

# Intensified sonochemical degradation of 2-Picoline in combination with advanced oxidizing agents

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## ABSTRACT

2-picoline is a very important pyridine derivative with significant applications though it is also poisonous and harmful having considerable adverse influence on aquatic life, environment and organisms. The need for developing effective treatment methodologies for 2-Picoline directed the current work focusing on degradation of 2-Picoline using the combination of ultrasound and advanced oxidants such as hydrogen peroxide ( $H_2O_2$ ), potassium persulphate (KPS), Fenton's reagent, and Peroxymonosulphate (PMS) along with the use of Titanium oxide ( $TiO_2$ ) as catalyst. Ultrasonic bath having 8 L capacity and operating frequency of  $40 \pm 2$  kHz has been used. The effect of parameters like power, initial pH, temperature, time and initial concentration of 2-Picoline were studied to establish best operating conditions which were further used in the combination treatment approaches of ultrasound with oxidising agents. The chemical oxygen demand (COD) reduction for the optimized approaches of ultrasound in combination with oxidizing agents was also determined. Degradation experiments were performed using oxidising agents also in absence of ultrasound to investigate the individual treatment capacity of the oxidants and also the synergetic index for the combination. Kinetic study demonstrated that second order model suited for all the treatment approaches except US/Fenton where first order model fitted better. Ultrasound in combination with Fenton reagent demonstrated a substantial synergy for the degradation of 2-Picoline compared to other treatment approaches showing highest degradation of 97.6 %, synergetic index as 5.71, cavitation yield of  $1.82 \times 10^{-5}$  mg/J and COD removal of 82.4 %.

## 1. Introduction

Water pollution is a great threat to environment and continuously increasing over the years due to discharge of hazardous pollutants from industries. Pyridine and Pyridine derivatives are highly toxic organic compounds and contributing significantly to the water pollution problems. 2-Picoline ( $C_6H_7N$ , molar mass of 93.13 g/mol and density of  $943 \text{ kg/m}^3$ ) is an important pyridine derivative and mostly used as solvent in chemical and agrochemical Industries [1]. 2-Picoline has a strong unpleasant smell and is highly dangerous to skin, eyes and respiratory system in the case of humans [2]. The identified concentration of pyridine derivatives in industrial wastewater is generally 20–300 mg/L though it increases to the range of 650–1000 mg/L during the spillages. Importantly, it is far higher than allowable concentration in wastewater (5 mg/L) for pyridine derivatives [3]. Significant industrial applications, existence in environment for considerable time and hazardous nature of pyridine derivatives encouraged development of efficient method for the treatment of wastewater having pyridine or its derivatives.

Several studies have been conducted to treat wastewater bearing pyridine and pyridine derivatives like ultrasound coupled with advanced oxidation [4], batch and column adsorption [5], biodegradation using enzymes [6], photo-Fenton [7] and ozonation [8] etc. Biodegradation generally does not treat larger concentration of effluent efficiently and operation is complicated, very slow and there is also difficulty in handling secondary waste. Adsorptive treatment approach result in better efficiency though it offers higher maintenance cost for washing adsorbent beds and also drawbacks with regeneration of adsorbent coupled with generation of solid waste. Photo-Fenton approach produces chemical waste sludge and also there is inefficient utilization of photo energy. Considering the drawbacks related to the conventional and applied methodology, use of process intensification approaches say on the basis of ultrasound with different oxidising agents need to be analyzed for obtaining efficient treatment approaches for pyridine derivative containing effluents.

Ultrasound assisted advanced oxidation method can considerably reduce the operation time and requirement of chemicals due to

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improved mass transfer and enhanced generation of radicals creating economically feasible oxidation processes. The earlier research based on removal of pyridine by Elsayed [4] using bath sonicator reported intensified degradation in the presence of oxidising agents such as hydrogen peroxide and Fenton reagent at irradiation power of 360 W and operating frequency of  $40 \pm 2$  kHz. Literature analysis associated with 2-Picoline removal revealed that very few illustrations for removal from wastewater are seen and that too based on adsorption [9] and biodegradation [10]. The present work is directed in analyzing the applicability of ultrasound for degradation of 2-picoline focusing on evaluating the effect of different operational parameters and intensification using advanced oxidants and additives for degradation of 2-Picoline. Chemical oxygen demand reduction has also been studied for the first time for the case of 2-Picoline degradation using ultrasound based oxidation methods highlighting the originality of the present work.

## 2. Methodology

### 2.1. Materials

2-Picoline and other chemicals used in present work were obtained from Merck India, Mumbai. Using distilled water, the stock solution of synthetic wastewater of 2-Picoline was prepared. The stock solution was subsequently diluted to produce the solutions with different concentrations of 2-Picoline used for conducting the experiments.

### 2.2. Ultrasonic system

The degradation experiments were conducted in ultrasonic bath of capacity 8L. The cavitation reactor operated at  $40 \pm 2$  kHz frequency and rated irradiation power of 120 W. The reactor has dimensions of  $0.30 \text{ m} \times 0.15 \text{ m} \times 0.18 \text{ m}$  and the ultrasound generator is a separate unit. The values of the operational parameters like time, power and temperature were set using control panel. A drainage valve opening is available at the bottom of the vessel. The 2-picoline containing wastewater was taken in 500 mL cylindrical flask and positioned at the middle of bath to get maximum benefit of cavitational activity. The location of maximum cavitational activity was based on the mapping studies performed earlier and relative position of the flask and transducer locations available in the ultrasonic bath [11–12]. The actual power available for degradation of 2-Picoline was 16 W as calculated using calorimetric method [13] indicating an energy efficiency of 22.9%.

### 2.3. Experimental procedure

The degradation experiments for 2-Picoline were initially performed at different time, temperature, power and pH using only ultrasound to understand the effects of these operating parameters on degradation. Temperature of the reaction mixture was measured using digital thermocouple and controlled by circulating cold water in bath. pH of 2-picoline wastewater solution was altered using appropriate quantity of sulphuric acid of concentration of 0.1 N or sodium hydroxide of 0.1 N strength based on requirement. Experiments were conducted over the range of parameters of pH as 2–10, time as 15 min–120 min, supplied ultrasonic power as 10 W–100 W, temperature as 20–50 °C and initial concentration of 2-picoline as 30 mg/L–60 mg/L. The best operating conditions established in the initial study as time of 90 min, temperature of 30 °C close to ambient temperature, power of 70 W and pH of 6.7 (natural pH of 2-picoline solution) were applied in the combination approaches with oxidant.

The combination studies of ultrasound with oxidants were performed using  $\text{H}_2\text{O}_2$ , Fenton reagent, KPS, PMS and also using a catalyst as titanium oxide. Chemical oxygen demand (COD) reduction at optimised conditions of ultrasound in combination with oxidising agents was also evaluated. Kinetic rate constant and cavitational yield for each treatment approach was also determined along with the synergetic index

based on rate constant values for the combination approaches.

All the experiments were repeated to check the reproducibility of the obtained data. It was seen that the data was reproducible with experimental errors between  $\pm 3\%$  of the reported values of the data in the discussion.

### 2.4. Analytical method

The samples were frequently taken at preselected time intervals and analysed after separation using centrifuge. The analysis of residue concentration of 2-Picoline was by using High Pressure Liquid Chromatography (HPLC) apparatus (supplied by Analytical Technologies Pvt. Ltd.) equipped with UV detector operated at  $\lambda = 262 \text{ nm}$  and a HPLC pump (P-3000 M). A C18 column ( $250 \text{ mm} \times 4.6 \text{ mm}$ ) was used for the analysis along with water and methanol (proportion of 70:30 v/v) as the mobile phase applied at flow rate of mixture as 1 mL/min. The column was properly cleaned before the analysis and after the analysis of 2-Picoline using methanol (standard HPLC grade). 2-Picoline sample quantity of 20  $\mu\text{L}$  was injected in the column for analysis. All samples were detected at the fixed wavelength of 262 nm.

## 3. Results and discussion

### 3.1. Influence of ultrasonic power

The cavitational activity is affected by the power dissipation and hence the degradation of any pollutant also depends on the supplied power. 2-Picoline degradation studies were carried out by varying the power from 10 W to 100 W. As per the results shown in Fig. 1 for the conditions of 50 mg/L as 2-picoline initial concentration, 90 min as irradiation time, pH of 6.7 and temperature of 30 °C, the extent of degradation enhanced from 10.4 % to 40.7 when power was increased from 10 W to 70 W. For the power greater than 70 W, the degradation of 2-Picoline did not increase appreciably with actual value as 41.4 % for irradiation power of 100 W. Thus the dominant positive effect of power on the extent of degradation of 2-Picoline is seen till irradiation power of 70 W. The observed trend is due to the enhanced cavitational effect at higher power over the range of 10 to 70 W which leads to increase in the formation of free radicals that result in accelerating the degradation of 2-Picoline. It was also observed the extent of degradation of 2-Picoline does not increase in appreciable amount (extent of degradation increases only by 1.8 %) beyond 70 W. Marginal change in degradation

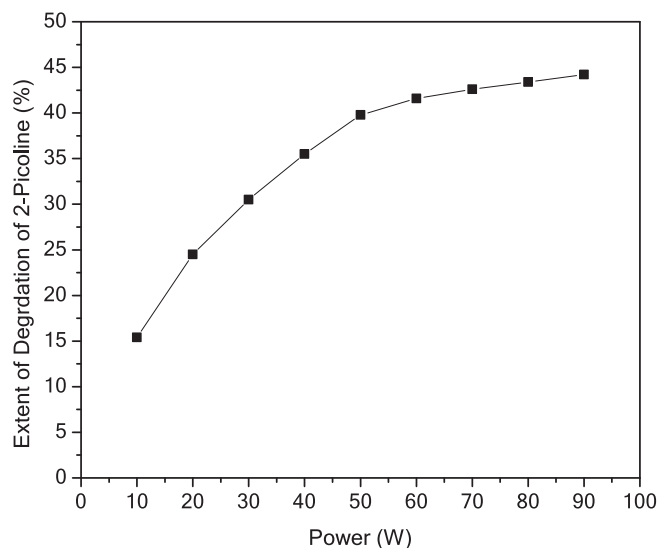


Fig. 1. Influence of ultrasonic power on degradation of 2-Picoline (time = 90 min,  $T = 30$  °C,  $c_i = 50 \text{ mg/L}$ , pH = 6.7).

beyond the power dissipation of 70 W is attributed to much more number of bubbles created at higher power which leads to coalescence resulting in increase in the size of the bubble which does not collapse efficiently [14]. Based on the obtained results, 70 W power was established as optimum and used in further experiments. Wang et al. [15] investigated decomposition of acid orange 7 using ultrasound and reported that the dye degradation enhances to 64 % with an increase in the power to 60 W whereas further change in power to 90 W resulted only a marginal change (actual value as 66 %). Dukkanci, and Gunduz [16] investigated degradation of oxalic acid using ultrasonic bath reactor and reported enhanced degradation from 03 to 16% by increasing the power from 70 to 112 W. One must understand that the effect of power is different for different pollutants and for different configuration of ultrasonic reactor and therefore the detailed study presented in the existing investigation is imperative.

