Intensification of hydroxyl radical production in sonochemical reactors

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Abstract

The efficacy of sonochemical reactors in chemical processing applications has been well established in the laboratory scale of operation though at a given set of operating parameters and no efforts have been directed in terms of maximizing the free radical production. In the present work, the effect of different operating parameters viz. pH, power dissipation into the system, effect of additives such as air, haloalkanes, titanium dioxide, iron and oxygen on the extent of hydroxyl radical formation in a sonochemical reactor have been investigated using salicylic acid dosimetry. Possible mechanisms for oxidation of salicylic acid in the presence of different additives have also been established. It has been observed that acidic conditions under optimized power dissipation in the presence of iron powder and oxygen result in maximum liberation of hydroxyl radicals as quantified by the kinetic rate constant for production of 2,5- and 2,3-dihydroxybenzoic acid. The study has enabled the optimisation of the conditions for maximum efficacy of sonochemical reactors where free radical attack is the controlling mechanism for the chemical processing applications.

Key words: Sonochemical reactors, Process Intensification, Salicylic acid dosimetry, Kinetics

1. Introduction

The underlying mechanism in the successful application of sonochemical reactors in different chemical processing applications such as chemical synthesis, wastewater treatment etc. has been the cavitation phenomena resulting in the generation of highly reactive hydroxyl radicals and local hotspots (high temperature and pressure). There have been many reports in the literature illustrating the use of sonochemical reactors for different applications and the aim has been to investigate the effect of several operating parameters such as frequency of irradiation, power dissipation into the system, initial concentration of the substrate, presence of dissolved species etc. on the effectiveness of the sonochemical reactors specific for a particular application under consideration [1-7]. The data thus reported cannot be generalized and engineers cannot use the data reliably for the efficient design and operation of sonochemical reactors. To overcome this paucity of design-related information, the present work has been specifically directed towards establishing the optimum set of operating parameters for maximizing the hydroxyl radical production rate in sonochemical reactors. The data presented in this work is generally applicable to all cases where the driving mechanism is free radical attack and may also be equally valid for situations where the governing mechanism is pyrolysis since the amount of free radicals generated and the magnitude of the temperature/pressure pulse produced in the system are inter-related though may not be governed by a one to one correspondence.

Salicylic acid dosimetry, i.e. monitoring the hydroxylation of salicylic acid, has been used as the tool to quantify the extent of hydroxyl radical production rate and hence compare the efficacy of a sonochemical reactor under different operating parameters. The dosimetry based on salicylic acid is very specific, meaning that the reaction products are exclusively caused by the hydroxyl radical oxidation reaction, usually addition of the hydroxyl radical to the aromatic ring. In these cases, it is commonly said that the hydroxyl radicals have been

trapped and hence the dosimeter can be described as a radical trap. The reaction products of salicylic acid dosimetry can be determined using HPLC with greater sensitivity than the spectrophotometrical measurements used with iodide and Fricke dosimeter [8].

Apart from optimizing the possible reaction operating conditions such as power dissipated into the system (frequency of irradiation is also another possible optimization parameter which cannot be varied in the present case due to restriction on the type of equipment) and pH, the effect of different additives has also been explored. The basis for the selection of these additives has been the fact that the presence of dissolved species and/or solid particles act as possible nuclei for cavitation resulting in an increase in the overall cavitational intensity. The effect of the presence of iron powder has also been investigated to possibly quantify the effectiveness of the combined operation of the acoustic cavitation and Fenton type oxidation mechanism.

2. Materials and methods

All experiments were carried out in a 300 mL glass beaker and sonicated using an ultrasonic probe (Cole-Parmer, UK) having a tip diameter of 1 cm operated at a frequency of 20 kHz with maximum power dissipation of 400W. The operating amplitude for power dissipation was selected as 50% (supplied power of 200W with calorimetric transfer efficiency of 32.5% i.e. actual dissipated power into the solution and hence available for cavitation events is 65W), which is the maximum available based on the ratings of the equipment. Preliminary studies indicated that the extent of liberation of hydroxyl radicals was directly proportional to the magnitude of power dissipation and hence the highest levels were selected for the experiments. Salicylic acid stock solution (0.5mM) was prepared in deionised water and, for all the experiments, the stock solution (200 mL) was subjected to

sonication under different experimental conditions. The reaction temperature was maintained at 23±2°C by immersing the reactor into an ice bath.

