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Identification of active sonochemical zones in a triple frequency ultrasonic reactor via physical and chemical characterization techniques



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ABSTRACT

Coupling multiple frequencies in ultrasonic systems is one of the highly desired area of research for sonochemists, as it is known for producing synergistic effects on various ultrasonic reactions. In this study, the characteristics of a hexagonal-shaped triple frequency ultrasonic reactor with the combination frequencies of 28, 40 and 70 kHz were studied. The results showed that uniform temperature increment was achieved throughout the reactor at all frequency combinations. On the other hand, sonochemiluminescence emission and degradation rate of Rhodamine B varies throughout different areas of the reactor, indicating the presence of acoustic 'hot spots' at certain areas of the reactor. Also, coupling dual and triple frequencies showed a decrease in the hydroxyl radical ($\cdot\text{OH}$) production, suggesting probable wave cancelling effect in the system. The results can therefore be served as a guide to optimize the usage of a triple frequency ultrasonic reactor for future applications.

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1. Introduction

Power ultrasound is widely used in different applications, such as cleaning [1], enhanced chemical reactions [2], wastewater treatment [3] etc. Over the past few decades, the use of ultrasound has become more established on the laboratory scale. Many researchers have produced reliable results upon using power ultrasound in various applications. However, due to the unique nature of ultrasonic wave, specific optimized ultrasonic setting is required for each unique application. In the field of removal of dye effluent, different ultrasonic settings were required for different dye removal. For example, Siddique et al. [4] have reported that the optimum ultrasonic frequency to remove reactive blue 19 dye was 80 kHz while Kobayashi et al. [5] have shown that sonication at 127 kHz and 490 kHz were able to remove methylene blue dye more effectively. In the field of sonochemical synthesis, it was reported that the effectiveness in synthesizing iron oxide nanoparticles loaded with folate and cisplatin increases with an increase in the ultrasonic frequency, under the same acoustic power [6]. On the other hand, Naddeo et al. [7] have reported that using a lower frequency ultrasound of 35 kHz slowed down the fouling formation in an ultrafiltration system, but higher frequency of 130 kHz favoured the removal of organic matter.

The unique optimized operating conditions of ultrasonic systems have gathered the attention of various researchers to combine different ultrasonic frequencies to enhance the efficiencies of their applications. In recent years, there has been an emerging trend of combining two frequencies for a particular sonication. Research has shown that coupling two different frequencies produced synergistic effects in an ultrasonic process, hence improving the overall efficiency of the process. For example, Koufaki et al. [8] coupled 20 kHz and 40 kHz ultrasound in synthesizing 3,5-disubstituted isoxazoles which resulted in a significant reduction in the reaction time. Sivakumar et al. [9] have reported the observation of synergistic effects upon combining 25 kHz and 40 kHz of sonication for the degradation of *p*-nitrophenol whilst Ninomiya et al. [10] have reported enhanced hydroxyl ($\cdot\text{OH}$) radical generation upon coupling 0.5 and 1.0 MHz ultrasound. On the other hand, Yasuda et al. [11] performed an extensive study on coupling different dual frequency modes ranging from 176 to 635 kHz and found that coupling similar frequencies resulted in better synergistic effects.

Further to the improvements of using dual frequency ultrasound, there have also been several reports on the use of triple frequency ultrasonic systems. Some researchers have reported an enhancement upon coupling three frequencies in their system. For example, Feng et al. [12] showed that combining 28, 1000 and 1870 kHz ultrasound produced 1.3–2.0 times more yield than the summation of individual frequency settings, whilst Zhao et al.

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[13] reported an enhancement in the degradation of nitrobenzene upon sonication with the frequency combinations of 20, 28 and 40 kHz. However, not all frequency combinations resulted in the enhancement. For example, Gogate et al. [14] combined 20, 30 and 50 kHz ultrasound and did not observe any synergistic effects on the destruction of Rhodamine B, even though the oxidation of potassium iodide showed significant synergistic effects.

Previous work performed by Manickam et al. [15] on the removal of chemical oxygen demand (COD) of palm oil mill effluent (POME) showed successful enhancement upon combining 28, 40 and 70 kHz ultrasonic irradiation, with the aid of H_2O_2 addition, in a triple frequency ultrasonic reactor (TFUR). In the work, it was also reported that the COD pattern fluctuated across the duration of the experiment for different frequency combinations, in the absence of H_2O_2 , suggesting that there may be some external factors causing the inhibition of COD removal. The inconsistencies in the experimental outcome for triple frequency ultrasonic systems bring the need for further investigation. Hence, in this investigation, a series of physical and chemical characterization is carried out at specific areas across the TFUR to have a clear understanding on the performance of ultrasonic reactor.

2. Materials and methodologies

2.1. Materials

The hydrogen peroxide (H_2O_2 , 30 w/v%) and sodium hydroxide (NaOH) pellets were obtained from R&M Chemicals, Malaysia. Luminol (3-aminophthalhydrazide) was obtained from Friedemann Schmidt Chemicals whilst the ethylene diamine tetraacetic acid (EDTA) and Rhodamine B powder were obtained from Sigma–Aldrich, Malaysia. All chemicals were used as-received without further purification.

The 16.5 L pilot-scale triple frequency ultrasonic reactor (TFUR, Sonictron, Malaysia) is a hexagonal shaped reactor (Fig. 1) that operates at 28 kHz, 40 kHz and 70 kHz. Each frequency mode has a maximum input power of 300 W. The TFUR can operate at seven different frequency modes of 28 kHz, 40 kHz, 70 kHz, 28 + 40 kHz, 28 + 70 kHz, 40 + 70 kHz and 28 + 40 + 70 kHz respectively. The vibrating plate on each transducer is a very thin plate of ca.

