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The effects of externally applied pressure on the ultrasonic degradation of Rhodamine B

Make Geng, Selma Mededovic Thagard [*]

Department of Chemical and Biomolecular Engineering, Wallace H. Coulter School of Engineering, Clarkson University, Potsdam, NY 13699, USA

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ABSTRACT

The present manuscript compares the ultrasonic degradation of Rhodamine B dye under atmospheric (1 bar) and elevated pressures (1.6 and 2 bar). The degradation was studied as a function of the bulk liquid temperature and initial dye concentration at two different values of mechanical amplitudes (ultrasonic intensities). Results indicate that at the low amplitude an increase in the applied pressure increases the dye removal rate, whereas at the high amplitude, the same increase in the pressure has a minimal effect on the degradation of the dye. Furthermore, at low amplitudes an increase in the bulk liquid temperature from 5 to 35 °C increases the dye degradation by 10%. At higher intensities, the same increase in temperature has negative or no effect on the dye removal. An increase in the initial dye concentration by one order of magnitude significantly lowers the dye degradation rate regardless of the applied amplitude. Though these results are caused by numerous physical and chemical processes taking place during ultrasonic cavitation, the number of cavitation sites, bubble temperature and consequently, the amount of oxidative species inside the bubble seem to be the most important ones in determining the extent of the degradation of molecules in the bulk liquid.

1. Introduction

Due to dyeing of fabric, wastewater from many textile industries contains color and as such cannot be disposed into the environment. Traditional methods for dye removal include biological treatment [1], coagulation [2], filtration [3] and adsorption [4,5]; however, because of high dye concentrations and the increased stability of synthetic dyes, these methods are becoming less effective for the treatment of colored industry effluents [6,7]. To overcome the problems associated with these traditional methods of dye removal, attention has been focused on advanced oxidation processes (AOPs), technologies based on in situ formation of highly oxidative hydroxyl radicals ($OH^{\cdot}$). Although different AOPs can yield $OH^{\cdot}$ using different precursors (i.e. O_3/H_2O_2, UV/H_2O_2, electrical discharge, etc.) [8–10], ultrasound, for example, creates these radicals by the passage of sound waves through the liquid water and the subsequent dissociation of vaporized water molecules [11,12].

Specifically, when sound waves pass through a liquid, in each point of the liquid consecutive compression and rarefaction (expansion) cycles take place. Because the acoustic energy cannot be absorbed by molecules, during the rarefaction cycle of the sound wave, the liquid is pulled apart, which generates a void and induces cavitation-the formation of small gaseous (micro) bubbles [13]. The cavitation process is characterized by two stages: (1) rapid increase in the size of a microbubble and (2) fast bubble collapse and the formation of a “hot spot”, a high-temperature residual bubble. The implosive collapse of the bubble raises the local temperature to at least 5000 K and pressures up to 1200 bars [12,14]. Consequently, under these extreme conditions, vaporized molecules are dissociated into free radicals and rapidly cooled (>1000 K/s) [15].

In the absence of substrates in the bulk liquid these radicals recombine to form stable byproducts such as hydrogen and hydrogen peroxide. However when a molecule such as an organic dye is present in the bulk liquid, it reacts with the radicals thereby preventing their recombination [12]. In this study we chose to investigate the degradation of Rhodamine B (RB), using it as a representative constituent of the textile industry effluent. RB is a fluorescent dye of the Xanthene class that is widely employed as a colorant in the industry of fine chemicals [16,17]. Though ultrasound has been used for decades to degrade various organic molecules and dyes [18–23], studies demonstrating its effectiveness in the degradation of RB are scarce. With the exception of few, majority of studies investigated the RB degradation in the presence of a catalyst and focused on heterogeneous aspects of the degradation [24–27]. One of the first studies conducted on the degradation of RB using ultrasound was done by Sivakumar and Pandit [28] who studied the effects of the power density/intensity of different ultrasonic equipment on the extent of RB degradation. Several

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[*] Corresponding author. Address: Department of Chemical and Biomolecular Engineering, Clarkson University, 8 Clarkson Avenue, Potsdam, NY 13699, USA. Tel.: +1 315 268 4423; fax: +1 315 268 6654.

E-mail address: smededov@clarkson.edu (S.M. Thagard).

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years later, Behnajady et al. [7] investigated the effect of operational and solution parameters on the degradation of the same dye and found the power density to be the most important one.

The objective of this study was to investigate the effect of hydrostatic pressure on the extent of degradation of RB under different operating parameters, including initial concentration of the dye, power intensity, and bulk liquid temperature. Published studies on the effects of applied pressure on sonochemical reactions have been mainly investigated using volatile molecules and ions [29–34]. Other studies include the degradation of phenol [35], ultrasonic hydrogenation of soybean oil [36,37], decomposition of nitrous oxide [38], agglomeration of nanoparticles [39], and destruction of microorganisms [40,41] under increased pressure. Also, a significant amount of work has been performed on the effects of applied pressure on bubble sonoluminescence [31,42–44]. Thus, the results obtained by working with a non-volatile molecule such as RB could provide more insights into the complex nature of sonochemical reactions. Because the power required to induce cavitation decreases as the operational pressure increases, sonochemical reactions under increased pressure are also interesting from a practical application standpoint.

