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Review of Research Topics for Scaling-up of Sonochemical Reactors (Sono-Reactors)

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ABSTRACT

This study is aimed to review the topics of chemical engineering to take in consideration for the scaling-up of reactors, in order to perform processes based on the application of the sonochemistry at industrial level. Sonochemistry is an emergent technology, defined as chemistry made with ultrasound. The characteristic ultrasound frequencies are in the range of 1-10MHz, and in particular for sonochemistry in the sub-range 16-100 KHz. Chemical effects of ultrasound exist when there are changes in the path-ways of reactions, yields and/or selectivities of the products due to the ultrasonic activation. At laboratory level, the sonochemistry has shown fantastic results, because it is based on the phenomenon of acoustic cavitation in liquids, thus, producing very high temperatures (some thousands of Kelvin degrees) and high pressures (some hundreds of atmospheres) during very short times (from tenths to hundreds of microseconds). Cavitation is the phenomenon with the most important effect for intensification of physical and chemical processing. Under these conditions, the yields of sonochemical reactions increase drastically, and their selectivities are improved, thus generating new mechanisms of reaction involving inorganic and organic syntheses. It is not easy to reproduce experimental results of quantification of sonochemical intensity, which is significant for the efficient scaling-up of sonochemical reactors (sono-reactors) for the progress of industrial applications of sonochemistry. This technology has application at industrial level for the treatment of waste-water and black-water. Sonochemistry can be considered as Green Chemistry, presenting the following advantages: low waste, low consumption of materials and energy with optimized use of non-renewable resources and use of renewable energies. Designs of large-scale use sono-reactors are based on intuition mainly, and their yields are impossible to predict. Few studies were aimed about optimum design and scaling-up of sonochemical reactors. The implementation of sonochemistry at the industrial level will be feasible when the use of cavitation energy can be adequately controlled. There is a need for standardized sonochemical reactors in order to be able to compare the results of yield and selectivity of sonochemical reactions. For sonochemical reactors a pilot and industrial scale the required volumes are 100 dm³ and 1 m³ approximately. Polymerization reactions, must be developed in a discontinuous or semi-continuous regime (Batch or semi-batch sono-reactors respectively), considering the kinetic and thermodynamic topics of the reactor, as also the effects of viscosity on transport properties. Organo-metals reactions, they have to be developed in a semi-continuous or continuous regime. In order to improve the sonochemical processes, we must take in consideration the optimizations of production and economic, including the ultrasonic energy in the energy balances, as well as in the conditions of operation. Among limitations found are the modeling and simulation of 2-D and 3-D of ultrasound waves in liquid medium for the study of pressure fields behaviors in sonochemical reactors, considering the quantification of cavitation intensities and fluid circulation. Due to the high temperatures inside of sono-reactor (although be for a period of μ s) and the associated safety hazards, application of thermal and electrical superconductors respectively, would be an important topic to investigate. The study of materials resistant to the stress by ultrasonic cavitation is also a new topic research open by sonochemistry.

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Introduction

Sonochemistry is defined as chemistry made with ultrasound. Ultrasound is a wave pressure consist in rarefactions and compressions cycles able of breaking the intermolecular Van der Waals forces. Sonochemistry had their origins between the last decades of the nineteenth century and early decades of the twentieth century: 1880-Curie (piezoelectric effect), 1883-Galton (development of the first transducer), 1894-Thornycroft and Barnaby (observation of the implosion of bubbles in water), 1912-Langevin (SONAR), 1927-Loomis (anomalous effect of soundwaves propagating through a liquid medium). However, it was no until the decade of 1980 that the Sonochemistry underwent important advances [1,2].

Sound is intrinsically different from electromagnetic radiation (radio-waves, infrared light, visible, ultraviolet, X-rays, gamma-rays, and cosmic-rays), because for the propagation is necessary a medium material. Soundwaves pass-through gases, liquids or solids. Thus, sound represents the transmission of mechanical energy and relies on the elastic and inertial properties of the medium through which it travels. To generate a sound field, one must do mechanical work on the medium, e.g., by setting a liquid into motion by the vibration of a submerged plate. Soundwaves are detected by human ears if they have frequencies above 16 Hz. A sensitivity of the human ear is in the range 16Hz-16KHz, a characteristic ultrasound frequency is in the range of 1-10MHz. The upper limit of ultrasound for gases is 5 MHz, and for solids and

liquids 500 MHz. In pure liquids and solutions, the generation and collapse of bubbles caused by ultrasound result in extraordinarily high local temperatures and pressures [3-5].

