



Ultrasound assisted advanced oxidation processes for intensified Acid Green-3 dye degradation

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ABSTRACT

Dyes are important source of contamination and pose serious environmental problems because of their colour and high chemical oxygen demand. The conventional processes offer many disadvantages like limited reactivity, generation of sludge and high treatment time directing significant interest into development of novel treatment techniques. The present work deals with developing an intensified treatment approach based on ultrasound in combination with advanced oxidation processes involving ozone, persulfate and peroxymonosulfate for treatment of Acid Green 3 dye (AG3) containing wastewater. AG3 has been selected as model compound due to the carcinogenic nature and demonstrated mutagenic properties to bacteria and yeast. Effect of important operating parameters like temperature, sonication power, solution pH, stirring rate, ozone flow rate, persulfate/ Fe^{2+} and peroxymonosulfate/ Fe^{2+} dosage on the extent of dye degradation has been studied. Using sonication alone, dye degradation of 51% was obtained at optimum conditions of initial concentration of 20 ppm, power dissipation of 120 W, initial pH of 5.8 and temperature of $30^\circ\text{C} \pm 2^\circ\text{C}$ in 120 min. Under optimized operating conditions, the combination studies of ozone/oxidants with ultrasound have been performed to get best possible synergistic results for the degradation of AG3. The combination approach of US/ O_3 resulted in 87.9% degradation in 90 min whereas combination of US/PS/ Fe^{2+} and US/PMS/ Fe^{2+} resulted in marginally lower extent of degradation as 87.2% and 85.1% respectively. Overall the effective use of combination approaches with higher extents of degradation was clearly demonstrated.

Keywords: Acid Green 3; Ultrasound; Ozonation; Sulfate radicals; Hybrid treatment; Process intensification

1. Introduction

Dyes are natural or synthetic organic compounds that provide bright and lasting colour to other substances. Dyes are used in various industries like the textile, paper, leather, plastic, rubber, cosmetics, pharmaceuticals and food industries with the textile industries being the topmost users of dyes. The wastewaters discharged from dyeing processes exhibit high biochemical oxygen demand as well as high chemical oxygen demand and offer significant disposal issues especially due to the colored nature and presence of high amounts of dissolved solids [1]. The conventional

processes currently applied in industries offer many disadvantages for treatment of dye containing wastewaters. Biological processes are not effective enough to decolourize dyes especially those with high stability while the other commonly used physical/chemical processes (coagulation, flocculation, adsorption on activated carbon and reverse osmosis) have limited applicability and create problems of secondary pollution. Excess sludge generation and generation of hazardous solid waste are the additional drawbacks as the disposal of the recovered/concentrated pollutant or the isolated sludge poses a major threat to the environment [2,3]. Thus, research into development of novel effective treatment

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schemes focusing on degradation of dyes rather than separation is very important.

Advanced oxidation processes (AOP) refer to processes based on the generation of hydroxyl radicals and subsequent attack on the pollutants. Some of the examples of AOP are Fenton processes, photocatalysis, ultraviolet irradiation (UV)/H₂O₂ and UV/O₃ processes [4]. Hydroxyl radicals are non-selective and much more powerful than molecular oxidants such as hydrogen peroxide or ozone [5]. AOP can also be classified as homogenous and heterogeneous. Homogenous processes include US, O₃/H₂O₂, UV/H₂O₂ etc. whereas some examples of the heterogeneous processes are US/TiO₂, UV/TiO₂ etc. AOP under appropriate treatment conditions, when applied to the dye containing effluents, can impart complete colour removal, detoxification and mineralization. In the current study, the treatment processes studied are based on the US operated individually and in combination with O₃ and sulfate based oxidizing agents as persulphate and peroxymonosulphate with an objective to maximize the dye degradation.

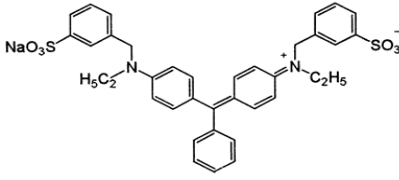
Dyes are classified according to their structure, solubility and application. Some of the most common types of dyes used in the textile industry are acid dyes consisting of azo, anthraquinone and triphenylmethane chromophores [6]. Most acid dyes are water-soluble anionic dyes used for processing of nylon, wool, silk, modified acrylics, paper, leather, food and cosmetics [6]. Acid dyes are resistant to degradation due to their stable aromatic structure and hence can easily pass through most traditional water treatment systems, which makes them as pollutants of most concern [7]. In the current study, Acid Green 3 (AG3) dye has been selected as the model compound. AG3 dye is an anionic triphenylmethane dye, which is considered to be one of the main offenders in environmental pollution [8]. Triphenylmethane dyes are proven animal carcinogens and indeed certain triphenylmethane dyes have been reported to promote tumor growth in some fish species [9]. Due to the significant hazards associated with the AG3 dye and considering the fact that acid dyes are most widely used within the textile industry and are one of the most difficult types of dye to treat, AG3 dye has been used as a model pollutant (representative of the acid dyes) in the current work. The literature analysis confirmed that studies have not been reported for the degradation of AG3 based on ultrasound either dealing with the understanding of effect of operating parameters or use of combination approaches trying to establish the synergism between the hybrid treatment approaches. Based on this analysis, the novelty of the current work can be clearly established.

2. Materials and methods

2.1. Materials

AG3 dye was obtained locally from Dyestuff Technology Department of the Institute of Chemical Technology, Mumbai. The specific properties of the dye used in the work are given in Table 1. Potassium peroxymonosulphate (99% purity) was obtained from Research Lab Fine Chem Industries, Mumbai. Ferrous sulphate (99.5% purity), potassium iodide and potassium persulphate (99.0% purity) were obtained from S D Fine-Chem Limited, Mumbai.

