

# Acid Orange 7 Dye Degradation Using Combined Acoustic Cavitation with Fenton and Photo Fenton Processes

Yogendra D. Thakare<sup>1</sup>, Sunita M. Jadhav<sup>2</sup>, Kishor S. Wani<sup>3</sup>

Assistant Professor<sup>1</sup>, Associate Professor<sup>2</sup>, Professor and Principal<sup>3</sup>

Department of Chemical Engineering

SSBT's College of Engineering & Technology, Bambhori, Jalgaon, MS, India<sup>1,3</sup>

Bharati Vidyapeeth Deemed University College of Engineering, Pune, MS, India<sup>2</sup>

## Abstract:

This paper evaluates the degradation of Acid orange 7 dye using combination of acoustic cavitation with Fenton and Photo Fenton processes. All experiments were performed on a laboratory scale set-up. The effects of different reaction parameters such as sonication power, concentration of dye, pH and the molar ratio of  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O} : \text{H}_2\text{O}_2$  for the oxidation of the acid orange 7 dye aqueous solutions has been assessed. Effective system conditions were found to be 750 W sonication power, 20 ppm dye concentration, pH of 3 and 1:20 molar ratio of  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O} : \text{H}_2\text{O}_2$ . The results show that the degradation of acid orange 7 dye was maximum for Acoustic cavitation + Photo Fenton process as compare to Acoustic cavitation + Fenton process and the conventional processes. Synergetic index of 3.15 and 4.33 have been obtained using Acoustic cavitation + Fenton and Acoustic cavitation + Photo Fenton processes respectively. The kinetic study indicated that the degradation rate of the acid orange 7 dye fitted to first order kinetics for all the processes studied. It was also observed that Acoustic cavitation based hybrid processes were more effective as compared to individual process.

**Keywords:** Acid Orange 7 Dye, Acoustic Cavitation/Ultrasonic Cavitation (US), Combination, Degradation, Fenton Process, Photo Fenton Process.

## I. INTRODUCTION

Wastewaters from textile and dye industries are highly coloured with significant amount of auxiliary chemicals. The discharge of these wastewater introduced intensive colour and toxicity to aquatic environment causing serious environmental problem [1, 2]. Dyes are widely used in the textile industries because of its simple dyeing procedure and good stability during washing process [3]. Due to the complex aromatic structure and stability of dyes, conventional biological treatment methods are ineffective for degradation [4]. Hence, the concentration remains constant in the environment [5].

There are many ways to treat the dye effluents, viz. biological methods, flocculation, reverse osmosis, adsorption on activated charcoal, chemical oxidation and advanced oxidation processes (AOPs) [6]. AOPs have been proven to be the most efficient way to degrade the dye effluents. AOPs are based on the use of the hydroxyl radical as primary oxidant of organic pollutants. These processes can lead to complete mineralization of organic molecules into  $\text{CO}_2$  and water [7-9]. Various types of oxidants including chlorine, hydrogen peroxide, ozone and chlorine dioxide are used for colour removal from wastewater [10].

Cavitation is the upcoming techniques that can be used for degradation of dye. It can be described as the formation of nuclei, growth and collapse of bubbles in liquid, releasing large magnitudes of energy. The collapse of the bubbles induces localized supercritical conditions, i.e. high temperature and pressure condition (about of 1000 atm pressure and about 5000 K temperature). The local effects of cavitation include generation of free radicals, hot spots and intense turbulence coupled with liquid circulation currents; the conditions being quite favorable for oxidation of pollutants

[11, 12]. During cavitation bubble collapse,  $\text{H}_2\text{O}$  undergoes thermal dissociation within the vapor phase to give hydroxyl radical and hydrogen atoms. In water and wastewater treatment applications, organic pollutants may be destroyed either in the cavitation bubble itself by pyrolytic decomposition (if the compounds are hydrophobic), at the interfacial sheath between the gaseous bubble and the surrounding liquid or in the bulk solution via oxidative degradation by hydroxyl radicals [13, 14].

When applied individually cavitation often gives lower rates of the degradation, but the efficiency of cavitation can be significantly enhanced by combining it with other advanced oxidation processes such as Fenton [15, 16] and Photo Fenton [17, 18]. Combination of cavitation with other AOPs often leads to an intensification of the degradation of organic pollutants due to the enhanced generation of the hydroxyl radicals [19].

In recent year attention have been focused on photochemical advanced oxidation processes using Fenton reagent with UV light for the treatment of wastewater. Fenton reagent had been found to be effective in degrading dye pollutants [20-23]. The oxidation power of Fenton reagent is due to the generation of hydroxyl radical ( $\text{OH}^\bullet$ ) during the iron catalyzed decomposition of hydrogen peroxide in acid medium [24].

The hydroxyl radical with a high oxidation potential (2.8 eV) attacks and completely destroys the pollutants in Fenton process. The degradation of pollutants can be considerably improved by using UV-radiation. This is due to the generation of additional hydroxyl radicals [25, 26]. This Photo Fenton process had been effectively used to degrade the pollutants.

Acid orange 7 dye is water soluble anionic dye, containing one or more acidic groups along with one azo group. Azo dyes constitute the largest class of dyes and are widely used in a variety of industries from textile to cosmetics. The chromophore structure of azo dyes is made of two aryl rings connected through an azo, -N=N-, bridge. The colour of the dye is due to azo (-N=N-) chromophore. Degradation would occur from the breakdown of azo group [27]. The exact structure of the Acid orange 7 dye has also been given in Figure 1.

