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Sonochemical synthesis of peracetic acid in a continuous flow micro-structured reactor

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HIGHLIGHTS

- Continuous microstructured reactor for the preparation of PAA in the presence of ultrasound.
- The effect of different parameters was studied on the formation of PAA.
- Reaction rate increases due to the formation of H_2O_2 because of cavitational events.
- Reaction time was less than 10 min compared to that of conventional batch reactors.

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ABSTRACT

In the present work, a continuous flow micro-structured reactor was used for the preparation of peracetic acid (PAA) in the presence of ultrasonic irradiations. The effect of several parameters such as acetic acid: hydrogen peroxide molar ratio (1:0.45–1:2.5), flow rate (20–40 mL/h), temperature (20–60 °C) and catalyst loading (340–707 mg/cm^3) were investigated in the presence of ultrasound during the preparation of peracetic acid. The deactivation of the Amberlite IR-120H catalyst was studied in micro-structured reactor. The optimum values of the molar ratio of acetic acid:hydrogen peroxide, flow rate, temperature and catalyst loading were found to be 1:1, 30 mL/h, 40 °C and 471 mg/cm^3, respectively. In the present study, the reaction time observed was less than 10 min compared to that of conventional batch reactors. This drastic decrease in the reaction time was attributed to the use of micro-structured reactor in which heat and mass rates are significantly higher compared to conventional reactors. Also, use of ultrasound drastically enhances the reaction rate due to the formation of H_2O_2 from the chemical effects of ultrasound.

1. Introduction

Peracetic acid is powerful, environmentally friendly and a very cheap oxidizing agent that has great commercial potential in many industries. It can be used as a bleaching agent and to prevent biofilm formation in paper and pulp industries, as a disinfectant in water treatment, for epoxidation of olefins and so on [1–5]. It is also an exceptional active reagent for epoxidation of unsaturated triglycerides for obtaining low cost plasticizers with good performance from natural and renewable sources [5]. Also, PAA pre-treatment has been proved to improve enzymatic digestibility of sugarcane bagasse without the need of high temperature [6,7]. Regardless of these applications of the peracetic acid, limited literature is available on the preparation of PAA. The kinetics of the formation of PAA has been studied by very few researchers, especially in conventional batch reactors. Zhao et al. [8] have studied and developed a homogeneous kinetic model for the preparation of PAA from acetic acid and hydrogen peroxide using Sulfuric acid as a catalyst in the liquid phase. It has been reported that the synthesis of PAA was first-order reactions with respect to reactant concentrations and H^+ concentration. It has been further reported that the rate-determining step in the synthesis of PAA is the reaction between H_2O_2 with active carbonyl intermediary. Further the kinetics of the formation of PAA in a batch process has been investigated by many researchers [9,10]. Peracetic acid is an unstable substance due to its fast thermal decomposition, and therefore, safety aspects in the production of PAA need to be considered. Due to this reason, studying the reactions on small scale is evident. Microreactor safety is based on a small reaction volume, which also

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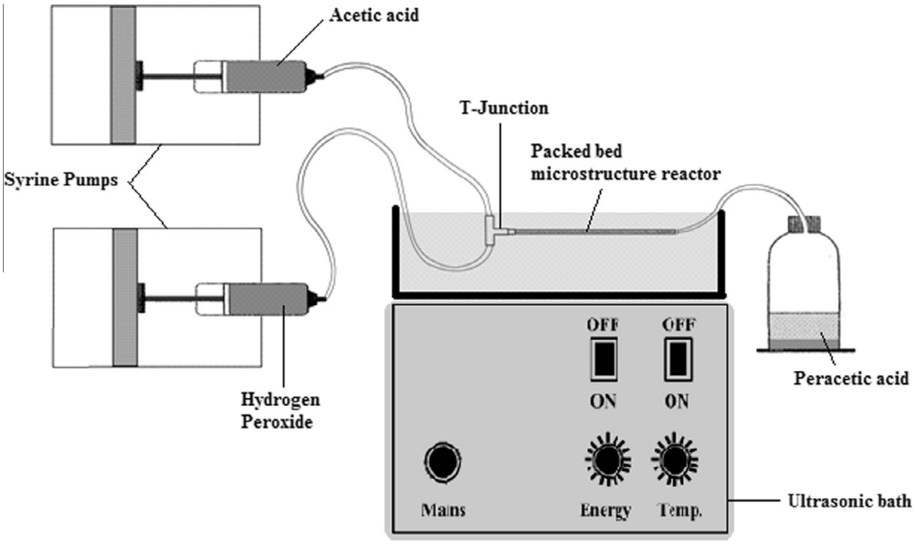