The concentrations of the salicylic acid and its hydroxylated products were quantified by using, high performance liquid chromatography (HPLC, WATERS 1575 Binary HPLC Pump with 717 plus Auto sampler and 2487 Dual λ Absorbance Detector/2475 Multi λ Fluorescence Detector). Initially calibration curves for dependency of peak area on concentration were established with standard solutions of salicylic acid as well as its hydroxylated products, 2,3-DHB and 2,5-DHB. The samples were collected every 30 min and filtered before analysis. Concentrations of reactants as well as the reaction products were then established using the calibration curves. It should be noted here that in addition to hydroxylated products, some traces of chlorinated products, in the case of chloroalkanes as additives, were also observed.

The effect of varying pH (operating range of 4.2 to 11), the presence of air (from a fish tank aerator), haloalkanes (dichloromethane and chloroform at concentrations of 0.5% by volume), TiO_2 (0.5% by weight), iron powder (0.3% by weight) and the introduction of oxygen on the extent of production of hydroxyl radicals as quantified by monitoring the generation of the hydroxylated products (2,3-DHB and 2,5-DHB) has been studied.

3. Results and discussion

The most plausible mechanism for the oxidation of salicylic acid (given in Figure 1) indicates the production of 2,3-DHB and 2,5-DHB with some traces of catechol [9]. The identification of the reaction products, as monitored using HPLC, indicated a continuous increase in the extent of generation of 2,3-DHB and 2,5-DHB. A sample profile is shown in figure 2, which indicates that generation of the 2,3 DHB isomer is more favoured under the action of ultrasound alone, which is unlike the normal distribution observed with salicylic

acid oxidation using Fenton oxidation where 2,5-DHB isomer is more preferred [10]. It is known that many parameters such as type of oxidative process, the presence of metals, time of oxidation, oxygen etc. control the distribution of the two isomers [11-12]. Hydrogen peroxide can also possibly form in the system due to the recombination reaction of the free radicals though it has not been accounted for since the major focus of the work was to quantify the intensification of hydroxyl radical production due to the use of different additives, which is aptly reflected by the magnitude of the hydroxylated products. A detailed discussion in terms of the dependency of the distribution of the isomers has also been dealt in details in subsequent sections.

3.1 Effect of operating pH:

The effect of operating pH on the rate constant for generation of 2,3-DHB (major product of salicylic acid oxidation) is shown in Figure 3. It can be seen from the figure, that lower pH (acidic conditions) results in higher rates of conversion of salicylic acid as indicated by higher kinetic rate constants for both the hydroxylated products. The extent of disappearance of salicylic acid also showed similar trends in terms of higher rate of disappearance at lower operating pH. Quantitatively, the rate constant for generation of 2,3-DHB reduced by about 15% with an increase in pH from 4.2 to 7.2 and further by about 20% when pH was increased to 11 indicating almost linear dependency of the rate constant on operating pH. It should be noted that although pH does not have any direct effect on the cavitational intensity in terms of the number of cavitation events or the pressure/temperature generated due to cavity collapse, lower pH i.e. acidic conditions helps to increase the concentration of the hydrophobic salicylic acid at the bubble interface leading to exposure of a higher quantum of the salicylic acid to the cavitating conditions. Thus, higher rates of oxidation of salicylic acid are expected as indicated by an increase in the rate constant of 2,3-DHB generation at lower operating pH. Similar results, in terms of higher efficiency of

sonochemical reactors for degradation of hydrophobic compounds at acidic conditions, have been reported in the literature [2,13]. As a result all further experiments were performed at this optimum pH of 4.2. It should be also noted here that the pKa value of the reactant also plays a major role in deciding the effect of pH. Neutral species and ionic species have different affinity towards cavitating bubbles and hence depending on the nature of the species (hydrophobic or hydrophilic), the operating pH needs to be selected so as to facilitate easy transfer of the reacting species at the zone of intense cavitating conditions [14,15]. In the present case, however, since all the operating pHs were above the pKa value for salicylic acid (2.97 is the pKa value whereas the pH was varied in the range 4.2 to 11), the effect of hydrophobic/hydrophilic nature of neutral or ionic species is not applicable.