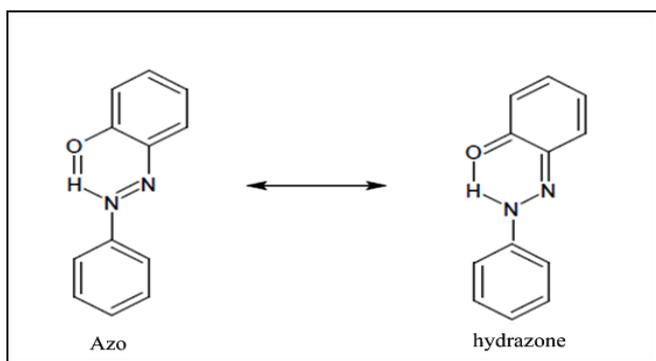


Figure 1 Structure of Acid Orange 7 dye

Various AOPs such as acoustic cavitation [28], H<sub>2</sub>O<sub>2</sub> [29, 30], Fenton [4, 29, 31], Photo Fenton [31], photolytic (UV) [30, 32], photolytic with H<sub>2</sub>O<sub>2</sub> (UV + H<sub>2</sub>O<sub>2</sub>) [33], photo catalytic [34-36], electrochemical [37] and electro Fenton [38] degradation processes have been reported in the literature for the degradation of acid orange 7 dye. However, the use of acoustic cavitation based hybrid techniques for the degradation of acid orange 7 dye has not yet been explored. The present work deals with the study of degradation of acid orange 7 dye by using of Acoustic cavitation and Acoustic cavitation based hybrid techniques such as Acoustic cavitation + Fenton and Acoustic cavitation + Photo Fenton process and observe the effect of key operating conditions on the kinetics of acid orange 7 dye degradation.

## II. MATERIALS AND METHODS

### 1. Materials

Acid orange 7 dye was obtained from Merck, Mumbai. Hydrogen peroxide (30% W/V H<sub>2</sub>O<sub>2</sub>) and Ferrous sulfate heptahydrate (FeSO<sub>4</sub> · 7H<sub>2</sub>O) were obtained from a Thomas baker, Mumbai. Stock solutions of acid orange 7 dye was prepared in distilled water. Before each run, 0.5 N H<sub>2</sub>SO<sub>4</sub> and 0.5 N NaOH were used to adjust the initial pH of the dye solution. H<sub>2</sub>SO<sub>4</sub> and NaOH used were obtained from Merck, Mumbai.

### 2. Experimental Setup

The cavitation reactor used in the present study was an ultrasonic horn. Ultrasonic processor of diameter 13 mm was operated at a frequency of 20 kHz with maximum power 750 W. All the experiments were conducted at 60% duty cycle (ultrasonic horn kept on for 6 second and off for 4 second). The height of the ultrasonic horn was adjusted using metal stand in such way that the tip of the probe was immersed 2 cm inside the liquid. Initially 230 ml of acid orange 7 dye solution was taken in a quartz glass reactor at natural pH 6 and temperature throughout the experiment was maintained at (28 ± 3 °C). Samples (volume 5 ml) were withdrawn at regular

intervals for analysis on UV- VIS spectrophotometer. Schematic representation of experimental set-up used in this study is as shown in Figure 2.

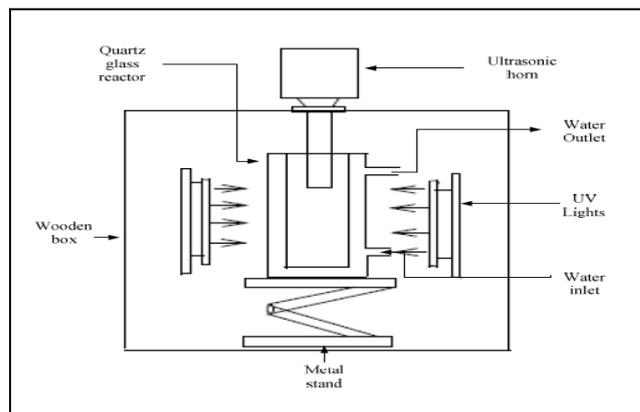


Figure 2 Schematic representation of the experimental setup

## 3. Analytical method

Change in the concentration of acid orange 7 dye obtained during its degradation using different processes was measured using a UV-Vis double beam spectrometer (PerkinElmer). Sample absorbance was measured at 485 nm which is the wavelength that corresponds to the maximum acid orange 7 dye absorbance in the visible region.

Effect of sonication power, concentration and initial pH on degradation of acid orange 7 dye was studied. Also effect of ferrous dosage on degradation of acid orange 7 dye using Acoustic cavitation + Fenton process and Acoustic cavitation + Photo Fenton process was studied and result obtained were compared.

## III. RESULT AND DISCUSSION

### Degradation kinetics:

Acid orange 7 dye degradation is a first-order kinetics [equation (1)], meaning that the rate of reaction depends only on the concentration of dye present in the solution. According to the kinetics, a plot of the natural logarithm of the concentration of the reactant against time results in a line whose slope represents the rate of degradation.

$$\ln(C_{A0}/C_A) = k \times t \quad (1)$$

The percentage of degradation was calculated according to equation (2).

$$\text{Degradation \%} = ((C_{A0} - C_A) / C_{A0}) \times 100 \quad (2)$$

C<sub>A0</sub>: initial concentration of the dye (mg/l); C<sub>A</sub>: concentration of the dye after treatment (mg/l).

k = rate constant (min<sup>-1</sup>), t = time (min).