2 mm thickness. Six single open-ended glass cylinders (internal diameter: 46.4 mm, outer diameter: 50 mm, length: 450 mm) purchased from Donewell Engineering & Services, Selangor, Malaysia, were used in the experiments and were placed at specific positions of the TFUR as shown in the schematic diagram in Fig. 1. All experiments were performed under a constant temperature of 25 ± 1 °C using the existing cooling coil system from the TFUR, unless stated otherwise.

2.2. Methodologies

2.2.1. Calorimetry

14 L of air saturated deionized water was placed into the TFUR, followed by 350 mL of deionized water into each of the six glass cylinders. The TFUR was sonicated at all seven different frequency modes for an hour each, without temperature regulation. Temperatures at all the six positions in the glass cylinders were recorded at 30 s intervals. The power output of the system, Q was calculated based on Eq. (1).

$$Q = \frac{mC_p\Delta T}{\Delta t} \quad (1)$$

where m is the total mass of water, C_p is the specific heat capacity of water ($4.18 \text{ kJ kg}^{-1}\text{°C}^{-1}$), ΔT is the temperature change (°C) and Δt is the time difference (s). The heat loss of the system was obtained by finding the temperature profile from heating the TFUR with the same volume of deionized water as the sonicated system with a 1000 W (Q_H) electrical heater for 15 min. The heat loss, Q_{HL} , can be calculated based on Eq. (2).

$$Q_{HL} = Q_H - \frac{mC_p\Delta T}{\Delta t} \quad (2)$$

The intensity of the ultrasonic system, I , can then be computed using Eq. (3).

$$I = \frac{Q + Q_{HL}}{A} \quad (3)$$

where $Q + Q_{HL}$ is the output power, P_{out} , and A is the cross-sectional area of the transducer, which are 0.083 m^2 , 0.1652 m^2 and 0.3304 m^2 for single, dual and triple frequency modes respectively.

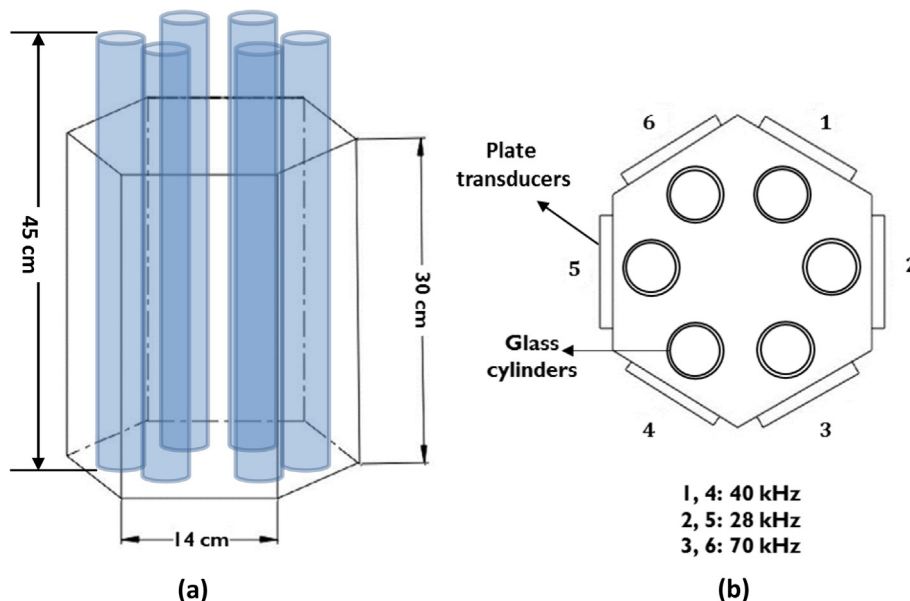


Fig. 1. Schematic diagram of the triple frequency ultrasonic reactor. (a) Side view of the hexagonal shaped reactor with 6 glass cylinders placed in the reactor; (b) top view of the reactor showing the sides of the reactor with different frequency emissions and the positions of glass cylinders and the piezoelectric ultrasonic transducers.

2.2.2. Luminol photography

Luminol photography was performed to map the areas of cavitation activities *via* analyzing the intensities from the sonochemiluminescence (SCL) produced. Luminol solution was prepared using 1 mM luminol, 0.1 mM EDTA and 0.1 mM H₂O₂ and adjusted to pH 12 using NaOH. In the first stage, the TFUR was filled with 16.5 L of luminol solution, in the absence of glass cylinders. The SCL images were captured from the top of the reactor using a digital single lens reflex camera (dSLR, Nikon D5100) mounted with a Nikon macro lens, using ISO setting of 6400, 18 mm focal length, aperture of F3.5 and exposure time of 30 s in a pitch dark environment. The temperature of TFUR was regulated at 25 °C using the cooling system of the reactor. A dark frame image was taken prior to each run, under similar operating conditions, in the absence of sonication. The intensity of SCL emission was calculated after subtracting the dark frame image using an image analysis software, ImageJ [16].

In the second stage, six glass cylinders were placed (Fig. 1), and were filled with 350 mL of luminol solution. The TFUR was pre-filled with 14 L of deionized water. SCL images were captured and the results were analyzed following the procedure as mentioned above.

2.2.3. Rhodamine B degradation

5 mg L⁻¹ of Rhodamine B (RhB) solution was prepared. The TFUR was pre-filled with 14 L of deionized water. 350 mL of RhB solution was poured into the six glass cylinders. 3 w/v% of H₂O₂ was added into the RhB solutions right before the start of the experiment. Sonication was performed at all the seven different frequency combination modes for an hour. Samples were taken every 10 min and the absorbance of RhB dye solution was analyzed using a UV–visible spectrophotometer (Varioskan Flash Multimode Reader, Thermo Fisher Scientific, USA) at 554 nm.

2.2.4. Statistical analysis

All the experiments were repeated three times, with the error bars showing the standard deviations of the repeated measurements. Statistical analyses were performed on all the experiments to assess their consistencies. One-way analysis of variance (ANOVA) was performed on all the comparable parameters at 95% confidence level to assess the significance among the readings obtained.