3.2 Effect of Air:

The presence of air bubbles in the system provides additional nuclei by virtue of heterogeneity resulting in an increase in the intensity of cavitation (increased number of cavitation events as compared to the absence of bubbling; this was also visually observed during the experimentation), which should lead to an increase in the amount of hydroxyl radicals generated in the reactor. Air was introduced using a fish tank aerator at very low flow rates. Due to the presence of air, the rate constant for the production of 2,3-DHB increased from 0.0504 μm/min to 0.0628 μm/min with a similar increase in the rate constant for 2,5-DHB from 0.022 μm/min to 0.0292 μm/min (results not shown). Similar results have been reported by Gogate *et al*. [16] for formic acid degradation and as higher gas flow rates were found to be detrimental for the ultrasonic horn type reactors possibly due to cushioning effect of the higher concentrations of air, in the present work, higher gas flow rates were not utilised in the current experiments. Using higher flow rates of air possibly also could result in the formation of a blanket of bubbles in the immediate vicinity of the transducer surface

thereby minimizing the transfer of energy into the system. Thus, it can be concluded that using air at very low flow rates results in intensification of the hydroxyl radical generation.

3.3 Effect of TiO_2

The presence of solid particles again provides additional nuclei for generation of cavities and hence should result in an increase in the cavitational intensity leading to better sonochemical effects. With this aim, the effect of the presence of TiO_2 particles at low loading of 1 g/L (again a higher loading of solid particles interferes in the effective transmission of the incident sound waves leading to lower energy dissipation rates) on the extent of oxidation of salicylic acid has been investigated. It has been observed that the rate constant for formation of 2,3-DHB marginally increased from 0.0504 μm/min to 0.053 μm/min though the rate constant for 2,5-DHB generation increased from 0.022 μm/min to 0.0307 μm/min. The change in the distribution of 2,3-DHB and 2,5-DHB (ratio of rate constants was 1.75 in the presence of TiO_2 particles as compared to 2.29 in its absence) can possibly be attributed to the fact that the high concentration of hydroxyl radicals in the presence of catalyst (solid surface facilitating adsorbed state of reactants) leads to selective attack at the 5-position as compared to the 3-position possibly due to steric hindrance of the carboxyl group in the latter case. The overall increase in the conversion of salicylic acid due to the presence of TiO_2 particles (hypothesis of higher cavitational intensity due to the presence solid particles) can be given credence by literature reports. Kubo *et al*.[5] have shown that the degradation efficiency of sonochemical reactors increases in the presence of TiO_2 particles and, furthermore, the rate constant for degradation of phenol also increases with a higher loading of TiO_2 particles. Similar observations have also been reported in our earlier work [17] where degradation of formic acid has been investigated in a multiple frequency sonochemical reactor. The use of TiO_2 particles for intensification of cavitational activity and hence the production of hydroxyl radicals is recommended particularly in the

case of wastewater treatment applications where synergistic effects of sonochemistry and photocatalytic oxidation are utilized for intensification of oxidation [18-19].

3.4 Effect of haloalkanes:

Haloalkanes, such as carbon tetrachloride, have also been used as additives for intensifying sonochemical reactions [20]. In the present work, the effect of the presence of dichloromethane and chloroform was investigated. Carbon tetrachloride though more effective in terms of extent of intensification has been not used in the present work due to possible carcinogenic effects and higher degree of pollution. When both the haloalkanes were present at concentrations of 0.5% by volume no appreciable increase in the rate constants for generation of 2,3-DHB was observed whereas the rate constant for 2,5-DHB generation marginally lowered. Experiments were also performed to check whether the observed trend was dependent on pH or on the concentration of salicylic acid and the results indicated that for all the combinations, the presence of haloalkanes did not result in any increase in the oxidation rates of salicylic acid. A possible explanation of this observation can be obtained from the fact that these haloalkanes being more volatile result in generation of more vaporous cavities, which collapse with lower cavitational intensity as indicated by the energy analysis of the collapsing cavities [21]. A careful examination of the reaction products indicated some traces of chlorinated products in the system. Data on disappearance of salicylic acid did confirm this fact though the change in the extent of disappearance was only marginal. This can be attributed to the fact that $Cl^{\bullet}$ radicals are also formed in the system which lead to some chlorination of the aromatic ring of salicylic acid. However this reaction is not as effective as hydroxyl radical attack, at least in the present case of salicylic acid oxidation. It should be noted that depending on the reactants under question, intensification in the overall rate of oxidation can indeed be achieved [20] due to the use of haloalkanes. Thus, use of haloalkanes for intensification of sonochemical reactions is only

