Sonochemical activity in ultrasonic reactors under heterogeneous conditions

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Abstract

Due to its physical and chemical effects, ultrasound is widely used for industrial purposes, especially in heterogeneous medium. Nevertheless, this heterogeneity can influence the ultrasonic activity. In this study, the effect of the addition of inert glass beads on the sonochemical activity inside an ultrasonic reactor is investigated by monitoring the formation rate of triiodide, and the ultrasonic power is measured by calorimetry and by acoustic radiation. It was found that the sonochemical activity strongly depends on the surface area of the ~~surface developed by the~~ glass beads in the medium: it decreases above a critical area value (around 10^{-2} m^2), partly due to wave scattering and attenuation. This result is confirmed for a large range of frequencies (from 20 to 1135 kHz) and glass beads diameters ~~glass beads~~ (from 8-12 µm to 6 mm). It was also demonstrated that above a given threshold of the ~~developed~~ surface area, only part of the supplied ultrasonic power is devoted to chemical effects of ultrasound. Finally, the acoustic radiation power appears to describe the influence of solids on sonochemical activity, contrary to the calorimetric power.

Highlights

- Ultrasonic power measured by calorimetry is not affected by glass beads addition
- Glass beads surface area is a relevant criterion to describe sonochemical activity
- Sonochemical activity decreases above a critical surface area for all frequencies
- Acoustic radiation power is relevant to describe glass beads effect on sonoactivity

Keywords: Ultrasound; Sonochemistry; Calorimetry; Acoustic radiation power; Heterogeneous media; Suspension

1. Introduction

Many applications are reported about low and high frequency ultrasound, applied in various sonochemical processes involving heterogeneous media. For example, nanostructured materials can be synthesized at ambient temperature and pressure, in a short reaction time, with the use of power ultrasound. It is even possible to control the size of powder and/or modify the material surface [1,2]. Ultrasound can also be used to enhance solid-liquid extraction: this ultrasound-assisted extraction allows to recover heat-sensitive bioactive

compounds at low temperature and promote the use of GRAS (generally recognized as safe) solvent [3]. Also in adsorption process, the regeneration of the adsorbent and the mass transfer were proven to be improved by means of ultrasonic waves [4]. Another example is sonocrystallisation, where ultrasound is used to decrease the induction time and the metastable zone, and to increase the nucleation rate. Crystals with controlled size and distribution are likely to be obtained [5].

Even if ultrasound in heterogeneous medium is widely used in such different domains, only few articles are dedicated to the study on the influence of heterogeneity on the sonochemical activity. Main studies previously reported are summarized in **Table 1**, where the surface area of the particles is calculated according to the data available in these papers. In 2002, Keck *et al.* investigated the influence of quartz particles (2 - 25 µm) on the chemical effects induced by ultrasound from 68 to 1028 kHz, under Ar/O_2 or N_2/O_2 conditions. The authors noticed the activity increases at 206 kHz due to a bubbles shape modification, which enables more radicals release in the bulk by increasing bubble interface [6]. They also reported that the ultrasonic activity was reduced for all the other frequencies, due to ultrasound attenuation. Tuziuti et al. (2005) studied the enhancement of sonochemical reaction by adding different amounts (0 - 100 mg) of alumina particles (1 - 80 µm). They observed that with an appropriate amount (20 mg) and size (20 µm) of particles, the sonochemical activity increases by increasing the population of cavitating bubbles [7]. Her et al. (2011) investigated the role of inert or TiO_2 coated glass beads (from 50 to 5000 µm diameters) on the H_2O_2 production. Their conclusion was that the inert glass addition increases the sonochemical activity at low frequency (28 kHz) by increasing the formation rate of cavitation bubbles. At higher frequencies (580 and 1000 kHz) this activity decreases, except for 100 µm (10-50 $g.L^{-1}$), due to wave-particle interference [8]. Stoian et al. (2018) studied the influence of particle addition (ion exchange resin, sand, and glass beads) with different diameters (207 - 1290 µm) and concentrations on the sonochemical activity in a full stirred reactor at 20 kHz. The authors found that the sonochemical activity of ultrasound is changed according to the particle concentration. They reported a first decrease due to wave attenuation, for volumetric solid concentrations (Cv) from 0 to 0.01. Then they reported an increase of the sonochemical activity for Cv from 0.01 to 0.4, due to the enhancement of cavitation bubbles. However, above Cv = 0.4, this activity decreased due to change of the medium viscosity [9]. More recently, Son et al. (2019) have investigated the cavitational activity in heterogeneous systems containing fine particles in a 28 kHz double-bath sonoreactor. Their results clearly suggested that there were no significant differences in calorimetric energies for both with and without particles conditions. Furthermore, the chemical activity was evaluated using sonochemiluminescence (SCL) and different trends were observed depending on the presence and size of beads [10].

In order to obtain complementary understanding on the effect of heterogeneity on ultrasound activity, this research aims to investigate the influence of the presence of divided solids on sonochemical activity within a low or high frequency ultrasonic reactor. Inert glass beads are used in order to simulate solid heterogeneity, with different diameter and concentration. Diameters were chosen considering the characteristic parameters of an ultrasonic system: its wavelength and the diameter of its acoustic cavitation bubbles. The global ultrasonic activity

and the chemical ultrasonic activity were quantified by different methods and they were systematically compared in homogeneous and heterogeneous conditions. The ultrasonic power was measured by calorimetry while the chemical activity was monitored by iodide dosimetry.

Table 1. Summary of main publications about ultrasound in heterogeneous media

Authors	Particles	Diameter (µm)	Concentration ($g.L^{-1}$)	Calculated area (m^2)	Frequency (kHz)	Gas condition	Reported effects
Keck et al. [6]	Quartz	2-25	1-25	0.15-10^4	68-206-353-620-1028	N_2/O_2 Ar/O_2	The particle addition reduces the sonochemical activity except at 206 kHz
Lu et al. [11]	Silica Alumina	2-130 130	2-200	0.92-6 10^3	20	Air	The sonoactivity is reduced, for all diameters and concentrations
Tuziuti et al. [7]	Alumina	1-80	10-100	0.38-15.2	42	Air	The sonoactivity is increased with an appropriate particle size and concentration
Her et al. [8]	Glass with and without TiO_2 coating	50-5000	10-200	48-4800	28-580-1000	Air	The sonoactivity is decreased with particle addition except at 28 kHz
Stoian et al. [9]	Resin Sand Glass	625 309 207-1290	12.2-610	12.2-30.2	20	Air	The sonoactivity is maximal for a 0.4 solid volumetric concentration
Son et al. [10]	Clay Glass	75 75-2000	100-333	0.12-3.2	28	Air	No difference in calorimetric energies. SCL depends on the presence and the size
This research	Glass beads	8-6000	0.003-80	1.5 10^{-4}-0.95	20-376-575-858-1135	Air Ar	

2. Materials and methods

2.1 . Ultrasonic reactors

Two different devices are used to generate ultrasound. The high frequency generator MFG and the corresponding transducers are provided by Meinhardt Ultrasonics (**Fig 1.a**). Two transducers are used in order to vary frequency: 376, 575, 858 and 1135 kHz are studied. These interchangeable flat transducers (50 mm diameter) are placed at the bottom of the vessel. The low frequency equipment is a homemade cup horn based on a 20 kHz Sonics Vibracell 75115 generator (**Fig 1.b**) with a 25 mm probe.