3. Results and discussion

3.1. Calorimetry

The overall temperature rise for each frequency mode of the TFUR at all the six positions in the glass cylinders is shown in Fig. 2. It could be seen that most of the temperature rise is almost similar at all the six positions of the TFUR, indicating that the sonicating system operates under uniform condition. The power dissipated into the system was calculated based on the average temperature gradient of all the six positions for a particular frequency setting.

The power dissipated due to heat loss, Q_{HL} , can be obtained based on Eq. (2), where $\frac{\Delta T}{\Delta t}$ is computed and is found to be 134 W.

Upon obtaining Q_{HL} of the system, the efficiency, η , of the TFUR for each setting is calculated using Eq. (4).

$$\eta = \frac{Q + Q_{HL}}{P_{in}} = \frac{P_{out}}{P_{in}} \times 100\% \quad (4)$$

where P_{in} is the power input to the system, which are 300 W, 600 W and 900 W for single, dual and triple frequency settings respectively, whereas P_{out} is the total power output.

Table 1 collates the overall power output and efficiencies of the TFUR at different frequency settings. From Table 1, it can be noted that the overall efficiencies of the system lie in the range of 62–95%, with 40 kHz mode being the least efficient in terms of power dissipation and 70 kHz mode as the most efficient setting.

3.2. Sonochemiluminescence from luminol photography

3.2.1. Sonochemiluminescence in the entire TFUR

Fig. 3 shows the SCL images from the top view of the TFUR upon sonication at different frequency modes. It can be noticed that the 'hot spots' for SCL varies significantly upon changing the frequency combinations. Further analyses were performed to identify the mean SCL emission from the images obtained, and the results in terms of SCL emission per unit power, have been represented in Fig. 4. Based on the results, coupling dual and triple frequencies did not show any enhancement in SCL emission. Contrarily, it had inhibited the production of SCL, which indicates a reduction in ·OH production under these frequency combinations. It can also be noted that there are specific 'hot spots' in the TFUR for a certain frequency combinations. For example, in the case of coupling of 28 kHz with other frequencies, the brightest SCL emission always occur at the sides of the reactor, as seen in Fig. 3(d) and (e). However, this is not the case for 40 kHz setting, where it shows the brightest SCL emission when it operates alone (Fig. 3(b)), but upon coupling with other frequencies, the SCL emission diminishes, as seen in Fig. 3(d) and (f).

3.2.2. Sonochemiluminescence in the glass cylinders

Suzuki et al. [17] have previously showed that the standing wave pattern of a dual frequency sonication system can be disturbed, which may result in a reduction in the sonochemical rates. Hence, in order to have a clearer sonochemical assessment on the TFUR, six glass cylinders were placed in the TFUR to further assess the sonochemical activities at these specific areas throughout the reactor. Fig. 5 collates the SCL emission of different frequency settings in the glass cylinders. The results are presented in terms of intensity of SCL emission per unit power output, P_{out} , of the TFUR, obtained from the results in calorimetry, which is termed sonochemical yield. Based on Fig. 4, it can be seen that single frequency settings generally produce higher yields as compared to coupling dual and triple frequencies.

The production of SCL is affected by the amount of ·OH radicals produced in the ultrasonic system. For the case of TFUR, it can be deduced that the ·OH radicals produced in dual and triple frequency modes were lesser as compared to the single frequency modes. This showed that coupling dual and triple frequencies of the TFUR led to adverse effects in terms of sonochemical yield. This may be due to a possible local heating when the system operates in dual and triple frequency modes, producing higher temperature at specific areas in the glass cylinders, resulting in a cushioning effect to the collapse of cavitation bubbles [18], hence producing lesser ·OH radicals in the system.

It is also worth noting that the total intensity of SCL emission vary significantly across different areas in the glass cylinders that were kept in the reactor (Fig. 6). This clearly shows that the sonochemical effects are focussed on selected areas across the reactor. Even in the absence of glass cylinders, the SCL results have shown that the sonochemical effects occur only at specific areas in the reactor (Fig. 3) and the presence of glass cylinders further enhances this SCL emission. The presence of glass cylinders, as shown in the setup in Fig. 1, diffracts the acoustic waves and leads to more focussed sonochemical 'hot spots'. One typical example of this could be seen from the sonication using 40 kHz (Fig. 5), whereby the glass cylinder at position 6 showed a significantly greater SCL emission as compared to all other areas throughout the reactor.

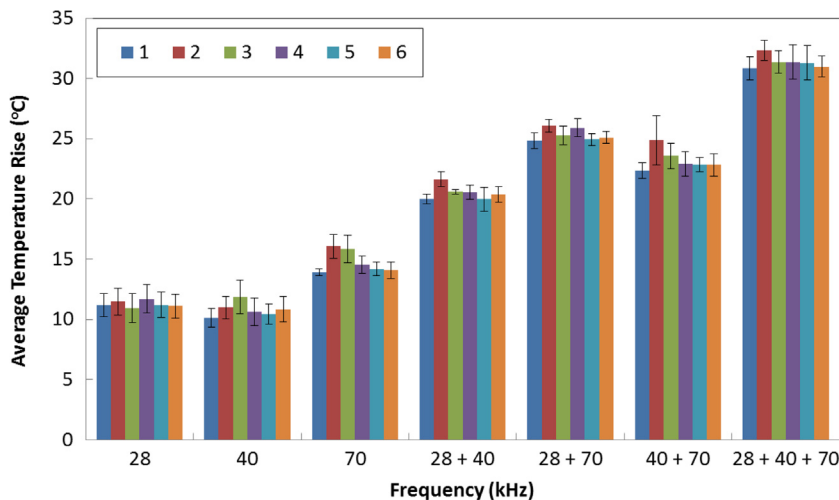


Fig. 2. Temperature rise across the six glass cylinders at different ultrasonic frequency setting upon sonication for an hour.

Table 1
Calorimetry results and the power efficiencies of different frequency modes.