Table 1
Properties of C.I. Acid Green 3 dye used in the work

ACID GREEN 3	
Synonyms	Acid Green 2G, CI 42085 Guinea Green B, Acid Green B
Molecular structure	
Molecular formula	C ₃₇ H ₃₅ N ₂ NaO ₆ S ₂
Molecular weight	690.8
λ _{max}	640 nm

2.2. Experimental methodology

Ultrasonic horn with tip diameter of 2 cm and operating frequency of 20 kHz, was used as source of ultrasonic irradiations. The reactor used to investigate dye degradation was a 4 neck round bottom glass reactor of 500 ml capacity. Ultrasonic horn was kept at the centre of the reactor and the tip was immersed to a depth of 0.5 cm. The reactor was placed in a water bath to maintain temperature and, magnetic stirring (MS) was provided for mixing. Different operating power dissipations were used in the study to understand the effect of ultrasonic power on degradation. In addition calorimetric study was used to quantify the exact power transferred into the solution and available for cavitation. Calorimetric studies established that the actual power dissipated into the solution was observed to be 8.65 W (for the specific case of rated power as 120 W) giving an energy transfer efficiency of 7.21%. For a typical treatment time of 120 min used for the only ultrasonic treatment, the amount of energy supplied was 28.8 kJ. For the combined operations, the amount of energy required for same dye degradation was lower due to faster rate of decolorization due to the synergistic effects of the combined approach.

Ozone generator (Model-DO400) used in the work was obtained from Eltech Engineering, Mumbai, and has a rated maximum output flow of 400 mg h⁻¹. The generation of ozone is based on the electrical discharge generating free oxygen which recombines to give ozone. A glass sparger was used to introduce ozone into the dye solution. Figs. 1a and b show the experimental set up used for only ultrasonic degradation and combined operation of US/O₃, respectively.

Ultrasonic bath with dimensions of length as 33 cm, width as 20 cm and height as 15 cm fitted and has a transducer of length 24 cm and 3 cm diameter (irradiation area as 205 cm²) attached to one end of the reactor was also used in the work for scale up studies. Ultrasonic bath has an operating frequency of 36 kHz and rated output power of 150 W. The bath is made up of stainless steel with a drainage valve provided at the bottom of the bath. The reaction mixture was cooled using external cooling agent such as ice to counter the heat generated into the system due to the action of ultrasound. A three blade turbine type impeller was used at a

speed of 500 rpm for uniform mixing at this scale of operation. Fig. 2 represents the schematic diagram of the experimental set up for the combined operation of US bath/O₃ [10].

2.3. Analysis

The absorption spectra (over the range of 200–800 nm) of the dye solution, was recorded using a UV-visible

spectrophotometer (VARIAN Cary 50 Conc). The concentration of dye was measured using a precalibrated chart generated based on known concentrations of dye and recording absorbance at the dominant wavelength of absorption as 640 nm. Total organic carbon (TOC) was determined using a TOC-L CPH analyzer (Shimadzu, Japan).

3. Results and discussions

3.1. Effect of temperature control and stirring

The study was initially carried out to understand the effect of controlling the operating temperature as on large scale operation cooling the effluent can be uneconomical. Similarly the effect of stirring was also studied in order to decide whether stirring is required in the sonolysis of the dye solution. Firstly, experiment with a fixed irradiation time of 120 min and power of 120 W with a duty cycle of 50% was performed with no temperature control with and without magnetic stirring (MS). Another set of experiment was performed with the same parameters as before, but with temperature maintained at 30°C ± 2°C. The obtained results were shown in Table 2 and it can be seen that the rate constants were high for sonication performed at controlled temperature. When the temperature was not controlled, an increase in the solution temperature was observed. The temperature rise was slightly faster in the batch were no stirring was provided. The temperatures went as high as 59°C for both the sets of with and without stirring. Cavitation has been reported to be efficient in generating suitable conditions for oxidation such as free radicals, hot spots and intense turbulence coupled with liquid circulation currents [11] with higher intensity at ambient temperatures as compared to higher temperatures and hence it is important to maintain low temperatures for obtaining high degradation rates. An increase in the solution temperature results in an increase in the vapor pressure of the liquid, resulting in higher vapour content in the cavitating bubbles leading to a cushioning effect. The maximum temperature and pressure created in such vaporous transient cavitation bubbles have been shown to be much lower resulting in a decrease in the overall cavitation activity [12].