recommended when the affinity of the $Cl^{\bullet}$ radicals towards the desired reactants is higher which can be established using preliminary kinetic studies unless data is available in the literature for specific application under question.

3.5 Effect of iron powder:

Iron powder should increase the number of cavitational events similar to the presence of TiO_2 particles by way of providing additional nuclei due to the deformities formed on the liquid surface. At the same time it is expected that a Fenton type mechanism can take place, by reaction of the iron powder with *in situ* generated hydrogen peroxide due to ultrasonic irradiation, leading to formation of more hydroxyl radicals. To quantify these phenomena, experiments with iron powder were investigated. The results for the formation of 2,5-DHB and 2,3-DHB for different experimental conditions are shown in figures 4 and 5 where it can be seen that the rate constant for both 2,5-DHB and 2,3-DHB are higher in the presence of iron powder. Also, the extent of increase is higher compared to that observed in the case of TiO_2 particles indicating the probable role of Fenton type chemistry in this instance. It should be also noted that the ratio of the distribution of 2,3-DHB to 2,5-DHB formed in the presence of iron powder is also marginally lower as compared to that observed in the absence of iron powder (2.15 as against 2.29) giving some credence for the hypothesis given earlier for the observed effect in the presence of TiO_2 particles.

The combined effect of air and iron powder has also been investigated to check whether the two mechanisms for intensification of hydroxyl radical production lead to synergistic effects. The data are shown in figures 4 and 5 and the rate constant for 2,5-DHB formation increased almost 2.5 times to 0.0567 μm/min whereas the rate constant for 2,3-DHB, surprisingly, decreased from a value of 0.0504 to 0.0242 μm/min. However, the overall conversion rates of salicylic acid were greater in the presence of air and iron powder compared to the absence of both the intensifying parameters. Whereas the exact mechanism

behind the alteration of the distribution of the two isomers is not evident, it is possibly attributed to the role of the Fenton type mechanism along with adsorption of the reactants onto the solid iron surface. The presence of oxidant in the form of air in combination with Fenton chemistry might also play some role in altering the distribution of the isomers. To conclusively establish the role of oxidants, some additional experiments have been performed in the presence of oxygen (higher oxidative capabilities as compared to air) and the data are also reported in figures 4 and 5. It can be seen that the rate constant for 2,5-DHB generation increased by almost 5 times whereas the rate constant for 2,3-DHB increased by almost 2 times as compared to the absence of both oxygen and iron powder. This again gives some credence to the fact that more oxidative capabilities and higher concentration of free radicals favours the formation of 2,5-DHB isomer as compared to the 2,3-DHB. Considering the overall conversion of salicylic acid, the presence of oxygen and iron powder was found to give three times higher rates as compared to the absence of both oxygen and iron powder.

4. Conclusions

Optimization studies related to the effect of different operating parameters on intensifying the extent of generation of hydroxyl radicals have lead to the following important design related information:

1. Acidic conditions with higher power dissipation levels results in a greater amount of hydroxyl radical generation.
2. The presence of air at low flow rates results in intensification in the cavitational activity and hence the rate of hydroxyl radical generation is also higher.
3. TiO_2 also intensifies the cavitational intensity though it also alters the mechanism of the oxidation, possibly by playing some role in the adsorption of the reactants.

4. Haloalkanes, such as dichloromethane and chloroform, do not increase the extent of oxidation of salicylic acid. It appears that the presence of haloalkanes is the preferred way of intensification only when the desired substrate has more affinity towards the hydroxyl radicals as compared to the haloalkanes and their degradation products.

5. Iron powder results in *in-situ* Fenton type reactions and this, in presence of oxidants like air or oxygen, further intensifies the rate of generation of hydroxyl radicals. Interestingly, this also alters the distribution of the isomers of DHB formed.