Fig. 1. Schematics of the experimental setup for the preparation PAA in micro-structured reactor.

leads to small inventory of dangerous chemicals. Moreover, the efficient heat transfer resulting from the high surface area-to-volume ratio offers efficient temperature control and, therefore, decreases the risk of run-away reactions. So, the present study preparation of PAA was carried in a microreactor. Also acoustic cavitations induced by ultrasound are among the well-explored research topics which represent green chemistry. The purpose of using ultrasound in present study was to check the feasibility of in situ generation and green provision of H_2O_2 during the course of reaction. Ebrahimi et al. [11] have performed continuous synthesis of performic and peracetic acids in a microstructured reactor using corresponding carboxylic acids and hydrogen peroxide in the presence of homogeneous sulfuric acid catalyst. Formation rates of performic and peracetic acids have been studied by Ebrahimi et al. [12] at different temperatures and catalyst concentrations. It has been reported that the reactions are faster than that in conventional reactors. Ebrahimi et al. [12] have also synthesized performic acid in a packed bed microstructured reactor in the presence of a cation exchange resin catalyst at different temperatures, catalyst concentrations, and residence times. It has been reported that with an increase in temperature and catalyst concentration accelerated the performic acid formation rate. Further Kockmann et al. [13] have reported the concept of the scale up of single channel microreactors which can be used to carry out chemical reactions in tiny channels using continuous-flow processes.

In the present work the effect of several parameters such as molar ratio, flow rate, temperature and catalyst loading has been investigated in the micro-structured reactor. The formed PAA is highly unstable and this reaction takes more time (more than 30 h) in batch processes [14]. Due to this higher reaction time, the decomposition of the product can occur. Further, it is very difficult to carry out this type of highly exothermic reaction in batch or continuous stirred tank reactor. Also, if the reaction is fast and strongly exothermic, hot spot and non-uniform temperature distribution might appear in batch or continuous stirred tank reactor. Such problems can be easily eliminated with the use of micro-structured reactor, which operates on a continuous basis [15]. Due to the small dimensions of the micro-structured reactor, the reaction conditions are easier to maintain because of higher heat and mass transfer rates. Further, the use of homogeneous catalysts such as sulfuric acid has a disadvantage like its subsequent separation from product. Therefore, in the present work, a solid Amberlite IR-120H catalyst is preferred.

Also, it has been reported that the use of ultrasound can lead to physical and chemical transformations in the reaction medium [16–22]. When the ultrasonic waves pass through a liquid medium, a large number of micro bubbles are formed which grow and finally collapse (cavitations) in a few microseconds releasing large magnitudes of energy. The adiabatic collapse of cavity results in the generation of very high local temperatures (>10000 K) and pressures (>1000 atm) and results in the formation of radicals ($^{\cdot}OH$ and $^{\cdot}H$), which leads to the formation of H_2O_2. This helps in the enhancement of the PAA formation reaction as formed H_2O_2 can be used in the reaction. Further, the physical effects (i.e. micro-turbulence and shock waves) generated by the ultrasonic irradiations keep the catalyst in suspended condition and decrease the mass transfer resistance that can enhance the PAA formation reaction. Ultrasound can enhance the mass transfer coefficient, specifically in case of liquid–liquid reactions. Small microfluidic devices has issue with micromixing, hence T junction is being used. However, if combination of ultrasound and microreactor is used then both higher micromixing and enhancement in mass transfer is also observed. This work is unique attempt in which two process intensification devices were used to facilitate the highly exothermic reaction. Though it is well known that microreactor and ultrasound independently enhance the selectivity and conversion however there are very few reports in which combination of the two devices studied [23,24].

With these objectives, the preparation of PAA was carried out in a micro-structured reactor in the presence of ultrasound using acetic acid and H_2O_2. The effects of different variables such as molar ratio, flow rate, temperature and catalyst loading have been investigated in micro-structured reactor. Further, the deactivation phenomenon of the used catalysts i.e. Amberlite IR-120H has been studied.