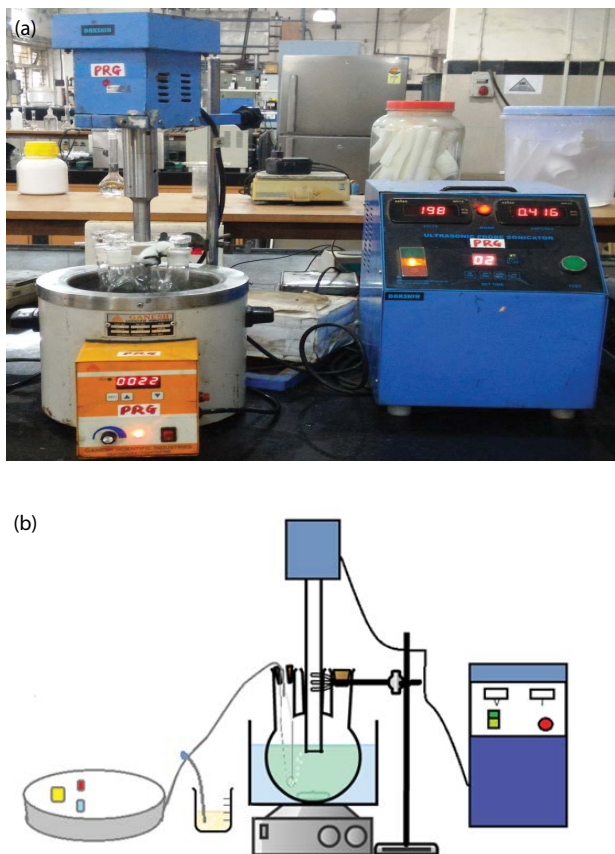


Fig. 1. (a) Experimental set up for ultrasonic degradation at laboratory scale and (b) Schematic representation of the experimental set up for the combination approach of US/O₃.

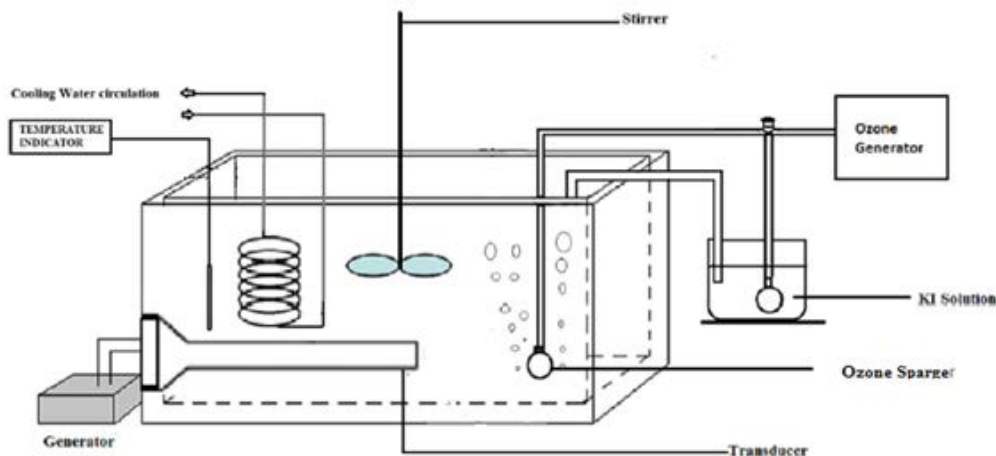


Fig. 2. Schematic diagram of the experimental set up for US bath/O₃ combination at large scale.

Table 2

Degradation rate constant, k and extent of degradation obtained using ultrasound with and without magnetic stirring at 30°C and under no temperature control

Temperature	Method	Extent of degradation (%)	Rate constant ($k \times 10^3, \text{min}^{-1}$)
Not controlled (final temperature of 59°C)	US	11.54	0.47
	US + MS	17.57	0.81
30°C	US	39.13	4.00
	US + MS	51.03	6.19

The results were presented in Table 2 also confirmed that higher extent of degradation was observed in the presence of agitation which can be attributed to better mixing effects. The pulsed mode sonication applied in the work and the intensity of liquid circulation generated at micro level is not capable of inducing bulk mixing and hence the continuous renewal of liquid at the cavitation zone (close to the transducer) is not obtained in the absence of mixing leading to lower degradation rates. Thus considering the solution volume of 250 ml and pulse mode sonication, additional stirring is a must for proper mixing and thus, it was decided to do all future experiments with MS.

3.2. Effect of temperature

Since controlling temperature was found to be beneficial, detailed study into effect of temperature on decolourization of AG3 dye was studied at different temperatures (20°C, 25°C, 30°C and 35°C) under constant initial concentration as 20 ppm and natural pH of 5.8. Fig. 3 illustrates the effects of temperature on the concentration of AG3 at different sonication times whereas Table 3 gives the results for the final extents of degradation. It was found that the concentration of AG3 in aqueous solution typically decreases with an increase in sonication time (Fig. 3) confirming the degradation of dye. The results depicted in

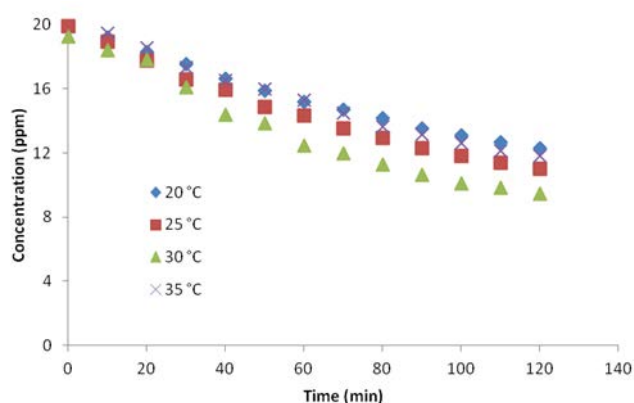


Fig. 3. AG3 concentration profile for ultrasonic degradation at different temperatures (C_0 : 20 ppm and pH: 5.8).