Frequency mode (kHz)	Power output (P_{out} , W)	Emitting surface area (m^2)	Intensity ($W\ cm^{-2}$)	Efficiency (%)
28	220.4	0.083	0.267	73.5
40	203.2	0.083	0.246	62.7
70	284.2	0.083	0.344	94.7
28 + 40	403.7	0.165	0.244	67.3
28 + 70	529.5	0.165	0.321	88.3
40 + 70	446.8	0.165	0.283	77.8
28 + 40 + 70	657.3	0.248	0.265	73.0

But when the glass cylinders were absent, the above phenomenon could not be observed (Fig. 3). This shows that even though uniform temperature rise could be observed throughout the entire reactor, there are still some specific areas at which higher SCL emission could be observed, and one of the probable reason could be due to the shape of TFUR. Tiong et al. [19] have previously indicated that the shape of an ultrasonic system plays a vital role in the acoustic pressure fields produced. Hence, the presence of glass cylinders may have resulted into more focussed acoustic field and lead to non-uniform SCL emission in this TFUR.

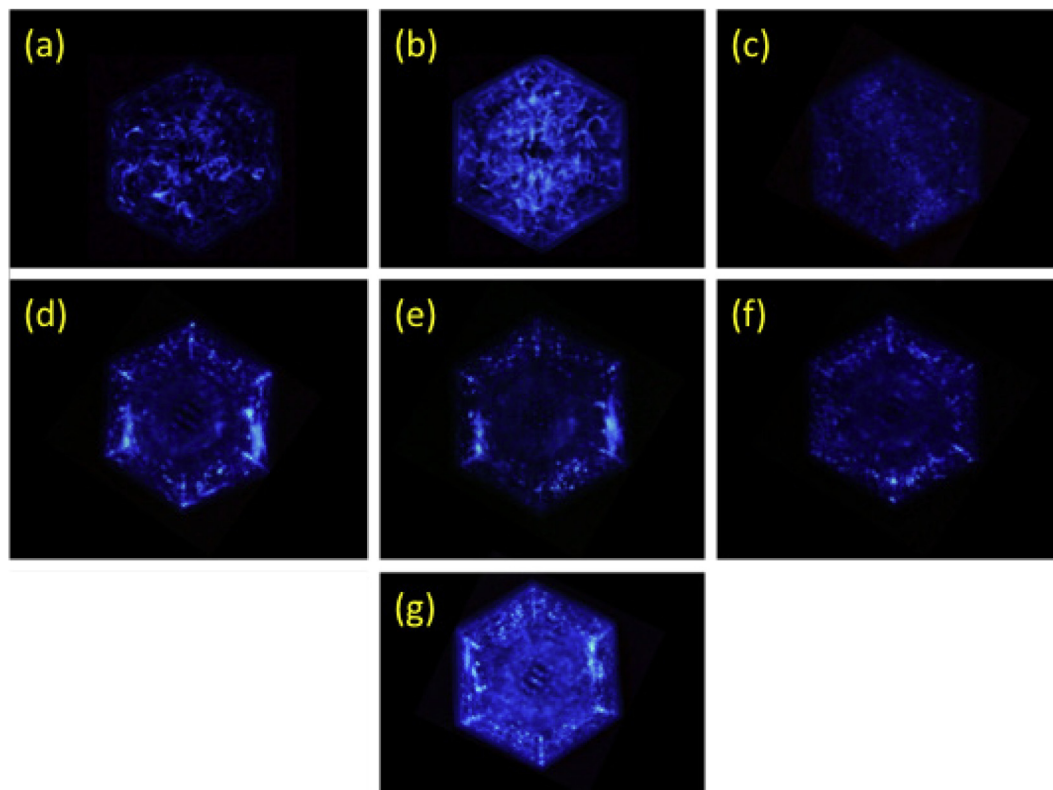


Fig. 3. Sonochemiluminescence images obtained using TFUR sonication under different frequency modes: (a) 28 kHz; (b) 40 kHz; (c) 70 kHz; (d) 28 + 40 kHz; (e) 28 + 70 kHz; (f) 40 + 70 kHz; and (g) 28 + 40 + 70 kHz.

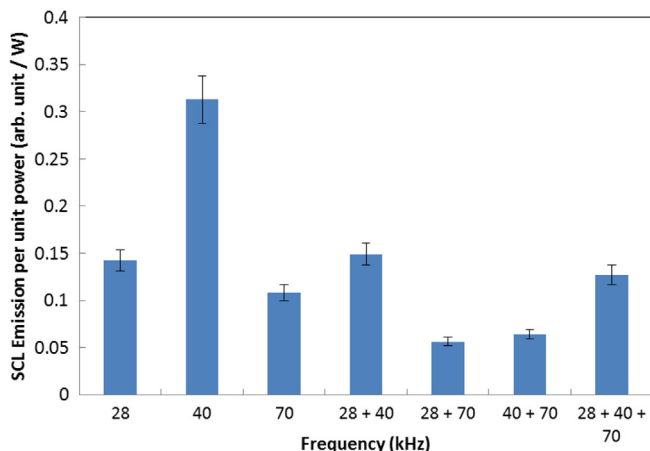


Fig. 4. SCL emission per unit power output throughout the entire TFUR upon sonication at different frequency modes.

3.3. Rhodamine B degradation

Rhodamine B is widely used in the field of sonochemistry [14,20–21]. Under ultrasonic conditions, the degradation of RhB could be accelerated, due to the formation of $\cdot\text{OH}$ radicals and shockwaves produced during the collapse of cavitation bubbles, aiding in the breakage of chromophores of the RhB structure [22]. In this investigation, the degradation of RhB in the presence of 3 w/v% H_2O_2 was studied. Fig. 7 shows the absorbance over time upon sonication at 28 + 40 kHz. Following the results obtained, the kinetics of degradation of RhB + H_2O_2 were plotted based on the first-order reaction, as shown in Eq. (5).

$$\ln \frac{[\text{RhB}]_t}{[\text{RhB}]_0} = -kt \quad (5)$$

where $[\text{RhB}]_t$ and $[\text{RhB}]_0$ are the concentrations of RhB dye at time, t and time zero respectively and k is the rate constant in min^{-1} .