The uses of ultrasound are function of its range of frequencies:

- From 16-100 KHz for use in cleaning, plastic welding, and sonochemistry
- From 2-10 MHz for use in medical analysis and chemical imaging.

The uses of ultrasound have been extended to the biology and biochemistry, chemical (organic and inorganic) syntheses, environmental chemistry, food chemistry, material processing, dentistry, medicine, materials science, aerogels, chemical engineering processes, geography, geology, among others. The sources of ultrasound are different from heat, light, and/or radiation ionizing in its duration, pressure, and energy. Ultrasound is produced when the electrical energy is used to cause movement of a solid surface, such as a piezoelectric ceramic (transducer, which converts one form of energy in another one). Piezoelectric materials are extended and shrunken when an electric field is applied. For high frequency ultrasound, alternating electric current is applied to a piezoelectric (e.g. PZT, a material consisting of zirconate titanate) attached to a metal. Ultrasound can easily be introduced into a chemical reaction if there is good control of the temperature and pressure. The international ultrasound symbol is).

The production of ultrasound is based on a physical phenomenon called cavitation, which is defined as the formation of vapor or gas bubbles and their corresponding activity in a liquid under any form of stress. Among the different classes of cavitation are mentioned: hydrodynamic, acoustic, optic, and from particles. For sonochemical applications hydrodynamic and acoustic cavitation are of the most importance. Cavitation consists in various processes: creation, increasing, and implosion of gas and vapor cavities in liquid, promoting effects of activation in chemical reactions. During the compression stage, the pressure is positive, on the other hand the expansion results in negative pressure (a vacuum), constituting a compression-rarefaction cycles that is generated within the cavities. During the rarefaction stage, is reached a maximum pressure value corresponding to the cavitation threshold of the bubble, which is function of the surface tension and temperature of the liquid. Then, the cavity acquires a critical size and implodes, releasing large amounts of heat and pressure in a short time. Because of the immense temperatures, pressures, and the extraordinary heat released during the collapse of bubbles, formed during cavitation, the ultrasound keeps a rare mechanism in order to generate chemistry of high energy. The temperature of implosion was about 5500 °C inside the cavity, and around the cavities is 2500 °C. The pressure estimated is about 500 atm. Compared to a single-phase fluid, gas bubbles in a liquid lead to a heavy change of phase velocity and sound attenuation. Gas bubbles in a liquid affect profoundly the acoustic behavior of the liquid.

Cavitation is the phenomenon with the most important effect for intensification of physical and chemical processing. The intensity of these physical and chemical effects depends on physical properties of media, and emitted frequency. The ultrasonic power or intensity has been considered as one of the factors with importance for the quantification of sonochemical intensity. Among the methods for quantification are calorimetry, measurements of cavitation noise/cavitation bubbles, and sonoluminescence. Thus, it is not easy to reproduce experimental results, limiting the progress of industrial application in sonochemistry. Among the phenomena generated by cavitation can be mentioned biological, emulsification, erosion,

molecular degradation, and sonochemical effects.

Characteristics of Sonochemical Reactions

Sonochemistry is a cleaner technology because present the following the advantages: low waste, intrinsically safe, low consumption of materials and energy with optimized use of non-renewable resources and preferential exploitation of the renewable type [6,7]. The main advantages of sonochemistry are:

- The ability to change the course of a reaction, in order to achieve new selectivities
- Improve speeds (saving-energy), yields and selectivities of chemical reactions (reduce waste production).
- The possibility of use of non-classical or cruder reagents being performed under unusual conditions (safety and saving-energy).
- The number of steps required for a synthetic route can sometimes be reduced.
- Some reactions can be directed to an alternative pathway of synthesis.