### Acoustic cavitation:

#### 1. Effect of sonication power on the degradation of acid orange 7 dye

The effect of sonication power on degradation of acid orange 7 dye was studied at different operating powers (250, 500 and 750 W) with initial concentration of 20 ppm, pH 6, at constant operating temperature of 28 ± 3 °C and 20 kHz sonication frequency. Sonication was carried out for 120 minutes. Figure 3 shows the effect of sonication power on the rate of degradation of acid orange 7 dye at different operating powers (250, 500 and 750W). It has been observed that the rate degradation of acid orange 7 dye increases with an increase in

the operating power. The maximum rate of degradation was observed at power dissipation of 750 W whereas minimum rate of degradation of acid orange 7 dye was observed at power dissipation level of 250 W.

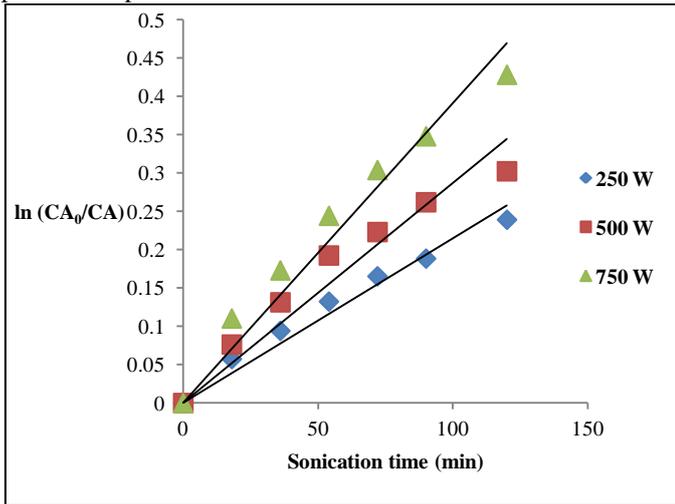


Figure 3 Effect of sonication power on the rate of degradation of acid orange 7 dye

Table 1 shows the effect of sonication power on the extent of degradation and first order reaction rate constant of acid orange 7 dye. It has been observed that as sonication power is increased from 250 to 750 W and extent of degradation of acid orange 7 dye increases from 21.28 % to 34.85 %. The increase in degradation of acid orange 7 dye with increasing power can be due to the enhancement in the number of cavities leading to higher cavitation activity and hence enhanced production of the hydroxyl radicals [39].

Table 1 Effect of sonication power on the degradation of acid orange 7 dye

Sonication power (W)	Extent of degradation (%)	First order reaction rate constant ( $k \times 10^{-3}, \text{min}^{-1}$ )
250	21.28	2
500	26.10	3
750	34.85	4

## 2. Effect of initial concentration of acid orange 7 dye on the degradation

The effect of initial dye concentration on the ultrasonic degradation of acid orange 7 dye was investigated at constant operating temperature of  $28 \pm 3$  °C, pH 6, power 750 W and 20 KHz frequency for 120 minutes sonication time. Figure 4 shows the effect of different initial concentration of acid orange 7 dye on the rate of degradation. It was found that with the increase initial concentration of acid orange 7 dye and the rate of degradation decreases.

Table 2 shows extent of degradation and first order reaction rate constant of acid orange 7 dye at its different initial concentration. It has been observed with the increase in the concentration of acid orange 7 dye from 20 to 40 ppm, the extent of degradation of acid orange 7 dye was decreased from 34.85 % to 28.12 %. It's because both pyrolysis and free radical reactions occur in the interfacial area of acid orange 7 dye. Further the major route for acid orange 7 dye degradation is chemical oxidation by hydroxyl radicals in the interfacial

area and bulk liquid. Pyrolysis (i.e., combustion) in the interfacial region is predominant at high solute concentration while at low solute concentration free radical reactions are likely to be predominant [40].

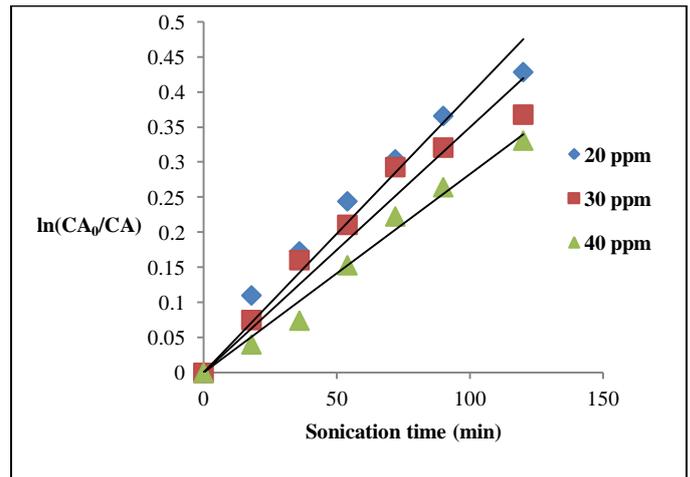


Figure 4 Effect of initial concentration of acid orange 7 dye on the rate of degradation

Table 2 Effect of initial concentration of dye on the degradation of acid orange 7 dye

Concentration (ppm)	Extent of degradation (%)	First order reaction rate constant ( $k \times 10^{-3}, \text{min}^{-1}$ )
20	34.85	4
30	30.76	3
40	28.12	2

## 3. The effect of initial pH on the degradation of acid orange 7 dye

Initial pH is an important parameter influencing the treatment efficiency. In this study, in order to investigate the effects of pH on degradation of acid orange 7 dye using acoustic cavitation, experiments were conducted at different pH values 2, 3, 4, 6, 8 and 10. These experiments were conducted at 20 ppm initial dye concentration, temperature of  $28 \pm 3$  °C for 120 minutes of sonication time. Figure 5 shows the effect of initial pH on the degradation (%) and the rate of degradation of acid orange 7 dye using acoustic cavitation.