From Fig. 8, it can be seen that the rate of degradation of RhB + H_2O_2 follows a *pseudo*-first order reaction, which agrees with the previous observations [23–25]. The sonochemical yield for the RhB + H_2O_2 degradation was calculated based on the first order rate constant, k , divided by power output. Fig. 9 collates the sono-

chemical yield upon sonication of RhB + H_2O_2 , under various frequency modes at all the six positions. Again, there is a general trend showing the percentage of dye degradation which differs significantly across the six glass cylinders. Comparing the overall results obtained from Fig. 9 on the degradation of RhB + H_2O_2 with the intensity of SCL emission in Fig. 5, it can be seen that certain cylinders tend to have higher SCL emission intensity, and subsequently showed higher degradation rates. For example, cylinders at positions 1 and 4 have much higher RhB degradation at frequencies 28, 28 + 40 and 28 + 70 kHz, and these were the positions that had also shown high SCL emission as well. However, there were some positions that did not show good correlation between SCL and RhB degradation, such as position 3 in 40 and 40 + 70 kHz configuration, where it showed high RhB + H_2O_2 degradation but significantly lesser in overall SCL emission at those areas. Nevertheless, these results have shown the general trend whereby positions with higher overall SCL emission intensities will have higher tendency to degrade RhB + H_2O_2 as they were at the ‘hot spots’, in terms of cavitation activity, for TFUR.

Similar to the SCL emissions, for the case of RhB degradation, single frequency settings (with the exception of 70 kHz) showed better performance in the dye degradation. Again, this may be attributed to the effect of local heating for both dual and triple frequency modes, which have resulted into less violent collapse of cavitation bubbles.

3.4. Further discussion

From the calorimetry results obtained, it can be seen that the variation in the temperature rise using different glass cylinders was not significant ($p < 0.05$), giving an indication that the TFUR operates at uniform temperature throughout all different areas. However, the results of SCL emission and RhB degradation showed that there are specific areas that produce higher sonochemical yield than others. The emission of SCL and degradation of RhB dye are greatly affected by the production of $\cdot\text{OH}$ radicals [14,20–22]. $\cdot\text{OH}$ radicals are produced upon the collapse of transient cavitation bubbles. Hence, for the case of the TFUR, there may be certain ‘dead spots’ around the reactor, resulting in the lowering of $\cdot\text{OH}$ radical yields in those specific areas.

Previous work on the TFUR has shown great improvements in the reduction of chemical oxygen demand (COD) on palm oil mill effluent (POME) upon sonication with triple frequency setting

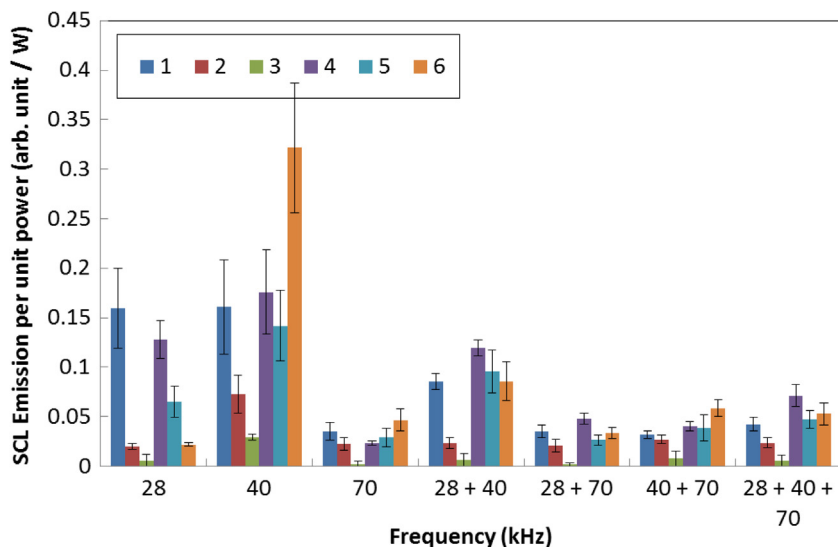


Fig. 5. Sonochemiluminescence emission per unit power output at six different positions in the TFUR upon sonication at different frequency settings.

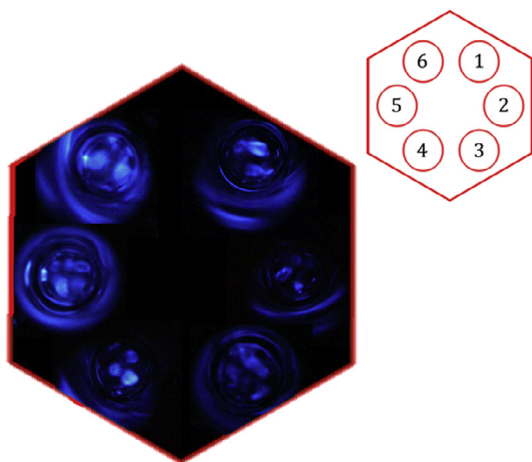


Fig. 6. SCL emission across the six glass cylinders upon sonication at 40 kHz, with red lines indicating the outline of the TFUR. Inset: positions of the six glass cylinders.

