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Advanced Fenton processing of aqueous phenol solutions: A continuous system study including sonication effects

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Abstract

Our previous report based on a batch reactor system for the Advanced Fenton Process (AFP) showed that pH, hydrogen peroxide and the organic substances treated are among the most important factors affecting the oxidation efficiency. As an extended study towards its commercialisation, this paper reports the effects of the main process parameters including those relating to a new AFP flow-through system. In order to systemise and correlate the results, the Taguchi experimental design method was used. Total organic carbon (TOC) removal was utilised as the measure of the oxidation efficiency and it was found that the removal of phenol from aqueous solution at pH 2.0 and 2.5 was very similar but hydrogen peroxide supply significantly affected the TOC removal with the change of flow rate from 14.4 mL/hr to 60 mL/hr. Also, the initial concentration of phenol was a highly significant factor, with higher concentrations resulting in a lower TOC removal rate. The temperature effects in the range of 14 °C to 42 °C were investigated and it was found that there

was accelerated oxidation of phenol in the early stages but after 90 minutes there was no significant difference between the results. Sonication with a bath type sonicator resulted in relatively small enhancements of TOC removal but further studies with cup-horn and probe type sonicators showed that TOC removal increased with higher intensity of sonication on additional input of hydrogen peroxide.

Keywords: wastewater, Fenton oxidation, iron corrosion, phenol, ultrasound, Taguchi experimental design

1. Introduction

In our previous work [1] we reported the results from batch reactor experiments to evaluate a novel chemical oxidation system referred to as the AFP (Advanced Fenton Process). The main parameters investigated were pH, H_2O_2 concentration and type of organic compound. Based on these results of the batch reactor experiments, this current work aims to evaluate the performance of a flow-through AFP system and further investigate the process parameters using phenol as a model pollutant. In order to enhance, mainly, the iron metal surface-mediated reactions ultrasonic irradiation has now been applied to the system and the flow rate of solution was considered as a process parameter because of its possible effect on mass transport and iron surface contact time.

Since many parameters are simultaneously investigated, the Taguchi experimental design method [2] was used for optimisation of the process conditions. The decomposition of phenol and other intermediates was determined by measuring the total organic content (TOC) of the solution after each treatment.

2. Experimental Section

2.1 Materials and methods

For all experiments, high purity deionised water (>17.7MΩ) (Nanopure, Elga) was used. All chemicals were reagent grade or better and used without further purification. H_2O_2 (AnalaR), ferrous sulphate, benzoic acid and sulphuric acid were purchased from BDH and phenol (redistilled, 99+%) was from Aldrich. Sodium persulfate, orthophosphoric acid (AnalaR) and potassium hydrogen phthalate (AnalaR) for TOC analysis were supplied by BDH. Non-galvanised iron metal bars (thickness 0.85mm, 2.5 cm x 9 cm) were cut from iron sheet supplied by Brown and Tawse (UK) (iron purity > 99.2 %). Great care was taken to reproduce consistent surface conditions for the iron bar. Before each run, the surface was abraded using, sequentially, three grades of sandpaper (Grit numbers P80, 120 then 240). Finally, the surface of the iron was dried with soft tissue, washed with deionised water and immediately immersed in the reaction solution.

2.2 Analytical and experimental conditions

Samples (1mL) were taken from the reaction solution at various times and 50μL were analysed immediately using a heated-persulfate type (100 ºC) TOC analyser (Model 700, OI Analytical). The total reactor working volume was 200mL and the iron bar surface loading was about 400cm^2/L for the continuous system, which consists of two symmetrical compartments and is shown schematically in Figure 1.

Temperature was normally maintained at 25 (±1) ºC using a water bath. Stock solution of H_2O_2 (3%) was used for hydrogen peroxide supply and a bath type sonicator (Kerry Ultrasonics, UK) was used for ultrasonic irradiation. The power

measured using the calorimetric method [3] was about 3.2W. For batch experiments using a cup-horn (diameter: 11.5cm) and probe type sonication, a multi-power level sonicator with 0 to 100% duty cycle (20kHz, 600 output power, Sonics and Materials, USA) was used. For a 30% duty cycle, the power measured was about 2.4W for power level 3 and 4.7W for power level 9. A 500mL Pyrex glass vessel was used as the reactor and the actual working volume was 400mL. Intensive mixing was used throughout using a mechanical stirrer (RZR1, Heidolph, Germany) at about 850 rpm for cup-horn type experiments. The iron metal surface loading was 72.6(±2.2) cm^2/L.