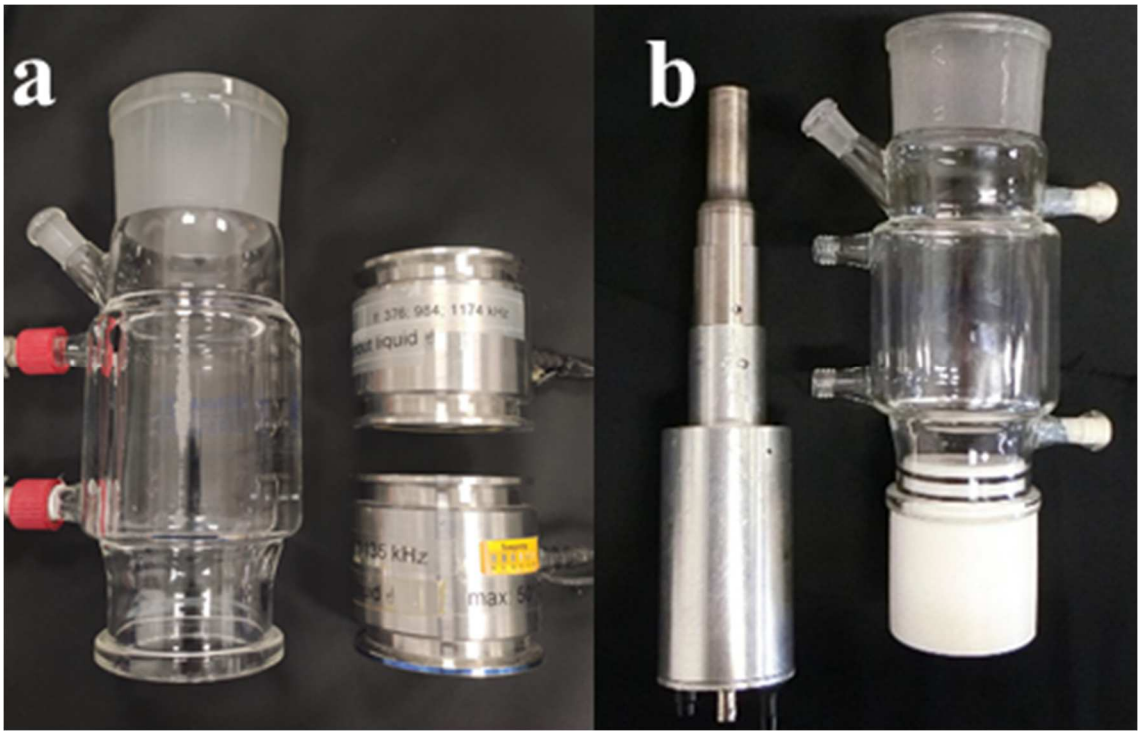

Fig. 1. Ultrasonic reactors (1.a: high frequency reactor, 1.b: low frequency reactor)

For both devices, the same 500 mL reactor vessel is used, with a double jacket in order to maintain a constant temperature at 20 ± 1 °C, thanks to a cryothermostat bath (Thermo Fisher Scientific Arctic A25). Each experiment last 30 minutes, and triplicates are carried on. As the used vessels are very similar, the reactor shape is not likely to influence the obtained results [12,13].

2.2 Glass beads

In order to simulate the heterogeneity in the medium, glass beads are used. They were chosen because they are easy to characterize through their diameter and chemically inert. Preliminary tests have shown triiodide adsorption is negligible (less than 1%) and SEM photographs have proven sonication has no effect on beads structure. These beads were used at different mass concentrations, ranging from 3.2 10^{-3} to 80 $g.L^{-1}$.

A wide range of glass beads diameters (between 8-12 and 6000 µm) was tested. The objective was to be in the same order of magnitude as the wavelength (from 1400 to 4000 µm for high frequency) and the cavitation bubbles diameter. From 213 to 1136 kHz, the cavitation bubbles diameter was estimated to be from 4 to 8 µm thanks to the work of Brotchie et al. [14], and it was also calculated from 2.8 (at 1174 kHz) to 164.5 µm (at 20 kHz) with Minnaert equation [15].

2.3 Calorimetry

The ultrasonic power (P_{US}) supplied to the medium was measured by calorimetry [16]. This method is classically used to thermally characterize an ultrasound device by monitoring the temperature change of the irradiated medium. ~~Carefully~~ The reactor is thermally insulated carefully by glass wool, and two temperature probes are placed within the reactor to confirm the temperature homogeneity inside the irradiated medium. Before calorimetry, the

temperature of the liquid inside the vessel is reduced by 5°C under the ambient temperature, and the monitoring stops when the temperature of the irradiated liquid is 5°C above the ambient temperature.

Assuming that the reactor is thermally insulated, the ultrasonic power is obtained by the following energy balance:

$$P_{US} = m_{water}\, C_{p,water} \frac{dT}{dt} \quad (1)$$

where m_{water} is the mass of water contained in the reactor (0.5 kg), $C_{p,water}$ is the heat capacity of water (4.18 $kJ.kg^{-1}.K^{-1}$) and $\frac{dT}{dt}$ is the slope of the experimental curve at the point where the temperature of the sonicated water equals the ambient temperature.

Nevertheless, the obtained value gives the net ultrasonic power ~~present~~ dissipated in the medium. The ultrasonic power absorbed by the reactor vessel must be estimated. So a calibrated resistance (11.5 Ohm) is used with a power supply (Française d'Instrumentation FI 3610) at 2.97 A and 34 V in order to measure the energy absorbed by the vessel. This energy is turned into an equivalent mass of water to be added at the energy balance as follows:

$$P_{US} = (m_{water} + m_{eq-water})\, C_{pWater} \frac{dT}{dt} \quad (2)$$

where $m_{eq\text{-}water}$ is the energy absorbed by the ~~reactor~~ vessel converted into an equivalent mass of water. Finally, the total ultrasonic power ~~generated~~ transferred by the transducer is calculated by equation (2).