2. Experimental details

2.1. Materials

The chemicals used in the preparation of PAA in the presence of cation exchange resin catalyst were anhydrous acetic acid and hydrogen peroxide (30 wt.%) purchased from S.D. Fine Chem. Cation exchange resin, Amberlite IR-120H, particles (mean diameter = 0.83 mm, density = 1.28 g/cm^3, functional group = sulfonic acid) was purchased from Rohm & Haas. For the analysis of PAA

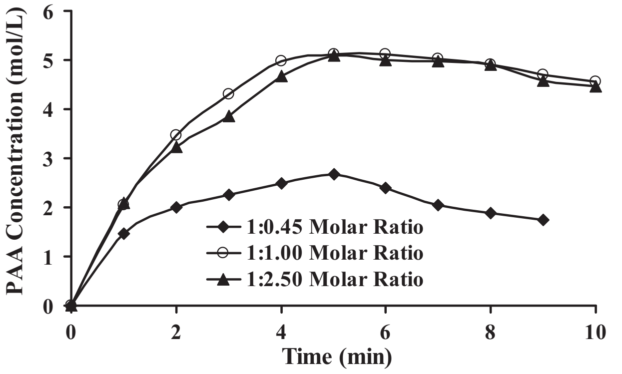

Fig. 2. Effect of molar ratio of acetic acid to hydrogen peroxide on PAA formation (catalyst loading = 471 mg/cm^3, total flow rate = 30 mL/h, residence time = 2.68 min, temperature = 40 °C).

formed, analytical grade ceric sulfate, potassium iodide and sodium thiosulfate were procured from Merck. sulfuric acid, starch indicator solution, ferroin (1,10-phenanthroline ferrous sulfate, 0.01 M in water) solution were used for the analysis of PAA. Deionized water was used in all the experiments.

2.2. Continuous experimental set-up and procedure

The reaction scheme for the synthesis of PAA is reported by Leveneur et al. [25]. The laboratory experiments were carried out in a continuous flow micro-structured reactor. The schematic of the experimental setup is shown in Fig. 1. The micro-structured reactor consists of a tubular glass reactor with 1.5 mm diameter and 30 cm in length, packed with Amberlite IR-120H catalyst. The feed of acetic acid and H_2O_2 is given through the Teflon T section to the micro-structured reactor. The micro-structured reactor was immersed in an ultrasound bath which is equipped with a temperature control arrangement. The experiments were performed for different molar ratios of acetic acid to hydrogen peroxide, total flow rate, temperatures (20–60 °C) and catalyst loading. The decomposition of the product was observed at higher temperatures (above 60 °C). The experiments were carried out under atmospheric pressure. The samples were collected from the outlet of the reactor at different time intervals and analyzed. Mole fractions of H_2O_2 and PAA were determined by the titration method reported by Greenspan and Mackellar [26].

3. Results and discussion

3.1. Effect of molar ratio of acetic acid:H_2O_2 on PAA formation

The effect of the molar ratio of acetic acid to H_2O_2 on PAA concentration is depicted in Fig. 2 (catalyst loading = 471 mg/cm^3, total flow rate = 30 mL/h (15 mL/h each of the reactant), temperature = 40 °C). As per the reaction scheme for the synthesis of PAA reported by Leveneur et al. [25], it has been observed that for the formation of one mole of PAA, one mole each of acetic acid and H_2O_2 is required. However in this study it is expected that the formation of H_2O_2 will take place due to sonolysis phenomena due to ultrasonic irradiations and this formed H_2O_2 will help to convert acetic acid to peracetic acid. Therefore, in the present study, some experiments are carried at lower molar ratio and it is believed that remaining part of the H_2O_2 will come through sonolysis phenomena. In the presence of ultrasonic irradiations, the extra formation H_2O_2 takes place due to the chemical effects of the ultrasound which in turn enhances the reaction rate. The physical effects of the ultrasound such as micro-turbulence and the jets formed reduce the mass transfer resistance and allow fast transport of H_2O_2 towards acetic acid and the reaction takes place. This reduces the reaction time significantly [14]. Further PAA concentration is found to be increased with an increase in the reaction time up to 5 min then it is found to decrease marginally. This is attributed to the decomposition of the formed PAA by hydrolysis reaction to give, again, acetic acid and H_2O_2 by backward reaction.