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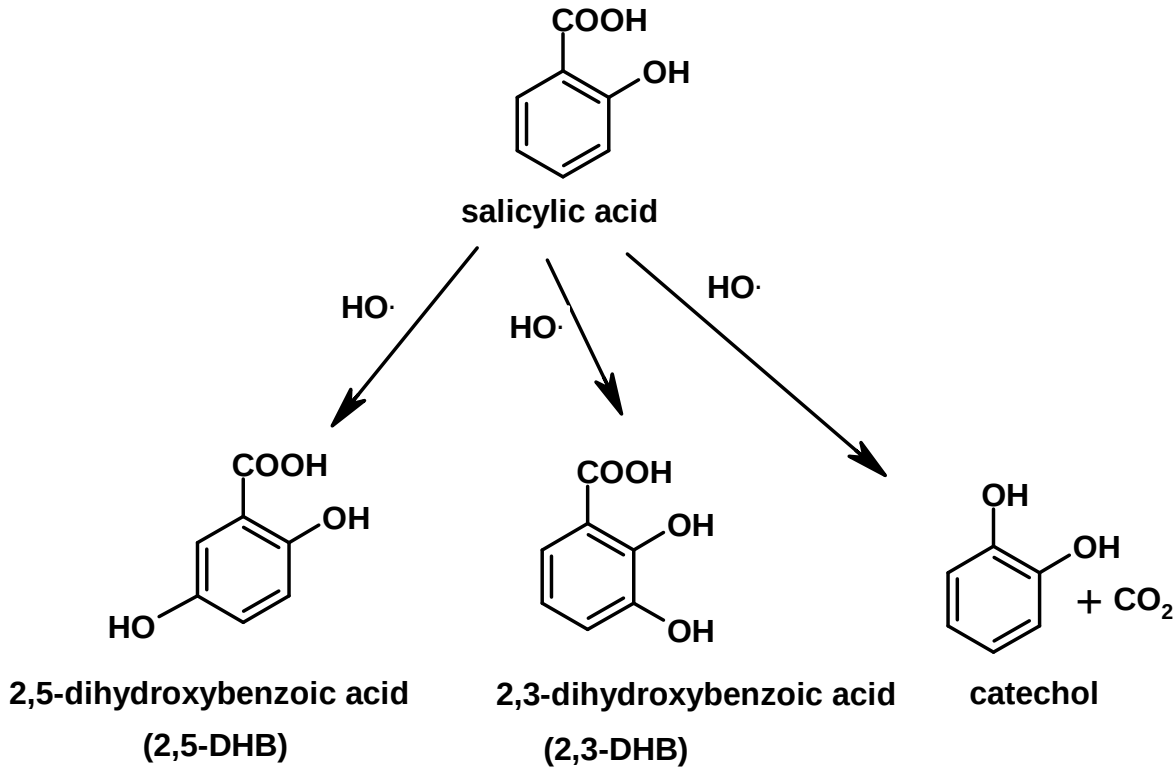