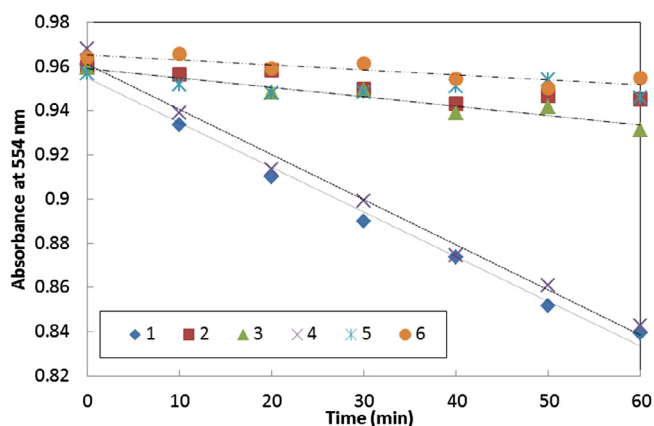


Fig. 7. Absorbance of Rhodamine B at 554 nm at six different positions upon sonication under the frequency combination of 28 + 40 kHz for an hour.

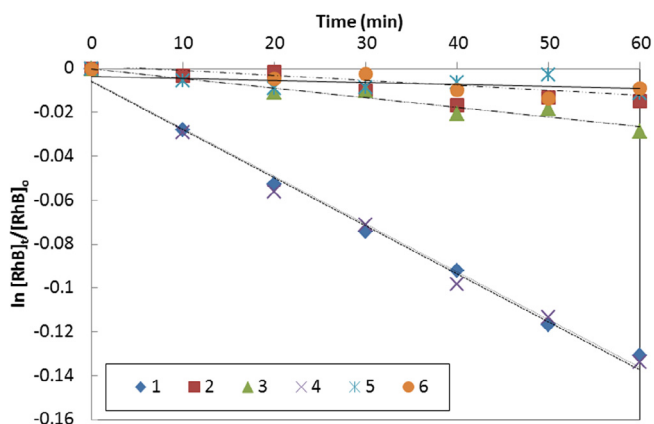


Fig. 8. Pseudo-first order plot for the degradation of Rhodamine B + H₂O₂ at six different positions upon sonication under the frequency combination of 28 + 40 kHz for an hour.

[10]. The authors have compared the effects of H₂O₂ to the reduction of POME upon sonication, and have attributed this to the aid of ·OH radicals in causing the reduction of COD in POME. In this study, however, the chemical reactions, in terms of ·OH radical production, did not show promising outcomes for dual and triple

frequency settings for both SCL emission and RhB degradation. This shows that there may be other factors contributing to the reduction of COD in POME, such as the physical effects of sonication (i.e. rise in temperature, acoustic streaming).

Another factor that may have contributed to the lack of chemical effects of coupling the frequencies could be the design of TFUR, where wave cancelling effect took place due to the hexagonal shape of the reactor, resulting in lowering of sonochemical yields. It may be noted that the shape of the TFUR plays a vital role in the sonochemical yield, hence care has to be taken on a proper design or rather the proper use of a multiple frequency ultrasonic reactor. To strengthen this argument, in a study performed by Lee and Oh [26], they have successfully shown that the position of an ultrasonic transducer plays a significant role in yielding synergistic or inhibition effect. In their case, coupling frequencies of 28 and 970 kHz positioned in opposite directions yielded more SCL emission whereas coupling 28 and 584 kHz transducers in both orthogonal and opposite directions showed inhibition in SCL emission. Hence, in this work, it could be that the position of the transducers and the shape of the reactor affecting the overall sonochemical yield.

Kanthale et al. [27] previously indicated that coupling dual frequencies in an ultrasonic system may lead to an increase in the maximum bubble collapse temperature, T_{max} , as compared to single frequency systems. A higher T_{max} in the system resulted from higher vapor entrapment within the bubble, forming larger bubble radius (R_{max}), thereby increasing the ratio of R_{max}/R_{min} , where R_{min} is the minimum bubble radius upon subjected to acoustic compression [27]. It was also noted by Kanthale et al. [27] that there was an increment in the sonoluminescence intensity at higher acoustic powers of single frequency systems, as compared to a dual frequency setting probably due to higher active cavitation bubble population when T_{max} is increased in the system, until a maximum R_{max}/R_{min} ratio of approximately 60 is reached, after which T_{max} decreased [27]. However, it was also noted by Ciuti et al. [28] that when the ultrasonic system operates using multiple frequencies, the total active bubble population increases which under high acoustic power may result into overpopulation of cavitation bubbles and hence into lower cavitation collapse intensity. This reported observation may be used to justify the phenomena found in our experimental data, where single frequency systems showed higher SCL emission and higher degradation rate of Rhodamine B, which may be due to less number of active cavitation bubble population as compared to multi-frequency systems.

Brothie et al. [29–31] have deduced that higher acoustic intensity in a multi-frequency ultrasonic system resulted into attenuation of sonoluminescence signal. They found that the synergistic effects were maximized in dual-frequency systems when the power was kept low approximately at 4–5 W, which based on their experimental setup turns out to emit acoustic intensities of approximately 0.5 W cm^{-2} [29]. Whereas, in the current study the power input was maintained at a constant value due to the limitations of experimental setup. The power used in the experiments range from ca. 220 to 660 W. Though it may seem that the higher power input may be the contributing factor to the attenuation of SCL emission, it has to be noted that the capacity of TFUR's is 16.5 L, and the overall acoustic intensity is at ca. $0.23\text{--}0.34 \text{ W cm}^{-2}$ (as shown in Table 1) which is still deemed to be well below the range of acoustic intensities required for the synergistic effects as reported by Brothie et al. [28]. Therefore, there may have been other contributing factors leading to the attenuation of SCL emission in this work.