2.4 KI dosimetry

Considered as reproductive, easy to set up and reliable [17], this technique is based on the irradiation of an aqueous solution of potassium iodide (KI) by ultrasound [18]. A fraction of iodide (I^-) is oxidized into diiodine (I_2) by radicals produced by cavitation bubbles implosion. Then the rest of iodine reacts with diiodine. So the final product triiodide (I_3^-) is generated according to the following reaction:

$$2\ HO^{\bullet} + 3\ I^- \rightarrow 2\ OH^- + I_3^- \quad (3)$$

From an initial solution of potassium iodide (10 $g.L^{-1}$), the absorbance of the yellow triiodide is measured at 355 nm (spectrophotometer Shimadzu UVmini 1240). Finally, its concentration is obtained thanks to its molar attenuation coefficient (ε = 26300 $L.mol^{-1}.cm^{-1}$).

For heterogeneous medium, addition of glass beads was considered since the obtained solution is homogenized even for the highest concentration. Therefore, hydrodynamic conditions are thereby nearly the same than under homogeneous conditions and the ultrasonic reactor can be considered as a batch reactor. So, the following equation is obtained thanks to the mass-balance based on triiodide production and provides the triiodine formation rate $r(I_3^-)$:

$$r(I_3^-) = \frac{1}{V} \cdot \frac{dn_{I_3^-}}{dt} = \frac{\Delta[I_3^-]}{\Delta t} \quad (4)$$

Moreover the concentration of triiodide increases linearly with sonication time (**Fig. 2**). Assuming the triiodide formation reaction follows a zero-order kinetics, triiodide formation

rate is likely to be directly estimated by the value of the slope of the obtained straight line, as proposed by [19].

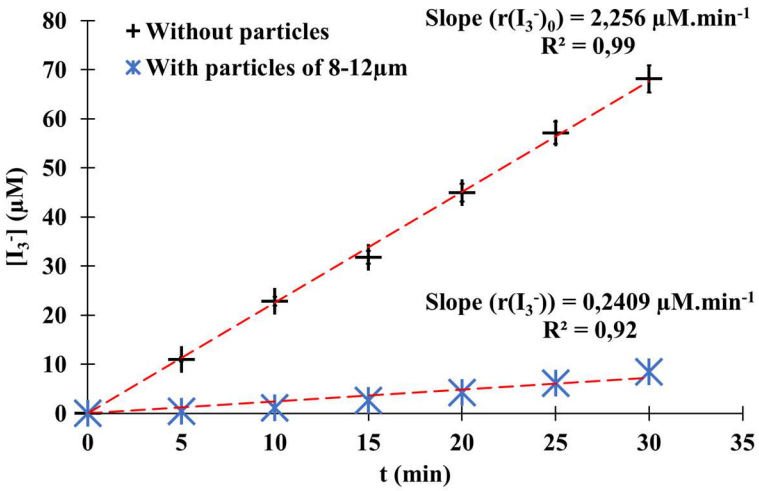

Fig. 2. Examples of chemical characterization by iodometry of an ultrasonic system at 575 kHz (d_p = 8-12 µm, V = 500 mL, P_{US} = 51.5 ± 0,5 W, T = 20 ± 1 °C)

~~In this study, two types of triiodide formation rate are defined.~~ In this study, we defined two different notations for triiodide formation rate: in the case of homogeneous media (without particles) the formation rate is represented by $r(I_3^-)_0$ whereas in the case of heterogeneous media (presence of glass beads) the formation rate is denoted $r(I_3^-)$.

2.5 Acoustic radiation power

When a solid target is immersed in a liquid irradiated by ultrasound, it undergoes a radiation force providing some information about the acoustic radiation power [20], denoted $P_{US\text{-}rad}$. This power is measured according to the International Electrotechnical Commission (IEC) 61161 norm [21]: a silicon target (diameter 6.5 cm) is set at the liquid surface and hooked to a precision balance (Kern-PCB 2500-2) in order to record its weight. Then the acoustic radiation power is calculated by the following equation

$$P_{US\text{-}rad} = \Delta m \cdot g \cdot c \quad (5)$$

where g is the gravitational acceleration (9.81 $m.s^{-2}$), Δm is the difference of weight with and without ultrasound (kg), and c is the sound velocity in water (1500 $m.s^{-1}$).
The acoustic radiation power depends on several parameters of the target (material, size, distance from the transducer …) [22-23] but the obtained values are in the same range as the power obtained by calorimetry, according to the literature [24-26]. In our case, experiments were only performed at 575 kHz, because target is damaged for higher frequencies.

2.6 Gas experiments

Most of experiments are achieved with an atmospheric open vessel, under air conditions, but sonochemical activity is influenced by dissolved gases. As a consequence, some experiments are carried on under argon. For these trials, water is preliminary deaerated and saturated by argon bubbling for 20 minutes. Then the sonication is performed with a slight argon current maintained just above the liquid surface, to avoid any oxygen and nitrogen dissolution.

3. Results and discussion

3.1. Ultrasonic power measured by calorimetry: effect of particles

In order to investigate the effect of heterogeneous media on P_{US}, calorimetric experiments were carried out first without heterogeneity (ultra-pure water), then in the presence of glass beads, with different diameters and different concentrations.

In a homogeneous medium (0 $g.L^{-1}$), the electrical input power was adjusted to obtain a similar ultrasonic power (around 50 W) for all the studied frequencies as shown in **Fig 3.a**.

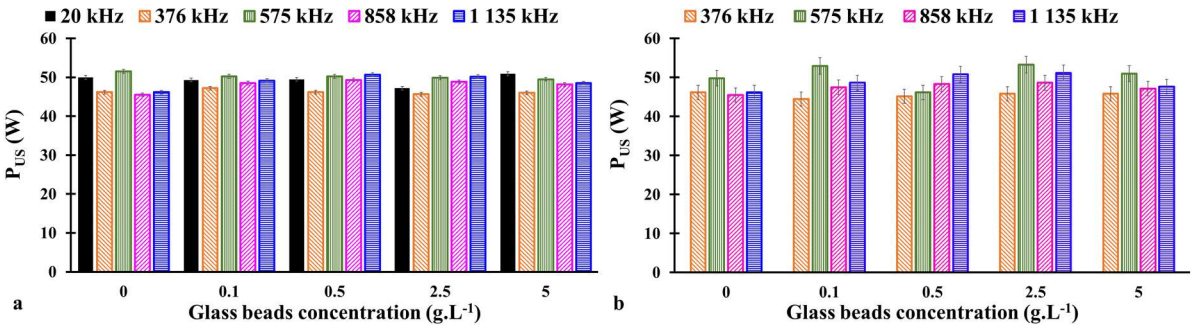

Fig. 3. Ultrasonic power measured by calorimetry. a: with 8-12 µm glass beads, b: with 90-150 µm glass beads

~~For the studied frequencies and~~ Then, at the same electrical power level, for all the studied frequencies and in presence of 8-12 µm diameter glass beads, the ultrasonic power was measured by calorimetry. ~~in heterogeneous medium~~ ~~was represented in~~ The result is displayed in **Fig. 3.a.** It can be observed that the addition of particles has no effect on P_{US} whatever the concentration is in the range from 0.1 to 5 $g.L^{-1}$, because the obtained calorimetric power is close to 50 W for all the concentrations. This result was corroborated by other glass bead diameters (**Fig 3.b**). Moreover, some complementary experiments were carried out for the 5 frequencies with an ultrasonic power of 22 W and the addition of particles has also no effect on P_{US}.