In particular, for sonochemistry is crucial the understanding of ultrasonic energy and their spatial and temporal distributions. Cavitation caused by ultrasound leads to physical and chemical effects:

- Physical effects: micro-streaming and mixing, which accelerate cleaning, extraction, and polymer degradation.
 - Chemical effects: the production of OH and H radicals (HO° and H° respectively) that can generate or influence some chemical reactions.
1. $\text{H}_2\text{O} \xrightarrow{\text{H}^\circ} \text{H}^\circ + \text{HO}^\circ$
 2. $2\text{HO}^\circ \xrightarrow{\text{H}_2\text{O}_2}$
 3. $2\text{HO}^\circ \xrightarrow{\text{H}_2\text{O}_2} \text{O}^\circ$
 4. $2\text{O}^\circ \xrightarrow{\text{O}_2}$
 5. $\text{O}_2 \xrightarrow{\text{O}^\circ} 2\text{O}^\circ$

Analysis of numerous experiments demonstrates that ultrasound does have not significant or specific effects on many reaction mechanisms. In many heterogeneous reactions the sound has the same effects that as high-speed agitation. Chemical effects of ultrasound exist when there are changes in the path-ways of reactions, yields and/or selectivities of the products due to the ultrasonic activation. Between they can be mentioned:

- If an elementary process of the chemical reaction is sensitive to ultrasound.
- When species generated by the cavitation collapse of bubbles act as intermediaries modifying the slowest step of the mechanism, which determines the global speed of chemical reaction (sono-catalysis).

What remains pending in sonochemical reactions is to investigate the effects at industrial processes level. Among the various applications that sonochemical reactions are:

- Organic synthesis: production of organometallic compounds
- Substitution, addition and elimination reactions
- Radicals formation reactions.
- Oxidation-Reduction reactions.
- Preparation of micromaterials and nanostructures.

Development of Sonochemical Reactor

Research and development of sono-reactors are often based on empirical reaction data, because many important effects are not understood yet. Few studies were directed toward engineering aspects of sonochemical reactors (Optimum Design and Scaling-up). The wanted result is the investigation of methods to design and scale chemical sono-reactors. There is a need for standardized

sonochemical reactors in order to be able to compare the results of yield and selectivity of sonochemical reactions. The structure of pressure fields in sono-reactors has to be known in detail, in order to be able to design them [8].

Sono-Reactor Design: A Crucial Step

Fine chemistry seeks the product more than the process, having great development at the countries. Nonetheless, if one seeks to develop the process rather than the product, trying improvements with change of scale corresponds to the context of the chemical engineering. Scaling-up represents a professional challenge for the chemical engineer, due to that the mathematical aspect (Increase of Geometrical Dimensions) is not enough, also is necessary take in consideration the technical, economic and environmental issues. Designs of large-scale use sono-reactors are based on intuition mainly, and their yields are impossible to predict. The enormous potential of sonochemical reactors at industrial level still not exploited yet. The applications of sonochemistry in the industrial field will expand considerably when the use of cavitation energy can be adequately controlled. Among the applications are: cleaning and decontamination; extraction and impregnation; crystallization and precipitation and electrochemistry. For the majority of cases, the design of the sono-reactors is based on the cavitation activity and intensity using solutions based on bubble dynamics equations as well as experimentation with different reactor types and reactions. In order to obtain reliable data under sonication, it is necessary to operate the sonochemical reactors under constant ultrasonic intensity, which is a key parameter for the study of acoustic physical properties: the acoustic pressure, vibrational amplitude, radiation pressure, and heat dissipated into solution. In addition to the reproducibility of the experimental results, we also need to develop large-scale sonochemical reactors for the practical applications. An intrinsic difficulty is the non-homogeneous distribution of energy, since ultrasound propagates in the same way as light. Then, the reactor will contain sonORIZED volumes and other "dead", which should be minimized by means of the reflection of the energy on the surface and walls via an adequate geometry of the reactor.

