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Influence of sonochemical reactor diameter and liquid height on methyl orange degradation under 200 kHz indirect sonication

Kandasamy Thangavadivel [a,*], Kenji Okitsu [a,**], Gary Owens [b], Peter J. Lesniewski [c], Rokuro Nishimura [a]

[a] Graduate School of Engineering, Osaka Prefecture University, 1-1 Gakuen-cho, Naka-ku, Sakai, Osaka 599-8531, Japan
[b] Mawson Institute, University of South Australia, Mawson Lakes Campus, Mawson Lakes, SA 5095, Australia
[c] Applied Physics, School of EIE, University of South Australia, Mawson Lakes Campus, Mawson Lakes, SA 5095, Australia

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ABSTRACT

The relatively high sonochemical activity in the frequency range 200–600 kHz, makes these high frequencies attractive for contaminant remediation. However, high frequency ultrasound also suffers from higher acoustic energy attenuation and inherent low intensity which limits the volume coverage and hence practical application. In this study, in order to clearly understand the relationship between the sonochemical activity and acoustic energy attenuation, calorimetric and degradation studies using methyl orange (MO) as a contaminant surrogate were investigated with indirect sonication at 200 kHz (transducer diameter: 65 mm) with various cylindrical glass reactors of different diameter (20, 48, 65, 95 and 117 mm) and liquid height (21, 58, 81 and 118 mm). It was clear that both reactor diameter and liquid height significantly influenced degradation efficiency. In addition to the inherent acoustic pressure distribution within the reactor due to the transducer acoustic pressure profile, the diameter of the reactor affected mainly attenuation of ultrasound in the radial direction, while attenuation in the axial direction was principally influenced by reactor height. A 95 mm diameter reactor with a ratio (reactor diameter/transducer diameter) of 1.45, exhibited the highest sonochemical efficiency and acoustic energy transfer efficiency across a range of liquid heights.

Introduction

Ultrasound technology using acoustic cavitation is widely used in the food industry, municipal sludge treatment plants, cleaning applications across the commercial and industrial sectors, as well as in laboratories to perform degasification, mixing, extraction and sonochemical research [1]. Often persistent organic chemicals, such as DDT [1,1,1-trichloro-2,2-bis(p-chlorophenyl) ethane], PFOS [perfluorooctanesulfonic acid] and PFOA [perfluorooctanoic acid] cannot currently be economically remediated using existing remediation technologies and high cost incineration is usually the only viable option [2]. However, if the incineration process is not controlled, this may also produce more hazardous products than the parent chemicals themselves. Ultrasound technology is an advanced oxidation technology which has shown potential for the remediation of persistent organic contaminants and will become a feasible alternative remediation technology in the near future [3]. While ultrasound technology can be used in isolation, it can also be combined with more traditional remediation technologies to enhance the overall remediation efficiency [4].

Acoustic energy, applied either directly or indirectly via a transducer into the sonochemical reactor, effectively produces acoustic cavitation and generates hydroxyl free radicals for the degradation of contaminants [1,5,6]. However, in order to enhance the overall performance, it is of paramount importance to transfer the maximum amount of acoustic energy to the reaction medium [3,7]. In the case of direct application of acoustic energy, non-uniform energy distribution within the reactor is the major limiting factor together with energy loss within the reactor and at the reactor boundary [8,9]. For indirect application of acoustic energy, in addition to the uniform distribution of ultrasonic energy within the reactor, efficient energy transfer from the transducer to the reacting medium via a water bath and the reactor wall are both important [3,10]. In all cases, energy transfer from the transducer to the reactor medium has to be maximised. The most common obstacle to be overcome in transference of available energy to the bath is the impedance mismatch between the solid head of the transducer and the liquid medium of much lower acoustic impedance. Many factors play a role here, including reactor material, thickness, geometry, transducer(s) position(s) within the reactor, frequency modulation of the transducer, liquid height, mode of ultrasound application (direct or indirect), operating

* Corresponding author. Tel.: +81 90 65556933.
** Corresponding author.
E-mail addresses: thangavadivel@yahoo.com (K. Thangavadivel), okitsu@mtr.osakafu-u.ac.jp (K. Okitsu).

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temperature and chemical and physical properties of the contaminants; all of which potentially influence efficient acoustic energy distribution within the reactor [11,12].

Acoustic intensity and sonochemical efficiency of model contaminants are widely used to assess the performance of sonochemical reactors [13]. Usually, chemical dosimetry, such as the Fricke or Weissler reactions, standard dye decompositions, and sonoluminesence measurements are used for quantifying radical production [14]. Cavities that reach a critical size will implode and release energy, where the amount of energy released at any point is related to the local cavitation intensity. Where the local acoustic pressure is highest, more violent and frequent collapse of the bubbles occur. Thus cavitation intensity is a measure of the intensity and frequency of bubble collapse which directly results in local acoustic pressure that can be measured calorimetrically.

Extensive modelling and simulation of sonochemical reactors have also been reported, but are mainly limited to low frequency systems because of the very fine mesh requirements at shorter wavelengths, where modelling of high frequencies results in excessively large mesh numbers and consequential long simulation times [15]. Furthermore, at high frequencies the volume coverage of the reactor is limited due to high attenuation of the ultrasonic wave within the reactor requiring relatively high intensities near the transducer housing to be effective [16,17].