### 3.2. Influence of solution pH

The pH is key parameter and it is extremely important to study its effect on degradation of any pollutant. Considering this requirement, experiments were performed by changing the initial value of pH from 2 to 11 using 0.1 N H<sub>2</sub>SO<sub>4</sub> or 0.1 N NaOH as required under fixed conditions of initial 2-Picoline concentration of 50 mg/L and at optimised power as 70 W. The results for the pH effect on degradation are depicted in Fig. 2 and it is shown that the maximum removal is obtained as 44.9 % at pH of 11. The lowest extent of removal (21.4 %) was noted at pH of 2. At pH 2, 2-Picoline molecule is protonated and hydrophilic which is not favourable condition for degradation and hence at lower pH, the degradation is lower at acidic conditions with pH below pK<sub>a</sub> value of 2-picoline (pK<sub>a</sub> = 5.96). The degradation was observed to be enhancing from 21.4 % to 43.2 % by increasing pH from 2 to 8 and beyond pH of 8, only marginal increase in degradation (43.2 % to 44.9%) was seen till pH changed to 11. In alkaline medium, 2-Picoline molecule becomes hydrophobic (de-protonated) which is desirable condition for degradation of 2-Picoline as higher concentration of 2-picoline will be seen at the cavity interface where maximum concentration of radicals is expected. As depicted in Fig. 2 the degradation of 2-picoline at natural pH (6.7) of 50 mg/L 2-picoline solution was observed as 42.6 %. It can be said that the increase in extent of degradation is very small for pH of 8 compared to natural pH and so further degradation experiments were carried out at natural pH to save required quantity of base required for pH adjustments also making the treatment cost effective. 2-Picolline has

N atom which is strongly electronegative than C molecule (sp<sup>2</sup> hybridised). In highly acidic environment, pyridium salt prevails which is more stable [17] and experiences oxidation at lesser rates in comparison to basic or neutral environment. Though most of the ultrasound degradation studies investigated in literature show best results in terms of degradation under acidic conditions, some studies showed favourable degradation in basic environment (though at dissimilar value of pH) for the amino or nitro compounds. For example, Elsayed [18] reported positive effect for higher extent of degradation of pyridine in basic conditions with the highest degradation using ultrasound treatment approach notified to be 25.1% at pH 8.5. Xu et al. [19] investigated the decomposition of ammonia-Nitrogen using ultrasound with the maximum degradation of 53 % reported at basic pH of 8.2. Analysing the results indeed confirmed the importance of the current study as the best pH condition is different dependent on specific effluent. Based on obtained results in the current work, subsequent experiments were performed at pH value of 6.7 (corresponding to the natural pH).

### 3.3. Influence of solution temperature

It is important to investigate the influence of temperature for sonochemical degradation as typically temperature will have counteracting effects on the degradation kinetics and cavitation activity. The effect of 2-Picoline solution temperature on extent of degradation using ultrasound was studied over the range of 20 °C to 55 °C keeping the other parameters fixed at optimised conditions and using 50 mg/L as the initial concentration of solution. The depicted results in Fig. 3 demonstrate that increasing 2-Picoline solution temperature from 20 °C to 40 °C drives the degradation to increase from 33.1 % to 44.3 %. However, with a subsequent increase in temperature to 45 °C and 55 °C, the degradation was found to be marginally lower as 43.6 and 43 % respectively. These results are better explained based on the hypothesis that as temperature increases from 20 °C to 40 °C, the degradation occurs at enhanced kinetic rate constant giving an increase in the rate. Also the cavitation action is not significantly affected in a negative manner leading to overall increase in the degradation. The increase in temperature till the optimum definitely results in an increase in the number of cavitation bubbles on sonolysis and also the rate of production of free radicals. Increasing temperature also reduces the viscosity of the solution leading to a decrease in the cavitation threshold limit [20]. In addition, with an increase in temperature, the kinetic rate constant also increases. All these effects demonstrate the positive effect of

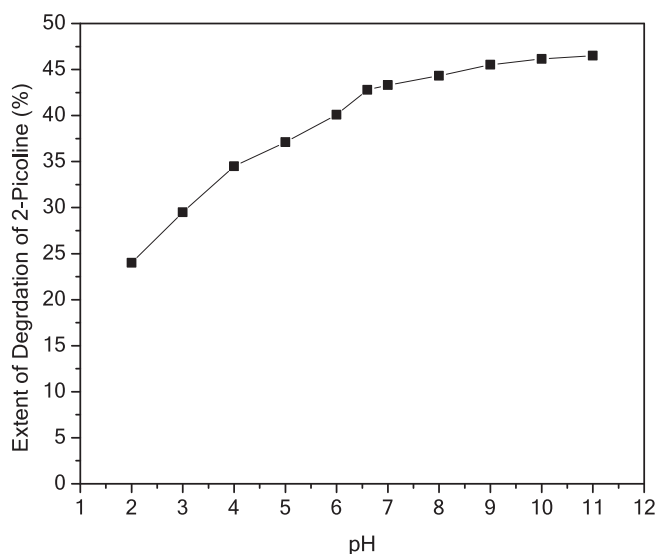


Fig. 2. Influence of pH on degradation of 2-Picoline (T = 30 °C, P = 70 W, time = 90 min, c<sub>i</sub> = 50 mg/L).

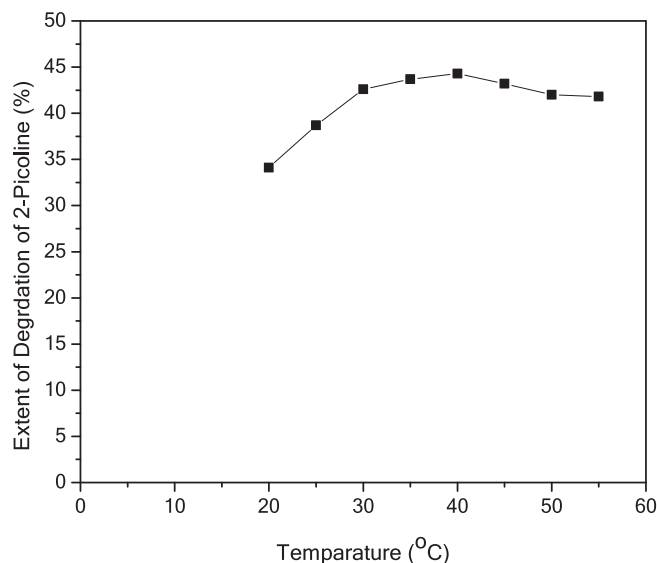


Fig. 3. Influence of operating temperature on degradation of 2-Picoline (pH = 6.7, P = 70 W, time = 90 min, c<sub>i</sub> = 50 mg/L).

temperature on the extent of degradation. However, at much higher temperatures, there are too many cavitation bubbles in the reactor leading to cushioned collapse and reduced cavitation intensity. Also, there is a formation of vaporous cavities which give lower collapse intensity [21]. Due to these effects, there is a reduced effect beyond the optimum temperature also seen in the current work where degradation of 2-Picoline declined above the optimum value as 40 °C.

It is also important to analyse the observed benefits in terms of increase in degradation with the additional requirements of energy for heating the solution which can be significant at commercial scales. The degradation was observed to be 42.6 % at 30 °C and 43.6 % at 45 °C (as seen from Fig. 3). Thus as only marginal increase is observed from 30 °C to 45 °C, it is recommended to use 30 °C (near to the ambient conditions) as the temperature of 2-Picoline solution so as to save additional energy input required for heating. Considering this analysis, 30 °C was used in subsequent experiments.

Barik and Gogate [22] reported similar results for 4-chloro 2-aminophenol showing positive effect on sonochemical degradation initially over the temperature range of 26 °C to 34 °C with the degradation increasing from 21.6 % to 33.1 %. Subsequent increase in the temperature to 38 °C resulted in reduced degradation as 29.2 %. Golash et al. [23] studied degradation of dichlorvos at different temperatures ranging from 15 °C to 45 °C in bath sonicator. The reported results showed that the degradation of dichlorvos enhanced from 38.1% to 50.1 % with a change in temperature of wastewater from 15 °C to 35 °C. Subsequently, marginal reduction in degradation was observed on further increasing the temperature to 40 and 45 °C. One must agree with the fact that influence of temperature on ultrasound degradation for pollutant depends up on different factors like solubility and nature of interaction among pollutant and free radical as well as reaction rate constant with the pollutant etc. Considering this analysis, trends must be established for the pollutant being considered establishing the importance of current work.