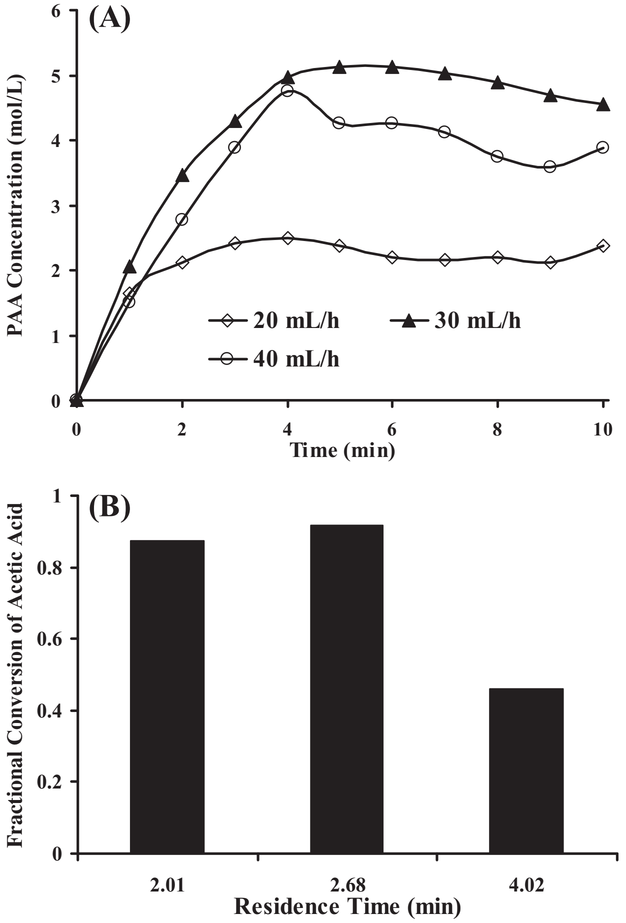

Fig. 3. Effect of reactants flow rate on (A) PAA formation and (B) Fractional conversion of acetic acid (catalyst loading = 471 mg/cm^3, molar ratio of acetic acid to H_2O_2 = 1:1, temperature = 40 °C).

3.2. Effect of flow rate on PAA formation

The effect of flow rate on PAA formation and % conversion of acetic acid is shown in Fig. 3 (catalyst loading = 471 mg/cm^3, molar ratio of acetic acid to H_2O_2 = 1:1, temperature = 40 °C). It is found that at the total flow rate equal to 20 mL/h (residence time = 4.02 min) with 1:1 M ratio of acetic acid: H_2O_2, the concentration of PAA is 2.375 mol/L and acetic acid conversion was 46%. It is lower as compared to other cases. This is attributed to the laminar flow in the micro-structured reactor at lower flow rate even though there is a presence of ultrasound. This offers more mass transfer resistance resulting in the less formation of PAA. Also, due to large residence time, decomposition reaction of PAA might be significant that results in lower PAA concentration. At the total flow rate equal to 30 mL/h (residence time = 2.68 min), higher concentration of PAA is observed (i.e. 5.125 mol/L) and acetic acid conversion was 92%, which is attributed to higher turbulence in the fluid due to higher flow rate and ultrasonic irradiations. Further the PAA concentration is found to decrease from 5.125 to 4.75 mol/L and acetic acid conversion from 92% to 87.5% with an increase in the flow rate from 30 to 40 mL/h, which is due low residence time of the reaction mixture. This results in the less formation of PAA in the reactor.

3.3. Effect of catalyst loading on PAA formation

The effect of the catalyst loading on the formation of PAA is shown in Fig. 4 (molar ratio of acetic acid to H_2O_2 = 1:1, temperature = 40 °C). In order to maintain the residence time at a fixed value of 2.68 min, the length of the reactor was varied as 20, 30 and 40 cm with a flow rate as 20, 30 and 40 mL/h, respectively. The PAA concentration at 340 mg/cm^3 catalyst loading is found to be 2.5 mol/L (conversion of acetic acid = 46%) and is increased to 5.125 mol/L (conversion of acetic acid = 94%) at 471 mg/cm^3 catalyst loading at 40 °C. It is attributed to more acid sites at higher loading of catalyst which leads to more formation of the PAA and equilibrium is reached sooner. However at 707 mg/cm^3 catalyst loading at 40 °C the concentration of PAA is found to be nearer to 5.00 mol/L (conversion of acetic acid = 92%), this is attributed to sufficient numbers of acid sites being provided with the loading of 471 mg/cm^3 catalyst. Also, even though more acid sites are available, the presence of limited amounts of acetic acid limits the formation of PAA in the reactor. Therefore the PAA concentration remains unchanged. In the present work, the equilibrium is reached in less than 5 min, indicating a faster reaction which is attributed to ultrasonic irradiations that form H_2O_2 and its chemical effects that enhance the reaction rate significantly.