Table 1 shows the experimental conditions for process parameters investigated in this work. The reaction time of 90 minutes was used for all reactions because it was found from preliminary experiments that the TOC removal rate after this time virtually ceased.

2.3 Taguchi methodology

The Taguchi method [2] uses an efficient experimental design to determine the optimal combination of a set of factors (A to E) to maximise a response variable (TOC). The combination found is that which maximises a signal to noise ratio (SNR_L) that provides a robust optimum [4], which is important as the process moves towards commercialisation.

In this paper we investigate the five main effects and all ten two-factor interactions leading to fifteen effects of interest. Hence the $L_{16}(2^{15})$ design [5,6] was used and three and higher interactions are ignored as is common with the Taguchi approach.

Table 2 shows the whole set of experimental runs carried out and for statistical reasons all runs were randomly conducted and also replicated 4 times. For all experimental runs, the final TOC removal was calculated at 90 minutes. The error range of TOC measurement was less than ±10%.

3. Results and Discussion

The results for all 16 experimental runs are presented in Table 2. A range of values from 7 to 50% was obtained for TOC removal. The average of TOC removal varied from 8.5 to 49.25% and the standard deviation from 0.50 to 5.74. From the average values of the results, run 15 gave the lowest TOC removal of phenol and 16 the highest.

3.1 Analysis of the experimental results using MINITAB™

A stepwise regression analysis for SNR_L showed that factors B ($t(12) = 10.19$; $p << 0.001$), C ($t(12) = -10.44$; $p << 0.001$), and their interaction ($t(12) = 7.49$; $p << 0.001$), were very highly significant whilst all remaining effects were insignificant (each $p > 0;.05$). The model with these three effects had an R^2 value of 95.7%, a highly significant overall F value ($F(3,12) = 89.60$; $p << 0.001$) and the Anderson-Darling test showed no departure from normality ($AD = 0.304$; $p > 0.05$).

Table 3 gives the mean %TOC for the combinations of H_2O_2 concentration and initial concentration of phenol. This shows that the best combination is H_2O_2 high and initial concentration of phenol low. The low-low and high-high combinations have a slightly less %TOC whilst the combination of H_2O_2 low and initial concentration of phenol high results in a much lower %TOC.

Thus the best combination is H_2O_2 high and initial concentration of phenol low but if this were difficult to achieve then it would still be acceptable to have low/low or high/high but definitely not H_2O_2 low and initial concentration of phenol high. Given these parameters then alteration of pH, ultrasound and flow rate will have little effect (within the ranges investigated) on TOC removal.

The flow rate of the solution can affect the process performance through changing the contact time of the solution on the iron metal surface. Also, the acceleration of washing-out of the iron metal surface may lead to improvement of the process efficiency. However, the results show that the increase of flow rate from 100mL/min to 500mL/min has relatively little effect on the overall TOC removal. In fact, since the solution was re-circulated through the system, higher flow rates gave the solution higher contact time with the iron bar. Although this caused relatively little change in TOC removal at 95 minutes, it clearly affected the TOC removal trend as shown in Figure 2. The higher flow rate showed a greater TOC removal between about 30 ~ 60 minutes.

3.2 Temperature effects

The effects of temperature as a process parameter on the oxidation efficiency were investigated. Figure 3 shows the results of increasing temperature from 14 ˚C to 25 ˚C to 42 ˚C. Around 20 minutes, the TOC removal at 42 ˚C was considerably higher than at 14 and 25 ˚C. However, after around 60 min, the TOC removal rate was very similar in all three cases. Hydrogen peroxide as a source of oxidants such as hydroxyl radicals is not a limiting factor because there was a continuous supply. It is suggested that as oxidation proceeds small molecules, which are resistant to further oxidation, are formed.

3.3 Sonication effects

From our previous results of continuous application of ultrasound by a bath type sonicator it was found that sonication did not lead to a significant increase in overall TOC removal efficiency [7]. This led to the current further work with higher intensity sonication equipment. The effects of ultrasound on homogeneous and heterogeneous processes have been investigated extensively by many researchers [1,8-11]. Since the AFP is both a homogeneous and heterogeneous system, the effects of sonication are more complex in this case. Consequently, in the current work only the effects of sonication on the overall TOC removal were considered.