All these observations put in evidence that the ultrasonic power measured by calorimetry is not influenced by the presence of glass beads. The same result was observed by Stoian et al. in terms of volumetric power [9]. The dissipated power ~~global energy available~~ in the system remains unchanged for all our experimental operating conditions. While such an observation is in good agreement with recent work by Son et al. [10], it is expected that complementary data dealing with the sonochemical activity should give more information.

3.2. Ultrasonic chemical activity measured by iodometry: effect of particles addition

The sonochemical activity was monitored by potassium iodide dosimetry and the formation rate $r(I_3^-)$ is a relevant indicator of the amount of radical species produced by sonolysis of water [27].

3.2.1. Sonochemical activity in homogenous media

For all the experiments, the reactors have the same shape and volume, and the same ultrasonic power is adjusted. So the frequency is assumed to be the single parameter likely to influence the sonochemical activity. The triiodide formation rates $(r(I_3^-)_0)$ are plotted according to the frequencies (**Fig 4**). As it can be seen, results show a maximal rate at 575 kHz with a value of 2.3 ± 0.1 $\mu M.min^{-1}$, and a minimal rate at low frequency with a value of 0.28 ± 0.01 $\mu M.min^{-}$

[1]. So, the optimal sonochemical activity is obtained at 575 kHz and the sonochemical activity is ~~divided by a factor of 10~~ ten-fold lower at 20 kHz. This result is in accordance with the literature: the same ~~decreasing factor~~ ratio between high and low frequencies was reported by Koda [18].

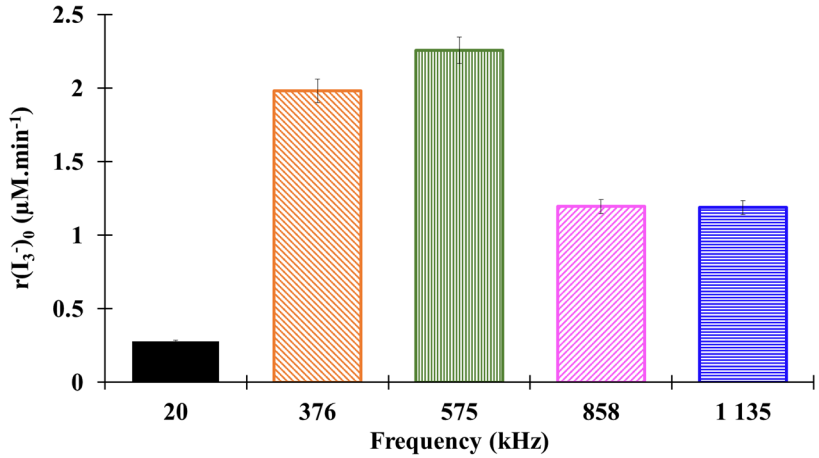

Fig. 4. Sonochemical activity measured by iodometry in homogeneous medium (V = 500 mL, P_{US} = 51.5 ± 0.5 W)

The maximal sonochemical activity between 300 and 600 kHz was previously reported by different authors [18, 28-30] and was explained by a larger population of active cavitation bubbles when the frequency increases. But this beneficial effect of the frequency is reduced for higher frequencies by the reduction of the growth time of cavitation bubbles, which leads to a reduction of sonochemical activity [31]. Therefore, our study mainly focused on the sonochemical activity at high frequency, and most of the results reported in this paper were obtained at 575 kHz.

3.2.2. Sonochemical activity in heterogeneous media

In order to investigate if the sonochemical activity is affected by solid heterogeneity, the rates of triiodide formation ($r(I_3^-)$) in the presence of glass beads were measured as previously detailed in this paper (**Fig. 2**). Experimental formation rates observed with 8-12 µm diameter glass beads are given in **Fig 5**. First of all, results exhibit that 575 kHz is the most efficient frequency for all the glass beads concentrations, as in homogeneous media. Secondly whatever the frequency is, it can be noticed that $r(I_3^-)$ decreases when the particles concentration increases. In the literature, this result is controversial because on the one hand the particle addition may promote the acoustic cavitation by reducing the cavitation threshold and may increase the number of nucleation sites or even modify the shape of imploding bubbles releasing more radicals [6,12]. On the other hand, at more concentrated media, the acoustic cavitation may decrease because of the wave attenuation [6-8].

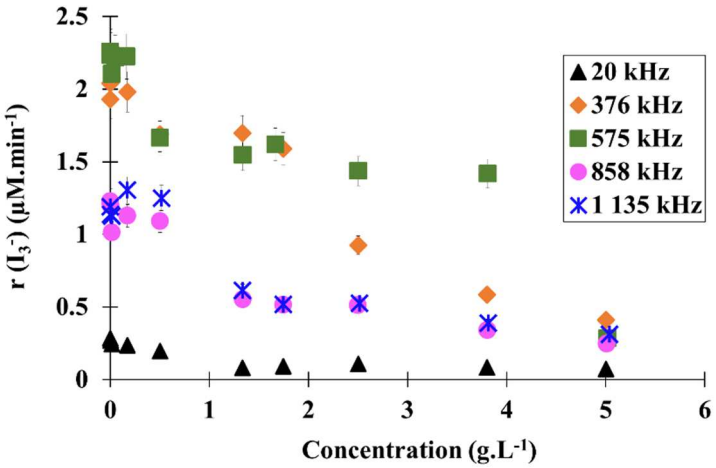

Fig. 5. Effect of glass bead concentration on triiodine formation rate, for different frequencies (d_p = 8-12 µm, V = 500 mL, P_{US} = 51.5 ± 0,5 W, T = 20 ± 1 °C)

Similar experiments were then performed with other glass beads diameters. To highlight the influence of these glass beads, results are presented using a ratio defined as the rate of triiodide formation in heterogeneous medium ($r(I_3^-)$) divided by the formation rate in homogeneous medium ($r(I_3^-)_0$). As shown in **Fig. 6** at low glass beads concentration, I_3^- formation rates ratio remains constant and close to 1, illustrating the sonochemical activity is not affected by the presence of particles, whatever the glass beads diameter. To our knowledge, this phenomenon has never been reported in the literature [6-9]. According to experimental results exhibited in **Fig. 6**, it seems that for each glass beads diameter, the I_3^- formation rates ratio decreases above a certain particle concentration~~, partially due to wave attenuation~~.

