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Intensification of cavitational activity in the sonochemical reactors using gaseous additives

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HIGHLIGHTS

- Evaluation of different gaseous additives for enhancing the cavitational effects.
- Optimum power dissipation, pH and temperature should be selected.
- Type of gas and its mechanism of intensification are important.
- Confirmation using simulations for volume fraction and pressure intensity.

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ABSTRACT

Sonochemical reactors have a significant potential for intensification of physical as well as chemical processes due to the effects of hotspots, intense turbulence and generation of free radicals. However, it is observed that commercial scale applications of these reactors are scarce possibly due to lack of uniform intensified activity at large scale and reliable design/operating strategies. The present work deals with investigations related to the intensification of cavitational activity based on the use of different gaseous additives with the results being equally applicable for all gas–liquid applications of sonochemical reactors. Model reactions of oxidation of potassium iodide and salicylic acid degradation have been used for quantification of cavitational activity. Initially, effect of different operating parameters such as temperature, power, duty cycle and initial concentration has been investigated. The different gaseous additives used in the work include air, oxygen, nitrogen and carbon dioxide. Effect of air flow rate on the cavitational activity has also been examined. Theoretical modeling studies based on the use of COMSOL have also been performed to explain the alteration of pressure field distributions due to the presence of gaseous additives. Overall it can be said that presence of gases enhances the cavitational activity and the effect is dependent on the nature of the gas and its physicochemical properties as well as the operating conditions in terms of the flow rate of the introduced gas. The work presents new design related information helpful for effective scale up and operation of sonochemical reactors.

1. Introduction

Very high energy densities can be produced over a small location using the cavitation phenomenon, which involves generation, growth and collapse of cavities in a liquid [1]. Ultrasound can be used to generate cavitational events and such reactors are typically described as sonochemical reactors. Ultrasound when transmitted through a liquid medium creates a time-varying pressure field which induces vibrational motion to the molecules leading to compression and stretching of the molecular structure. If the intensity of ultrasound in a liquid is increased continuously, at certain intensity, the intramolecular forces are not able to hold the molecular structure intact and cavitation nuclei are formed. The generated nuclei respond to the varying sound field in the liquid by expanding and contracting, i.e. it is excited by a time-varying pressure and undergoes the different stages of the cavitation phenomena finally collapsing and releasing large magnitude of energy due to the adiabatic collapse, which is suitable for significant intensification of many chemical and processing applications [2,3]. The physical effects of local turbulence and liquid microcirculation at very high velocities can intensify the processes limited by mass transfer including chemical reactions whereas the chemical effects such as the generation of hot spots (conditions of very high temperatures and pressures) and reactive free radicals, can intensify the chemical processing applications limited by intrinsic chemical kinetics [2]. In reality, the combination of the physical and chemical effects of cavitation leads to net intensification of the process.

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The factors causing hindrance to successful application of sonochemical reactors on an industrial scale are multifold [4]. Firstly, there is a lack of suitable large-scale design strategies. Also, intense cavitational activity occurs very close to the transducer which is the device used for generating ultrasound and the overall activity is much lower on a larger scales of operation thereby limiting the application. The intense activity near the transducer could prove detrimental to the functioning of transducer and lead to frequent erosion of the ultrasonic surfaces especially under conditions of higher power input. Also there is an uneven distribution of the cavitational activity and this problem is severe in the case of large scale reactors leading to much lower effectiveness for the desired application. One of the other important reasons for lack of successful application is the lower rates of processing at large scale applications, which can be overcome by the use of different additives as process intensifying parameters. The present work has been concentrated in evaluating the efficiency of different gaseous additives at laboratory scale operation, which is first such targeted effort to the best of our knowledge. Quantification of the cavitational activity has been made with the help of hydroxyl radical dosimeters.

Specific hydroxyl radical dosimeters are adequate methods to standardize the characterization of sonochemical reactors and also to compare the effectiveness of the different reactor configurations [5–9]. The numerical results of cavitational activity distributions can also be confirmed with the experimental results based on the dosimetry with an objective of establishing the important design related information for sonochemical reactor [8]. Monitoring the generation of OH radicals in sonochemical reactors is also essential to know the potential applicability as an advanced oxidation process. In cavitation processes, the hydroxyl radicals are generated inside the bubbles. Therefore, in order to react with the substances in the liquid phase the radicals have to diffuse through the gas–liquid interface and the liquid phase. Thus, dosimetry in cavitational reactors has to guarantee the accessibility of the substrate to the ·OH radicals. Taking into account the previous studies [6–8], the present study is focused on salicylic acid and iodide dosimetry as the method to estimate the ·OH radicals generation in the cavitation process. These approaches offer some advantages like easy quantification of hydroxylated products that are obtained exclusively due to the action of ·OH radicals and no intermediate products affect the results.