First of all, the results of the continuous reactor experiment in the absence and presence of ultrasound irradiation were compared. Figures 4a and 4b show the results of total iron concentration measurements and TOC removal respectively. Under ultrasound irradiation, a marked increase of iron concentration in the solution was observed. The results in Figure 4a show that there is a significant effect of sonication on the corrosion process of iron surface. It was extensively described by Tomlinson [9] that ultrasound can increase the corrosion of metal surface. The main reason for

enhanced corrosion by sonication is ascribed to removal or destruction of passivation films on the metal surface by cavitation effects. In such a case, active corrosion increases at the pristine metal surface. On the other hand, as seen in Figure 4b, the TOC removal trend was similar regardless of the total iron concentration in the solution. This may be ascribed to recalcitrance of the fragmented small molecules formed as the result of phenol oxidation.

The sonication by a bath type sonicator did not give sizable improvement of the TOC removal but this may not be the same when high intensity of ultrasound is utilised. Therefore, a cup-horn type sonicator was used to compare the effects of sonication intensity on the oxidation efficiency. Figure 5 shows the results of the TOC removal during the ultrasonic irradiation by a cup-horn type sonicator at three different power levels. There were marked variations of temperature by sonication with the adjustment of the power level but no sizable changes of TOC removal. Considering the results shown in Figure 4a, along with those presented here, it appears that there may be an increase in iron concentration in the solution due to the higher power level but without sizable increase of TOC removal.

It was thought that an increased input of hydrogen peroxide during experiments might affect the overall TOC removal through generation of more hydroxyl radicals by Fenton-type reactions enhanced by sonication. Therefore, multiple injections of hydrogen peroxide into the reaction system were made during the oxidation of phenol solution. Figure 6a shows the results from multiple injections of hydrogen peroxide under ultrasound irradiation by a probe type sonicator. Hydrogen peroxide was added at 0, 40, 80, 100, 120, 140, and 160 min. After addition of hydrogen peroxide at 80 min, the TOC removal rate increased rapidly and reached 75% around 100 min.

These results indicate that sonication can make a great contribution to enhanced mineralisation of organic substances with increased input of hydrogen peroxide but little contribution without hydrogen peroxide. It also confirms results obtained by others [12-14] that small, stable molecules act as a barrier to complete mineralization. The input of hydrogen peroxide after 120 min did not result in any sizable increase of TOC removal. This slow process of TOC removal after 100 min may be due to recalcitrance of small molecules formed through hydroxyl radical driven oxidation reactions.

4. Conclusions

In this work, a model pollutant, phenol, was treated by a novel oxidation process (the Advanced Fenton Process; AFP) and its efficiency was monitored by TOC removal from the solution. The continuous AFP, as presented in this paper, has shown a high potential as an alternative for oxidative destruction of toxic pollutants such as phenol. The identified process parameters of the AFP included hydrogen peroxide supply, initial concentration of phenol, sonication, pH, temperature and iron surface contact time. Under the experimental conditions used in this work, the pH change from 2.0 to 2.5 hardly affected the overall TOC removal of phenol solution. Also, the temperature increase from 14 ºC to 42 ºC seemed to cause little significant increase in TOC removal at around 100 min reaction time, in spite of a marked increase of TOC removal rate in the early stage of the treatment. However, the initial concentration of phenol and hydrogen peroxide supply significantly affected the TOC removal rate. This addresses the importance of the stoichiometric relationship between hydrogen peroxide and organic substances. A generalised approach will be sought to deal with this stochiometric relationship (including iron metal surface loading and iron

concentration in solution) to support commercialisation of the AFP. Ultrasonic effects were quite marked with the cup-horn and probe-type sonicators but relatively small enhancements of TOC removal were observed with a bath type sonicator. Further studies are ongoing with scaled-up equipment including alternative ways of inputting cavitation.

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Table 1: Levels of experimental parameters.

Table 2: A design of $L_{16}(2^{15})$ by the Taguchi method

Table 3: Mean of %TOC removal for the combinations of factors: H_2O_2 concentration and initial concentration of phenol

Figure 1: Schematic diagram for the continuous reactor system. (**A**: reactor, **B**: peristaltic pump, **C**: constant temperature water bath, **D**: submergible magnetic stirrer, **E**: pH meter, **F**: hydrogen peroxide storage vessel, **G**: iron bar, **H**: bath type sonicator)

Figure 2: Comparison of the TOC reduction trends with the change of flow rate. (For the experimental numbers, *see* Tables 1 and 2.)