Table 3

Degradation rate constant, k and extent of degradation using only ultrasound at different temperature

Temperature (°C)	Extent of degradation (%)	Rate constant ($k \times 10^3, \text{min}^{-1}$)
20	39.50	4.74
25	44.75	5.41
30	51.03	6.19
35	42.80	5.2

Table 3 shows that the maximum extent of degradation as 51.03% was obtained at temperature of 30°C. Initially, as the temperature was increased from 20°C to 30°C, the rate of degradation also increased. The rate of reaction of the generated hydroxyl radical with dye molecules increases with an increase in the temperature and hence this contributes to enhanced degradation till the optimum temperature [13]. Beyond the observed optimum of 30°C, a further increase in the temperature to 35°C resulted in reduction in the extent of degradation (actual value is 42.8%). The lowering of the degradation can be attributed to fact that with an increase in the temperature beyond the optimum, vaporous cavities are generated leading to lower cavitation intensity and hence lower extent of radicals being formed. Due to the reduction in the availability of free radicals and the degree of cavitation effects, the extent of dye degradation decreases. Similar results were also reported by Lan et al. [14] with an increase in the temperature from 15°C to 22°C resulting in a increase in the extent of degradation from 62.7% to 66.5% and subsequent increase to 35°C reducing the extent of degradation to 57.8%.

Kinetic studies were also undertaken and based on the integral analysis of the obtained data; it was observed that first order kinetics explained the decolourization process satisfactorily. Fig. 4 illustrates the profiles for the first order degradation of AG3 dye using ultrasound at various temperatures. The maximum rate constant of $6.19 \times 10^{-3} \text{min}^{-1}$ was observed at optimum temperature of 30°C and the fittings showed a regression coefficient of 0.98. The obtained values of rate

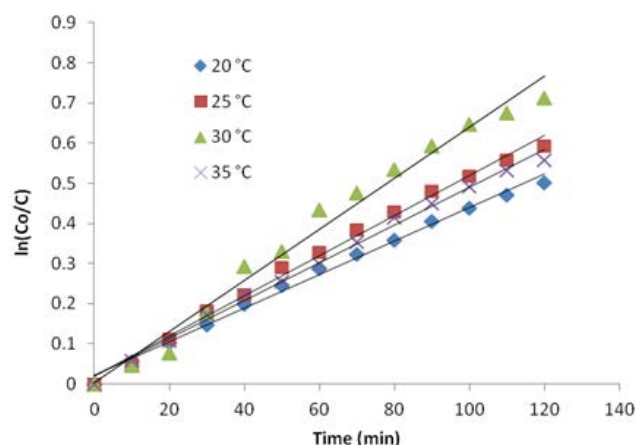


Fig. 4. First order kinetic studies for degradation of AG3 dye using ultrasound at various temperatures (C_0 : 20 ppm and pH: 5.8).

constants were lower at all the other temperatures studied in the work. Based on these results, all the further experiments have been carried out at an operating temperature of 30°C.

3.3. Effect of power dissipation

The effect of sonication power on the rate of degradation of AG3 was studied at different operating powers (40, 80, 120 and 140 W) with initial concentration of 20 ppm, temperature of 30°C and natural pH of the dye solution. Fig. 5 depicts the data for time profiles of concentration variation while Table 4 shows the obtained data for degradation rate constant, k and final extent of degradation at different sonication power. The obtained results presented in Fig. 5 and Table 4 showed that, with an increase in the power dissipation from 20 to 120 W, the extent of degradation also increases whereas further increase to 140 W resulted in lower extent of degradation. The increase in rate of dye degradation 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. On increasing the sonication power beyond the optimum level of power dissipation, there is a formation of a cloud of cavities due to large number of cavities in small volume, which reduces the efficiency of cavity collapse [11]. Also too much accumulation of the cavities near to the transducer results in decoupling effects meaning reduced energy transfer into the solution and this results in a decrease in degradation efficiency. The maximum degradation of 51.03% was

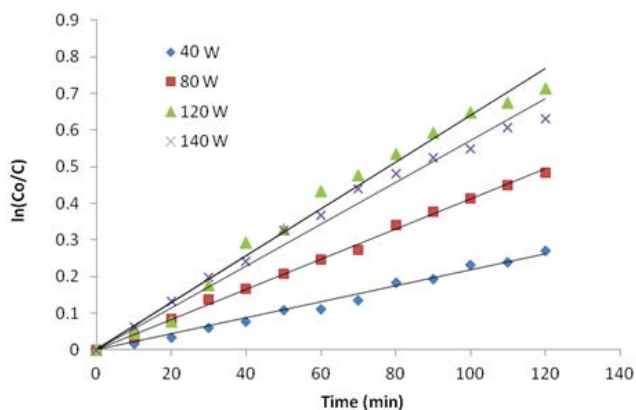


Fig. 5. Effect of power dissipation on the kinetic rate constant of degradation of AG3 dye using sonolysis. (C_0 : 20 ppm, T : 30°C and pH: 5.8).

Table 4

Degradation rate constant, k and extent of degradation using only ultrasound at different sonication power

Sonication Power (W)	Extent of degradation (%)	Rate constant ($k \times 10^{-3}$, min^{-1})
40	23.67	2.06
80	38.42	4.11
120	51.03	6.19
140	46.88	6.05

observed at power of 120 W whereas minimum degradation of 23.67% was obtained at 40 W. Chen et al. [15] reported a similar observation for the study on degradation of an azo dye, direct sky blue 5B. The extent of degradation was reported to increase as power increased from 200 to 400 W whereas further increase in the power to 600 W, resulted in slight decrease in the dye degradation. It is important to see that the optimum value of the operating power was different in present case clearly demonstrating that even if the trends are similar, studies are required for specific compounds and type of ultrasonic reactors.