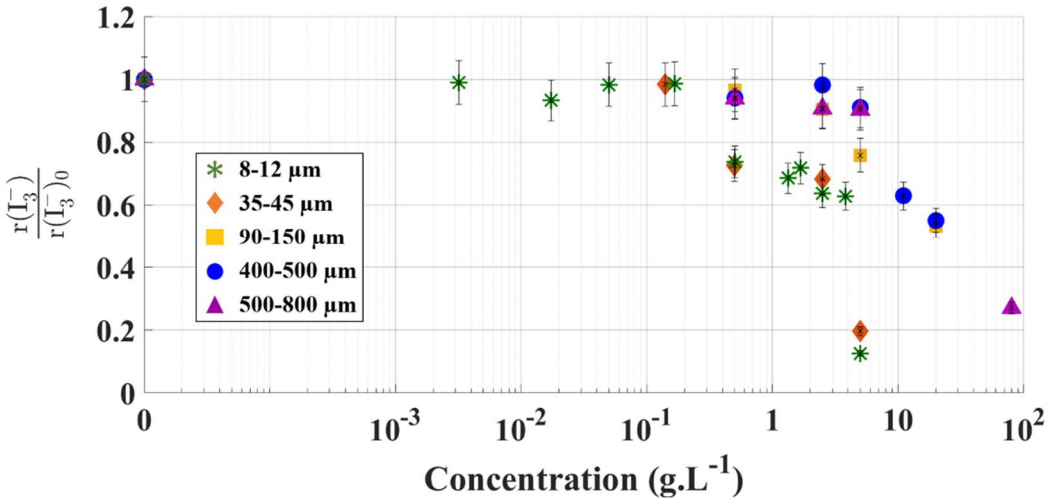

Fig. 6. Effect of the glass bead concentration on the triiodine formation rate, for different diameters (f = 575 kHz, V = 500 mL, P_{US} = 51.5 ± 0.5 W, T = 20 ± 1 °C)

For all these experiments, both diameter and concentration of particles are likely to be different. So, in order to take into account these two parameters simultaneously, the area of the ~~developed~~ surface due to the presence of beads inside the reactor was considered as a new criterion to express the results. It is defined as the area of the surface induced by the amount

of glass beads introduced within the reactor, and it is calculated thanks to the following equation.

$$\text{Surface area: } A = \frac{6}{\rho_{glass}\, d_p} m_p \quad (6)$$

with m_p: total mass of particles, d_p: mean particle diameter and ρ_{glass} = 2500 kg.m^{-3}.

Results obtained at 575 kHz are exhibited on **Fig. 7**. Whatever the particles diameter is, the I_3^- formation rates ratio is close to 1 at low ~~developed~~ surface area value. It means the ultrasonic activity is not influenced by the particles addition. Nevertheless, chemical effect of ultrasound decreases sharply above a typical value of the surface area. This critical value was found to be between 10^{-2} and 3.10^{-2} m^2, varying according to the bead size.

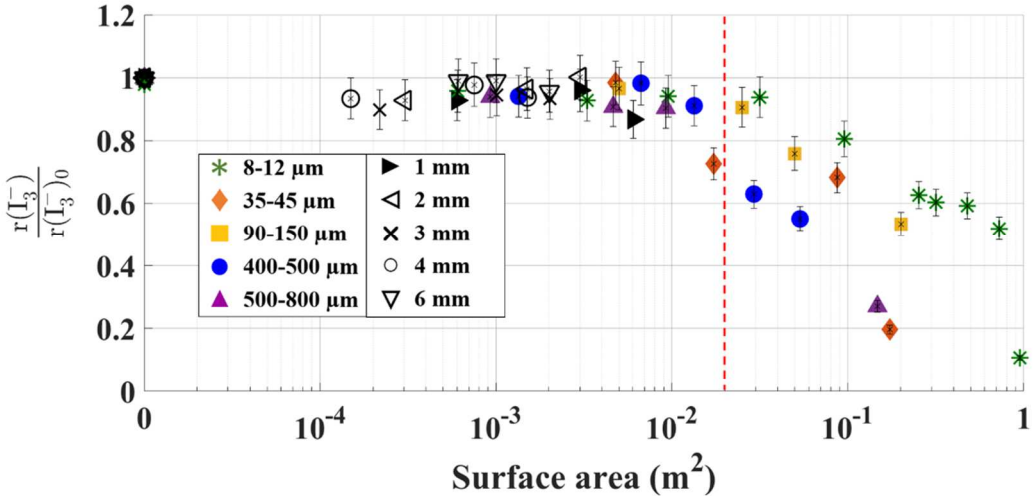

Fig. 7. Normalized I_3^- formation rates, for different surface areas and diameters. (f = 575 kHz, V = 500 mL, P_{US} = 51.5 ± 0.5 W, T = 20 ± 1 °C)

According to the literature, the effect of inert particles on sonochemical activity is considered to result from two types of interaction. The first interaction takes place between the waves and the particles, and it provokes an attenuation and a scattering of the ultrasonic waves for concentrated suspensions [6-9] (Table 1). The second interaction takes place between the particles and the cavitation bubbles: the particles can interfere at the different stages of the cavitation bubble lifetime. (i) At the initial nucleation step, the solid particles can be supposed to act as additional nucleation sites [32], so their presence will improve the sonochemical activity by increasing the number of bubbles. (ii) At the growing stage, it was reported that small and low-density particles can be located at the ultrasonic wave antinodes where the tiny bubbles grow and become active resulting in a detrimental competition [33]. (iii) At the last phase of the cavitation bubble lifetime, the presence of particles is generally supposed to promote asymmetric implosions enhancing thereby the sonochemical activity [6–8].

In our case, below the critical area, the sonochemical activity remains unchanged. On the one hand, this is due to the fact that the particles did not play the role of nucleation site, because the used glass beads are smooth and not small enough, which can reduce the probability of the cavitation occurrence according to the work of Zhang et al. [34]. On the other hand, there is

no wave scattering and attenuation due to the low particle concentration. Furthermore, no second interaction can be expected at this level because the glass beads are too dense to be trapped at the wave antinodes. Nevertheless, as they can be dragged away by the acoustic streaming, the particles did not play the role of solid wall, which enhance radical release by modifying the shape of imploding bubbles as described by Keck [6] or Tuziuti [7].