### 3.4. Influence of time and initial concentration of 2-Picoline

It is important to investigate the influence of treatment time and initial concentration of 2-Picoline as industrial wastewater generally contains pollutant at different concentrations. The degradation experiments of 2-Picoline was performed first to establish optimised treatment time at 50 mg/L as the initial 2-Picoline concentration under conditions of pH as 6.7, temperature of 30 °C and power of 70 W. The trends for the

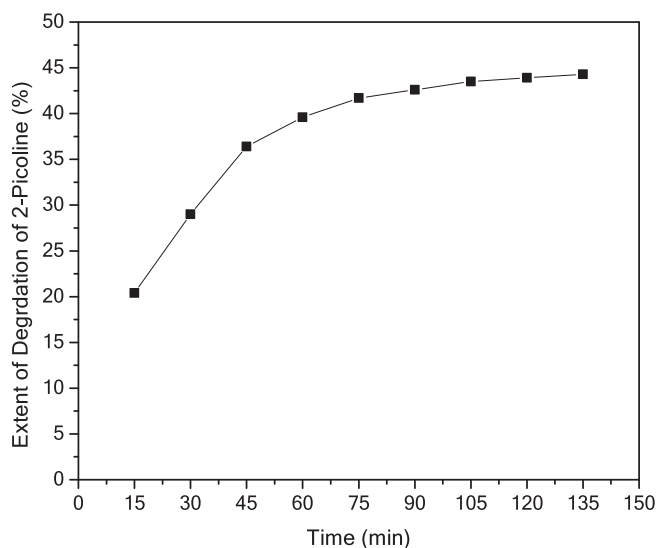


Fig. 4. Influence of irradiation time on degradation of 2-Picoline (T = 30 °C, pH = 6.7, P = 70 W).

influence of contact time shown in Fig. 4 demonstrate that 2-Picoline degradation increases from 20.4 % to 42.6 % as the time increases from 15 min to 90 min. Very small increment in the extent of degradation (42.6 % to 44.3 %) was noticed further with increasing the time from 90 min to 135 min. The degradation does not exactly increase with time beyond 90 min may due to formation of degradation products in the solution which react with hydroxyl radicals at a faster rate. Based on the obtained results, subsequent experiments were performed at 90 min as the optimised time.

Degradation experiments of 2-Picoline were also performed at different initial concentrations ranging from 30 mg/L – 60 mg/L by keeping other conditions at optimised values. The obtained data elucidated that the extent of 2-Picoline degradation was observed to increase to 53.2 % (actual removal was 24.3 mg/L as shown in Fig. 5) from an initial value of 40 % (actual removal was 15.3 mg/L) by enhancing initial concentration of 2-Picoline from 30 mg/L to 60 mg/L at optimised operating conditions. One must understand that actual amount of 2-picoline degradation (in terms of moles degraded) is high at higher concentration (see the data in Fig. 5) even though the extent of degradation is lower. The extent of degradation reduces at higher initial concentration as at higher concentration, larger amount 2-picoline molecules are present in the solution which cannot react effectively with limited supply of hydroxyl radicals based on fixed cavitation intensity. Elsayed et al. [24] investigated the degradation of pyridine in ultrasonic bath over the range of concentration as 10 to 100 mg/L and reported that the degradation of pyridine was 52 % at 10 mg/L, which reduced to 15 % at 100 mg/L as the initial concentration. Further experiments to understand the effect of oxidising agents in the present work were carried out using 30 mg/L initial concentration of 2-Picoline as maximum degradation was noticed.

The degradation of 2-Picoline can be well demonstrated by second order kinetic model as represented by following equation.

$$\frac{1}{C_e} = \frac{1}{C_i} + kt$$

Where,  $C_i$  is initial concentration,  $C_e$  is concentration at time  $t$  and  $k$  the second order rate constant. The obtained trends for the plot  $\frac{1}{C_e}$  vs  $t$  are shown in Fig. 6 for the approach of only sonochemical degradation. The values of  $k$  and  $R^2$  (regression coefficient) are given in Table 1. Based on obtained results of  $R^2$  (close to unity), it was clear that the degradation mechanism follows second order kinetics. The study of kinetics is the key as it provides the crucial design information to scale up the

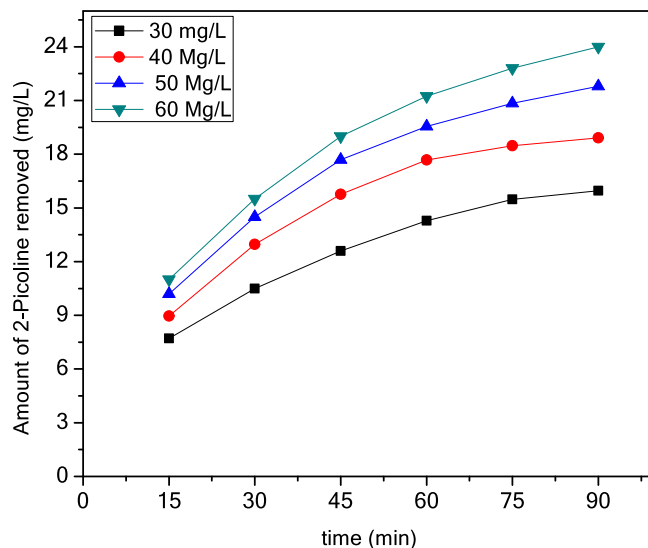


Fig. 5. Influence of Initial concentration on amount of 2-Picoline removed (T = 30 °C, pH = 6.7, P = 70 W).

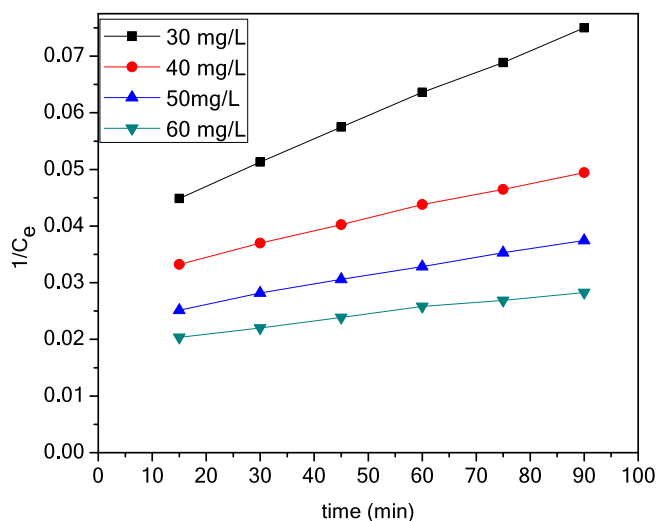


Fig. 6. Plot of Second order kinetic fitting for degradation of 2-Picoline using only ultrasound ( $T = 30\text{ }^{\circ}\text{C}$ ,  $\text{pH} = 6.7$ ,  $P = 70\text{ W}$ ).

Table 1

Extent of Degradation of 2-Picoline and first order rate constant for different treatment approaches.

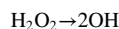
Operative parameters: Initial Concentration ( $c_i$ ): 30 mg/L, t: 90 min, pH:6.7, T: 30 $^{\circ}\text{C}$			
Treatment Approach	Extent of Degradation (%) of 2-Picoline	Rate constant	$R^2$
US Only	53.2	$0.00360\text{ L mol}^{-1}\text{ min}^{-1}$	0.992
Only $\text{H}_2\text{O}_2$	21.3	$0.00008\text{ L mol}^{-1}\text{ min}^{-1}$	0.999
Only Fenton	32.2	$0.0002\text{ L mol}^{-1}\text{ min}^{-1}$	0.992
Only KPS	20.1	$0.00008\text{ L mol}^{-1}\text{ min}^{-1}$	0.994
KPS/ $\text{FeSO}_4$	27.7	$0.0001\text{ L mol}^{-1}\text{ min}^{-1}$	0.993
Only PMS	18.2	$0.00006\text{ L mol}^{-1}\text{ min}^{-1}$	0.993
Only $\text{TiO}_2$	17.2	$0.00007\text{ L mol}^{-1}\text{ min}^{-1}$	0.997
PMS/ $\text{FeSO}_4$	24.7	$0.00001\text{ L mol}^{-1}\text{ min}^{-1}$	0.996
$\text{TiO}_2/\text{H}_2\text{O}_2$	19.6	$0.00008\text{ L mol}^{-1}\text{ min}^{-1}$	0.995
US/ $\text{H}_2\text{O}_2$	85.3	$0.00210\text{ L mol}^{-1}\text{ min}^{-1}$	0.996
US/Fenton	97.6	$0.0400\text{ min}^{-1}$	0.999
US/KPS	81.4	$0.00170\text{ L mol}^{-1}\text{ min}^{-1}$	0.996
US/KPS/ $\text{FeSO}_4$	90.4	$0.00330\text{ L mol}^{-1}\text{ min}^{-1}$	0.997
US/PMS	80.1	$0.00168\text{ L mol}^{-1}\text{ min}^{-1}$	0.995
US/PMS/ $\text{FeSO}_4$	87.5	$0.00280\text{ L mol}^{-1}\text{ min}^{-1}$	0.998
US/ $\text{TiO}_2$	75.1	$0.00130\text{ L mol}^{-1}\text{ min}^{-1}$	0.997
US/ $\text{TiO}_2/\text{H}_2\text{O}_2$	81.3	$0.00180\text{ L mol}^{-1}\text{ min}^{-1}$	0.997

sonochemical reactor in terms of the required residence time and capacity.

### 3.5. Influence of advanced oxidising agents in combination with ultrasound on degradation of 2-Picoline

#### 3.5.1. Influence of hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) in combination with ultrasound

Hydrogen peroxide is an oxidising agent which can dissociate in aqueous solution under the action of ultrasound producing hydroxyl radicals as per the following reaction:



The studies related to effect of variation in the loading of hydrogen peroxide on degradation of 2-Picoline were performed at pH of 6.7, temperature of  $30\text{ }^{\circ}\text{C}$ , initial concentration of 30 mg/L, ultrasonic power of 70 W and time 90 min. The results obtained in the study are shown in Fig. 7 for different  $\text{H}_2\text{O}_2$  loadings over the range of 4 mg/L to 20 mg/L. According to the results, the degradation of 2-Picoline increased sharply from 57.3 to 85.2 % with a change in the oxidant concentration from 4 mg/L to 12 mg/L. Further increase in  $\text{H}_2\text{O}_2$  concentration to 16 mg/L and 20 mg/L resulted in a slight drop in 2-Picoline degradation. The initial increase in degradation of 2-Picoline is attributed to enhanced hydroxyl radical formation at enhanced loading of  $\text{H}_2\text{O}_2$  leading to higher degradation. The decrease in degradation beyond 12 mg/L (at 16 mg/L = 83.2% and 20 mg/L = 81.1%) is explained by the scavenging action of the residual hydrogen peroxide. The obtained results confirmed that 12 mg/L can be selected as optimum dose for efficient degradation. Similar trends have been reported by Zhang et al. [25] for the degradation of azo dye studied over the range of loading of  $\text{H}_2\text{O}_2$  as 0.8–2.4 mM. The degradation was noticed to increase to 92.4% with an increase in loading to a value of 1.94 mM and further increase in  $\text{H}_2\text{O}_2$  loading to 2.4 mM resulted in lowering the extent of degradation to 78.5 %. Ayare et al. [26] reported that the COD removal increases from 41 % to 48 % by increasing hydrogen peroxide loading from 1000 mg/L to 1200 mg/L for the case of treatment of Phosphonate containing industrial wastewater. A further increase in loading of  $\text{H}_2\text{O}_2$  to 1400 mg/L resulted in lowering of the extent of the COD removal to 44 %. Hydrogen peroxide has also capability to degrade the compounds alone (without ultrasound) and hence experiments were also carried out using only  $\text{H}_2\text{O}_2$  at optimised concentration of 12 mg/L for conditions of fixed initial concentration of 2-Picoline solution as 30 mg/L. For this set of