Figure 3: The TOC removal profile at different temperatures 14 ºC, 25 ºC and 42 ºC (All experiments were conducted using the continuous reactor under sonication by the bath type sonicator. Initial pH = 2.5; H_2O_2 (3%) = 60mL/h; $[phenol]_o$ = 0.5mM; flow rate = 500mL/h).

Figure 4: (a) The effect of ultrasound irradiation on the total iron concentration in the solution during the AFP oxidation of phenol solution using the continuous reactor. (b) Comparison of TOC removal in the presence and absence of ultrasound irradiation (pH = 2.5; H_2O_2 (3%) = 60mL/h; $[phenol]_o$ = 0.5mM; flow rate = 500mL/h)

Figure 5: Oxidation of phenol solution under ultrasound irradiation by a cup-horn type sonicator with increase of power level. (a) TOC removal profile and (b) temperature rise profile (initial pH = 2.5; $[H_2O_2]_o$ = 1900mg/L; 30% duty cycle for all runs)

Figure 6: Oxidation of phenol solution under sonication by a probe type sonicator (a) TOC removal profile (b) temperature rise profile. (H_2O_2 addition: 1900 mg/L at 0, 40, 80, 100, 120, 140, 160 min, respectively. Initial pH = 2.5; $[phenol]_o$ = 0.5mM)

Table 1

Factors		Levels	
		Low	**High**
A	pH	2.0	2.5
B	H_2O_2 (3% stock solution)	14.4ml/hr	60ml/hr
C	Initial concentration of phenol	0.5mM	5mM
D	Ultrasound	OFF	ON
E	Retention time of solution (flow rate)	0.4min (500mL/min)	2min (100mL/min)

Table 2

Run Number	**A**	**B**	**C**	**D**	**E**	**TOC Mean**	**TOC SD**	**SNR_L**
1	Low	Low	Low	Low	Low	34.50	1.73	30.73
2	Low	High	High	High	High	45.75	1.71	33.19
3	High	Low	Low	Low	High	43.25	0.96	32.71
4	High	High	High	High	Low	39.75	5.74	31.77
5	Low	Low	High	High	Low	11.75	2.22	21.02
6	Low	High	Low	Low	High	47.50	2.08	33.52
7	High	Low	High	High	High	13.75	2.87	22.42
8	High	High	Low	Low	Low	45.50	1.91	33.14
9	Low	Low	Low	High	High	35.25	2.75	30.88
10	Low	High	High	Low	Low	32.75	3.30	30.19
11	High	Low	Low	High	Low	40.75	2.63	32.16
12	High	High	High	Low	High	34.50	2.08	30.72
13	Low	Low	High	Low	High	11.75	2.06	21.10
14	Low	High	Low	High	Low	42.50	2.08	32.54
15	High	Low	High	Low	Low	8.50	1.29	18.36
16	High	High	Low	High	High	49.25	0.50	33.85

(See Table 1 for factors, TOC = %TOC removal rate)

Table 3

H_2O_2 (3% stock solution)	Initial concentration of phenol	Mean TOC
Low	Low	38.44
Low	High	11.44
High	Low	46.19
High	High	38.19

