fig. 1

Fig. 2