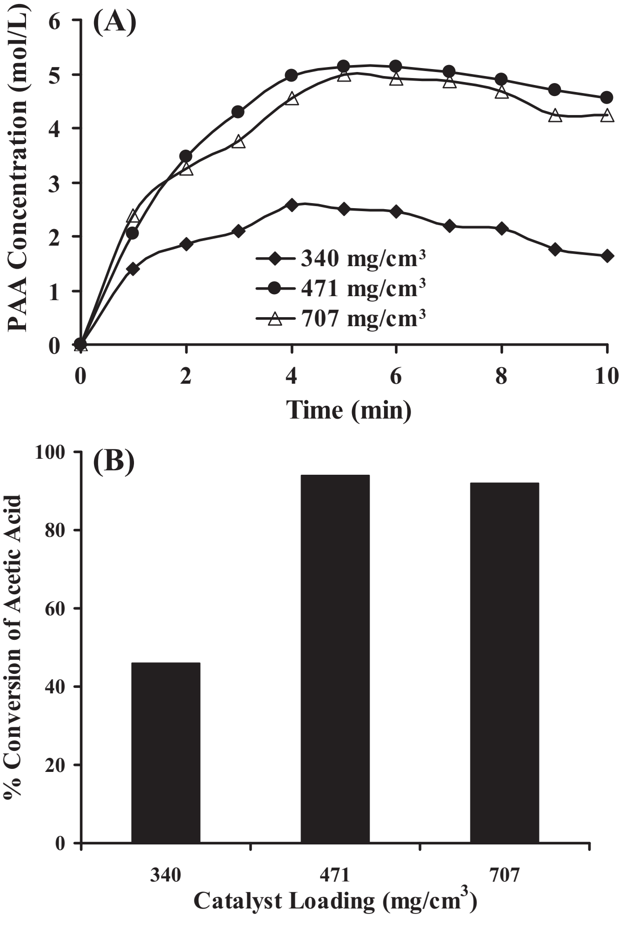

Fig. 4. Effect of Amberlite IR-120H catalyst on (A) PAA formation and (B) % conversion of acetic acid (molar ratio of acetic acid to H_2O_2 = 1:1, residence time = 2.68 min, temperature = 40 °C).

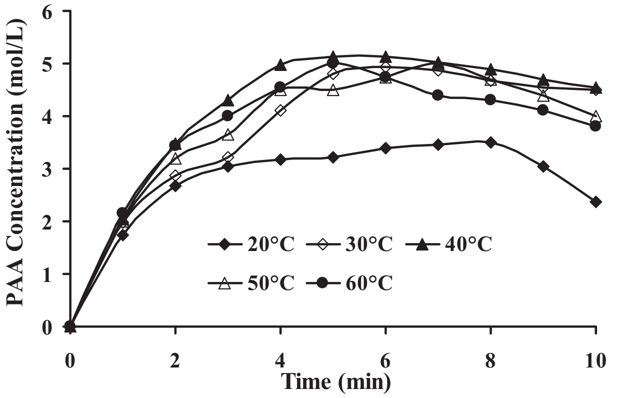

Fig. 5. Effect of reaction temperature on PAA formation (flow rate = 30 mL/h, molar ratio of acetic acid to H_2O_2 = 1:1, residence time = 2.68 min, catalyst loading = 471 mg/cm^3).

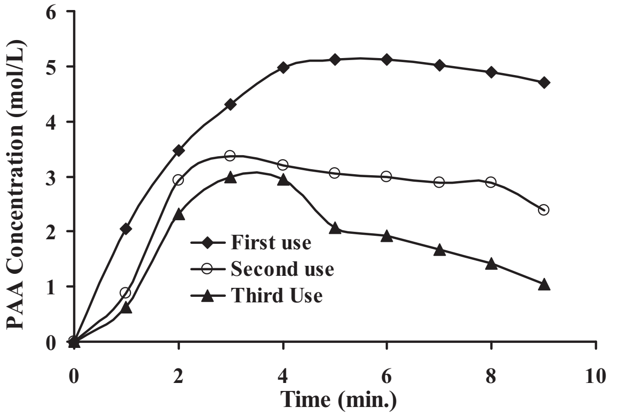

Fig. 6. Deactivation of Amberlite IR-120H catalyst on PAA formation (flow rate = 30 mL/h, molar ratio of acetic acid to H_2O_2 = 1:1, catalyst loading = 471 mg/cm^3, residence time = 2.68 min, temperature = 40 °C).