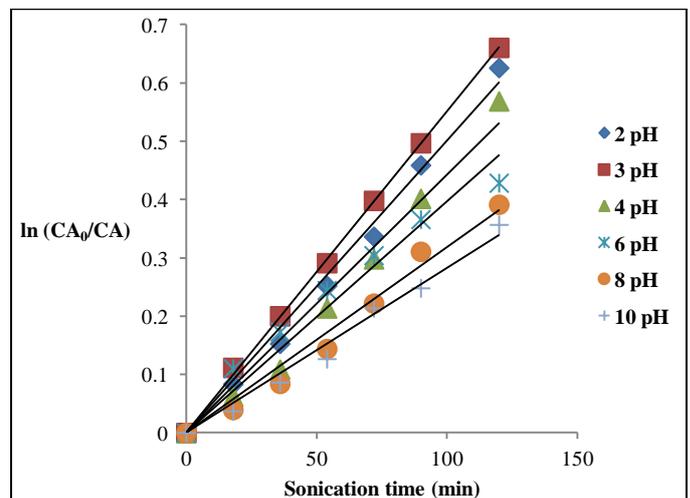


Figure 5 Effect of initial pH on the rate of degradation of acid orange 7 dye

Table 3 shows that the degradation of acid orange 7 dye is very rapid under acidic pH 3, 48.34 % degradation after 120 min of sonication was obtained at constant reaction temperature ( $28 \pm 3$  °C) and with 20 mg/L of initial dye concentration. At lower pH, there is domination of the molecular form of acid orange 7 dye. This molecular form of acid orange 7 dye induces its evaporation into the cavity. Thus, the overall decomposition of acid orange 7 dye at low pH is considered to take place in both the gaseous and interfacial film regions by pyrolysis and free radical attack which may result into rapid degradation of acid orange acid 7 dye. Another reason may be that the oxidization potentials of  $\text{OH}^\bullet$  radicals are higher in acidic medium as compared to that in the basic medium [41-43].

Table 3 Effect of initial pH on the of degradation acid orange 7 dye

pH	Extent of degradation (%)	First order reaction rate constant ( $k \times 10^{-3}$ , $\text{min}^{-1}$ )
2	46.51	5.21
3	48.34	5.50
4	43.36	4.47
6	34.85	3.57
8	32.39	3.36
10	30.01	2.97

## US + Fenton Process:

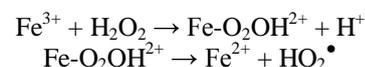
### 1. Effect of ferrous dose on the degradation of acid orange 7 dye

Fenton process utilizes the reactivity of hydroxyl radicals generated in acidic conditions by iron catalyzed decomposition of hydrogen peroxide for the degradation of organic pollutant. Amount of ferrous ion is one of the main parameters to influence the Fenton processes. More hydroxyl radicals are produced with the increase in the concentration of ferrous ions ( $\text{Fe}^{2+}$ ). Effect of Ferrous dose on the extent of degradation of acid orange 7 dye has been investigated for various molar ratios (1:50, 1:40, 1:30 and 1:20) of Ferrous sulphate heptahydrate ( $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ ) to hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) in the presence of acoustic cavitation (Time: 18 min). Figure 6 shows the effect of ferrous dosage on the rate of degradation of acid orange 7 dye. It has been observed that the rate of degradation of acid orange 7 dye increases with an increase in the doses of ferrous under acoustic cavitation with optimum concentration of hydrogen peroxide (260 mg/L). The degradation of acid orange 7 dye is faster in the early stage of the reaction than in the later stage. Most of the hydrogen peroxide dose was consumed in the early stage of the Fenton reaction. Since ferrous ion catalyses hydrogen peroxide to form hydroxyl radical quickly in the first stage of reaction, more degradation occurs in the early stage of reaction [44].

Fenton reaction can be described using equation,



Resulting  $\text{Fe}^{3+}$  ions can react with  $\text{H}_2\text{O}_2$  to produce the intermediate complex  $\text{Fe-O}_2\text{OH}^{2+}$ , which can easily get converted into  $\text{Fe}^{2+}$  and  $\text{HO}_2^\bullet$  under cavitation.



Generated  $\text{Fe}^{2+}$  ions can again react with  $\text{H}_2\text{O}_2$  to generate even more number of hydroxyl radicals. In addition to this, some part of  $\text{H}_2\text{O}_2$  directly decomposes to hydroxyl radicals in presence of acoustic cavitation as shown in below,



Hence, the combination of Acoustic cavitation and Fenton process accelerates the rate of generation of hydroxyl radicals [45, 46].