However, above the critical area value, the sonochemical activity is dramatically decreased, that cannot be only due to the wave scattering and attenuation ~~like it was~~ as reported in the literature [6-9,11], because our highest particle concentration (80 $g.L^{-1}$) is lower than the concentrations used by these researchers (Table 1). For example, Stoian [9] worked with a concentration between 12.2 $g.L^{-1}$ and 610 $g.L^{-1}$ and Tuziuti [7] used a concentration from 10 to 100 $g.L^{-1}$. Finally, it can be thought that the particles may induce an asymmetric implosion, likely to decrease sonochemical activity, according to different studies [11, 35].

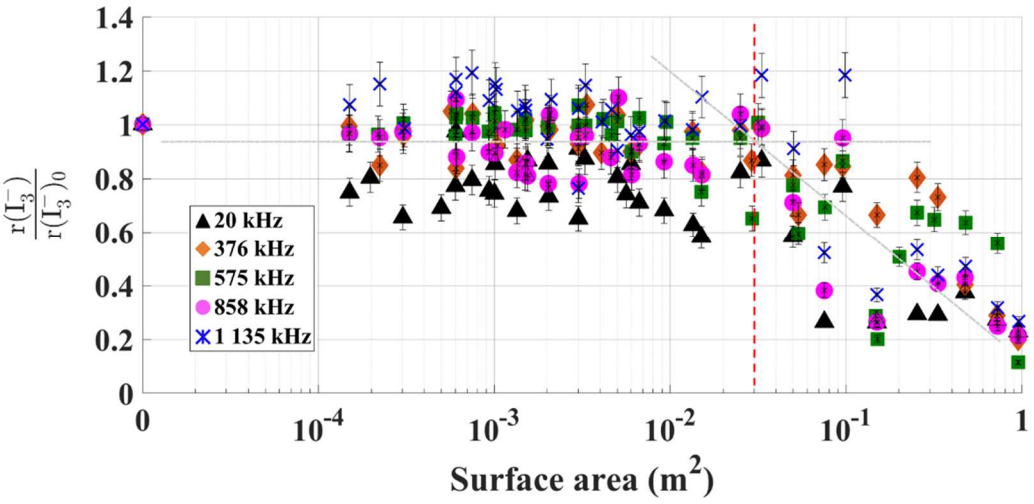

Fig. 8. I_3^- formation rates ratio at different frequencies for different surface areas and diameters. (V = 500 mL, P_{US} = 51.5 ± 0.5 W, T = 20 ± 1 °C, d_p from 8-12 µm to 6 mm)

As surprisingly shown in **Fig. 8**, the same trend was observed for all the ultrasonic frequencies used in this work: the sonochemical activity first remains unchanged and then sharply decreases above the same critical surface area inside the reactor. So, for these studied frequencies, the addition of inert glass particles reduces the sonochemical activity above a critical area, estimated to be 3.10^{-2} m².

3.2.3. Effect of gas on sonochemical activity in heterogeneous media

As for a homogeneous medium, sonochemical activity in a heterogeneous medium is influenced by dissolved gases. According to the gases, oxidant species are not the same, so chemical reactions pathways are modified. For instance, sonication of water under air leads to the formation of different species, among which nitrites and nitrates whereas sonication under argon is known to be •OH specific [36]. So experiments were carried on under argon conditions (section 2.6) with and without 8-12 µm glass beads, with a 51.5 ± 0.5 W calorimetric power at 575 kHz.

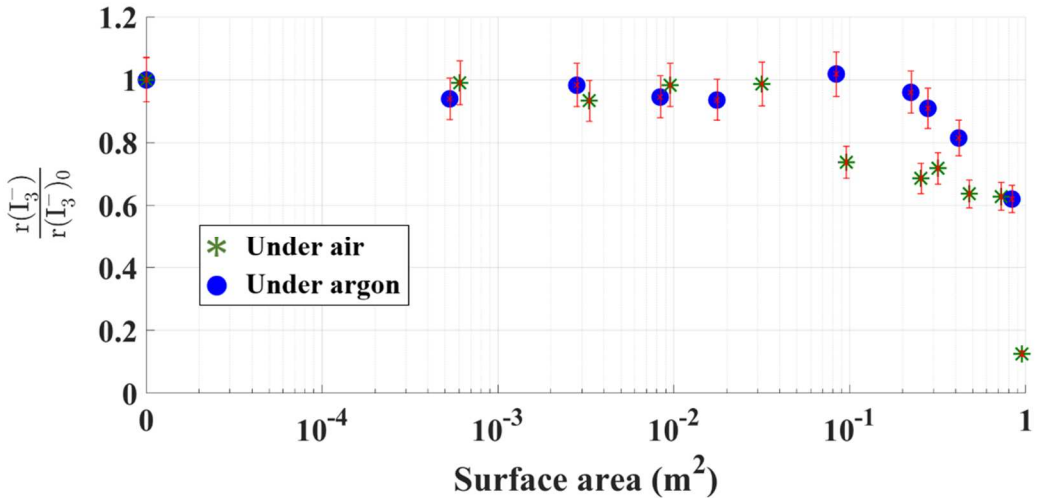

Fig. 9. Combined effect of gas and glass beads presence on triiodine formation rate (d_p = 8-12 µm, f = 575 kHz, V = 500 mL, P_{US} = 51.5 ± 0.5 W, T = 20 ± 1 °C)

Without any beads, triiodine formation rate decreases from 2.3 ± 0.1 µmol.min^{-1} under air condition to 0.65 ± 0.04 µmol.min^{-1} under argon condition. Under argon condition, there is no contribution of the oxidant reagents generated by oxygen (•OOH, •OH et O) as reported in the literature [37-42], so the triiodine formation rate declines.

In the presence of glass beads, results obtained under air and argon conditions were compared (**Fig. 9**). Both curves exhibit the same trend: a first plateau where the sonochemical activity remains constant followed by a drastic decrease above a critical value of the ~~developed~~ surface area. As previously explained, this reduction of activity is probably due to wave attenuation and to less energetic bubbles implosions [35, 43-45]. Under argon conditions, the value of the critical ~~developed~~ surface area (close to 3.10^{-1} m²) is higher than the value observed for air conditions (close to 3.10^{-2} m²). For argon, even if the sonochemical activity is initially lower, its decrease appears to be less important. It can be explained by the higher temperature reached when cavitation bubbles implode, due to this mono-atomic gas presence inside these bubbles [26, 46-49] that counteracts the detrimental effect of glass beads.

Even if iodometry under argon condition is much more •OH specific compared to air condition, the same trend is obtained for both conditions. So air iodometry is likely to be used to describe the effect of glass beads addition within an ultrasound reactor.