Large-Scale Sonochemical Reactor

In order to extend the industrial applications of sonochemistry, the knowledge of acoustic properties, cavitation intensity and fluid circulation are very important for the modeling of pressure field, approaching to the real conditions that occurs in a sonochemical reactor, thus, enabling an efficient scaling-up. An important issue related to scale-up of the sono-reactors is the elucidation of the effect of liquid height and irradiation volume on sonochemical reactions. For the studies of chemical effects at laboratory-scale were used sonochemical reactors of volume 1 dm³ (1dm=0.1m). For sonochemical reactors a pilot and industrial scale the required volumes are 100 dm³ and 1 m³ approximately. The large-scale sonochemical reactors have been developed for low frequencies at range 20–50 kHz. (the transducers can be attached at each side wall of the reactor). Design of large-scale sonochemical reactors represent a true challenge due to need of high curvature of the walls to solve optical problems, and to minimize the perturbations linked to the stirring effects induced by ultrasound irradiation. The typical apparatus for sonochemistry consists of sonochemical reactor, temperature control unit, ultrasonic generator, and power amplifier. A piezoelectric ceramic or magneto-strictive transducer is incorporated into the reactor and is used as an ultrasound source. For low frequencies, the horn-type and Langevin-type transducers are used. For higher frequency, PZT (Platinum-zirconate-titanate) is used. The shape of reactor vessel and the irradiation method

are necessary to design a sonochemical reactor. Cylindrical and cubic sonochemical reactors are useful for practical applications due to this feasibility to be designed at a large scale. Hexagonal reactors also have been designed, in order to enhance the cavitation effects [9,10].

The structure of pressure fields is significant in order to design sonochemical reactors. The heterogeneous distribution of acoustic field (as also of the energy) in sonochemical reactors is a limiting factor for their scaling-up at industrial level. In order to solve this problem, is possible obtain a mapping of mass-transfer coefficients it by use of electrodes. By expressing these results as function of Sherwood number, is going to be feasible the comparison between experimental reactors. The geometric structure of the ultrasonic field depends on the homogeneity or heterogeneity of density distributions of cavitation bubbles. Blake (1994) and Leighton (1994) developed a mathematician model in order to predict the spatial distribution of cavitation events in sonochemical reactors. With this model was feasible calculate the pressure field in these reactors, which helps to the understanding of behavior of sonochemical reactions at pilot level. The propagation of ultrasonic waves requires that its medium of transport has elastic properties. The intensity is function of density and speed of sound of the medium. In turn, the speed of sound in the medium is function of the compressibility and density of the medium.

Optimal Sono-Reactor Design

Once determined what type of sonochemical reaction occurs, subsequently is optimized the type and shape of sonochemical reactor (sono-reactor).

Technical Decision in the Choice of Chemical Reactor

Choice of the most convenient type of reactor is exclusively due to technical considerations. The adaptation for a particular problem can be based on simple and intuitive arguments. Although the technical decision to be taken is not necessarily the economic optimum, it will be closely related with that chemical reactions are going on. The reactors used in the industry for safety reasons are the continuous tank agitated (CSTR), instead of those of tubular flow (PFR). In chemical reactions, the concentration of the desired product achieves a maximum for a critical time of operation. Therefore, to obtain the maximum yield of the limiting reagent in its transformation to the desired product, the reaction process must have a time no longer nor shorter than the critical time. In a sonochemical reactor as in any real continuous reactor there is distribution of residence times (FDTR). Thus, certain particles pass through the reactor with residence times equal, higher and lower than the critical time. Although the minimum residence time coincides with the critical time, this leads to a decrease in performance, to say greater the dispersion of residence times with respect to the critical time, lesser will be performance. The measure of dispersion can be obtained and measured by applying the statistical mathematical criterion of the standard deviation or distribution of the variance [11].

Performance=(Concentration of the Desired Product at Maximum Critical Time)/(Concentration of Limiting Reagent at Critical Time)

Among the real reactors, only the discontinuous one (Batch reactor) with appropriate agitation ensures a FDTR (Function Distribution of Times of Residence) with minimal dispersion. Thus, this is the reactor that achieves the highest performance values when operating with residence time equal to the critical time. For the continuous reactors, If, due to the large amount of

product to be obtained, cannot be possible to use the tubular flow reactor, the association of agitated tank reactors arranged in series may be the most suitable configuration.