Fig 1

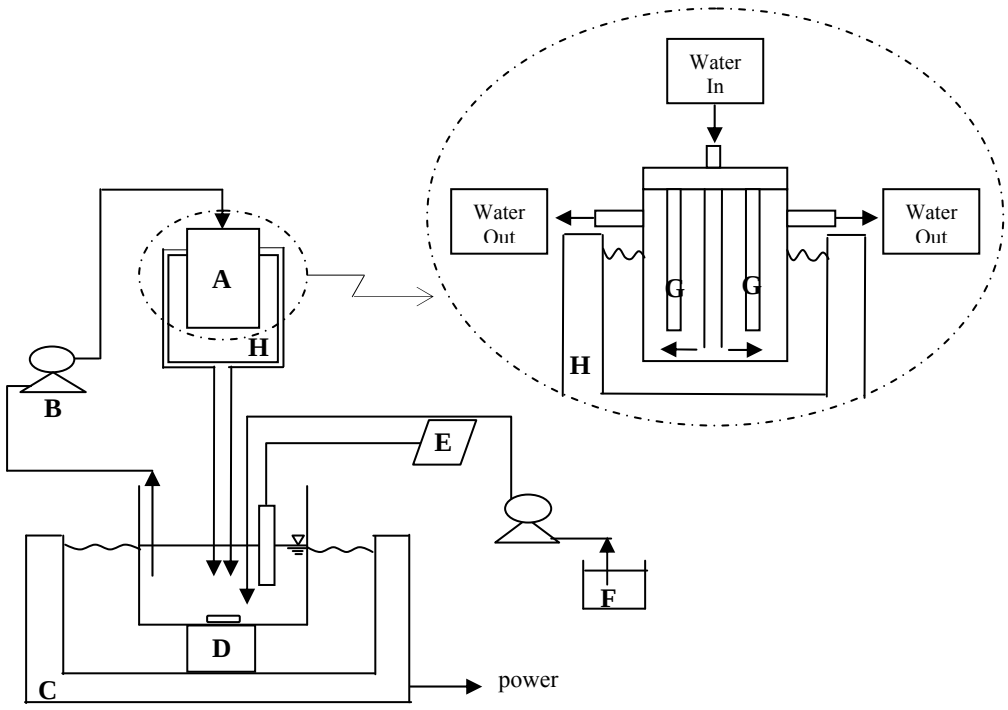
Water In
Water Out
Water Out
G
G
H
A
H
B
E
F
D
C
power

Fig 2

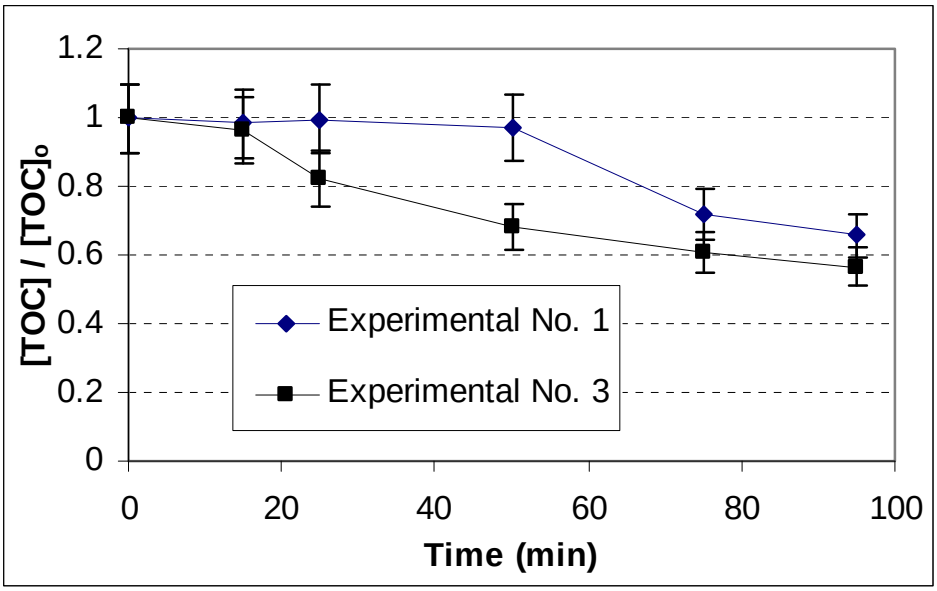
1.2
1
0.8
0.6
0.4
0.2
0
[TOC] / [TOC]o
0
20
40
60
80
100
Time (min)
Experimental No. 1
Experimental No. 3