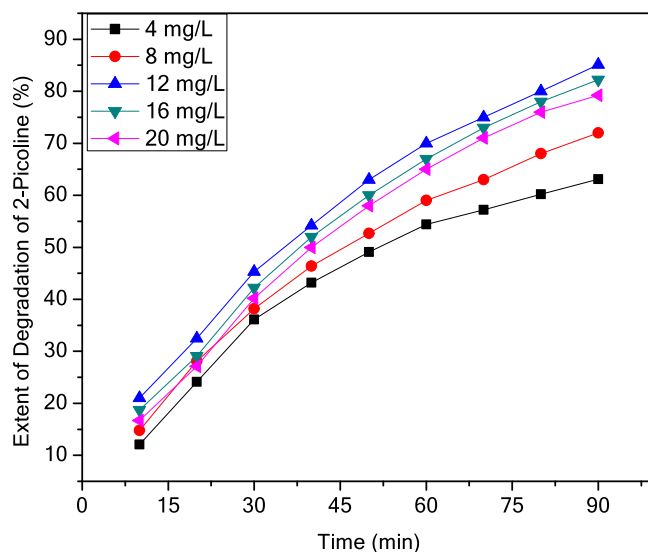


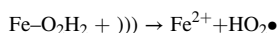
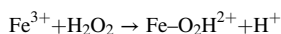
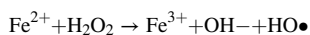
Fig. 7. Influence of  $\text{H}_2\text{O}_2$  concentration on degradation of 2-Picoline using ultrasound ( $T = 30\text{ }^{\circ}\text{C}$ ,  $\text{pH} = 6.7$ ,  $P = 70\text{ W}$ ,  $c_i = 30\text{ mg/L}$ ).



studies, the extent of degradation was found to be 21.3 %, which was much lower compared to that obtained for the combination meaning that ultrasound induced dissociation of  $\text{H}_2\text{O}_2$  plays a key role in driving the degradation of 2-Picoline. The synergetic index and obtained second order rate constant for the different approaches shown in Table 1 also confirm the role of ultrasound and  $\text{H}_2\text{O}_2$  at optimum concentrations in enhancing the degradation of pollutants.

### 3.5.2. Influence of Fenton reagent in combination with ultrasound

Typical concentration range for  $\text{FeSO}_4$  was selected from 4 mg/L to 24 mg/L at fixed concentration of hydrogen peroxide as 12 mg/L established as optimised concentration in the earlier study. The other maintained conditions were pH of 6.7, temperature of 30 °C, time of 90 min and initial concentration of 2-picoline as 30 mg/L. The mechanism explaining the enhanced generation of free radicals in the case of ultrasound and Fenton's reagent has been described earlier [27]. The possible increase in the degradation using combined operation of Fenton chemistry with ultrasound is mainly attributed to increased production of hydroxyl radicals due to the inter-conversion of  $\text{Fe}^{2+}$  to  $\text{Fe}^{3+}$  and back by the action of ultrasound.



As depicted in Fig. 8, the degradation was observed to increase from 63.2% to 97.6 % with an increase in the addition of  $\text{FeSO}_4$  (at fixed  $\text{H}_2\text{O}_2$  loading as 12 mg/L) from 4 mg/L to 16 mg/L. Further increase in the loading of  $\text{FeSO}_4$  to 20 mg/L and 24 mg/L at optimised loading of  $\text{H}_2\text{O}_2$  (12 mg/L) resulted in marginal reduction in degradation of 2-Picoline with actual values as 97 % and 96.5 % respectively. The increase in the degradation till 16 mg/L as the  $\text{FeSO}_4$  concentration is attributed to formation of higher number of free radicals. Thus, it looks like that 16 mg/L dosage of  $\text{FeSO}_4$  with 12 mg/L of  $\text{H}_2\text{O}_2$  is adequate for generating enough hydroxyl radicals and drive the 2-Picoline degradation faster. At higher concentrations of  $\text{FeSO}_4$  added to the wastewater, scavenging effect is observed which reduces the degradation slightly. Similar trends have been reported by Joshi et al. [28] for the treatment of the land fill leachate with study at fixed concentration of hydrogen peroxide as 5 mg/L and at different concentrations of  $\text{FeSO}_4$  (20 mg/L, 35 mg/L and 50 mg/L). Quantitatively, the degradation changed from 57% to 74.5% for a change in loading of  $\text{FeSO}_4$  from 20 mg/L to 35 mg/L, however

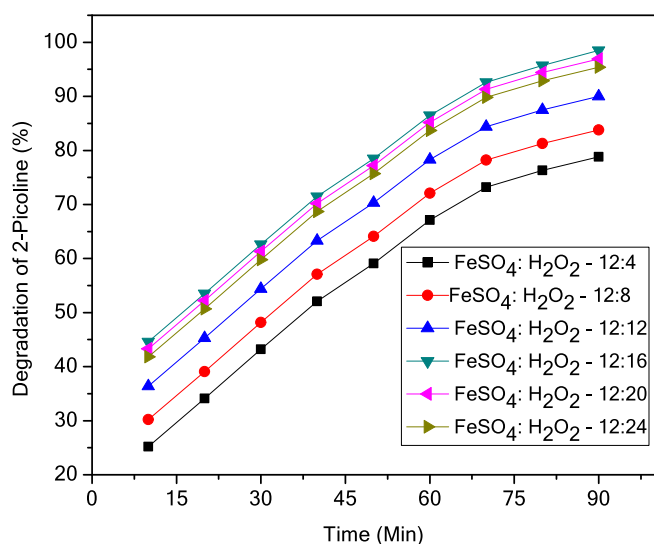


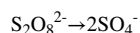
Fig. 8. Influence of Fenton reagent concentration on degradation of 3MP using ultrasound ( $T = 30^\circ\text{C}$ ,  $\text{pH} = 6.7$ ,  $P = 70\text{ W}$ ,  $c_i = 30\text{ mg/L}$ ).

marginal decrease in extent of degradation (actual value as 70.1%) was observed for further increase to 50 mg/L as the  $\text{FeSO}_4$  concentration. Again the quantitative variations in observed degradation with addition of Fenton's reagent confirm the existing study as innovative.

The degradation in absence of ultrasound at obtained optimised concentration of  $\text{FeSO}_4$  coupled with fixed  $\text{H}_2\text{O}_2$  loading as 12 mg/L was evaluated and it was found to be 32.2 % again confirming the role of ultrasound in intensifying the degradation for the combination approach. The synergetic index and obtained first order rate constant are shown in Table 1. Comparison of different approaches involving ultrasound,  $\text{H}_2\text{O}_2$  and Fenton presented in Fig. 9 reveal that ultrasound combination with Fenton is the best approach, which is also confirmed by the synergistic index values reported in the Table 1.

### 3.5.3. Influence of persulphate (KPS) addition in combination with ultrasound

Sulphate based oxidising agents like persulfate (KPS) have shown promise in application for wastewater treatment due to some advantages like stability, ease of storage, chances of in-situ activation, higher solubility in aqueous solution, production of strong sulphate radicals and much lower sludge compared to biological treatment or Fenton chemistry [29]. The typical activation reaction for the production of sulphate radicals can be depicted as below.



Experiments were performed at different KPS loading from 4 mg/L to 28 mg/L using 30 mg/L as the initial concentration of 2-Picoline solution, pH of 6.7, temperature of 30 °C, time of 90 min and power dissipation of 70 W. The obtained results for the 2-Picoline degradation are depicted in Fig. 10. The degradation of 2-Picoline was found to increase from 58.2% to 81.4 % by increasing the KPS concentration from 4 mg/L to 20 mg/L. A further increase in KPS loading to 24 mg/L and 28 mg/L resulted in a marginal decrease in the degradation of 2-Picoline to 80.8 % and 79.5 % respectively which was attributed to scavenging action of  $\text{SO}_4^{\bullet -}$  by surplus  $\text{S}_2\text{O}_8^{2-}$  existing in 2-picoline solution. Considering the observed results, 20 mg/L can be selected as optimised concentration of KPS. The obtained trends are matching to the trends reported by Patil and Shukla [30] where the extent of degradation of reactive yellow dye increased from 43.6 to 93.2% with an increase in the KPS dose from 0.7 to 3.7 mM. A further increase in dose to 4.4 mM resulted in reduced degradation of dye with actual value as 80.9 %. It is also important to note that few researchers reported that no scavenging effect of KPS is

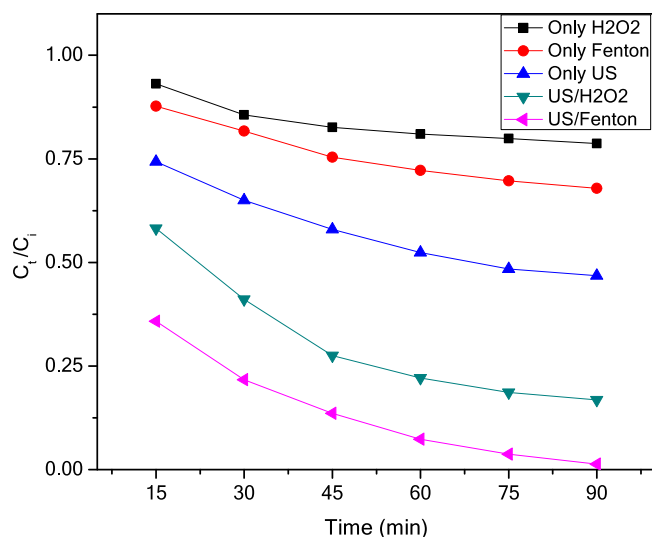


Fig. 9. Results for degradation of 2- Picoline using different approaches involving ultrasound,  $\text{H}_2\text{O}_2$  and Fenton ( $T = 30^\circ\text{C}$ ,  $\text{pH} = 6.7$ ,  $P = 70\text{ W}$ ,  $c_i = 30\text{ mg/L}$ ).