As in Sonochemistry one of their main applications constitute the polymerizations, we will be mentioned that in them the commercial purpose thereof is to obtain a specific polymer, presenting also the molecular weight distribution of the corresponding copolymers a minimum dispersion. Based on these ideas, the actual discontinuous reactor is more appropriate than the continuous stirred tank reactor (CSTR). In polymeric reactions, in which their products are normally very viscous, the tubular flow reactor (PFR) is not used because its hydraulic regime is the laminar type. As a consequence of this laminar regime the high molecular weight polymers circulate closer of the wall of reactor, while those polymers of insufficient molecular weight are close to the axis. In CSTR model, the concentration of reagents remains constant over time, while in the discontinuous reactor the concentration decreases. This fact needs to take in consideration for polymerization reactions. The type of reactor does not any influence if the polymerization has no termination process, as is the case of polycondensations. On the other hand, if the polymerizations occur with mechanisms in which free radicals or ions intervene, the type of reactor is very important. Under these conditions, for many types of polymerizations, the molecular weight distributions for reactions with initiation and termination mechanisms have less dispersion in a CSTR than a discontinuous model.

Economic Decision in the Choice of Chemical Reactor

In the case of dealing with sonochemical processes, we must take in consideration the economic factor in the design of the sono-reactor. Optimization studies in chemical reactors generally seek to obtain the maximum benefit of a process or the maximum reduction of its costs, increasing the chemical performance of the reaction, size of reactors, criteria of control of operations, security, etc. All these factors must be taken into account in the objective function for the optimization of reactor. The greatest endeavors made for optimize these objective functions are oriented in:

Production Problems

- To obtain the maximum amount of product per unit of time and volume of reactor, if there are side reactions during the operation.
- When initial costs far exceed reagents, energy.

Performance Problems

When the reaction time does not matter, as the case of complex organic reactions, in which the costs of heat reagents, energy transformed abroad, devaluation of the product by coexistence of by-products have a very high importance.

For both types of optimization problems, it is necessary the selection of an optimum temperature or an optimal sequence of temperatures.

Proposal of the Chemical Reactor for the Use of Ultrasound (Sono-Reactor)

Very important for the optimization of sonochemical processes is the knowledge of how the ultrasonic energy has influence on their thermodynamics and reaction kinetics, in order to choose the most adequate models of sonochemical reactors that meet the requirements of the operational conditions, as also the materials used for its construction, optimizing costs and production. On the theoretical basis, we can work with a cylindrical reactor, in regimes

ideal discontinuous (Batch), semi-continuous (Semi-Batch) and continuous regime (CSTR, PFR).

For the sono-reactor, we can use a configuration consisting in two concentric rotary cylinders. On the inner surface of the internal cylinder will be fixed homogeneously the catalyst. Placing the transducers in symmetrical mode of the external cylinder, in order to distribute the ultrasonic energy homogeneously. In order to minimize the dead sonorized volumes, instead of the big transducer usually used can be replaced by an arrangement of small transducers. Additionally, the two concentric rotary cylinders possibility the reflection of the ultrasonic energy on the surface of cylinders. In the case of polymerizations (Batch and Semi-Batch), we can use a combination of mechanical agitation and ultrasonic waves, to optimize performance. For mechanical agitation, externally can be generated by the rotation of cylinders. For the wastewater or blackwater cleaning can be used a CSTR model using the configuration of concentric cylinders rotating in the same or inverse directions. Figures 1 and 2 illustrate the model of a sono-reactors in continuous and discontinuous regimes:

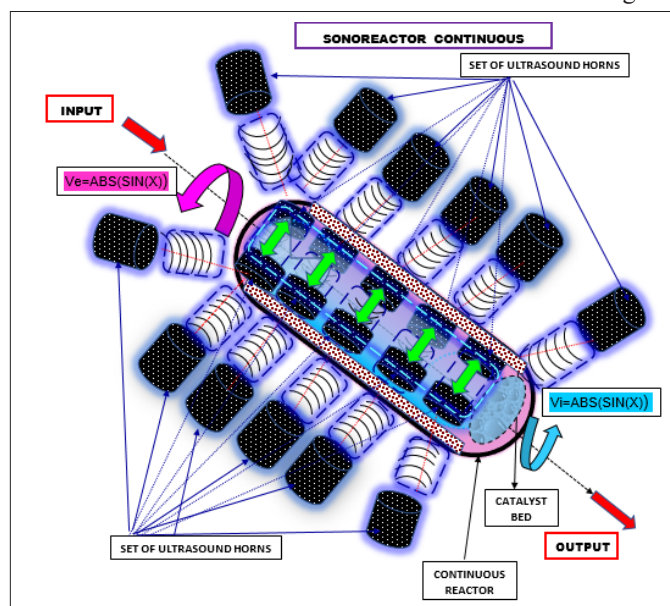


Figure 1: Model of Sono-Reactor in Continuous Regime (CSTR, PFR).