3.4. Effect of pH

The initial pH of the solution is another important parameter in deciding the extent of decolourization of AG3 dye. In the present study, the effect of pH was investigated over the range of 2.8 to 11. The experiments were performed under conditions of initial concentration as 20 ppm and optimized temperature and power of 30°C and 120 W respectively for a treatment time of 120 min. The obtained results have been presented in Fig. 6 for the concentration time profiles whereas Table 5 shows the data on degradation rate constant, k and extent of degradation at different pH. The rate of decolourization was higher in acidic medium compared to the basic medium. As AG3 is acidic in nature, the maximum degradation of dye is expected in acidic medium (at pH 2.8, 4.5 and 5.8) compared to the higher pH range (9.2 and 11), where there can be a change in state of the dye

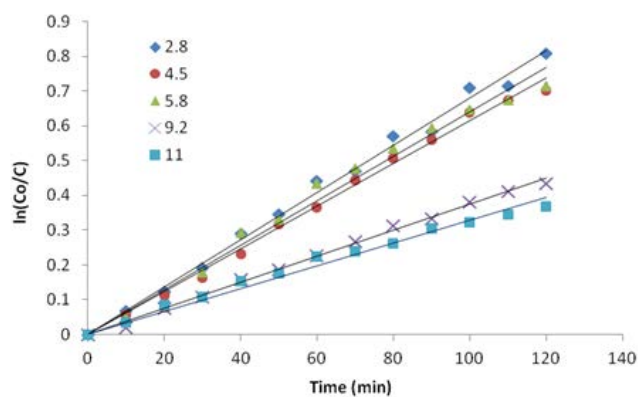


Fig. 6. Effect of pH on the kinetic rate constant of degradation of AG3 dye using sonolysis (C_0 : 20 ppm, T : 30°C).

Table 5

Degradation rate constant, k and extent of degradation using only ultrasound at different pH

pH of solution	Extent of degradation (%)	Rate constant ($k \times 10^3$, min^{-1})
2.8	55.45	6.80
4.5	50.48	6.03
5.8	51.03	6.19
9.2	35.17	3.61
11	30.74	3.51

molecule. It has been also observed that the extent of degradation for lower pH was almost similar. At lower pH values, the form of AG3 is such that it can easily go into the active zone of cavitation and hence the degradation at low pH is higher. Also, the oxidation potential of hydroxyl radicals is higher at lower pH compared to higher pH. The maximum colour removal was observed when pH value was 2.8 though only marginally different removal was obtained at pH of 5.8. The extent of degradation at pH 5.8 was 51.03% and it was considered as optimum pH for further investigations. It is important to note here that adjusting pH to strong acidic conditions may not be always suitable especially at larger scales of operation and the potential benefits of faster degradation needs to weighed against costs of chemicals involved for adjusting pH and further associated processing steps like neutralization before actual discharge into the natural sources. In the present work, since there is not much change in the extent of degradation on using stronger acidic conditions, pH of 5.8 was established as optimum and used in subsequent studies.

In the present work, in the basic conditions, lower decolourization efficiency was observed which is consistent with reported literature illustrations [11,15]. However, there are also some reports available on dyes which show higher degradation using ultrasound both in the acidic as well as basic medium compared to the neutral range [16,17] and hence it is important to investigate the effect of pH for the desired dye in question. Also the optimum value of pH for best degradation and extent of changes in the degradation often depend on the dye establishing the importance of the current work.

3.5. Ozonation alone and in combination with ultrasound

Experiments for investigating the degradation of AG3 using only ozone were performed with initial AG3 concentration of 20 ppm and at natural pH of 5.8. Different values of the ozone flow rate as 100, 200 and 300 mg h⁻¹ were used in the work. Table 6 represents the obtained results in all the three cases confirming that 100% decolourization has been achieved at all the flow rates. As the ozone flow rate was increased, the rate of decolourization increased and the time required attaining complete colour removal reduced. As the flow rate increased, there was improved mass transfer of ozone leading to faster degradation of AG3 dye solution [18]. The results are in accordance to that mentioned in the literature [19]. Fig. 7 illustrates the variation of the dye concentration of AG3 at varying ozone flow rate of O₃. In all the cases, concentration decreased exponentially with respect to time. Kinetic studies also confirmed that the degradation

followed second order rate kinetics and for representative 100 mg h⁻¹ ozone flow rate, it was established that the kinetic rate constant was 0.0004 L mg⁻¹ min⁻¹ with correlation coefficient value as R² = 0.98. The optimum ozone concentration should be established as a compromise between energy consumption to generate ozone and the amount of ozone in the gas exhaust or the reduction in the treatment time [20]. Considering that flow rate of 100 mg h⁻¹ was able to give complete color removal and there was not significant reduction in the required time at higher flow rates, 100 mg h⁻¹ was chosen as the optimum ozone flow rate as this can lead to lower amount of ozone in the exhaust and also lower costs of operation.

Combination of ultrasound with ozonation was also studied at the optimized parameters, that is, ultrasonic power of 120 W, natural pH of 5.8, temperature maintained at 30°C ± 2°C and ozone flow rate of 100 mg h⁻¹. It was observed that maximum degradation of 87.88% was observed in 90 min of US/O₃ treatment, which means that ozone alone gave marginally better degradation compared to the combination US/O₃ in the same treatment time. Martins et al. [21] also reported that the degradation of a triphenylmethane dye, pararosaniline (C.I. Basic Red 9 monohydrochloride) by ozonation was more efficient than ultrasonic irradiation alone or ultrasound combination with O₃. It is also important to note that, in literature, it has been also demonstrated that synergistic effect was achieved by combining ozone with ultrasonic irradiation [22] for the case of methyl orange. Typically, ozone reacts in two different forms either directly with the pollutant molecules or after the formation of hydroxyl radicals or in some combination that is, using the dual oxidation mechanism. The governing mechanism decides the possible effects for the combination approach and it is important to investigate the application of combination for the specific pollutant in question. For the Acid Green 3 pollutant, it was demonstrated that using combination of US/O₃ at optimized parameters does not yielded much favorable results as compared to use of ozone alone.