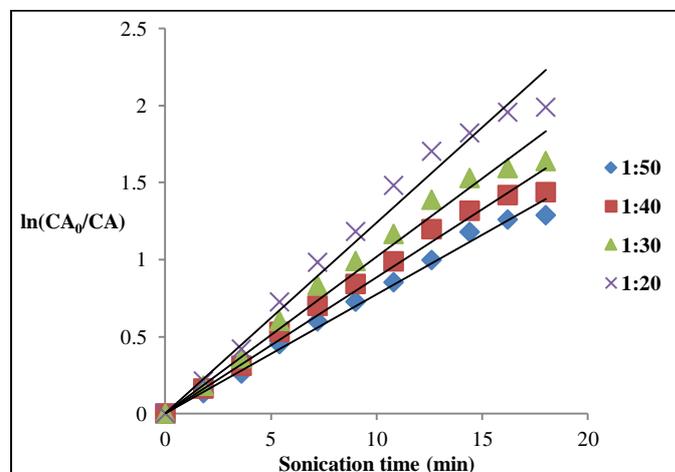


Figure 6 Effect ferrous doses on the rate of degradation of acid orange 7 dye

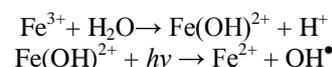
## US + Photo Fenton Process (Sonophotofenton Processes):

### 1. Effect of ferrous dosage on the degradation of acid orange 7 dye

The degradation of acid orange 7 dye was investigated using sonophotofenton process at different molar ratios of  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O} : \text{H}_2\text{O}_2$  ranging from 1:50 to 1:20. Two 8 W low-pressure mercury UV lamps (Philips) were used at 254 wavelengths for UV irradiation and ultrasonic processor for cavitation. Figure 8 shows the effect of the processes on the degradation of acid orange 7 dye. It has been observed that the rate of degradation of acid orange 7 dye increases with increase in the loading of  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  under sonophotofenton process with optimum concentration of  $\text{H}_2\text{O}_2$  (260 mg/L). In Fenton process ferrous salts react with hydrogen peroxide to generate the hydroxyl radicals as follows



The rate of dye degradation can be considerably increased via photochemical reaction in the photo-Fenton's process. In this case, the regeneration of catalyst i.e.  $\text{Fe}^{2+}$  ions, with production of new  $\text{OH}^\bullet$  radicals from  $\text{Fe}^{3+} / \text{Fe}(\text{OH})^{2+}$  by UV irradiation [51,52],



Hydrogen peroxide readily decomposes into hydroxyl radicals in the presence of acoustic cavitation and UV lights.



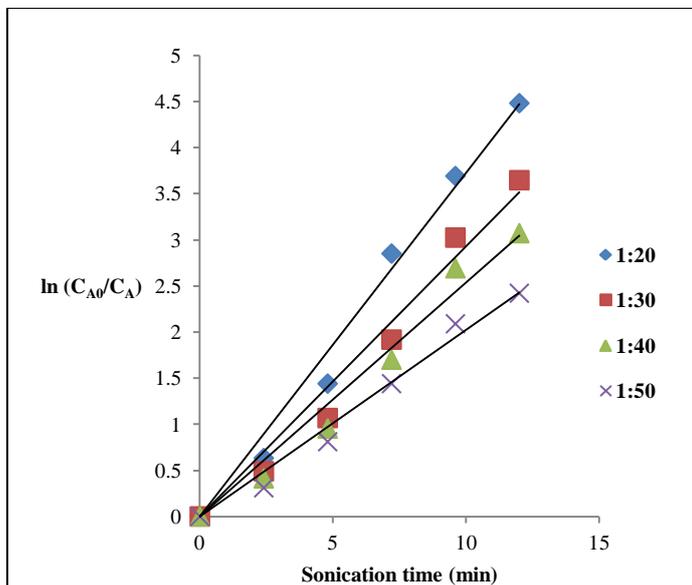


Figure 8 Effect ferrous loading on the rate of degradation of acid orange 7 dye

### Synergetic Effect:

#### 1. Combination of US + Fenton Process

Table 4 shows the effect of US, Fenton and US + Fenton Process on extent of degradation and first order reaction constant of acid orange 7 dye. It has been observed that 10.56 % and 61.91 % degradation of acid orange 7 dye obtained after 18 min of operation using acoustic cavitation and conventional Fenton process (with magnetic stirrer) respectively, significantly increased to 86.30 % by applying the combination of acoustic cavitation with Fenton process. Substantial synergetic effect has been observed using acoustic cavitation + Fenton process, since the value of reaction rate constant of  $6 \times 10^{-3} \text{ min}^{-1}$  and  $33 \times 10^{-3} \text{ min}^{-1}$  obtained in case of acoustic cavitation and conventional Fenton process (with magnetic stirrer) substantially increased to  $123 \times 10^{-3} \text{ min}^{-1}$  when acoustic cavitation was combined with Fenton process. The synergetic effect of combining acoustic cavitation with Fenton process based on reaction rate constant obtained is -

$$\text{Synergetic Coefficient} = \frac{k_{(\text{US} + \text{Fenton process})}}{k_{\text{US}} + k_{(\text{Fenton process})}} = \frac{123 \times 10^{-3}}{(6 + 33) \times 10^{-3}} = 3.15$$

Synergetic effect observed has been credited to the fact that the combination of acoustic cavitation with Fenton process generates higher concentration of hydroxyl radicals as compared to acoustic cavitation and Fenton processes. The increased concentration of hydroxyl radicals along with their effective utilization due to higher intensity of turbulence created by acoustic cavitation significantly accelerates the rate of degradation of acid orange 7 dye. In addition, the quantity of the ferrous sulphate required as a catalyst can be reduced significantly due to the combined acoustic cavitation + Fenton process as compared to Fenton process for obtaining same extent of degradation [19, 47].

Similar trends of results are reported in the literature for the degradation of Reactive Brilliant Red dye [48], Acid Blue 25 dye [49] and C.I. Acid Red 88 [50] dye by applying combination of acoustic cavitation and Fenton process.