Different types of gaseous additives used in the present work include air, oxygen, nitrogen and carbon dioxide. The presence of gaseous additives can ease the process of cavity generation and intensify cavitational activity in the reactor. Some of the additives can also result in enhanced generation of free radicals or generation of additional oxidizing species in the system or alter the distribution of the reactants at the site of cavity collapse. The main objectives of the work were the quantification of cavitational activity using salicylic acid and potassium iodide dosimetry; understand the effect of presence of different gases on the degree of intensification experimentally supported with theoretical simulations and also investigate the effect of flow rate of air on the cavitational activity under the optimized conditions.

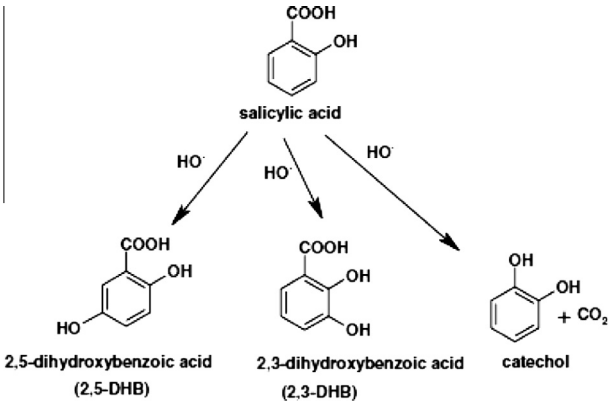
2. Materials and methods

2.1. Reaction scheme

Reactions considered for the quantification of cavitational activity are oxidation of potassium iodide and salicylic acid dosimetry. The reaction scheme for oxidation of potassium iodide can be shown as follows:

$$I^- + OH^\cdot \rightarrow OH^- + I^\cdot$$
$$I^\cdot + I^- \rightleftarrows I_2^{\cdot-}$$
$$2I_2^{\cdot-} \rightarrow I_2 + 2I^-$$
$$I_2 + I^- \rightleftarrows I_3^-$$

Similarly, reaction scheme for salicylic acid dosimetry can be shown as follows:



It can be seen that both the reactions are driven by hydroxyl radicals and hence are true indicator of the cavitational activity existing in the sonochemical reactors and can quantify the degree of intensification that can be achieved using gaseous additives.

2.2. Materials

Analytical Reagent (AR) grade potassium iodide (KI), salicylic acid (SA), sodium hydroxide and phosphoric acid were procured from S.D Fine Chem. Pvt. Ltd. Mumbai, India. Potassium iodide and salicylic acid were diluted to required concentrations using distilled water (freshly prepared in the laboratory using Millipore apparatus) for experimental studies. Compressor was used for introduction of air whereas the other gases viz. oxygen, nitrogen and carbon dioxide were introduced through cylinders obtained from Alchemie Gases Ltd. Mumbai. All the chemicals were used as received from the suppliers.

2.3. Analytical procedure

Analysis of iodine liberation due to the potassium iodide oxidation was performed using Thermo Scientific SPECTROSCAN UV 2600 spectrophotometer and analysis for the samples of salicylic acid dosimetry was performed using high pressure liquid chromatography (HPLC). Column used for the HPLC was C18 column having inner diameter of 4 mm and length as 25 cm. The mobile phase used was a mixture of phosphate buffer (pH = 2.5) and methanol (45:55%), isocratically delivered (constant composition and flow rate) by a pump at a flow rate of 1 ml/min. The wavelength set for UV detection was 291 nm.

2.4. Experimental set-up of ultrasonic horn

The ultrasonic horn equipped with a generator was procured from Dakshin India Ltd., Mumbai. The reactor operates at a frequency of 20 kHz and the maximum rated power output of the generator is 240 W. The tip diameter of the transducer was 2.1 cm with an active acoustical vibrational area as 3.46 cm^2. Experiments were conducted using 300 ml reaction solution of 100 ppm, 300 ppm, 500 ppm concentrations of potassium iodide and 100 ppm concentration of salicylic acid. It was observed that during sonication, reaction temperature increased due to heat dissipation induced by cavitational events and hence to achieve a