3.3. The real ultrasonic power devoted to sonochemistry

Whatever the frequency is, for all the beads diameters and concentrations, the calorimetric ultrasonic power (P_{US}) released inside the reactor in heterogeneous medium was constant (section 3.1) while the sonochemical activity decreased above a critical value of ~~developed~~ surface area (section 3.2) in the same conditions. From a chemical engineer viewpoint, it could be helpful to estimate the proportion of the ultrasonic power supplied to the reactor that is assumed to be devoted to chemical effect. So, calibration experiments were made without glass beads: the ultrasonic power and the triiodide formation rate were both measured for several electrical power inputs. The obtained data enables to link $r(I_3^-)_0$ and P_{US} for the different ultrasound frequencies **Fig.10**.

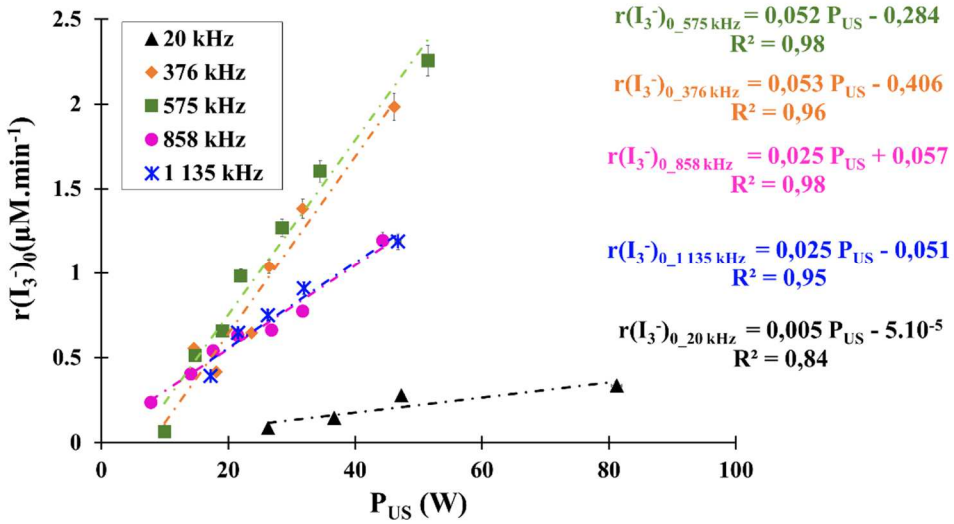

Fig. 10. I_3^- formation rate as a function of calorimetric ultrasonic power for the same electric power in homogeneous medium (0 g.L^{-1}, V = 500 mL, T = 20 ± 1 °C)

For all the frequencies, it can be noted the triiodine formation rate increases with the ultrasonic power once the cavitation threshold is overpassed [50]. Above this threshold, the observed increase of the sonochemical activity can be attributed to the growing of acoustic bubbles population [51]. It was therefore assumed that without particles the ultrasonic power measured by calorimetry is partly turned into sonochemical activity due to the relationship between these both ~~parameters~~ variables as suggested by results in **Fig. 10**. Then the linear approximations of these curves were used as calibration curves (**Fig. 11**) to estimate the proportion of the equivalent ultrasonic power devoted to chemical activity under heterogeneous conditions, denoted $P_{US\text{-}chemical}$. Even if such an assessment tool may be ~~criticisable~~ questionable, it can be regarded as a useful tool for preliminary diagnosis tests for ultrasonic reactors performances.

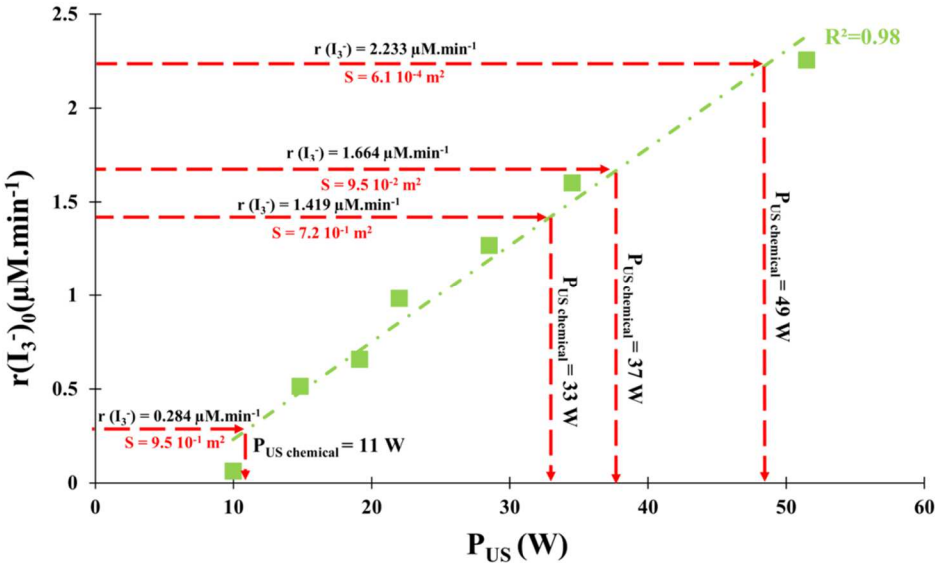

Fig. 11. Instance of calibration (f = 575 kHz, 0 g.L^{-1}, V = 500 mL, T = 20 ± 1 °C) to estimate the equivalent ultrasonic power devoted to chemical activity under heterogeneous conditions.

This procedure was then extended to all our experimental results under heterogeneous conditions. It was thereby possible to estimate a power fraction defined as the equivalent

ultrasonic power devoted to cavitation ~~sonochemical activity~~ divided by the total ultrasonic power estimated by calorimetry. This methodology leads to curves given in **Fig. 12** where the power fraction is given as a function of the ~~developed~~ surface area by solid particles within the reactor.

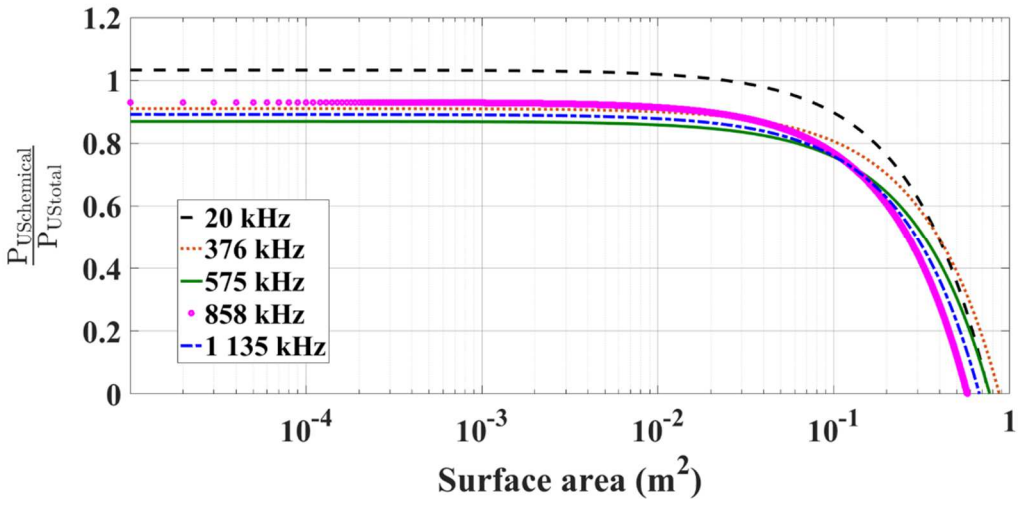

Fig. 12. Dependence of the ultrasonic power devoted to the sonochemical activity on the ~~developed~~ surface area.