Table 4 Effect of US, Fenton and US + Fenton Processes on the degradation of acid orange 7 dye

Types of process	Molar ratio (FeSO <sub>4</sub> .7H <sub>2</sub> O : H <sub>2</sub> O <sub>2</sub> )	First order reaction rate constant ( $k \times 10^{-3}, \text{ min}^{-1}$ )	Degradation (%) after 18 minutes
US	-	6	10.56
Fenton (with magnetic stirrer)	1:20	33	61.91
US + Fenton	1:50	77	72.39
	1:40	88	76.22
	1:30	101	80.56
	1:20	123	86.30

#### 2. Combination of US + Photo Fenton Process

Table 5 shows the effect of US, Photo Fenton, US + Photo Fenton on extent of degradation and first order reaction constant of acid orange 7 dye. It has been observed that 7.04 % and 78.71 % degradation of acid orange 7 dye obtained after 12 min of operation using acoustic cavitation and conventional photo Fenton process respectively, significantly increased to 98.89 % by applying the combination of acoustic cavitation with Photo Fenton process. Substantial synergetic effect has been observed using acoustic cavitation + Photo Fenton process, since the value of reaction rate constant of  $4 \times 10^{-3} \text{ min}^{-1}$  and  $82 \times 10^{-3} \text{ min}^{-1}$  obtained in case of acoustic cavitation and conventional Photo Fenton process (with magnetic stirrer) substantially increased to  $372 \times 10^{-3} \text{ min}^{-1}$  when acoustic cavitation was combined with photo Fenton process.

The synergetic effect of combining acoustic cavitation with Photo Fenton process based on reaction rate constant obtained is -

$$\text{Synergetic Coefficient} = \frac{k_{(\text{US} + \text{UV} + \text{Fenton process})}}{k_{\text{US}} + k_{(\text{UV} + \text{Fenton process})}} = \frac{372 \times 10^{-3}}{(4 + 82) \times 10^{-3}} = 4.33$$

Synergetic effect observed can again be attributed to the effective utilization and higher generation of hydroxyl radicals, regeneration of catalyst i.e. Fe<sup>2+</sup> ions and effective mixing generated by cavitation [19].

Similar trends of results are reported in the literature for the degradation of Malachite Green dye [12] by applying combination of acoustic cavitation and Photo Fenton process.

Table 5 Effect of US, Photo Fenton and US + Photo Fenton Processes on the degradation of acid orange 7 dye

Types of process	Molar ratio (FeSO <sub>4</sub> .7H <sub>2</sub> O : H <sub>2</sub> O <sub>2</sub> )	First order reaction rate constant ( $k \times 10^{-3}, \text{ min}^{-1}$ )	Degradation (%) after 12 minutes
US	-	4	7.04
Photo Fenton (with magnetic stirrer)	1:20	82	78.71
US + Photo Fenton	1:50	202	91.15
	1:40	254	95.36
	1:30	293	97.39
	1:20	372	98.89

#### IV. CONCLUSION

The following important conclusion can be established for the degradation of acid orange 7 dye.

1. Acoustic cavitation degradation of acid orange 7 dye is maximum at 750 W sonication power, 20 ppm dye concentration, pH 3 and 260 mg/L optimum H<sub>2</sub>O<sub>2</sub> concentration.

2. The combination of acoustic cavitation with Fenton and Photo Fenton processes found to give higher degradation rate of acid orange 7 dye than for conventional processes,  
Acoustic cavitation + Photo Fenton process = 98.89 %  
Photo Fenton process (with magnetic Stirrer) = 78.71 %  
Acoustic cavitation + Fenton process = 86.30 %  
Fenton process (with magnetic Stirrer) = 61.91 %  
Acoustic cavitation only = 10.56% (18 min sonication time)  
= 07.04% (12 min sonication time)

3. Significant synergetic effect has been observed since synergetic coefficient found were,  
US + Photo Fenton process = 4.33  
US + Fenton process = 3.15

The result shows that combination acoustic cavitation (US) with Fenton and Photo Fenton process is effective for the degradation of acid orange 7 dye. Thus the combination can give better results than individual process.