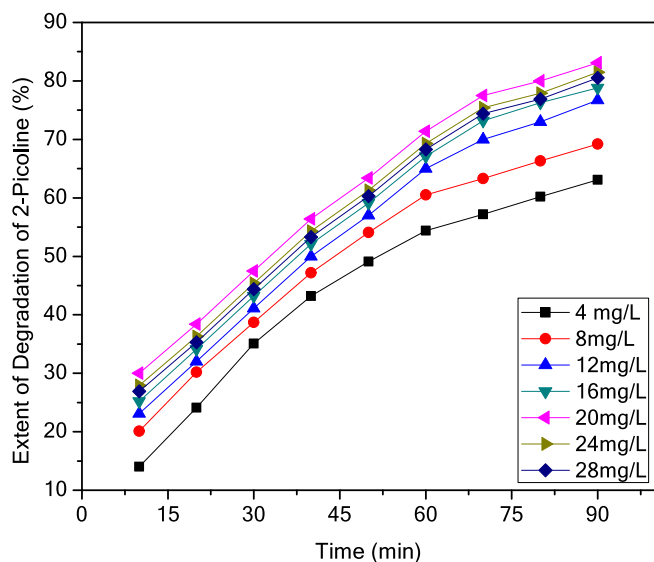


Fig. 10. Influence of KPS concentration on degradation of 2-Picoline using ultrasound ( $T = 30\text{ }^{\circ}\text{C}$ ,  $\text{pH} = 6.7$ ,  $P = 70\text{ W}$ , time = 90 min,  $c_i = 30\text{ mg/L}$ ).

seen at higher doses. For example, More et al. [31] reported that US/KPS combination enhanced treatment of crude soybean oil. The degumming extent enhanced from 88.9 % to 94.8 % with an increase in KPS loading from 0.6 to 1.4 g/L and a marginal increase to 95% was observed for further increase in KPS loading to 2 g/L without any negative scavenging action. It is thus important to note that the optimum loadings are different for different pollutants and activation mode.

Experiments were also carried out in the present investigation using optimized KPS (24 mg/L) without ultrasound to know the effect of using only KPS as oxidant on the extent of degradation of 30 mg/L of 2-Picoline solution at pH of 6.7, temperature of  $30\text{ }^{\circ}\text{C}$  and time of 90 min. The degradation of 2-Picoline was observed as only 20.1% again establishing the need of ultrasound to yield beneficial results in the combination. The synergetic index and obtained second order rate constant values for different approaches involving KPS are shown in Table 1.

#### 3.5.4. Influence of persulphate (KPS) in combination of ferrous sulphate ( $\text{FeSO}_4$ ) and ultrasound

Ultrasound assisted degradation of 2-Picoline having initial concentration of 30 mg/L was studied at optimised concentration of KPS (20 mg/L) and  $\text{FeSO}_4$  (16 mg/L) at fixed condition of pH as 6.7, temperature as  $30\text{ }^{\circ}\text{C}$ , time as 90 min and ultrasonic power as 70 W. The possible activation driving the production of sulphate radicals in the presence of  $\text{FeSO}_4$  and ultrasound can be represented using the reaction given below.



The obtained results revealed that the extent of degradation of 2-Picoline was 90.4 %. It is noteworthy to discuss that the combined operation of KPS/ $\text{FeSO}_4$  results in higher degradation compared to only KPS attributed to generation of higher quantity of  $\text{SO}_4^{\cdot -}$  radicals as  $\text{FeSO}_4$  is acting as additional activator ultimately increasing the formation of free radicals and enhancing the degradation. Chincholi and Gogate [32] also reported that the degradation of Acid Green-3 dye using US/KPS approach was 26.5 % and the degradation enhanced to 67.11% for the combination of US/KPS/ $\text{FeSO}_4$ .

Experiments were also carried out using optimized concentration of KPS/ $\text{FeSO}_4$  without ultrasound to know the role of ultrasound. The observed extent of degradation for 30 mg/L of 2-Picoline solution at conditions of pH as 6.7, temperature of  $30\text{ }^{\circ}\text{C}$  and time of 90 min was only 27.7 % again clearly illustrating role of ultrasound in activation. The obtained values of synergetic index for the combination and second

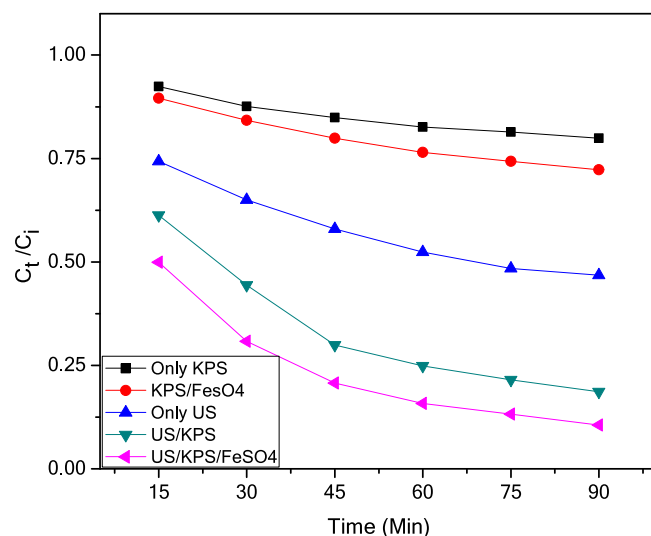
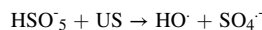


Fig. 11. Results for degradation of 2-Picoline using different approaches involving ultrasound,  $\text{FeSO}_4$  and KPS ( $T = 30\text{ }^{\circ}\text{C}$ ,  $\text{pH} = 6.7$ ,  $P = 70\text{ W}$ , time = 90 min,  $c_i = 30\text{ mg/L}$ ).

order rate constants for different approaches involving the ultrasound, KPS and  $\text{FeSO}_4$  shown in Table 1 as well as the data of concentration ratio of 2-picoline represented in Fig. 11 confirm the maximum effects for the combined approach of ultrasound, KPS and  $\text{FeSO}_4$ .

#### 3.5.5. Influence of peroxymonosulfate (PMS) in combination with ultrasound

PMS is also another sulphate based oxidising agent and advantageous to be used similar to KPS. The decomposition reaction of PMS in the presence of ultrasound can be represented as follows.



The effect of different initial concentrations of PMS over range of 4 mg/L to 32 mg/L in combination with ultrasound on the 2-picoline degradation was investigated at pH of 6.7, temperature of  $30\text{ }^{\circ}\text{C}$ , time of 90 min and power of 70 W. The obtained results depicted in Fig. 12 reveals that the degradation increases from 54.2 % to 80.1 % on increasing the PMS loading from 4 to 24 mg/L in the presence of

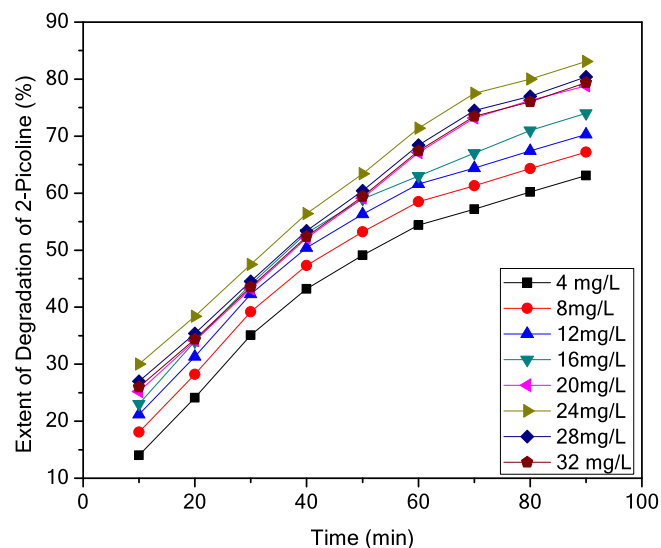


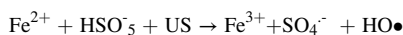
Fig. 12. Influence of PMS concentration on degradation of 2-Picoline using ultrasound ( $T = 30\text{ }^{\circ}\text{C}$ ,  $\text{pH} = 6.7$ ,  $P = 70\text{ W}$ ,  $c_i = 30\text{ mg/L}$ ).

ultrasound. Importantly, marginal decrease in degradation was observed on further increasing the dose to 28 mg/L (79.2 %) and to 32 mg/L (78.7 %) due to scavenging action of extra PMS in wastewater solution. It can be stated here the actual loading of PMS is specific to particular pollutants through the general trends are matching with the literature. Yixin et al. [33] reported that ultrasonic degradation of atrazine enhances from 28.90 % obtained at PMS loading of 50  $\mu\text{mol/L}$  to 58.7 % at 400  $\mu\text{mol/L}$  and subsequently as the loading increases beyond 400  $\mu\text{mol/L}$ , the degradation remained unchanged due to scavenging action of unutilised PMS in the solution.

Experiments were also conducted with only PMS in absence of ultrasound at conditions of pH of 6.7, temperature of 30 °C and time of 90 min. The degradation was noticed as 18.2 %, which is much lower compared to that observed in the presence of ultrasound. The synergetic index and obtained second order rate constant for the various approaches involving PMS are shown in Table 1 which also confirms the beneficial results seen for the ultrasound combination with PMS compared to the individual operations.

### 3.5.6. Influence of PMS/Ferrous sulphate ( $\text{FeSO}_4$ ) combination with ultrasound

2-Picoline degradation at initial concentration of 30 mg/L was also evaluated using the combination of ultrasound with PMS (24 mg/L) and  $\text{FeSO}_4$  (16 mg/L) under fixed conditions of pH as 6.7, temperature as 30 °C, time of 90 min and ultrasonic power as 70 W to establish the possible synergetic effect. The PMS decomposition in presence  $\text{FeSO}_4$  and ultrasound can be well represented by the reaction given below:



The observed extent of degradation for the combination was noted as 87.5 %. The beneficial effect for the combination was attributed to the fact that  $\text{FeSO}_4$  acts as activator to PMS resulting in increasing the formation of  $\text{SO}_4^{\cdot-}$  free radicals eventually increasing the degradation of 2-Picoline. Similar kind of trends were reported by Liu et al. [34] where the extent of degradation of azo dye as 81.3 % using US/PMS approach enhanced to 90 % for combination treatment approach of US/PMS/ $\text{FeSO}_4$ .