Finally, as exhibited in **Fig. 12**, the power fraction remains constant at first, but decreases sharply after a critical ~~developed~~ surface area. Therefore, the ultrasonic power distribution changes: mainly devoted to sonochemistry for low ~~developed~~ surface areas (below 10^{-2} m^2) it is dissipated into mechanical effects for higher areas. So, using this type of diagram can be helpful to determine the predominant effect of ultrasound in an heterogeneous medium simulated by glass beads and thereby to determine the efficiency of our sonochemical reactor.

3.4 Acoustic radiation power

In order to estimate directly the sonochemical activity from physical tests, special attention has been given to the radiation power, because the calorimetric ultrasonic power seems not to be adapted for the entire range of studied ~~developed~~ surface areas (sections 3.1 and 3.2).

At 575 kHz, acoustic radiation power and calorimetric power were compared for homogeneous medium. The obtained values (P_{US} = 51.5 ± 0.5 W and $P_{US\text{-}rad}$ = 51.0 ± 1.0 W) proves our analytical method is efficient. Then the acoustic radiation power was measured at 575 kHz in the presence of 8-12 µm glass beads, at different concentrations, for the same calorimetric power (P_{US} = 51.5 ± 0.5 W). Normalized results of triiodine formation rate, calorimetric power and radiation power were compared (**Fig. 13**).

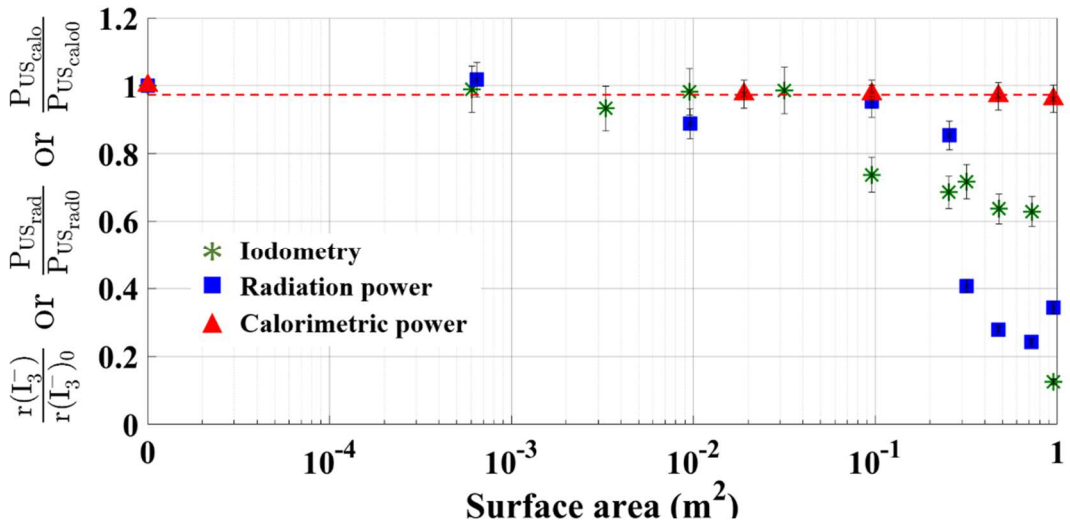

Fig. 13. Comparison of triiodine formation rate, calorimetric power and radiation power in heterogeneous medium (d_p = 8-12 µm, f = 575 kHz, V = 500 mL, T = 20 ± 1 °C)

The calorimetric power remains constant as mentioned previously (section 3.1), but the acoustic radiation power appears to follow the same trend as the sonochemical activity measured via the triiodine formation rate. At low ~~developed~~ surface area, the radiation power remains constant (ratio close to 1), so the presence of particles does not perturb ultrasound waves propagation. Nevertheless, above a critical value of ~~developed~~ surface area (around 10^{-1} m^2), radiation power decreases drastically. This is due to wave-matter interactions, mainly scattering and attenuation, induced by glass beads [44-45, 52]. Hence glass beads, whose acoustic impedance is different than water acoustic impedance, disturb wave propagation towards the target. As a conclusion, at the studied frequency, contrary to the calorimetric power, the acoustic radiation power is a relevant parameter to describe the influence of solids on sonochemical activity.

4. Conclusions

The aim of this paper was ~~to acquire a better knowledge on~~ to study the sonochemical activity in heterogeneous medium, ~~according to the~~ varying concentration (0-80 $g.L^{-1}$) and diameter (8-12 to 6000 µm) of chemically inert glass beads. A wide range of ultrasonic frequency (20 to 1135 kHz) was used. The ultrasonic power was measured by calorimetry or by radiation, and the sonochemical activity was monitored by iodide oxidation ~~following the formation rate of triiodide~~.

Whatever the concentration and diameter of glass beads are, the ultrasonic power measured by calorimetry was not affected by ~~particles~~ glass beads addition~~, even when the power supply was reduced~~. ~~One might here consider that such a result could be expected since the ultrasonic power measured by calorimetry only gives general information on the overall energy available in the system without any distinction on its nature. However, the results from the chemical characterization have shown dependence between the area of the surface developed by the particles and the chemical activity of ultrasound.~~ On the contrary, the chemical characterization has shown dependence between the surface area of ~~the surface developed by~~

the particles and the chemical activity of ultrasound. Indeed, the sonochemical activity remains constant below a surface area threshold ~~critical area value~~ and it sharply decreases above it. In our case, it seems the addition of particles did not increase bubbles population by playing the role of nucleation sites. Above the critical surface area, the activity decrease is due to wave scattering and attenuation on the one hand, and bubble stabilization on the other hand, which reduced the energy release.

Glass beads addition has the same effect on the sonochemical activity and on the acoustic radiation power, while the measured calorimetry is unchanged. As a consequence, the acoustic radiation power is a relevant parameter to describe the influence of solids on sonochemical activity.

The criterion suggested by our results is the surface area ~~developed by~~ of the particles within the reactor, whose advantage is to take into account both size and concentration of the heterogeneous media. Once a threshold of the ~~developed~~ surface area is overpassed, a switch in the proportion of mechanical and chemical energy leads to a decrease of the sonochemical activity.

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