3.4. Effect of temperature on PAA formation

The effect of the temperature on the formation of PAA is shown in Fig. 5 (flow rate = 30 mL/h, molar ratio of acetic acid to H_2O_2 = 1:1, catalyst loading = 471 mg/cm^3). It has been observed that the PAA concentration is 3.5 mol/L at the end of 8 min at 20 °C and is found to be increased to 5.125 mol/L with an increase in the temperature to 40 °C. It is attributed to the enhancement in the reaction rate with an increase in the temperature. Further, at 60 °C, it decreases marginally to 5.00 mol/L. It is credited to decomposition reaction at higher temperature (above 60 °C). Therefore the PAA concentration is found to be lower at 50 and 60 °C compared to 40 °C. Also, with an increase in the temperature the vapor gets filled in the cavitating bubble leading to milder collapse that leads to lesser formation of H_2O_2 in the reaction medium. However, at 40 °C i.e. at lower temperature, the vapor pressure is less, therefore the amount of vapor present in cavitating bubble enhances thus leading to intense collapse of the cavity which leads to chemical change results in the formation of more amount of H_2O_2 in the reaction medium and that the reaction rate at reaction temperature equal to 40 °C.

3.5. Deactivation of catalyst in continuous micro-structured reactor

In the present work the deactivation and reusability of cation-exchange resin i.e. Amberlite IR-120H has been investigated. The

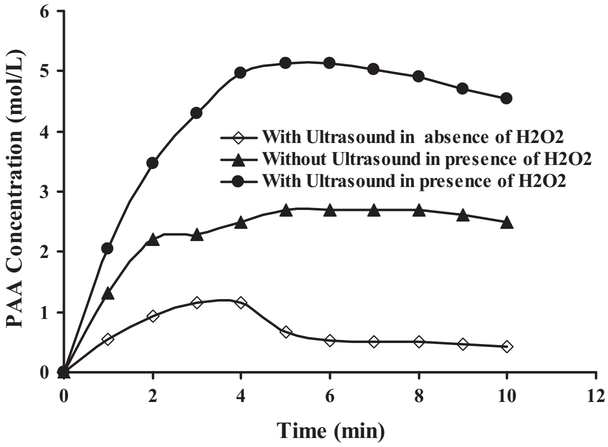

Fig. 7. PAA formation in microreactor in the presence of ultrasound without H_2O_2, in presence of ultrasound with H_2O_2 and in the absence of ultrasound with H_2O_2 (flow rate = 30 mL/h, catalyst loading = 471 mg/cm^3, residence time = 2.68 min, temperature = 40 °C).

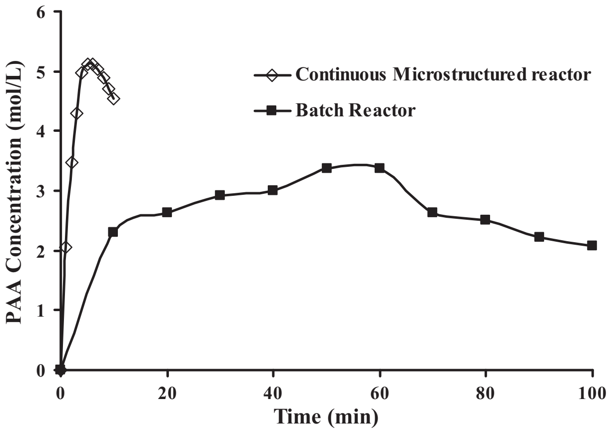

Fig. 8. Comparative study on PAA formation in the presence of ultrasound in micro-structured reactor (flow rate = 30 mL/h, catalyst loading = 471 mg/cm^3, residence time = 2.68 min, temperature = 40 °C) and in the presence of ultrasound in batch reactor (temperature = 40 °C, catalyst loading = 471 mg/cm^3).