3.6. Activated persulfate treatment

Different concentrations of potassium persulfate (KPS) and activator ferrous sulphate (FeSO₄) were used in the

Table 6
Extent of degradation using only ozone treatment at different ozone flowrate

O ₃ flow rate (mg h ⁻¹)	Extent of degradation (%)	Time (min)
100	100	110
200	100	70
300	100	30

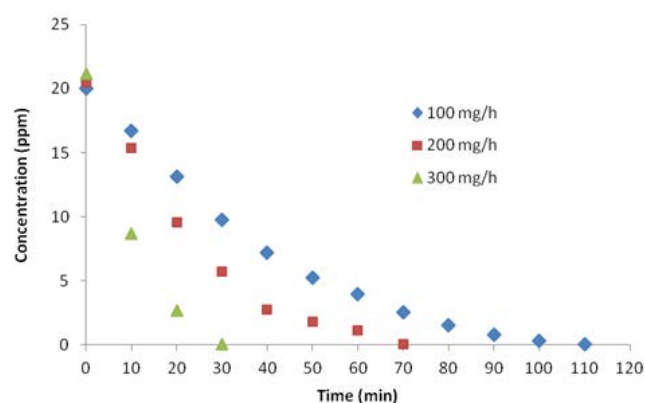


Fig. 7. AG3 concentration profile for ozone treatment at varying ozone flow rate (C₀: 20 ppm and pH: 5.8).

study to establish the efficacy of activated persulfate treatment. The experiments were performed with an initial AG3 concentration of 20 ppm, with stirring but no temperature or pH control. Table 7 shows the obtained results for extent of degradation (%) at different treatment times (min) and different loadings of KPS and FeSO_4 . It can be seen from Table 7 that, treatment using FeSO_4 (quantity added as 0.025 g or 100 mg L^{-1} loading) alone led to degradation of only 2.89%. Dye degradation of 26.5% was achieved when KPS (0.025 g as the quantum or 100 mg L^{-1} loading) alone was added to the dye. Different combination approaches involving various concentrations of KPS and FeSO_4 were also studied keeping the ratio of KPS: Fe^{2+} constant as 1:1 throughout. When the dye solution was treated with KPS/ FeSO_4 (100 mg L^{-1} each), extent of degradation of 67.11% was achieved. It can be said that use of FeSO_4 in combination with KPS accelerated the degradation of AG3 due to the activation effects on KPS giving the formation of sulphate radicals which are stronger oxidizing agents. Kuśmierk et al. [23] also reported acceleration in degradation of 2-chlorophenol by persulfate on addition of FeSO_4 . It was also observed in the present work that though the extent of degradation increased, yellow color was introduced to the treated effluents along with the formation of precipitates which means that excess sulphate is being used. It is reported that sulfate anion is generated as a principal byproduct from the reactions involving $\text{SO}_4^{\cdot -}$ [24] and when allowed to stand, these particles settled to the bottom. Off course clear solution was obtained on subsequent removal of yellow particles leading to complete colour removal for the treated effluent but still solid hazardous waste was generated. Considering these facts, the quantum

of KPS and FeSO_4 used in the study were revised to 0.005 g each, and it was observed that almost similar extent of degradation was achieved with no suspended yellow particles unlike in the case before. Fig. 8 depicts spectrum of decolourization of Acid Green 3 on treatment with KPS/ Fe^{2+} at optimized parameters at different time intervals. The representative spectrum has been reported to clearly demonstrate the reduction in the absorbance across the spectrum meaning all the color bearing components are being reduced with treatment.

It was also thought to further reduce the dosage and experiments were performed adding 0.001 g each of KPS and FeSO_4 but it was observed that there is a significant drop in the degradation comparable to the one where only KPS was added meaning that activation is not sufficient. Considering the obtained results, the optimized dosage of KPS/ FeSO_4 was established as 20 mg L^{-1} each with the ratio of dye: KPS: FeSO_4 as 1:1:1. Similar dosage of KPS/ FeSO_4 has also been reported in literature as the best operating condition [25] with higher dosage being reported to lead to insignificant increase in decolourization rate. Kuśmierk et al. [23] reported that optimum molar ratios for the degradation of 2-chlorophenol using persulfate were 1:200:2 for KPS: 2-chlorophenol: FeSO_4 combination. It is also important to understand that the optimum oxidant ratios are different depending on the pollutant establishing novelty of the current results.

Ultrasound was also combined with the combination of KPS/ FeSO_4 and studies for this approach were performed at the optimized parameters of ultrasonic power of 120 W, natural pH of 5.8, temperature maintained at $30^\circ\text{C} \pm 2^\circ\text{C}$ and KPS/ FeSO_4 loading of 0.005 g each. Maximum degradation of 87.15% was achieved for the combination of US/KPS/ FeSO_4 . It was also observed that the degradation rate was very fast in the first 10 min and then slowed down with time. Similar results for the enhanced degradation in the presence of ultrasound were also reported for the degradation of Acid Orange 7 by Wang et al. [25] under optimum set of conditions as initial concentration of 30 mg L^{-1} , KPS loading of 0.3 g L^{-1} and FeSO_4 loading of 0.5 g L^{-1} , ultrasonic power dissipation of 60 W and pH of 5.8. The intensified degradation in the presence of ultrasound can be attributed to the enhanced production of sulphate radicals based on additional activation mechanism induced by ultrasound. It is important to note that the intensification in the extent of degradation will be dependent