It was previously reported by Gogate et al. [14] that combining three different frequencies has inhibited the degradation of RhB. They have deduced that the inhibition could be due to less violent collapse of cavitation upon combining the three frequencies

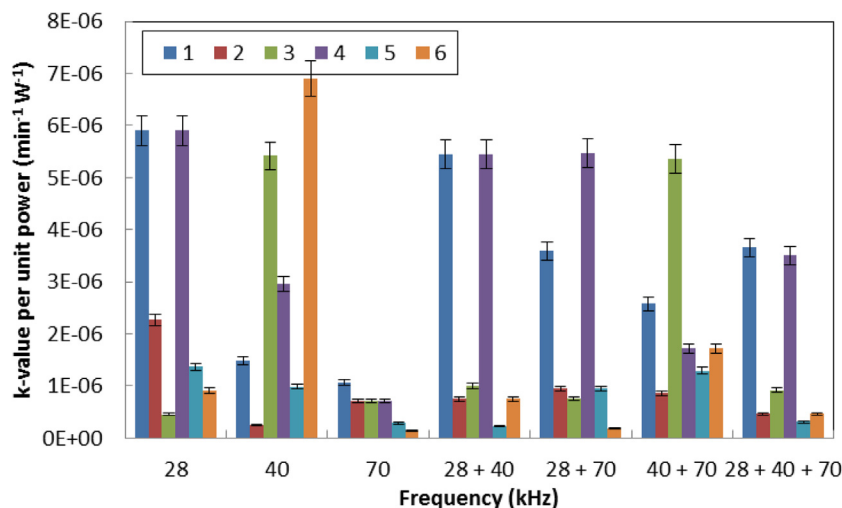


Fig. 9. Rhodamine B degradation in terms of sonochemical yield upon sonication for an hour under different frequency settings.

together, resulting in lower percentage degradation of RhB. In this investigation, three different frequency combinations were used, but the end result was similar as those reported by Gogate and co-workers [14]. Moreover, Suzuki and co-workers have also previously showed that the standing wave pattern of a dual frequency sonication system can be disturbed and resulted into a reduction in the sonochemical rates [17]. Both SCL and RhB showed lesser sonochemical effects upon combining dual or triple frequencies. These studies support that combining these frequencies may have resulted into wave cancelling effect, henceforth showing a higher reduction in the sonochemical yields.

In general, even though coupling dual and triple frequencies did not show desirable sonochemical yields, this work has successfully shown that there are specific 'hot spots' around the TFUR yielding much higher sonochemical yields compared to other areas. This is a phenomenon that is worth noting because, even though the temperature profile from calorimetry showed uniform increment across all six areas of the glass cylinders, they all still yielded different amount of $\cdot\text{OH}$ radicals significantly. It is of common knowledge that acoustic streaming creates a turbulent stirring effect on ultrasonic systems [32]. However, since this TFUR is on a relatively larger scale as compared to the normal laboratory scale ultrasonic systems, this may have resulted in a less turbulent stirring in the system, causing non-uniform sonochemical effects throughout the entire reactor.

4. Conclusions

This study enables to have a clearer understanding of the performance of TFUR. In general, calorimetry results have shown that the temperature rise was uniform across the entire TFUR, and the acoustic intensities ranged between 0.23 and 0.34 W cm^{-2} for all the frequency combinations, resulting in power efficiencies ranging from 62% to 95%. The SCL emission and RhB degradation, however, showed that there is a significant difference in the sonochemical yields across the six glass cylinders. Also, coupling dual and triple frequencies resulted into adverse effects in terms of sonochemical yields. This may be attributed to the design of TFUR, causing a wave cancelling effect upon coupling different frequencies. There were certain 'hot spots' that resulted into higher $\cdot\text{OH}$ radicals in terms of brighter SCL emissions and higher degradation of RhB. This showed that TFUR may not have undergone uniform mixing, resulting in higher sonochemical activities in certain areas. It may also be the shape of the TFUR causing some 'dead

spots' around the reactor. Investigations are underway to further rectify the actual cause of this and further optimization of this ultrasonic system is under exploration.

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References

- [1] K.S. Suslick, M.M. Fang, T. Hyeon, M.M. Mdleleni, Applications of sonochemistry to material synthesis, in: L.A. Crum, T.J. Mason, J.L. Reisse, K.S. Suslick (Eds.), *Sonochemistry and Sonoluminescence*, Kluwer Academic Publishers, 1999.
- [2] K.S. Suslick, *Sonochemistry*, Science 247 (1990) 1439–1445.
- [3] H. Destailats, M.R. Hoffmann, H.C. Wallace, Sonochemical degradation of pollutants, in: M.A. Tarr (Ed.), *Chemical Degradation Methods for Wastes and Pollutants: Environmental and Industrial Applications*, CRC Press, 2003.
- [4] M. Siddique, R. Farooq, Z.M. Khan, S.F. Shoukat, Enhanced decomposition of reactive blue 19 dye in ultrasound assisted electrochemical reactor, *Ultrason. Sonochem.* 18 (1) (2011) 190–196.
- [5] D. Kobayashi, C. Honma, A. Suzuki, T. Takahashi, H. Matsumoto, C. Kuroda, K. Otake, A. Shono, Comparison of ultrasonic degradation rates constants of methylene blue at 22.8 kHz, 127 kHz, and 490 kHz, *Ultrason. Sonochem.* 19 (4) (2012) 745–749.
- [6] R. Dolores, S. Raquel, G.-L. Adianez, Sonochemical synthesis of iron oxide nanoparticles loaded with folate and cisplatin: effect of ultrasonic frequency, *Ultrason. Sonochem.* 23 (2015) 391–398.
- [7] V. Naddeo, L. Borea, V. Belgiomo, Sonochemical control of fouling formation in membrane ultrafiltration of wastewater: effect of ultrasonic frequency, *J. Water Process Eng.* 8 (2015) e92–e97.
- [8] M. Koufaki, T. Fotopoulou, G.A. Heropoulos, Synergistic effect of dual-frequency ultrasound irradiation in the one-pot synthesis of 3,5-disubstituted isoxazoles, *Ultrason. Sonochem.* 21 (1) (2014) 35–39.
- [9] M. Sivakumar, P.A. Tataka, A.B. Pandit, Kinetics of p-nitrophenol degradation: effect of reaction conditions and cavitation parameters for a multiple frequency system, *Chem. Eng. J.* 85 (2002) 327–338.
- [10] K. Ninomiya, K. Noda, C. Ogino, S.-I. Kuroda, N. Shimizu, Enhanced OH radical generation by dual-frequency ultrasound with TiO_2 nanoparticles: its application to targeted sonodynamic therapy, *Ultrason. Sonochem.* 21 (1) (2014) 289–294.
- [11] K. Yasuda, T. Torii, K. Yasui, Y. Iida, T. Tuziuti, M. Nakamura, Y. Asakura, Enhancement of sonochemical reaction of terephthalate ion by superposition of ultrasonic fields of various frequencies, *Ultrason. Sonochem.* 14 (2007) 699–704.
- [12] R. Feng, Y. Zhao, C. Zhu, T.J. Mason, Enhancement of ultrasonic cavitation yield by multi-frequency sonication, *Ultrason. Sonochem.* 9 (5) (2002) 231–236.
- [13] L. Zhao, W. Ma, J. Ma, J. Yang, G. Wen, Z. Sun, Characteristics mechanism of ceramic honeycomb catalytic ozonation enhanced by ultrasound with triple