#### V. REFERENCES

1. M. Muruganandham, M. Swaminathan, Decolourisation of Reactive Orange 4 by Fenton and Photo-Fenton oxidation technology. *Dyes and Pigments*, 63 (2004) 315-321.
2. J. Pierce, Colour in textile effluents-the origins of the problem, *Journal of the Society of Dyers and Colourists*, 110 (1994) 131-133.
3. D. Shugui, Z. Yuanyi, C. Yongsheng, C. Lixia. Study on the relationship between structure of synthetic organic chemical and their biodegradability, *Environmental Chemistry*, 14 (1995) 354-367.
4. A. R. Rahmani, M. Zarrabi, M. R. Samarghandi, A. Afkhami, H. R. Ghaffari, Degradation of Azo Dye Reactive Black 5 and Acid Orange 7 by Fenton-like mechanism, *Iranian Journal of Chemical Engineering*, 7 (2010) 87-94.
5. B. Neppolian, H. C. Choi, S. Sakthivel, B. Arabindoo, V. Murugesan, Solar light induced and TiO<sub>2</sub> assisted degradation of textile dye Reactive Blue 4, *Chemosphere*, 46 (2002) 1173-1181.
6. S. Samira, P. Akash Raja, C. Mohan, J. M. Modak, Photocatalytic degradation of Crystal Violet (C.I. Basic Violet 3) on Nano TiO<sub>2</sub> containing anatase and rutile phases (3:1), *Thermodynamics & Catalysis*, 3 (2012).
7. D. E. Kritikos, N. P. Xekoukoulotakis, E. Psillakis, D. Mantzavinos, Photocatalytic degradation of Reactive Black 5 in aqueous solutions: Effect of operating conditions and coupling with ultrasound irradiation. *Water Research*, 41 (2007) 2236-2246.
8. F. Harrelkas, A. Paulo, M. M. Alves, L. El Khadir, O. Zahraa, M. N. Pons, F. P. van der Zee, Photocatalytic and combined anaerobic-photocatalytic treatment of textile dyes, *Chemosphere*, 72 (2008) 1816-1822.
9. D. B. Voncina, A. Majcen-Le-Marechal, Reactive Dye decolorization using combined Ultrasound/H<sub>2</sub>O<sub>2</sub>, *Dyes and Pigments*, 59 (2003) 173-179.
10. Y. D. Thakare, S. M. Jadhav, Degradation of Brilliant Green Dye using cavitation based hybrid techniques, *International Journal of Advance Engineering and Technology*, 4 (2013) 31-36.
11. Y. G. Adewuyi, Sonochemistry: Environmental science and engineering applications, *Ind. Eng. Chem. Res.*, 40 (2001) 4681-4715.
12. C. Berberidou, I. Poullos, N. P. Xekoukoulotakis, D. Mantzavinos, Sonolytic, Photocatalytic and Sonophotocatalytic degradation of Malachite Green in aqueous solutions, *Applied Catalysis B: Environmental*, 74 (2007) 63-72.
13. P. R. Gogate, R. K. Tayal, A. B. Pandit, Cavitation: A technology on the horizon, *Current Science*, 91 (2006) 35-46.
14. P. R. Gogate, A. B. Pandit, A review of imperative technologies for wastewater treatment II: hybrid methods. *Advances in Environmental Research*, 8 (2004) 553-597.
15. P. N. Patil, P. R. Gogate, Degradation of methyl parathion using hydrodynamic cavitation: effect of operating parameters and intensification using additives, *Separation and Purification Technology*, 95 (2012) 172-179.
16. K. Joshi, P. R. Gogate, Degradation of Dichlorvos using hydrodynamic cavitation based treatment strategies, *Ultrasonics Sonochemistry*, 19 (2012) 532-539.
17. R. A. Torres, G. Sarantakos, E. Combet, C. Petrier, C. Pulgarin, Sequential helio-photo-fenton and sonication processes for the treatment of Bisphenol A, *Journal of Photochemistry and Photobiology*, 199 (2008) 197-203.
18. Y. Segura, R. Molina, F. Martinez, J. A. Melero, Integrated heterogeneous Sono-photo Fenton processes for the degradation of phenolic aqueous solutions, *Ultrasonics Sonochemistry*, 16 (2009) 417-424.
19. S. Raut-Jadhav, V. K. Saharan, D. V. Pinjari, S. H. Sonawane, D. R. Saini, A. B. Pandit, Intensification of degradation of Imidacloprid in aqueous solutions by combination of hydrodynamic cavitation with various advanced oxidation processes (AOPs). *Journal of Environmental Chemical Engineering*, 1 (2013) 850-857.
20. W. G. Kuo, Decolorizing dye wastewater with Fenton's reagent. *Water Research*, 26 (1992) 881-886.

