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Ultrasound-assisted degradation of methyl orange in a micro reactor

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ABSTRACT

In this study, an aqueous solution containing methyl orange (MO) was indirectly sonicated in a polydimethylsiloxane/glass micro reactor using a 200 kHz transducer. A removal efficiency (RE) of about 9% was observed in 90 min when 5 mg L^{-1} MO solution was circulated at a flow rate of 0.76 mL min^{-1} at pH 2 and 20 °C. While a lower RE was observed with an increase in solution temperature, an increase in MO concentration, flow rate and acoustic power led to an increase in RE. The addition of 100 mg L^{-1} of CCl_4 increased RE by 4% under similar experimental conditions. The mechanism of MO degradation involved sonochemically generated oxidising radicals, which was confirmed by the formation of H_2O_2 during sonolysis of water and reduction in RE with the addition of a radical scavenger.

Introduction

Excellent physical and chemical effects of acoustic cavitation in an aqueous medium provide unique opportunity for ultrasound technology to be used in various fields [1]. Cleaning, food processing and activated sludge remediation industries greatly benefit from the physical effect of acoustic cavitation in an aqueous medium [1]. It is widely established that sonication at a higher frequency range from 200 to 600 kHz yields relatively higher amount of OH radicals during sonolysis of water [2]. However, compared to conventional advanced oxidation technologies, such as ozone and UV, overall effectiveness of ultrasound technology is much inferior [3]. Often ultrasound technology is being used along with other advanced oxidation technologies to synergistically enhance the efficiency because sonication provides excellent mixing effect apart from moderate OH radical contribution for oxidation processes [1,3].

With an increase in ultrasound frequency, the transducer element becomes thinner and often becomes more fragile and hence limits the use of higher acoustic energy [4]. Along with relatively longer treatment times (about 20–90 min) in batch and continuous processes [5], sensitivity to reactor volume variation [6] and environmental factors, such as temperature and pressure also hinder sonolysis to be a viable standalone advanced oxidation technology [7]. Higher axial and radial attenuation of acoustic energy within a reactor leads to existence of heterogeneous cavitation activity throughout the reactor and hence results in a lower overall cavitation yield [8,9].

In recent years, the use of micro reactors has increased rapidly in the chemical, medical, biotechnology and pharmaceutical industries [10]. Because of their smallest size, higher area to volume ratio, excellent heat and mass transfer, possibility of precious control of operating parameters such as temperature, pressure and excellent mixing, micro reactors give higher yields and selectivity of the reaction products [11]. It is relatively easy and economical to fabricate a micro reactor in a suitable material and hence no health and safety risk involved [11,12]. Existing technology ensures the higher reproducibility of micro reactor unit with great precision [11]. Very low capital, operation and maintenance cost compared to conventional reactors make the micro reactors as viable attractive option [11]. In general, these micro reactors have channels of few micrometre to few hundred micrometre width and height. It is reported that a micro reactor gives several order magnitude higher reaction rate compared to a normal conventional reactor and hence helps to intensify the process greatly [11].

By combining ultrasound with micro reactor technology, there is an excellent possibility to overcome the limitations of conventional ultrasound technology such as heterogeneity of cavitation activities, localised variation in temperature, pressure and acoustic power and attenuation of acoustic energy. This may

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eventually lead to the successful usage of chemical effect of ultrasound in practical reality as a standalone technology. In a micro reactor, the temperature homogeneity can be achieved quickly and this is a great advantage in the sonicated micro reactor, because it is generally difficult to control the solution temperature precisely in conventional sonochemical reactors. For example, Abulizi et al. reported about 12 °C increase in the solution temperature in 5 min sonication at 20 kHz even in a temperature controlled water bath at 25 °C [13]. Since the temperature change in the irradiated solution strongly affects the chemical effects of cavitation, the combined use of the micro reactor and ultrasound would have an advantage in the precise temperature control which should result in good reproducibility, efficiency and selectivity.

There are a few studies on combining ultrasound and micro reactors [11,14,15]. Acoustic cavitation is used to enhance mixing reactants in a micro reactor and hence the reaction rate [11]. A few studies have reported on the occurrence of cavitation within sonicated microreactors [11,16,17]. A sonicated micro reactor mainly uses surface wave to promote acoustic cavitation within micro channels [18–20]. The use of sonicated micro reactors for the degradation of organic contaminant in aqueous solutions has not been reported in the literature. In this study, we have investigated the degradation of methyl orange (MO), a model dye pollutant, under various operating conditions in an indirectly sonicated micro reactor under recycling condition.

Material and methods

Chemicals

MO ($C_{14}H_{14}N_3NaO_3S$), analytical grade sulfuric acid (H_2SO_4), carbon tetrachloride (CCl_4) and 1-hexanol [$CH_3(CH_2)_5OH$] were supplied by Wako Pure Chemical Industries Ltd, Japan. Milli-Q water with a resistivity of 18.2 MΩ centimetres was used to prepare all aqueous solutions as well as flushing the reactor and tubing. H_2SO_4 was used to adjust solution pH. CCl_4 was used to promote degradation with radical reactions and 1-hexanol was used as a radical scavenger.