Most laboratory batch reactors have volumes less than 500 mL and one can safely assume that the cavitation threshold is exceeded throughout the reactor under laboratory experimental conditions [19]. In order to scale up the sonochemical process, the use of larger batch reactors with sizes up to 250 L has recently been reported [3]. Current laboratory data on remediation of contaminants using high frequency ultrasound (200–600 kHz), while promising in terms of kinetic parameters, often lacks information on acoustic energy consumption which is essential for inter laboratory comparisons and scaling up the process [2,10]. A number of studies [3,6,9,18,20,21] interested in the optimisation of reactor diameter and liquid height for various reactors found that mechanical agitation minimised the standing wave effect up to a specific mixing speed.

Indirect sonication is typically applied in laboratory sonochemical reactors using a water bath submerged transducer where the reactor diameter and height vary considerably [4]. Thus to obtain optimal reactor performance, studies of reaction efficiency with different reactor diameter and liquid height are important, especially at higher frequencies where acoustic energy attenuation is very high. The aspect ratios (reactor diameter/transducer diameter, liquid height/reactor diameter) are vital in terms of optimum performance of the laboratory reactor and also scale up of the sonochemical reactor in large scale application. In this study, we evaluated the performance of sonochemical reactors of various diameters and with varying liquid height both by using the calorimetric method as well as by measuring methyl orange (MO) degradation at pH 2 under atmospheric conditions.

Materials and methods

Chemicals

Analytical grade MO and 98% sulphuric acid were both procured from Wako Pure Chemical Industries Ltd., Japan. Milli-Q water, with a resistivity of 18.2 MΩ cm, was used to prepare all stock solutions and perform the calorimetric study.

Ultrasonic equipment

The experimental apparatus used in this study has been previously fully described [21]. The ultrasound source of a 65 mm diameter transducer (KAIJO 4611 MFG. No. 00102) had a frequency of 200 kHz and a nominal power of 200 W (KAIJO Model 4021, Lot. No. 11EA00105). The water bath (40 cm × 40 cm × 20 cm) was maintained at 20 ± 1 °C using TAITEC's cool pump (Model CP-150R). Ultrasound was applied indirectly to glass reactors of various diameters (20, 48, 65, 95 and 117 mm) (Figs. S1 & S2, Table S1; Supplementary information) with liquid heights of 21, 58, 81 and 118 mm which corresponded to 2.75, 7.75, 10.75 and 15.75 λ, respectively. A liquid height of 118 mm (abbreviated as H118) was not physically achievable in the 117 mm diameter reactor (abbreviated as D117). During sonication the reactor was maintained at either 4 mm (for D20, D48 and D65) or 8 mm (for D95 and D117) above the transducer. The transducer and the 1 mm thick Pyrex glass bottom plate of the reactor were positioned parallel to each other throughout the experiment. The liquid height was the vertical distance between the bottom plate's top surface to free surface of water (water/air) in the reactor.

Calorimetric measurement

Each reactor was filled with Milli-Q water to the required level and allowed to stabilise to room temperature over 30 min in a water bath without temperature control. Ultrasound energy was then applied at full power and the temperature in the middle of the liquid column 10 mm away from the centre line of the reactor was continuously recorded using a thermo couple for 90 s with every 1 s data (date logger used). To ensure that the maximum amount of ultrasonic power was applied to the liquid in the reactor, the centre line of the transducer and the reactor were carefully vertically aligned with the reactor maintained at a fixed distance (4 or 8 mm) above the transducer throughout all experiments. This transducer and reactor arrangement was also used for MO degradation.

Calorimetric power (P_{cal}) was determined using Eq. (1) [22,23],

$$P_{cal} = M \times C_p \times \frac{dT}{dt} \quad (1)$$

where M is the mass of water in grams, C_p is the specific heat capacity of water = 4.19 J/g K and dT/dt is the initial rate of solution temperature increase.

Since P_{cal} is directly related to temperature change, and temperature increases with cavitation intensity, P_{cal} is a useful measure of cavitation intensity.

Calorimetric energy intensity (CEI), as defined by Eq. (2) [1,2,16], is a good indicator of overall energy distribution within the reactor,

$$\text{CEI} = \frac{P_{cal}}{\text{Reactor volume}} \quad (2)$$

where the reactor operating volume is in litres.

MO degradation

An aqueous solution of MO was transferred into the reactor to reach the required level, and the reactor was then positioned 4 mm (reactor D20, D48 and D65) or 8 mm (reactor D95 and D117), vertically above the transducer. After stabilising the reactor in the 20 °C water bath for at least 30 min, sonication was commenced at full power and aliquots of solution (2 mL) were periodically (at 0, 3, 5, 10, 15, 20, 25 min) taken using a stainless steel needle with polypropylene syringe for analysis. Since the 20 mm diameter reactor had a very low volume (4–23 mL), after analysis the sample was put back into the reactor and sonication continued. Under our experimental condition, HNO_2 and HNO_3 are both formed by sonication. To prevent the effect of such acids on the concentration measurement of MO, the pH of the solution was adjusted to pH 2 before sonication [24]. The absorbance of MO at 510 nm was used