Fig 3

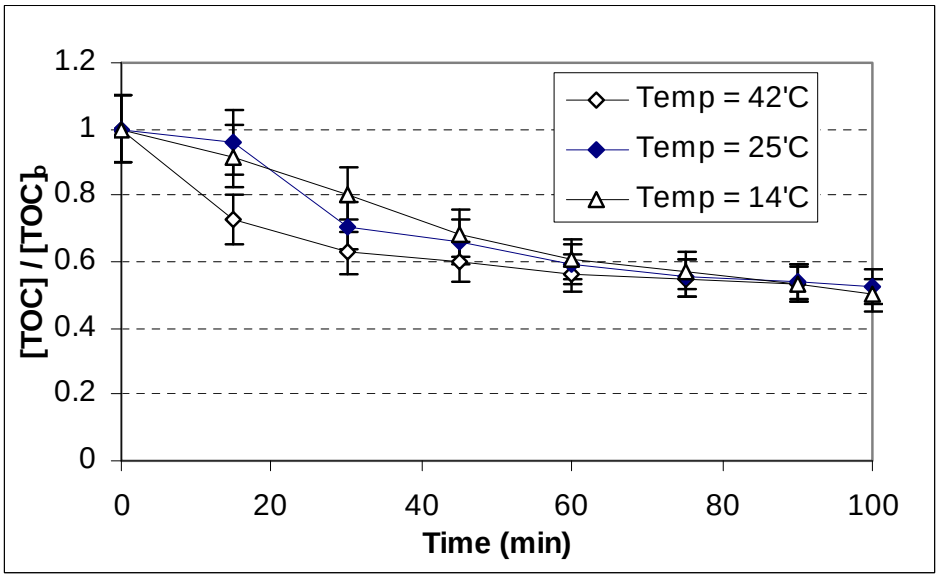

Fig 4a

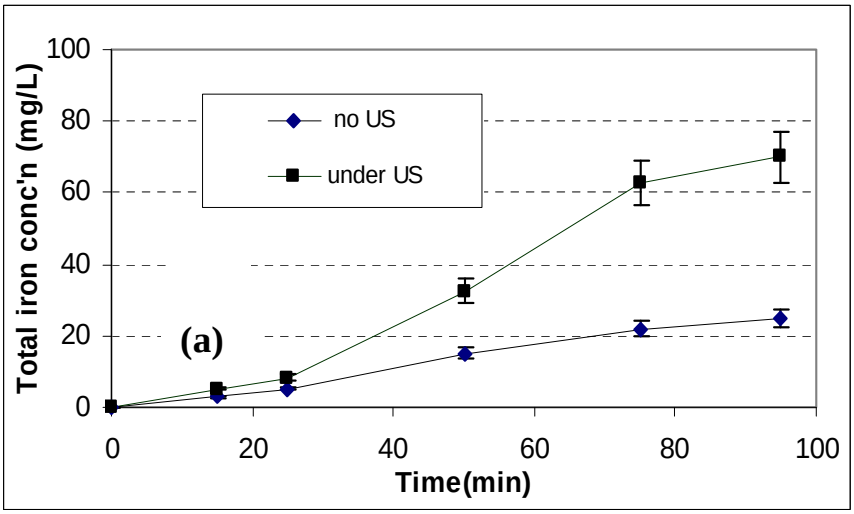

Fig 4b

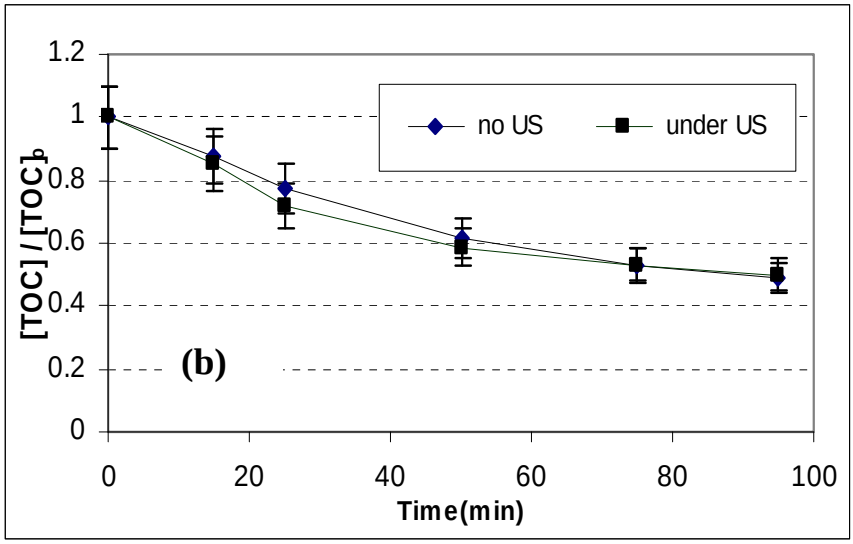

Fig 5a