- frequencies for the degradation of nitrobenzene in aqueous solution, *Ultrason. Sonochem.* 21 (1) (2014) 104–112.
- [14] P.R. Gogate, M. Sivakumar, A.B. Pandit, Destruction of Rhodamine B using novel sonochemical reactor with capacity of 7.5 l, *Sep. Purif. Technol.* 34 (2004) 13–24.
- [15] S. Manickam, N.b. Zainal Abidin, S. Parthasarathy, I. Alzorqi, E.H. Ng, T.J. Tiong, R.L. Gomes, Role of H_2O_2 in the fluctuating patterns of COD (chemical oxygen demand) during the treatment of palm oil mill effluent (POME) using pilot scale triple frequency ultrasound cavitation reactor, *Ultrason. Sonochem.* 21 (4) (2014) 1519–1526.
- [16] M.D. Abamoff, P.J. Magelhaes, S.J. Ram, Image processing with Image, *J. Biophotonics* 11 (2004) 36–39.
- [17] T. Suzuki, K. Yasui, K. Yasuda, Y. Iida, T. Tuziuti, T. Torii, M. Nakamura, Effect of dual frequency on sonochemical reaction rates, *Res. Chem. Intermed.* 30 (7–8) (2004) 703–711.
- [18] D.M. Mattox, *Handbook of Physical Vapor Deposition (PVD) Processing*, Elsevier, United Kingdom, 2010.
- [19] T.J. Tiong, G.J. Price, S. Kanagasigam, A computational simulation study on the acoustic pressure generated by a dental endosonic file: effects of intensity, file shape and volume, *Ultrason. Sonochem.* 21 (5) (2014) 1858–1865.
- [20] T.J. Tiong, G.J. Price, Ultrasound promoted reaction of Rhodamine B with sodium hypochlorite using sonochemical and dental ultrasonic instruments, *Ultrason. Sonochem.* 19 (2012) 358–364.
- [21] S. Manickam, A.B. Pandit, Ultrasound enhanced degradation of Rhodamine B: optimization with power density, *Ultrason. Sonochem.* 8 (3) (2001) 233–240.
- [22] T.J. Tiong, L.E. Low, H.J. Teoh, J.-K. Chin, S. Manickam, Variation in performance at different positions of an ultrasonic VialTweeter—A study based on various physical and chemical activities, *Ultrason. Sonochem.* 27 (2015) 165–170.
- [23] M.-F. Hou, L. Liao, W.-D. Zhang, X.-Y. Tang, H.-F. Wan, G.-C. Yin, Degradation of rhodamine B by Fe(0)-based Fenton process with H_2O_2 , *Chemosphere* 83 (9) (2011) 1279–1283.
- [24] X. Wang, J. Wang, P. Guo, W. Guo, C. Wang, Degradation of rhodamine B in aqueous solution by using swirling jet-induced cavitation combined with H_2O_2 , *J. Hazard Mater.* 169 (1–3) (2009) 486–491.
- [25] N. Daneshvar, M.A. Behnajady, Khayyat Ali M. Mohammadi, M.S. Seyed Dorraji, UV/ H_2O_2 treatment of Rhodamine B in aqueous solution: Influence of operational parameters and kinetic modelling, *Desalination* 230 (1–3) (2008) 16–26.
- [26] M. Lee, J. Oh, Synergistic effect of hydrogen peroxide production and sonochemiluminescence under dual frequency ultrasound irradiation, *Ultrason. Sonochem.* 18 (3) (2011) 781–788.
- [27] P.M. Kanthale, A. Brotchie, M. Ashokkumar, F. Grieser, Experimental and theoretical investigations on sonoluminescence under dual frequency conditions, *Ultrason. Sonochem.* 15 (2008) 629–635.
- [28] P. Ciuti, N.V. Dezhkunov, A. Francescutto, F. Calligaris, F. Sturman, Study into mechanisms of the enhancement of multibubble sonoluminescence emission in interacting fields of different frequencies, *Ultrason. Sonochem.* 10 (6) (2003) 337–341.
- [29] A. Brotchie, M. Ashokkumar, F. Grieser, Effect of water-soluble solutes on sonoluminescence under dual-frequency sonication, *J. Phys. Chem. C* 111 (2007) 3066–3070.
- [30] A. Brotchie, F. Grieser, M. Ashokkumar, Sonochemistry and sonoluminescence under dual-frequency ultrasound irradiation in the presence of water-soluble solutes, *J. Phys. Chem. C* 112 (2008) 10247–10250.
- [31] A. Brotchie, R. Mettin, F. Grieser, M. Ashokkumar, Cavitation activation by dual-frequency ultrasound and shock waves, *Phys. Chem. Chem. Phys.* 11 (2009) 10029–10034.
- [32] S. Hyun, D.-R. Lee, B.-G. Loh, Investigation of convective heat transfer augmentation using acoustic streaming generated by ultrasonic vibrations, *Int. J. Heat Mass Transfer* 48 (2005) 703–718.