Table 7
Extent of degradation at different loadings of KPS ($\text{K}_2\text{S}_2\text{O}_8$) and FeSO_4

$\text{K}_2\text{S}_2\text{O}_8$ (g)	FeSO_4 (g)	Extent of degradation (%)
–	0.025	2.89
0.025	–	26.5
0.025	0.025	67.11
0.005	0.005	66.7
0.001	0.001	26.26

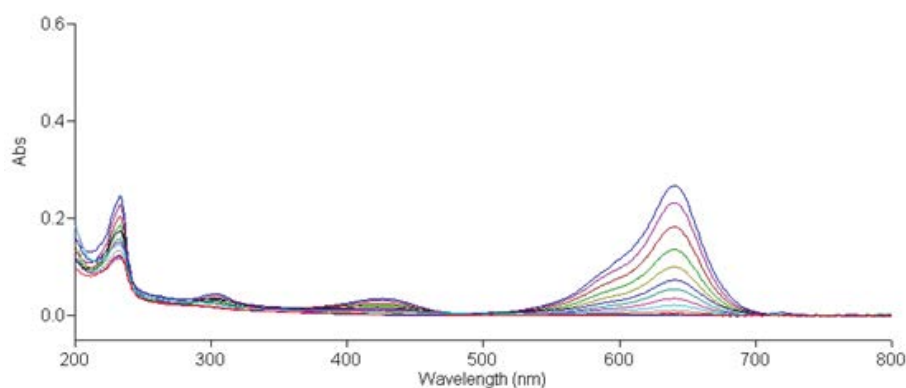


Fig. 8. Spectrum of decolourization of Acid Green 3 on treatment with KPS/ FeSO_4 at optimized parameters.

on the utilization of sulphate radicals by the pollutant and hence specific investigations are always important.

3.7. Activated Peroxymonosulfate treatment

Different concentrations of potassium peroxydisulfate (PMS) and the FeSO_4 were also used in this study for establishing the efficacy for treatment. The experiments were performed at an initial AG3 concentration of 20 ppm, with stirring but no temperature or pH control for 30 min. The results obtained are shown in Table 8. Similar to the combination of KPS/ FeSO_4 , it was observed that using higher concentrations of PMS/ FeSO_4 resulted in higher degradation but also gave yellow colored residue. The optimized dosage of PMS/ FeSO_4 was established as 0.005 g each which gave a degradation of 58.79% without the formation of yellow suspension. Lower dosage compared to this optimum resulted in lower extent of degradation. Also the combination of PMS/ FeSO_4 was better as compared to the individual use of PMS or FeSO_4 attributed to the activation effects giving the desired production of sulphate radicals. Kurukutla et al. [26] reported that 99% decolorization of Rhodamine B could be achieved using PMS/ FeSO_4 in only 2 min under optimum oxidant dosage and yellow color was obtained at excess addition of PMS and FeSO_4 . The comparison of the obtained results in the present work and literature clearly established different quantitative trends in terms of degree of intensification demonstrating the importance of the study.

Ultrasound was also combined with PMS/ FeSO_4 at the optimized parameters as natural pH of 5.8, temperature maintained at $30^\circ\text{C} \pm 2^\circ\text{C}$ and PMS/ FeSO_4 quantity at 0.005 g each. Maximum degradation of 85.05% was observed for the combination treatment approach of US/PMS/ FeSO_4 . Again the observed intensification due to the use of PMS is attributed to the activation effects of ultrasound similar to that explained for the KPS. It is also interesting to note that extent of degradations for the combination approach of US/PMS/ FeSO_4 and US/KPS/ FeSO_4 were almost similar indicating that the type of sulphate source does not play an important role in the presence of two activators as ultrasound and FeSO_4 . For the use of one activator as FeSO_4 , use of KPS showed better efficacy as compared to PMS as the extent of degradation were about 20% higher possibly attributed to higher sulphate content in KPS at same added quantity

3.8. Scale-up studies

Investigation for demonstrating the effectiveness of the sonochemical reactors for large scale treatment of AG3

containing wastewater has been performed by carrying out experiments in the available large scale ultrasonic bath with an operating frequency of 36 kHz, rated power output of 150 W and capacity of 7 L. Experiments were performed using different approaches of only US, US/ O_3 , US/KPS/ FeSO_4 , US/PMS/ FeSO_4 at optimum pH and temperature already established in the earlier detailed investigations at the laboratory scale. Extent of degradation observed for only sonication was about 22.9% as against 51.03% obtained using ultrasonic horn (Table 9). The difference in degradation can be attributed to the fact that in the case of ultrasonic horn intense cavitation can be achieved due to high power density (power dissipation per unit volume) as compared to that observed in the case of ultrasonic bath [27].

The actual power dissipation for the ultrasonic horn (20 kHz) with supplied power of 120 W and operating capacity of 200 ml was 8.65 W giving an energy efficiency of 7.21% and power density of 43.25 W/L. At an operating capacity of 7 L, the power dissipation in the ultrasonic bath was found to be 27.75 W giving an energy efficiency of 18.5% and power density of 3.96 W/L for the ultrasonic bath (36 kHz, 150 W). Hence, even though the energy efficiency is higher for the ultrasonic bath the actual extent of degradation was lower attributed to lower power density. Similar results for lower extent of degradations were also observed for the combination approaches of US/ O_3 , US/KPS/ FeSO_4 and US/PMS/ FeSO_4 . It is important to understand that the extent of reduction in the degradation due to the large scale operation was lower for the combination of US/ O_3 and even lower for the other two combinations of US/KPS/ FeSO_4 and US/PMS/ FeSO_4 . This is attributed to the fact that the role of ultrasound is only supplementary in the combinations and main contribution is by virtue of the chemical oxidants.