Figure 1: Products from the oxidation of salicylic acid (SA) with HO• radicals

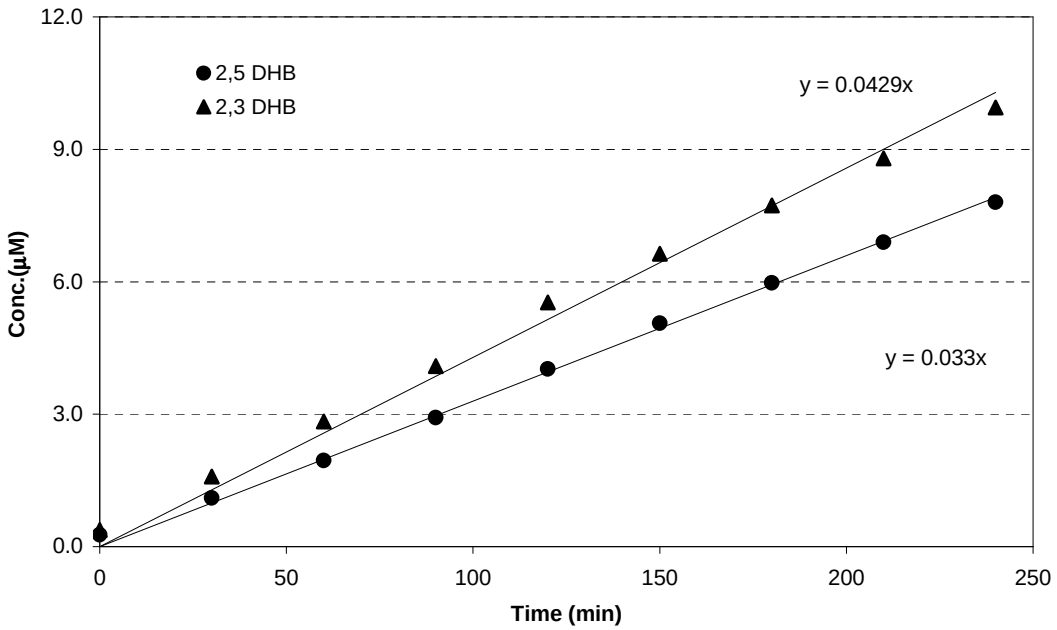

Figure 2: Concentration profile of products from the hydroxylation of salicylic acid under ultrasonic irradiation alone (Experimental conditions: SA = 0.5 mM, amplitude = 50%, volume of solution = 200mL, pH = 7.2)

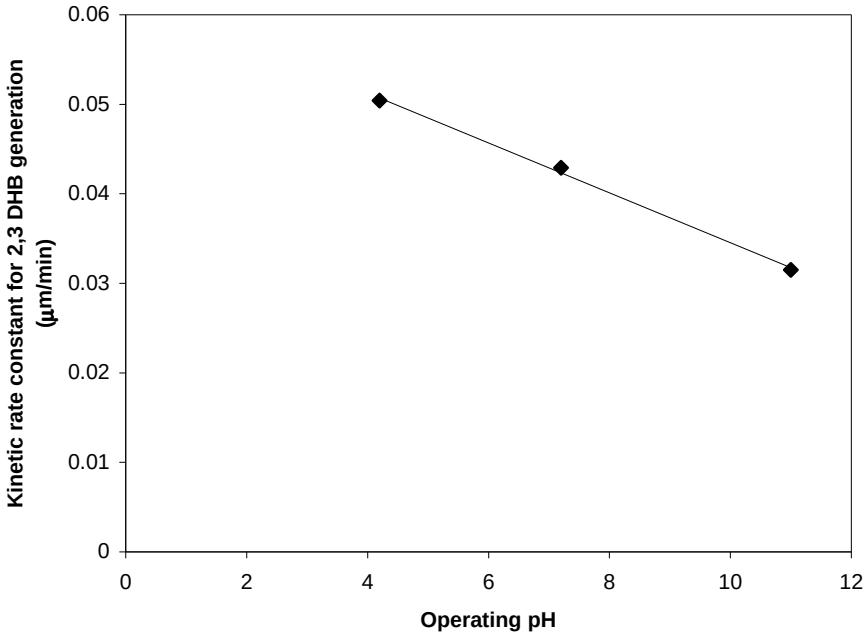

Figure 3: Effect of pH on the formation of 2,3-DHB from salicylic acid in the presence of ultrasonic irradiation alone (Experimental conditions: SA = 0.5 mM, amplitude = 50%, volume of solution = 200mL)