Indirectly sonicated micro reactor

A schematic diagram of the micro reactor used in this study is shown in Fig. 1. The ultrasound source was a 65 mm diameter transducer (KAIJO 4611 MFG. No. 00102) which had a resonance frequency of 200 kHz that could be operated at a maximum power of 200 W (KAIJO Model 4021, Lot. No. 11EA00105). A water bath (26 cm × 36 cm × 12 cm), maintained at 20 ± 1 °C using TAITEC's cool pump (Model CP-150R), was used to house the micro reactor and the transducer. A micro reactor (model J2-1, Fluidware Technologies Inc., Japan; 4 micro channels with 100 μm height and 50 mm straight distance between inlet and outlet) was used throughout this study. As shown in Fig. 1, during operation, the bottom of the reactor plate was horizontally positioned 8 mm above the transducer, and the centre line of the transducer and reactor was aligned vertically to ensure maximum energy transfer to the micro reactor. As shown in Fig. 2, the micro reactor consisted of 4 channels on the surface of a 2 mm thick plate of polydimethylsiloxane (PDMS) and a 1 mm thick glass substrate was used to cover the channels. The PDMS and glass were glued together by epoxy. Silicone tubes were used to connect the channels to a pump (Model number of pump and micro controller were SDMP 306 and MPC-200A, respectively, Takasago Electric Inc.).

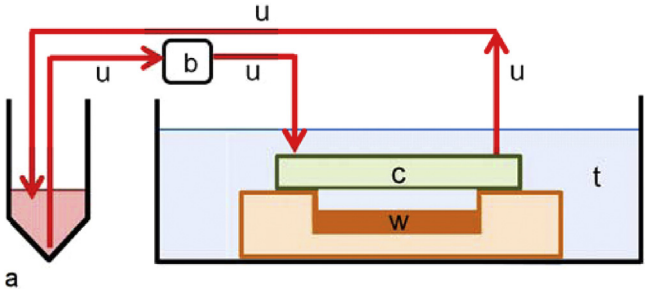
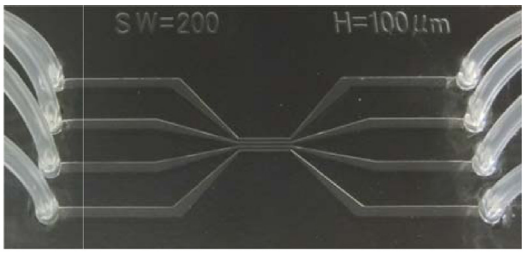
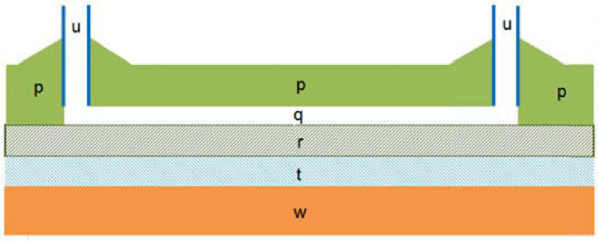


Fig. 1. Schematic diagram of MO recirculation system via indirectly sonicated 4 channels micro reactor in a constant temperature water bath. a – 15 mL glass tube, b – micro pump, c – micro reactor (1 mm thick glass substrate and 2 mm thick PDMS include 100 μm height micro channel), w – 200 kHz transducer, t – water bath, u – silicone rubber tube.



A: View of 4 channels micro reactor circuit.



B: Cross sectional side view of micro reactor and transducer

Fig. 2. Sketch of the indirectly sonicated micro reactor and transducer arrangement.
[p – PDMS (2 mm thick), q – micro channel (100 μm height), r – glass substrate (1 mm thick), u – silicone rubber tube, t – cooling water (coupling medium, 8 mm vertical distance between transducer and glass substrate), w – transducer]

Initially, based on the micro pump's operating specifications, a flow calibration curve was prepared for the whole operating range of the pump using Milli-Q water at 20 °C. The micropump performance was checked by recording a calibration curve between the voltage and real flow rate at constant frequency (40 Hz). The flow rates were confirmed by measuring the weight of pure water collected under different flow rates at the outlet of the micro reactor. Based on this data, we used 100, 150, 200 and 250 V to control the flow rates at 0.76, 1.32, 2.01 and 2.92 mL min^{-1}, respectively. To our knowledge, the PDMS/glass micro reactor with recycle mode was used for the first time in this study for organic pollutant degradation under indirect sonication.

MO degradation and H_2O_2 production

Based on the literature survey as well as our previous studies, 1, 5 and 10 mg L^{-1} MO concentrations were chosen [21]. These concentrations enabled us to achieve reasonable MO concentration reduction during 90 min treatment. A UV–vis spectrophotometer (Shimadzu UV-2550) with a 1 cm path length quartz cuvette was used to measure the MO concentration using its absorbance at 510 nm at pH 2.

A known concentration of a 3 mL MO solution (e.g., 5 mg L^{-1}) at pH 2 was placed in a glass tube. Then, by using the micropump, the