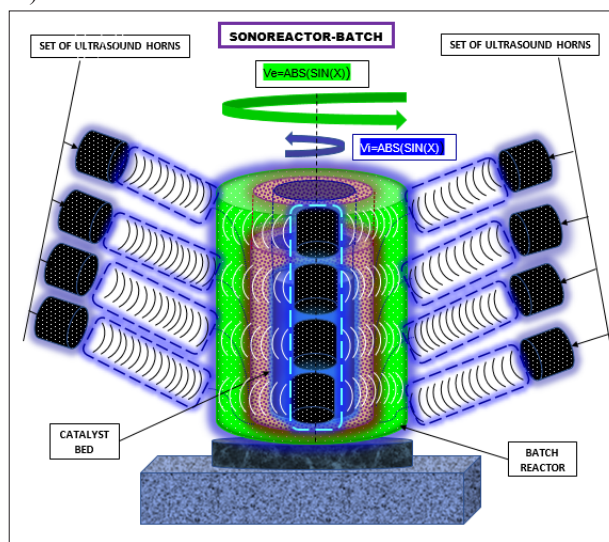


Figure 2: Model of Sono-Reactor in Discontinuous Regime (Batch).

Conclusions

- Sonochemistry is an emergent technology with many advantages comparing with the existing technologies. In many cases, it is a good alternative to replace mechanical agitation.
- Sonochemistry is a cleaner technology than the others because generates less waste than other technologies. Sonochemistry possess a mechanism that makes most of the intermediate species generated be almost or entirely consumed.
- In the aspect of concentration profiles, the following are taken in consideration:
- For polymerization reactions, they must be developed in a discontinuous (Batch reactor) or semi-continuous (semi-batch reactor) regime. Therefore, it has to be considered the kinetic aspects of the reactor and the effects of viscosity on transport properties, in order to develop concentration profiles either be analytically or by computer simulations.
- For organo-metals reactions, they have to be developed in a semi-continuous regime or continuous regime (stirred tank reactor-CSTR or piston flow reactor-PFR).
- In order to improve the sonochemical processes, we must take in consideration the production and economic optimizations, including the ultrasonic energy in the energy balances, as well as in the conditions of operation.
- In order to perform an optimum scaling-up to an industrial sono-reactor, we must go deeper into the kinetic and thermodynamic topics that constitutes foundations to the fully development of sonochemical processes.

Recommendations

- Development of simulations, taking into account the two-dimensional and three-dimensional behavior of ultrasound waves in liquid medium.
- Analysis of thermodynamics for irreversible processes, in order to better understand the sonochemical reactions.
- Learn more about the rationale use of ultrasound and transducers in order to build sono-reactor at pilot scale for the study of different chemical processes.
- The cavitation intensity for sonochemical reactors is influenced by the shape of the reactors, electric power input, height of liquid from a transducer, and the ultrasonic energy consumed in solution. In order to the design and scaling-up of sono-reactors, the study of cavitation intensity and fluid circulation have to take in consideration.
- For the case of micro-materials and nano-structures are necessary the use of supramolecular chemistry and fractal geometry that will help to describe more accurately these processes.
- One crucial point is finding out the adequate type of energy source for the functioning of sono-reactor, improving the conversion via transducer to the ultrasonic energy. This can be done combining conventional sources or non-conventional, such as the magnetic and or solar energies.
- Due to the high temperatures inside of sono-reactor (although be for a period of μ s), the accumulation of heat at industrial level can convert in an important problem to resolve, especially for polymerizations. A solution would be the application of thermal superconductors in order to optimize the heat transport. For safety reasons of sono-reactor, research in electrical superconductors would be an important topic.
- In order to design a sono-reactor, apart from the economic factor, we must take in consideration that due to the cavitation generated by the ultrasonic energy, the ultrasound frequency can equal the characteristic threshold frequency of material, from which reactor was made, producing the resonance phenomenon. Consequently, the sono-reactor is going to be

cracked. In that concerning about the construction materials for sono-reactor, sonochemistry opens-up a new chapter: materials resistant to the ultrasound.

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