Since the power dissipation for ultrasound and capacity of operation were different, it was also thought desirable to compare the efficacy of the two ultrasonic reactors in terms of the cavitation yield (mg W^{-1}) defined as amount of pollutant degraded per unit rate of power dissipation. The cavitation yield obtained for large scale ultrasonic bath was observed to be 1.116 mg W^{-1} whereas for the laboratory scale ultrasonic horn it was observed to be 0.236 mg W^{-1} . Thus the cavitation yield for the ultrasonic bath was almost 5 times higher for the ultrasonic bath where larger area of transducers was used for transmission. It can be thus emphasized that for the scale up of sonochemical reactors, reactor with higher irradiation area will be better [10]. Similar results of better

Table 8
Extent of degradation at different loadings of PMS and FeSO_4

PMS (g)	FeSO_4 (g)	Extent of degradation (%)
–	0.025	2.89
0.025	–	39.06
0.025	0.025	70.26
0.005	0.005	58.79
0.001	0.001	19.59

Table 9
Extent of degradation and cavitation yield for combined approaches at large scale operation

Method	Extent of degradation (%)	Cavitation yield (mg W^{-1})
US	22.9	0.236
US/ O_3	78.2	0.805
US/KPS/ FeSO_4	65.90	0.679
US/PMS/ FeSO_4	80.10	0.825

efficacy in terms of cavitation yield were also observed for the other combination approaches investigated in the work. The cavitation yield was higher for the combination of US with O_3 , KPS/ $FeSO_4$ and PMS/ $FeSO_4$ as compared to the only US based treatment. Quantitatively, combination of US with O_3 increased the cavitation yield by about 2.3 times, while combination with KPS/ $FeSO_4$ and PMS/ $FeSO_4$ increased the value by 2.56 and 2.5 times, respectively. The cavitation yield calculations have also thus confirmed the superiority of combining US with other oxidants in terms of enhancing the degree of intensification as compared to only US based processes.

3.9. Mineralization

The mineralization efficiency of different approaches was also found out by calculating the TOC reduction in the samples treated using different approaches. The obtained results have been represented in Table 10. It can be seen that maximum mineralization is obtained when US was combined with ozone with the TOC reduction of 83.72% and 58.97% for the case of US horn and US bath, respectively. For the other oxidants as well, higher TOC reduction was obtained as compared to the use of only ultrasound. Higher TOC reduction was also seen at smaller treatment volumes attributed to higher power density for the ultrasound. It was observed that ultrasound alone doesn't lead to good mineralization but on combination, almost 1.7 to 2.3 times better mineralization was achieved depending on the scale of operation and type of combination (ozone or KPS or PMS). Kurukutla et al. [26] also reported 93% mineralization based on TOC measurements for the combined approach of US/KPS/ $FeSO_4$, which was higher as compared to the individual approaches of treatment. It is thus clearly seen that similar to decolorization, the mineralization results also depend on the type of pollutant used as well as the treatment combination applied. Lower extents of mineralization as compared to the removal of the parent pollutant as acid green dye in the present case are explained on the basis of the degradation pathways. Typically, complex dyes are initially converted into benzophenones and its derivatives, phenols and its derivatives, benzoic acid, quinones and its derivatives as the first level of oxidation intermediates. These aromatic compounds also undergo ring opening under continued treatment with the hydroxyl radicals or the oxidants forming short chain carboxylic acids, aldehydes etc which also continue oxidation finally yielding CO_2 and water. The rate of conversion of

the intermediates is lower as compared to the parent compound justifying the lower TOC reduction as compared to the extent of AG3 degradation. As the main focus was on decolorization and engineering aspects to establish the optimum conditions/combinations for maximum decolorization, detailed investigation into the mechanistic aspects related to exact identification of intermediates was not undertaken in the present work.

4. Conclusions

In the present study, the efficacy of sonication, ozonolysis, sulfate based AOPs operated individually and in different combinations has been evaluated for the degradation of AG3 at small scale (250 ml) as well as large scale (7 L) operation. For the ultrasound induced degradation, acidic conditions were more effective whereas optimum temperature and power dissipation were found to be the best giving maximum degradation. Ozone was found to be significantly efficient in degradation with use of 100 mg h^{-1} flow rate giving complete degradation even for the individual ozone treatment. For most of the combination approaches except for ultrasound and ozone, beneficial results of higher extent of degradation were observed. For example, combination of ultrasound with KPS/ $FeSO_4$ or PMS/ $FeSO_4$ resulted in much higher degradation of around 85% as compared to around 60% observed without the use of ultrasound. Scale up studies performed using large scale ultrasonic bath at 7 L capacity also confirmed that combination approaches were more suitable at the larger scale of operation. Cavitation yield calculations clearly established the better efficacy for the large scale reactor where higher areas of transducer are used giving higher cavitation activity. Overall, an effective combination treatment approach was developed and demonstrated for effective treatment of wastewater containing AG3 dye. both in terms of decolorization and mineralization.

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Table 10
TOC reduction data for different treatment approaches

Method	TOC reduction (%)	Method	TOC reduction (%)
250 ml capacity		7 L capacity	
US	36.3	US	31.33
US/ O_3	83.72	US/ O_3	58.97
US/KPS/ Fe^{2+}	55.25	US/KPS/ $FeSO_4$	45.79
US/PMS/ Fe^{2+}	58.42	US/PMS/ $FeSO_4$	42.06

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