Experiments were also carried out using optimized concentrations of PMS/ $\text{FeSO}_4$  without ultrasound at conditions of 30 mg/L as the initial concentration of 2-Picoline solution, pH as 6.7, temperature as 30 °C and time 90 min. The observed degradation of 2-Picoline was only 24.7 %

confirming that ultrasound is indeed necessary for the intensified formation of free radicals. This requirement is also evident from the value of the synergetic index and obtained second order rate constant shown in Table 1 as well as the data of residual concentration of 2-Picoline represented in Fig. 13.

### 3.5.7. Influence of Titanium dioxide ( $\text{TiO}_2$ ) as catalyst in combination with ultrasound

The effect  $\text{TiO}_2$  catalyst on degradation of 2-Picoline was investigated at different loadings of  $\text{TiO}_2$  (5 mg/L to 50 mg/L as the studied range) at conditions of pH of 6.7, 30 mg/L as the initial concentration of 2-Picoline, temperature of 30 °C, time of 90 min and ultrasonic power of 70 W. Increasing the addition of heterogeneous catalyst improves the removal efficacy of pollutants as there are extra active sites for activation. It was observed that degradation of 2-Picoline increased from 55.7 to 75.1 % when  $\text{TiO}_2$  addition in 2-Picoline wastewater solution was increased from loading of 5 mg/L to 40 mg/L. The obtained results can be attributed to the fact that addition of catalyst leads to increase in number of nuclei for cavitation [35] and also to enhancement in active sites.  $\text{TiO}_2$  catalyst also assists in the decomposition of  $\text{H}_2\text{O}$  which leads to formation of more free radicals; all the effects contribute to enhanced degradation of 2-Picoline. At loadings of 45 mg/L and 50 mg/L of  $\text{TiO}_2$ , degradation only slightly increased to 74 % and 73.4% respectively (Fig. 14) which may be due to the mechanism that excess presence of  $\text{TiO}_2$  solid catalyst particles scatters the incident sound waves thus reducing the available energy for cavity formation and this disadvantageous effect is dominant at greater loading. From the obtained results, it can be concluded that 40 mg/L is optimum dose. The obtained trends for the optimum are consistent with the trends reported by Mishra et al. [36] where rhodamine B degradation enhanced from 10 % to 41.2 % with addition of  $\text{TiO}_2$  from 0.5 g/L to 2 g/L and subsequently a marginal decrease (38.2 %) in degradation was reported on further increasing the catalyst loading to 4 g/L.

Experiments were also performed using only  $\text{TiO}_2$  catalyst in absence of ultrasound at pH of 6.7, temperature of 30 °C and time of 90 min keeping the optimum dose of  $\text{TiO}_2$  catalyst as 40 mg/L. The observed degradation as 17.2 % explained the importance of using ultrasound and also the obtained benefits for the combination approach in terms of the synergetic index and obtained second order rate constant are clear from the data shown in Table 1.

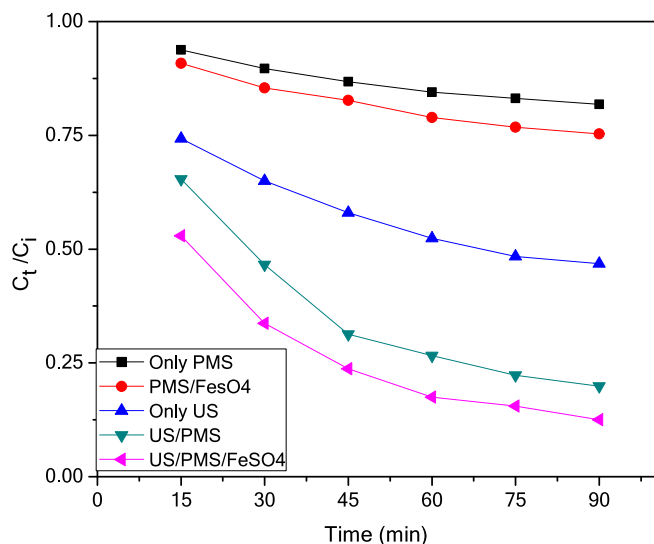


Fig. 13. Results for degradation of 2-Picoline using different approaches involving ultrasound,  $\text{FeSO}_4$  and PMS ( $T = 30^\circ\text{C}$ ,  $t = 90$  min,  $\text{pH} = 9$ ,  $C_i = 100$  mg/L).

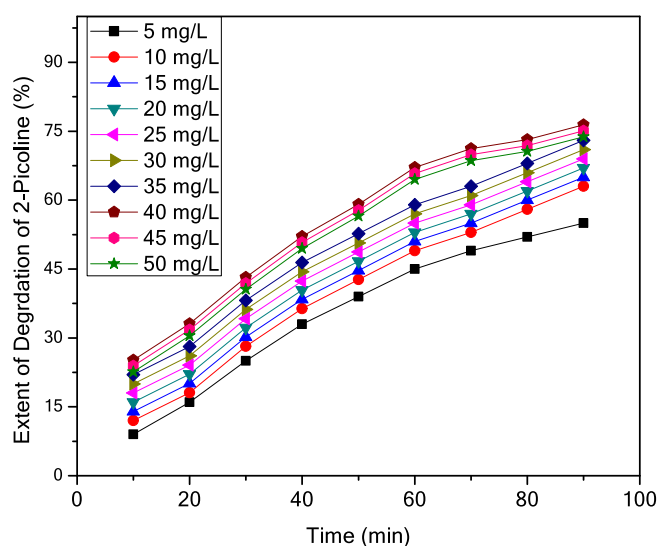


Fig. 14. Influence of Titanium oxide catalyst loading on degradation of 2-Picoline using ultrasound ( $T = 30^\circ\text{C}$ ,  $\text{pH} = 6.7$ ,  $P = 70$  W,  $C_i = 30$  mg/L).



### 3.5.8. Influence of combination of Titanium dioxide (TiO<sub>2</sub>) with hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>)

Degradation of 2-Picoline was also studied for the combination of TiO<sub>2</sub> and H<sub>2</sub>O<sub>2</sub> in the presence of ultrasound at conditions of pH of 6.7, temperature of 30 °C, 30 mg/L as the initial concentration, time of 90 min and ultrasonic power as 70 W. The degradation was observed as 81.3 % showing a small increase due to the presence of TiO<sub>2</sub> (76.7% is the degradation obtained in the absence) which can be attributed to the fact that the presence of TiO<sub>2</sub> catalyses the dissociation and increases the formation of free radicals which leads to increase in degradation. Khokhawala et al. [37] also reported that degradation of phenol for US/TiO<sub>2</sub> was 25.1 % whereas for the treatment approach of US/TiO<sub>2</sub>/H<sub>2</sub>O<sub>2</sub> higher degradation as 41 % was seen.

Experiments were also carried out using obtained optimized loadings of TiO<sub>2</sub>/H<sub>2</sub>O<sub>2</sub> without ultrasound to know the effect of using ultrasound for degradation. The conditions used for experiments were pH of 6.7, temperature of 30 °C, 30 mg/L as the initial concentration of 2-Picoline solution and time of 90 min. The degradation of 2-Picoline was seen as 19.6 % which again confirmed the necessity of using ultrasound. The synergetic index and obtained second order rate constants for the combination approach involving ultrasound, TiO<sub>2</sub> and H<sub>2</sub>O<sub>2</sub> is shown in Table 1, which confirm the beneficial results for combination approach of US/TiO<sub>2</sub>/H<sub>2</sub>O<sub>2</sub>. Similar confirmation is also seen based on the residual concentration data for 2-Picoline as shown in Fig. 15.

## 4. Analysis of Chemical oxygen demand (COD) reduction

COD measures the quality of wastewater in terms of total concentration of organics and the reduction of COD reveals the mineralization. COD analysis was performed using standard dichromate method. The COD for 2-Picoline at initial concentration of 30 mg/L before degradation was observed to be 42.1 mg/L. The obtained data for COD analysis after degradation using different treatment process have been shown in Table 2. Pyridine and its derivatives are resistant to dichromate oxidant and generally give low COD results [38] as also seen in the current work. The extent of COD removal was typically lesser as compared to the removal of the parent compound indicating the formation of intermediates which are being mineralized at slower rate. The trends in COD reduction were consistent with the trends for removal of 2-picoline and maximum COD reduction was obtained for the approach of US/Fenton.

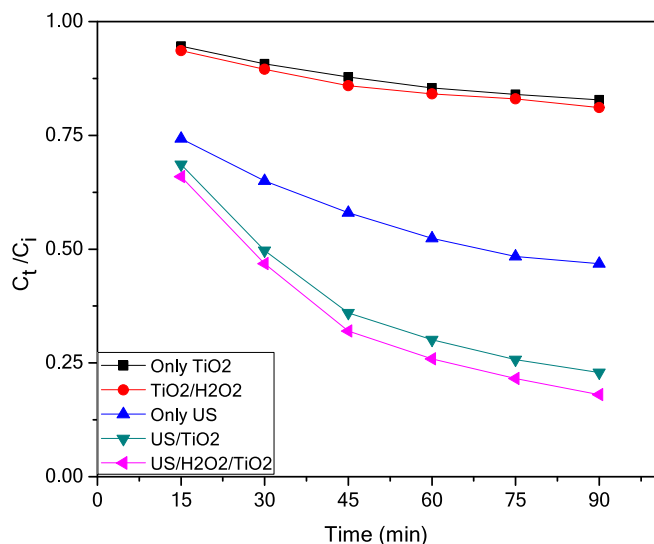


Fig. 15. Results for degradation of 2- Picoline using different approaches involving ultrasound, H<sub>2</sub>O<sub>2</sub> and TiO<sub>2</sub> (T = 30 °C, t = 90 min, pH = 9, C<sub>i</sub> = 100 mg/L).