2. Experimental

2.1. Materials

Rhodamine B (RB, $C_{28}H_{31}N_2O_3$–Cl, CAS: 81-88-9) was purchased from Sigma–Aldrich and used as received. RB solutions were made from deionized water of conductivity <1 $\mu S\,cm^{-1}$.

2.2. Apparatus and procedure

Sonolyses were performed with an UIP1000hd sonicator (Hielscher Ultrasonic) operating at 20 kHz. The complete ultrasonic system consisted of an electrical generator and an ultrasonic transducer. The transfer of the oscillations from the transducer to the medium was achieved via a sonotrode whose mechanical amplitude was regulated via a rotary potentiometer between 50% and 100%. The 100% value corresponded to 150 μm amplitude. The sonotrode was immersed in a 300 mL stainless steel flow cell (Hielscher Ultrasonic) and operated in recirculation mode. Prior to sonication, 1 L of RB solution was recirculated through the reactor (Masterflex Precision pump) and was allowed to equilibrate at the set temperature. The temperature inside the reactor was maintained by flowing water around the reactor jacket using an external refrigerated circulator (Fischer Scientific 9500). The temperature of the RB solution was measured at the reactor exit. The pressure of the fluid inside the reactor was regulated and measured by an external valve and a pressure gage, respectively. All the sonication experiments were performed for one hour with RB samples taken at 10 min intervals. The absorbance of RB was monitored by an UV–VIS spectrophotometer (Shimadzu UV-1800) at 554 nm. The absorbance values were converted to the concentration values on the basis of Lambert–Beer's law. pH and conductivity of the RB solution were measured at the beginning and the end of every experiment. Power input from the sonicator into the reactor was measured with a PowerMeter (Hielscher Ultrasonic).

3. Results and discussion

Fig. 1 shows the correlation between the mechanical amplitude of the sonotrode and the resulting ultrasonic intensity at three different values of hydrostatic pressure. The ultrasonic intensity I is defined as the ratio between the power input to the sonicated medium and the transmitting area. It should be noted that the highest pressure value shown in Fig. 1 is 2 bar which corresponds to the highest value achievable by the pump used in the study. Clearly, for all three hydrostatic pressure values an increase in the mechanical amplitude leads to an increase in the sonication intensity. At low mechanical amplitudes most of the power is dissipated in the movement of the liquid without generating powerful cavitation events. This of course requires minimal power input. As the amplitude increases, cavitation gets more intense (the zone undergoing cavitation increases) and now the majority of sonication power is directed towards producing cavitation. However, as the value of the mechanical amplitude starts to increase further, the liquid cannot maintain contact with the vibrating surface and starts to decouple. At this point, the transfer of the sonication power into the bulk of the liquid can no longer be increased and instead additional power focuses on the liquid solid (sonontrode) interface. As a result, at higher values of amplitude, more power is required to maintain the cavitation events which results in an increase in the sonication intensity.

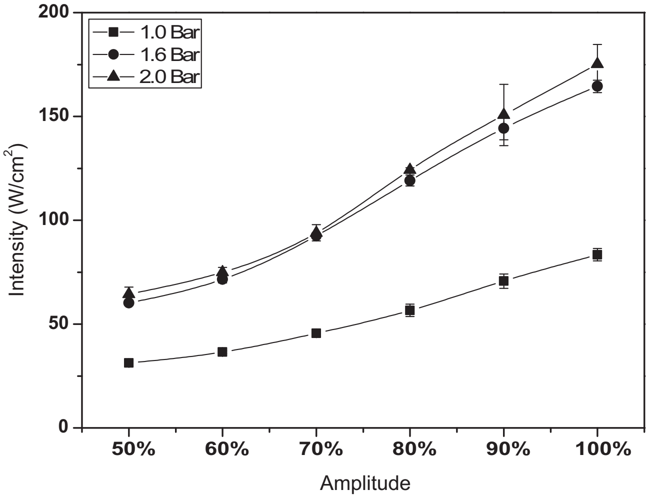

Fig. 1. Relationship between the ultrasonic intensity and the mechanical amplitude.

According to Fig. 1, an increase in hydrostatic pressure from 1 to 1.6 bar also results in a significant increase in sonication intensity. Contrarily, a further pressure increase from 1.6 to 2 bar has an almost negligible effect on the further increase in the intensity. Experimental studies suggest that an increase in externally applied pressure (hydrostatic pressure) results in fewer cavitation sites due to the increase in threshold for cavitation [11,31,45]. Thus, to ensure cavitation, the power, that is, the intensity of the sonication, must also be increased. Minute differences in the intensity observed between 1.6 and 2 bar could be caused either by too low a pressure incremement used in the experiments or by a cavitation threshold in which, after reaching a certain intensity value necessary to achieve cavitation, further increase in the applied pressure does not require more power (intensity). A similar explanation was given by Henglein and Gutierrez [31] while studying the oxidation of iodide by 1 MHz ultrasound. Due to the observation that the most pronounced differences in the ultrasonic intensity were achieved at 50% and 100% amplitudes, further results in this study compare the sonochemical effect at these two values.

3.1. Amplitude

Fig. 2(a) and (b) show the effect of hydrostatic pressure on the degradation of RB at two different amplitudes. As shown in Fig. 2(a), at 50% amplitude, an increase in hydrostatic pressure