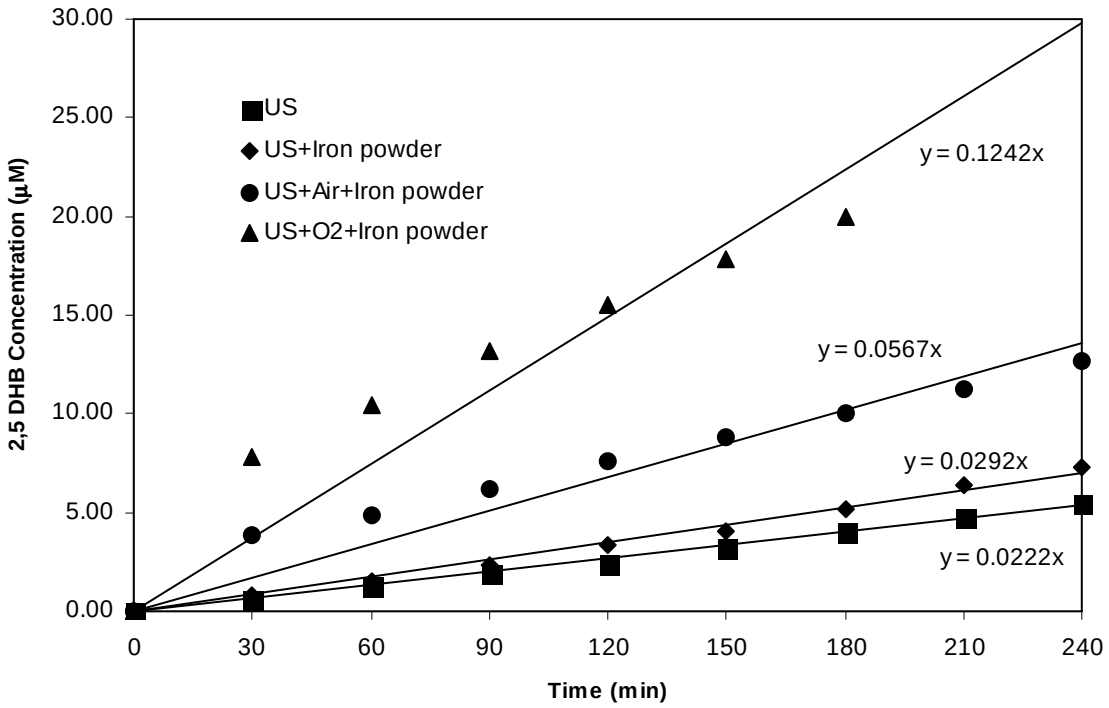

Figure 4: Comparison of the formation of 2,5-DHB under different experimental conditions in the presence of ultrasound and iron powder (Experimental conditions: SA = 0.5 mM, amplitude = 50%, volume of solution = 200mL)

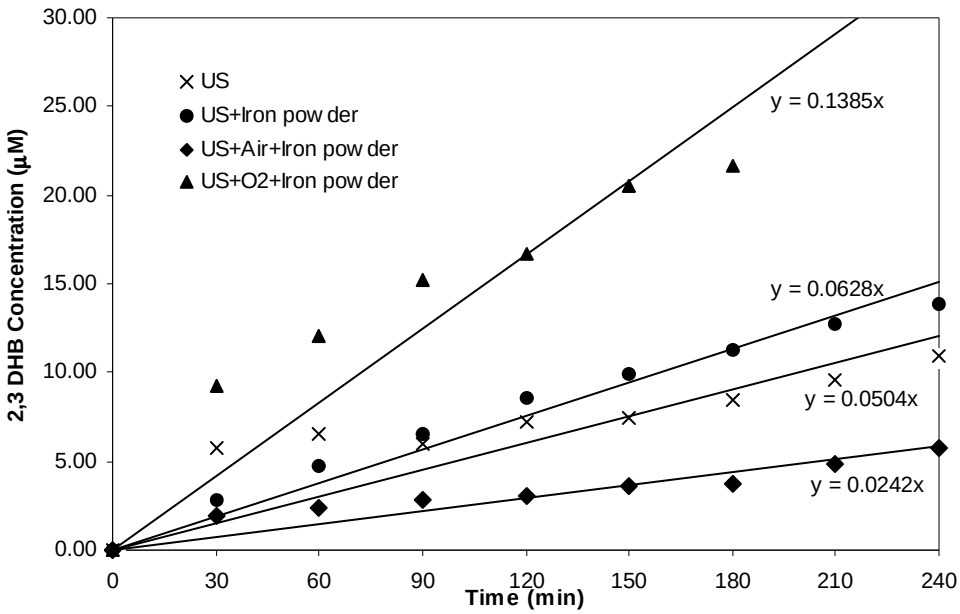

Figure 5: Comparison of the formation of 2,3-DHB under different experimental conditions in the presence of ultrasound and iron powder (Experimental conditions: SA = 0.5 mM, amplitude = 50%, volume of solution = 200mL)