Table 2

Results for Chemical Oxygen Demand removal for different treatment approaches.

Operative parameters: Initial Concentration (C <sub>i</sub> ): 30 mg/L, t: 90 min, pH:6.7, T: 30 °C	
Treatment Approach	Extent Of COD Removal (%)
US Only	47.1
US/H <sub>2</sub> O <sub>2</sub>	72.9
US/Fenton	82.4
US/KPS	67.1
US/KPS/FeSO <sub>4</sub>	76.5
US/PMS	62.4
US/PMS/FeSO <sub>4</sub>	64.7
US/TiO <sub>2</sub>	60.1
US/TiO <sub>2</sub> /H <sub>2</sub> O <sub>2</sub>	62.4

## 5. Degradation products

The sample of 2-Picoline solution obtained after treatment was analysed using HPLC. The Peak of original 2-Picoline is shown in Fig. 16a where it is seen that 2-Picoline is detected at 3.9 min. Fig. 16b-f show HPLC peaks for sample analysis after degradation of 2-Picoline using different approaches. For the treated solutions, the formation of new peaks around 5.2 min was attributed to the formation of pyruvic acid [39]. It is also interesting to note that the peak intensity for 2 picoline at 3.9 min is reducing to different extents for different approaches attributed to different levels of removal. The tentative degradation path way for 2-Picoline is shown in Fig. 17. The degradation involved the formation of 2, 3-dihydroxy-6-picoline followed by ring cleavages between hydroxyl group further forming Oxopentanoic acid and then Pyruvic acid. The projected cleavage path (Fig. 17) is similar to the pathway proposed by Gupta et al. [40] for biodegradation 2-Picoline using *Arthrobacter* sp. KM-4.

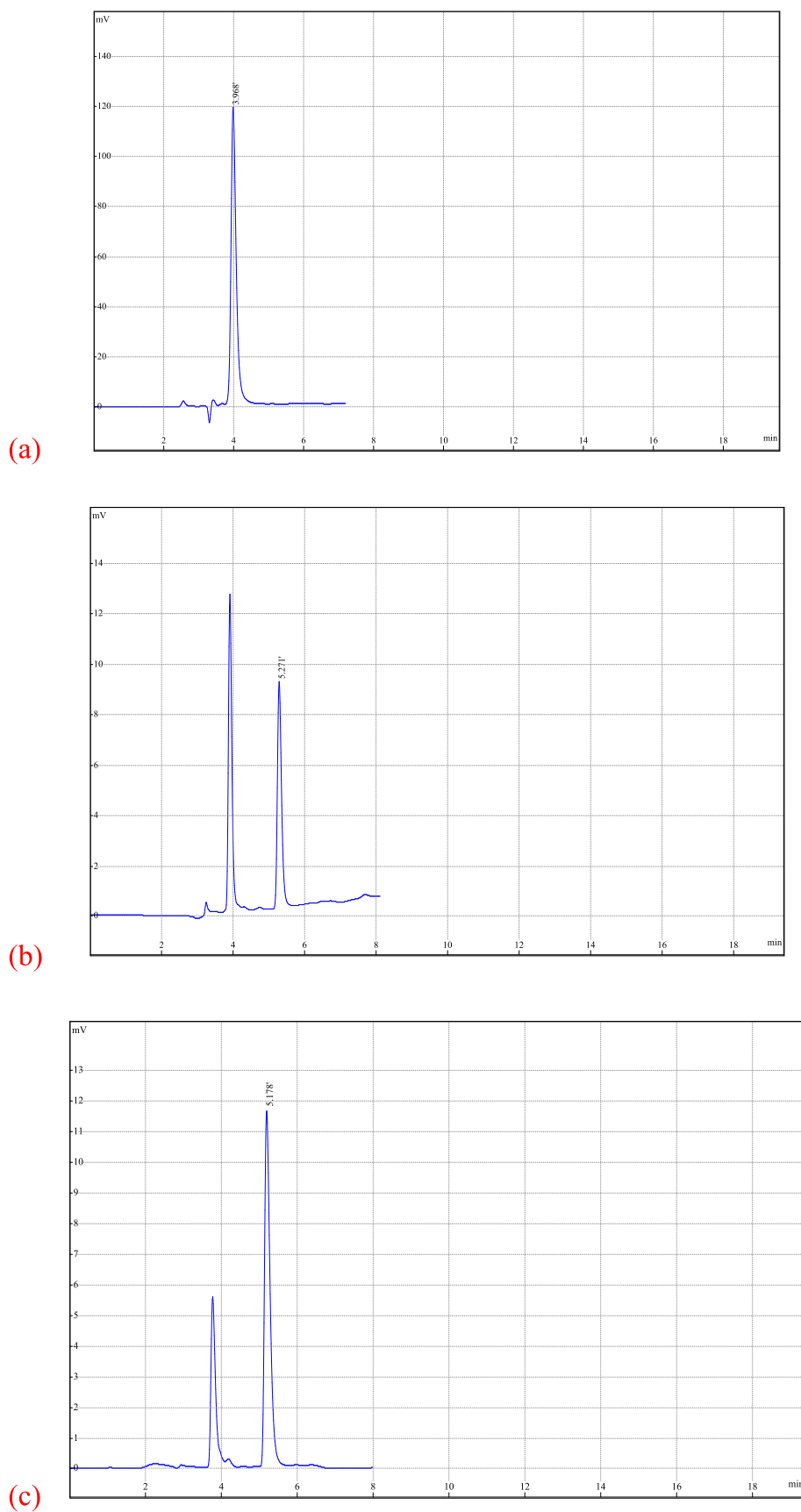
## 6. Cavitation yield and synergetic index calculations

The cavitation yield based on extent of degradation of 2-Picoline and energy consumption for all approaches was evaluated and the obtained data is shown in Table 3. The obtained results clearly demonstrate that the US/Fenton treatment approach provides highest cavitation yield ( $1.82 \times 10^{-05}$  mg/J) for treatment of 400 mL of 2-Picoline wastewater solution. The energy consumption for stirring for all treatment approaches and power dissipated by ultrasound generator was considered to estimate the cavitation yield. The detailed sample calculation is provided in Appendix-1.

Synergetic index was also established for all combination approaches based on optimised concentration of all oxidising agents and represented in Table 3. The highest synergetic index (5.71) was obtained for US/Fenton. The detailed calculation to establish synergetic index is shown in Appendix-2. Overall it can be concluded that US/Fenton is best treatment approach for degradation of 2-Picoline compared with all other treatment approaches in terms of cavitation yield, Synergetic index, highest degradation of 2-Picoline and greater removal of COD.

## 7. Conclusions

The treatment of 2-Picoline containing wastewater was analysed under different operative conditions and using different approaches involving ultrasound and combination with oxidants or catalyst. The maximum degradation (97.6 %) and COD removal of 82.4 % was obtained for US/Fenton approach at optimised parameters as pH of 6.7, temperature of 30 °C, time of 90 min and dissipated power of 70 W for treatment volume of 400 mL having initial concentration of 2-Picoline as 30 mg/L using bath sonicator. The degradation was followed to favour second order kinetics for all treatment approaches (except US/Fenton where first order kinetics prevailed). The cavitation yield based on energy consumption and synergetic index based obtained rate constant



**Fig. 16.** HPLC analysis of original 2-Picoline solution (a) and after treatment using different approaches ( $T = 30^{\circ}\text{C}$ ,  $t = 90\text{min}$ ,  $\text{pH} = 9$ ,  $c_i = 30\text{mg/L}$ ) (b) US only (c) US/ $\text{H}_2\text{O}_2$  (d) US/Fenton (e) US/KPS (f) US/PMS (g) US/ $\text{TiO}_2$ .