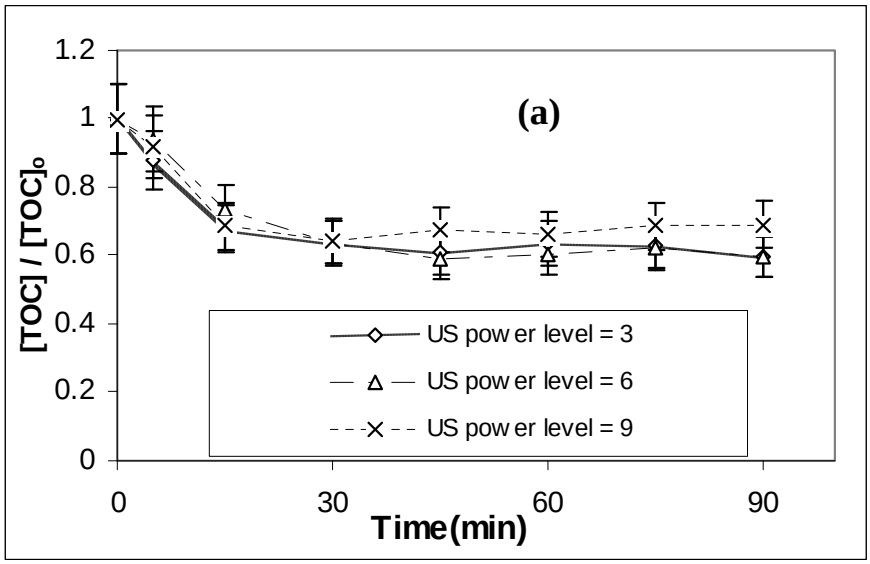

Fig 5b

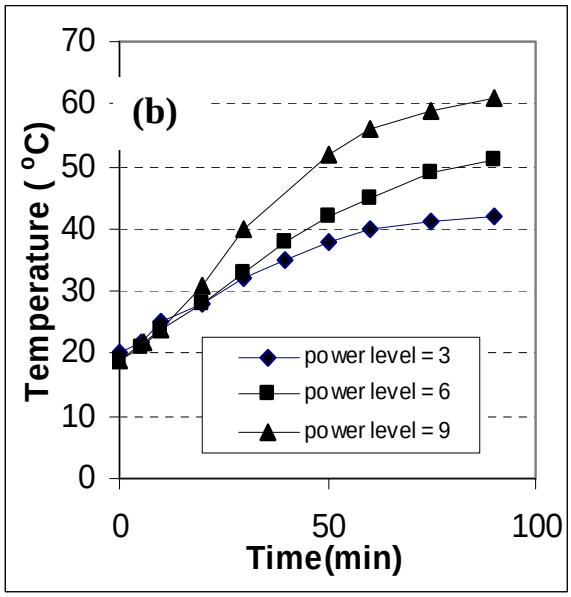
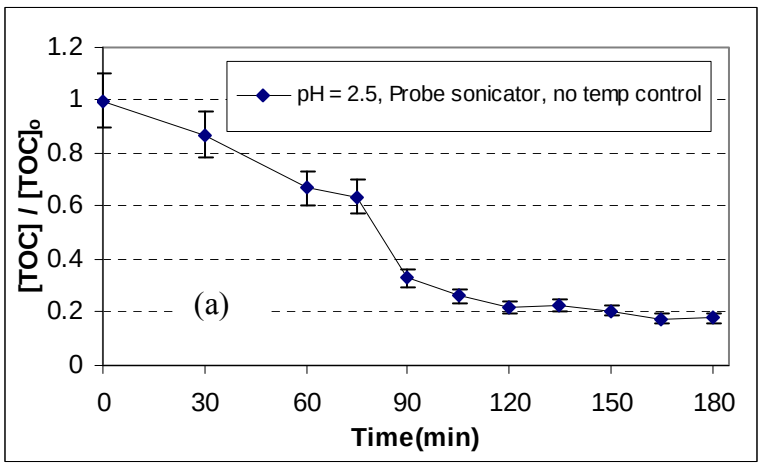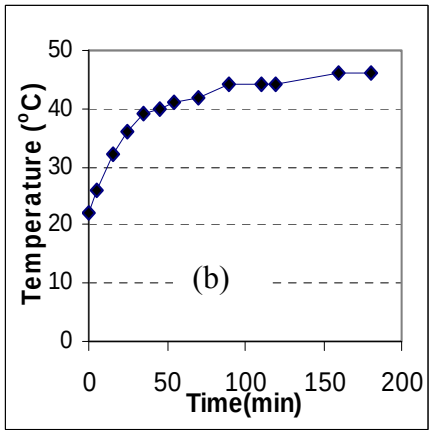
Fig 6a and b