experiments were carried out under the same operating conditions (flow rate = 30 mL/h, molar ratio of acetic acid to H_2O_2 = 1:1, catalyst loading = 471 mg/cm^3, temperature = 40 °C). The reused catalyst was washed with water, then dried in oven at 70 °C for 48 h and reused. The comparison between the activity of fresh and reused catalyst are depicted in Fig. 6. From Fig. 6, it can be predicted that the activity of the catalyst decreases with its usage. The PAA concentration in the first use of catalyst is 5.125 mol/L. It is 3.375 and 3.00 mol/L for second and third use respectively. The deactivation of Amberlite IR-120H catalyst occurs through the neutralization of the sulfonic acid groups, catalyst shrinkage, or loss in pore sites [27]. Further the use of catalysts was significantly increased due to ultrasonic irradiation, as all the catalyst particles remained suspended in the reaction medium and whole area was available for the reaction. Therefore, a drastic decrease in the PAA concentration was observed in second use of the catalyst as compared to the first use.

3.6. Effect of ultrasound on H_2O_2 formation

The effect of use of ultrasound on the formation of H_2O_2 i.e. in turn on PAA formation is depicted in Fig. 7. In the presence of ultrasound and absence of H_2O_2 reactant, the PAA concentration was found to be 1.15 mol/L. This is attributed to the formation of H_2O_2 due to the cleavage of water molecules due to cavitational effects of ultrasonic irradiations according to the mechanism provided in the literature. The cleavage of water molecules leads to the formation of OH$^\cdot$ and H$^\cdot$ radicals and further combination two OH$^\cdot$ radicals results in formation H_2O_2 which is one of the reactants of the PAA formation reaction. This formed H_2O_2 favors the formation of PAA product according to the reaction scheme provided in the literature. Further, in the absence of ultrasound with H_2O_2, the PAA concentration was found to be 2.70 mol/L, which is marginally higher than that in the presence of ultrasound without H_2O_2. Also, in the presence of ultrasound with H_2O_2, the PAA concentration was found to drastically increase to 5.125 mol/L. This is credited to the combined effect of H_2O_2 added and formed in the presence of ultrasound on PAA formation rate. Further, due to this excess H_2O_2, the reaction becomes pseudo-first order and that favors formation of PAA and suppresses the backward reaction and leads to higher concentration of PAA in the final product.

3.7. Comparative study of PAA formation in batch and micro-structured reactor

The comparative study of PAA formation in the batch and micro-structured reactor in the presence of ultrasound is depicted in Fig. 8. It clearly shows the effect of the micro-structured reactor on the formation of PAA. It is observed that the reaction completes in less than 10 min in micro-structured reactor while in case of batch rector the time required was around 100 min. Further the PAA formation in the micro-structured reactor is around 5.125 mol/L whereas in case of batch reactor it is 3.375 mol/L. This clearly indicates that the use of micro-structured reactor favors the formation of PAA compared to batch reactor with better selectivity. Further higher rates of mixing, mass and heat transfer plays an important role in micro-structured reactor during formation of PAA. Another possible reason for the lesser PAA formation in batch reactor is the backward reaction i.e. hydrolysis reaction. PAA is an unstable compound so due to higher reaction time in batch reactor, the PAA formation is less compared to micro-structured reactor. This can be avoided in micro-structured reactor because of lesser reaction time.

4. Conclusion

The preparation of PAA was carried out successfully in the micro-structured reactor in the presence of Amberlite IR-120H catalyst and ultrasonic irradiations. The advantages of the solid Amberlite IR-120H catalyst over the liquid catalyst are the ease of separation of the catalyst and the absence of corrosion. The use of Amberlite IR-120H catalyst offers high catalytic activity in the presence of ultrasonic irradiations. The optimum PAA concentration occurs at a flow rate of 30 mL/h, molar ratio of acetic acid to H_2O_2 1:1, temperature 40 °C and catalyst loading of 471 mg/cm^3. Ultrasonic irradiations play an important role during the formation of PAA in a micro-structured reactor as it produces H_2O_2 due to cavitation which in turn enhances the reaction rate. Further the use of micro-structured reactor in the presence of ultrasonic irradiations enhances the reaction rate significantly and the reaction gets completed in less than 10 min compared to that of conventional batch reactors. The deactivation of Amberlite IR-120H catalyst occurs through neutralization of the sulfonic acid groups, catalyst shrinkage, or loss in pore sites.

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