21. S. H. Lin, C. F. Peng, Treatment of textile wastewater by Fenton's reagent, *Journal of Environmental Science and Health*, 30 (1995) 89-98.
22. S. H. Lin, C. F. Peng, A continuous fenton's process for treatment of textile wastewater, *Environmental Technology*, 16 (1995) 693-699.
23. E. G. Solozhenko, N. M. Soboleva, V. V. Goncharuk, Decolourization of Azo dye solutions by Fenton's oxidation, *Water Research*, 29 (1995) 2206-2210.
24. S. F. Kang, C. H. Liao, S. T. Po, Decolorization of textile wastewater by photo-Fenton oxidation technology, *Chemosphere*, 41 (2000) 1287-1294.
25. S. M. Kim, A. Vogelphohl, Degradation of organic pollutants by the photo-Fenton process, *Chemical Engineering Technology*, 21 (1998) 187-191.
26. G. Ruppert, R. Bauer, G. Heisler, The photo-Fenton reaction an effective photochemical wastewater treatment process, *Journal of Photochemistry and Photobiology A: Chemistry*, 73 (1993) 75-78.
27. X. Zhong, L. Xiang, S. Royer, S. Valange, J. Barrault, H. Zhang, Degradation of C.I. acid orange 7 by heterogeneous fenton oxidation in combination with ultrasonic irradiation. *Journal of Chemical Technology and Biotechnology*, 86 (2011) 970-977.
28. H. Liu, G. Li, J. Qu, H. Liu, Degradation of Azo dye Acid orange 7 in water by Fe<sup>0</sup>/granular activated carbon system in the presence of ultrasound, *Journal of Hazardous Materials*, 144 (2007) 180-186.
29. H. Zhang, J. Zhang, C. Zhang, F. Liu, D. Zhang, Degradation of C.I. acid orange 7 by the advanced fenton process in combination with ultrasonic irradiation, *Ultrasonics Sonochemistry*, 16 (2009) 325-330.
30. S. Yang, P. Wang, X. Yang, L. Shan, W. Zhang, X. Shao, R. Niu, Degradation efficiencies of azo dye acid orange 7 by the interaction of heat, UV and anions with common oxidants: Persulfate, peroxymonosulfate and hydrogen peroxide, *Journal of Hazardous Materials* 179 (2010) 552-558.
31. L. Guo, F. Chen, X. Fan, W. Cai, J. Zhang, S-doped  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> as a highly active heterogeneous fenton-like catalyst towards the degradation of acid orange 7 and phenol, *Applied Catalysis B: Environmental*, 96 (2010) 162-168.
32. H. Park, W. Choi, Visible light and Fe(III)-mediated degradation of acid orange 7 in the absence of H<sub>2</sub>O<sub>2</sub>, *Journal of Photochemistry and Photobiology A: Chemistry*, 159 (2003) 241-247.
33. Galindo, Catherine, Jacques, Patrice, Kalt, Andre, Total Mineralization of an azo dye (Acid Orange 7) by UV/H<sub>2</sub>O<sub>2</sub> Oxidation, *Journal of Advanced Oxidation Technologies*, 4 (1999) 400-407.
34. S. F. Villanueva, S. S. Martinez, TiO<sub>2</sub>-assisted degradation of acid orange 7 textile dye under solar light, *Solar Energy Materials and Solar Cells*, 91 (2007) 1492-1495.
35. R. Jaimes-Ramírez, J. Vergara-Sánchez, S. Silva-Martínez, Solar assisted degradation of acid orange 7 textile dye in aqueous solutions by Ce-doped TiO<sub>2</sub>, *Mexican Journal of Scientific Research*, 1 (2012) 42-55.
36. A. Troupis, T.M. Triantis, E. Gkika, A. Hiskia, E. Papaconstantinou, Photocatalytic reductive-oxidative degradation of acid orange 7 by polyoxometalates, *Applied Catalysis B: Environmental*, 86 (2009) 98-107.
37. A. Fernandes, A. Morao, M. Magrinho, A. Lopes, I. Gonçalves, Electrochemical degradation of C. I. acid orange 7, *Dyes and Pigments*, 61 (2004) 287-296.
38. A. Ozcan, M. A. Oturan, N. Oturan, Y. Şahin, Removal of acid orange 7 from water by electrochemically generated fenton's reagent, *Journal of Hazardous Materials*, 163 (2009) 1213-1220.
39. N. Daneshvar, M. H. Rasoulifard, A. R. Khataee, F. Hosseinzadeh, Removal of C.I. acid orange 7 from aqueous solution by UV irradiation in the presence of ZnO nanopowder, *Journal Hazardous Material*, 143 (2007) 95-101.
40. M. Sivakumar, A. B. Pandit, Ultrasound enhanced degradation of rhodamine B: optimization with power density, *Ultrasonics Sonochemistry*, 8 (2001) 233-240.
41. G. Tezcanli, N. H. Ince, Degradation and toxicity reduction of textile dye stuff by ultrasound, *Ultrasonics Sonochemistry*, 10 (2003) 235-240.
42. A. Gutowska, J. Kau, W. Zna-Czaplin, Degradation mechanism of reactive orange 113 dye by H<sub>2</sub>O<sub>2</sub>/Fe<sub>2</sub> and ozone in aqueous solution, *Dyes and Pigments*, 74 (2007) 41-46.
43. J. Wang, B. Guo, X. Shang, Z. Shang, J. Han, J. Wu, Sonocatalytic degradation of methyl orange in the presence of TiO<sub>2</sub> catalysts and catalytic activity comparison of rutile and anatase, *Ultrasonics Sonochemistry*, 12 (2005) 331-337.
44. Y. Yang, L. Xu, Reusing hydrolyzed reactive dye bath for nylon and wool dyeing, *American Dyestuff Reporter*, 3 (1996) 27 - 34.
45. M. Neamtu, A. Yediler, I. Siminiceanu, A. Kettrup, Oxidation of commercial reactive azo dye aqueous solutions by the photo-fenton and fenton-like processes, *Journal of Photochemistry and Photobiology A: Chemistry*, 161 (2003) 87-93.
46. E. R. Bandala, M. A. Pelaez, A. J. CGarcia-Lopez, M. J. Salgado, G. Moeller, Photocatalytic decolourisation of synthetic and real textile wastewater containing benzidine-based Azo dyes, *Chemical Engineering and Processing* 47 (2008) 169-176.

47. S. Raut-Jadhav, V. K. Saharan, D. Pinjari, S. Sonawane, D. Saini and A. B. Pandit, Synergetic effect of combination of AOP's (Hydrodynamic Cavitation and  $H_2O_2$ ) on the degradation of neonicotinoid class of insecticide, *Journal of Hazardous Materials*, 261 (2013) 139-147.
48. X. Wang, Z. Yao, J. Wang, W. Gou, G. Li, Degradation of reactive brilliant red in aqueous solution by ultrasonic cavitation, *Ultrasonic Sonochemistry*, 15 (2008) 43-48.
49. H. Ghodbane, O. Hamdaoui, Degradation of Acid blue 25 in aqueous media using 1700 kHz ultrasonic irradiation: Ultrasound / Fe (II) And Ultrasonic / $H_2O_2$  Combinations, *Ultrasonic Sonochemistry*, 16 (2009) 593-598.
50. Ya-Li Song, Ji-Tai Li, Hua Chen, Degradation of C.I. Acid Red 88 aqueous solution by combination of fenton's reagent and ultrasound irradiation, *Journal of Chemical Technology and Biotechnology*, 84 (2009) 578–583.
51. H. Katsumata, S. Koike, S. Kaneco, T. Suzuki, K. Ohta, Degradation of Reactive yellow 86 with photo-fenton process driven by solar light, *Journal of Environmental Sciences*, 22 (2010) 1455–1461.
52. Y.D. Thakare, V.R. Diware, K.S. Wani, Decolorization of Malachite green dye using UV +  $H_2O_2$  and Photo Fenton Processes, *International Journal of Engineering Trends and Technology*,(2016) 90-96.