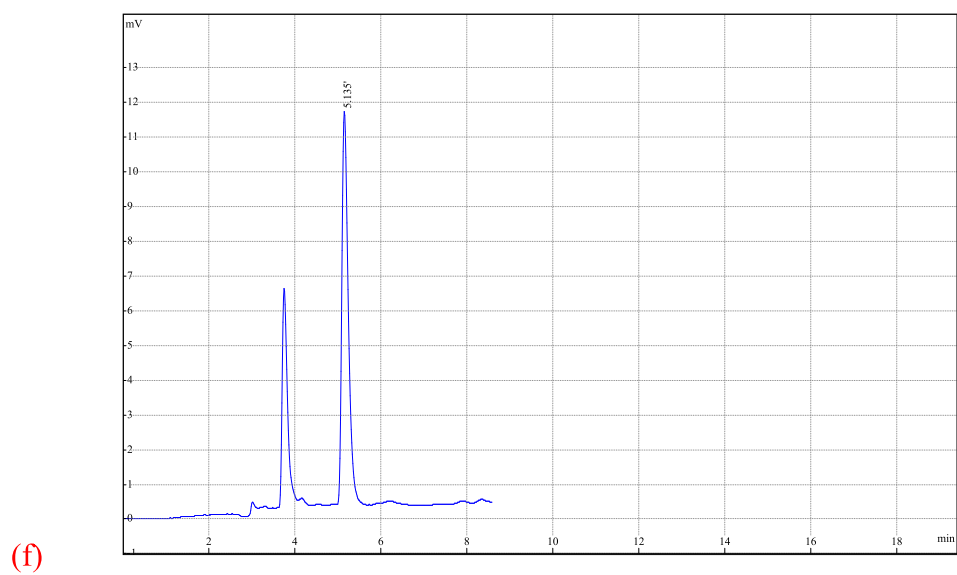
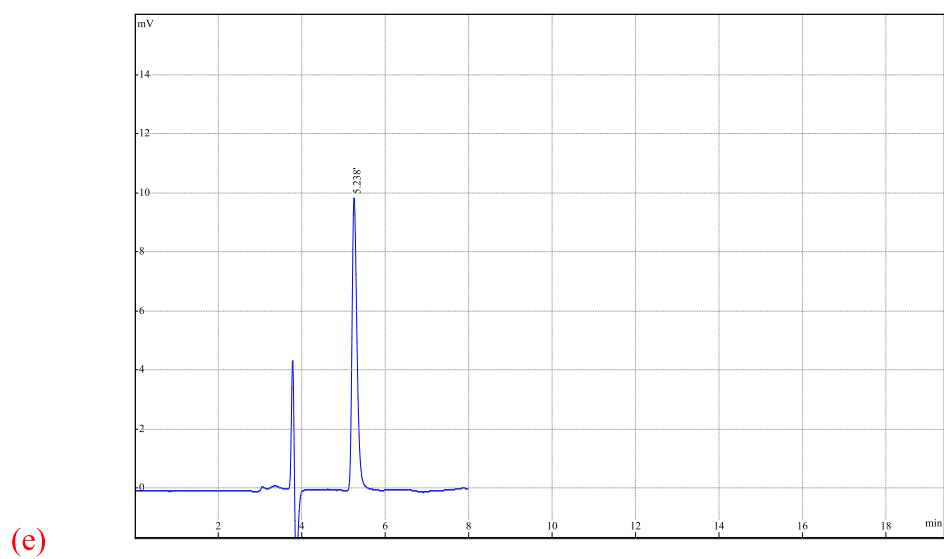
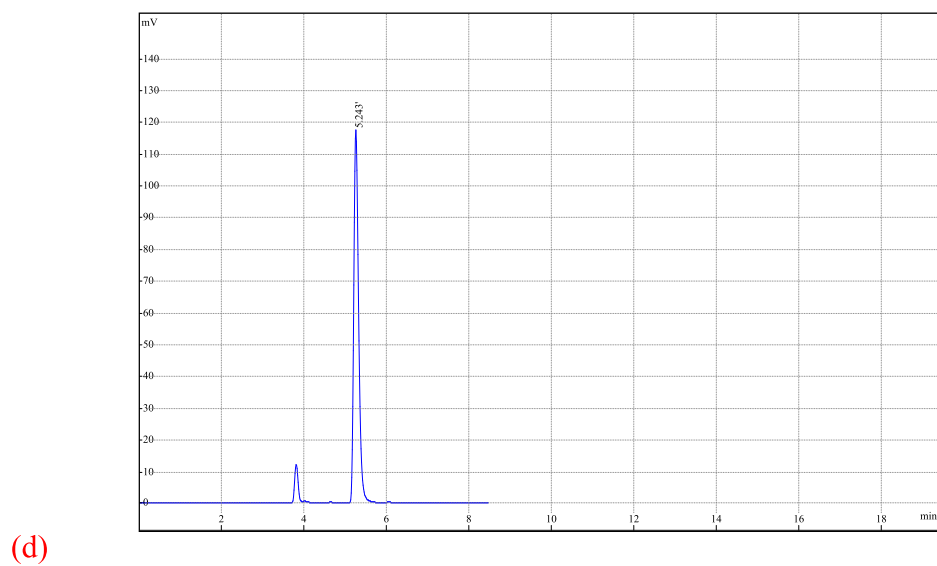


Fig. 16. (continued).

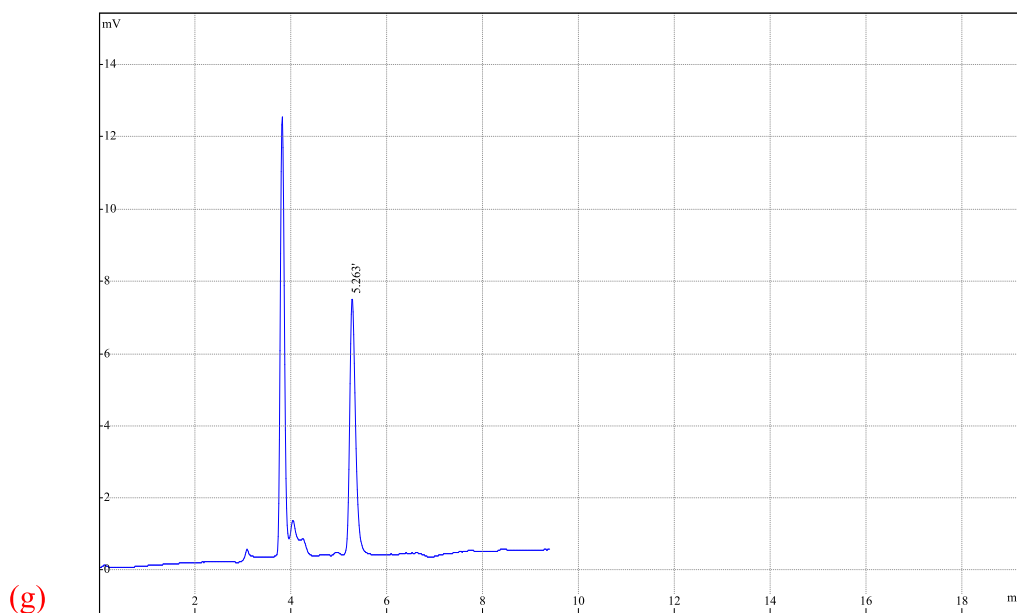


Fig. 16. (continued).

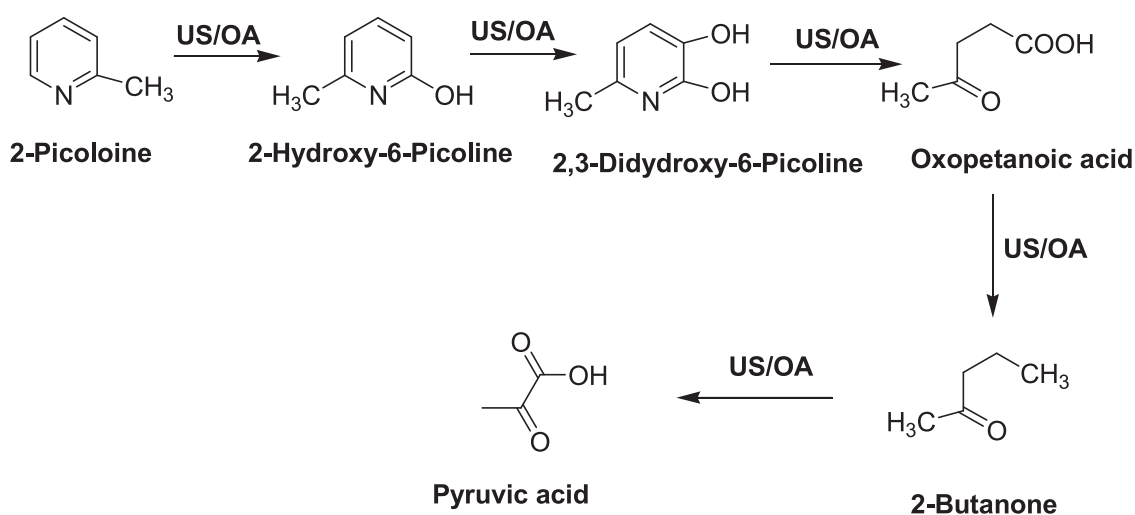


Fig. 17. Tentative Degradation Pathway of 2-Picoline.

Table 3

Cavitation Yield and Synergetic Index for different treatment approaches.

Operative parameters: Initial Concentration ( $c_i$ ): 30 mg/L, t: 90 min, pH:6.7, T: 30 °C		
Treatment Approach	Cavitation Yield	Synergetic Index
US Only	$9.851 \times 10^{-06}$	—
Only H <sub>2</sub> O <sub>2</sub>	$3.94 \times 10^{-06}$	—
Only Fenton	$5.96 \times 10^{-06}$	—
Only KPS	$3.72 \times 10^{-06}$	—
KPS/FeSO <sub>4</sub>	$5.12 \times 10^{-06}$	—
Only PMS	$3.37 \times 10^{-06}$	—
Only TiO <sub>2</sub>	$3.18 \times 10^{-06}$	—
PMS/FeSO <sub>4</sub>	$4.57 \times 10^{-06}$	—
US/H <sub>2</sub> O <sub>2</sub>	$1.55 \times 10^{-05}$	3.40
US/Fenton	$1.82 \times 10^{-05}$	5.71
US/KPS	$1.50 \times 10^{-05}$	2.90
US/KPS/FeSO <sub>4</sub>	$1.78 \times 10^{-06}$	5.00
US/PMS	$1.67 \times 10^{-05}$	3.00
US/PMS/FeSO <sub>4</sub>	$1.62 \times 10^{-05}$	4.50
US/TiO <sub>2</sub>	$1.42 \times 10^{-05}$	2.80
US/TiO <sub>2</sub> /H <sub>2</sub> O <sub>2</sub>	$1.52 \times 10^{-05}$	2.90

were determined for all treatment approaches. The best treatment methodology based on obtained results of degradation, highest cavitation yield ( $1.82 \times 10^{-05}$  mg/J) and synergetic index (5.71) was also US/Fenton. Overall it can be concluded that ultrasound in presence of oxidising agents is effective treatment approach in terms of degradation extent and energy utilisation compared to individual treatment approach.

#### CRediT authorship contribution statement

**G.B. Daware:** Methodology, Investigation, Writing – original draft.  
**P.R. Gogate:** Conceptualization, Writing - review & editing, Supervision.

#### Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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## Appendix I:

Time for treatment = 90 min (5400 sec),  
 Treatment volume of 2-Picoline = 400 mL  
 Initial concentration of 2-Picoline = 30 mg/L and after 90 min treatment, the observed concentration = 14.01 mg/L.  
 2-Picoline degraded in 90 min = 15.99 mg/L  
 Dissipated power for sonicator = 70 W.  
 Stirring Power = 50 W  
 Total Power used = 120 W  
 Power dissipated per unit volume =  $120/0.4 = 300 \text{ W/L}$   
 $= 300 \times 5400 = 1620000 \text{ J/L}$   
 Cavitation Yield = (the amount of 2-Picoline degraded/power consumed (J))  
 $= 15.99/1620000 = 9.87 \times 10^{-6} \text{ mg/J.}$

## Appendix II. : Synergetic index (f):

Treatment approach of US/Fenton  
 Rate constant for only US ( $k_{US}$ ) =  $0.0040 \text{ min}^{-1}$   
 Rate constant for Fenton ( $k_{Fenton}$ ) =  $0.003 \text{ min}^{-1}$   
 Rate constant For US/Fenton system,  $k_{(US/Fenton)} = 0.040 \text{ min}^{-1}$

$$f = \frac{k_{(US/Fenton)}}{k_{US} + k_{Fenton}}$$

$$f = \frac{0.040}{(0.0040 + 0.0030)}$$

$$f = 5.71$$

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