



Sonochemical degradation of 3-methylpyridine (3MP) intensified using combination with various oxidants

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ABSTRACT

3-Methyl pyridine (3MP) is a toxic and hazardous organic compound having considerable negative impact on environment and living organisms. The objective of this work to report a novel treatment strategy based on sonochemical degradation of 3MP, in combination with oxidants such as hydrogen peroxide, Fenton's reagent, peroxymonosulphate (PMS), and potassium persulphate (KPS) as well as solar irradiations. A bath sonicator operating at 25 kHz frequency and rated power dissipation of 100 W was applied in the work to study different approaches with an objective to enhance the removal of 3MP in lesser time. Effect of operating parameters such as pH (over the range of 2–10), treatment time, temperature (25–55 °C) and ultrasonic power (25 W to 150 W) on the degradation has been studied and the best conditions were used in subsequent combination approaches. It was demonstrated that ultrasound in combination with PMS, ferrous sulphate (FeSO_4) and solar irradiations (approach of US/PMS/ FeSO_4 /solar irradiation) is the best treatment strategy yielding maximum degradation as 97.4% with highest cavitation yield as 1.920×10^{-4} mg/J and highest synergetic Index as 2.70. Kinetic analysis revealed that first order mechanism fitted well to all the approaches involving different combinations of ultrasound, oxidising agents and solar irradiation. Degradation products were also analysed that established the degradation mechanism as C_2 and C_3 ring cleavages forming 1, 4-dihydro-3-methylpyridine followed by Levulinic acid as non-toxic main by-product. Overall the work clearly demonstrated an effective treatment approach involving combined sonication with oxidants for remediation of 3MP also providing insights on kinetics and mechanism of degradation.

1. Introduction

Water pollution is the problem that has increased over the years due to continued industrialisation and advent of newer molecules. Handling and disposal of hazardous chemicals as well as treatment of effluent containing these compounds is a major concern for industries. Pyridine and Pyridine derivatives are rated as one of the most significant hazardous chemicals and are having many industrial uses like intermediates, solvent, raw material to fertiliser, pesticides, pharmaceutical and dye industries [1] making it as important class of chemicals. United States Environmental Protection Agency [USEPA] has rated pyridine as extremely hazardous to living organisms and environment [2]. Pyridine and its derivatives are heterocyclic aromatic compounds having pungent and unlikeable smell [3]. It can cause toxic effects to human nervous system, kidney and skin [4]. Typically, pyridine and pyridine derivatives are found at loadings over the range of 20 to 300 mg/L, though the emergency spills can increase its concentration to considerable extent, such as 1000 mg/L [5]. The maximum allowable

concentration of pyridine and its derivatives in the treated wastewater is 5 mg/L. Significant industrial applications and higher water solubility means there is a considerable possibility of finding pyridine derivatives in the wastewater and this has motivated researchers to develop effective treatment options for tackling wastewater containing pyridine and its derivatives.

Several researchers have reported the use of different chemical and physical methods to treat pyridine and pyridine derivatives including adsorption [6], microwave [7], biological oxidation [8], microbial fuel cell (MFC) [9], photo-Fenton oxidation [10], ultrasonic irradiations [11], ozonation [12] etc. Biodegradation is generally slow and complex method requiring good knowledge and proper maintenance of micro-organisms. Adsorption methods are widely used but disposal of adsorbent loaded with the pollutant is a major concern and also in most of the cases, complete regeneration of adsorbent is not possible. MFC involves higher operating cost and operational constraints at lower temperature as most of the microbial reactions are slow at lower temperature. Photo-Fenton processes generally require high operating cost

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and low utilization rate of light energy. It can be thus said that most of the reported methods for the treatment of pyridine derivatives have problems related to the operation and hence are not so efficient to be developed as commercial scale solution. Use of ultrasound does offer significant potential and the efficacy for degradation of hazardous pollutants based on the cavitation effects however not many studies have been reported for the specific case of pyridine derivatives. Ultrasound induced degradation study for pyridine derivatives was only reported [11] for the specific case of pyridine, where the study was performed using ultrasound operated at 40 kHz frequency and 360 W as power dissipation. The study also reported the combination of ultrasound with oxidising agents like hydrogen peroxide and Fenton reagent. The present work has concentrated on ultrasound induced degradation of 3-Methyl pyridine (3MP) as there are no reports dealing with use of ultrasound for degradation of 3MP either individually or in combination with oxidants. Use of combined approaches with oxidants has also been investigated in the current work as in the literature, ultrasound combination with oxidants has been reported to be very effective for treatment of wastewater containing dyes [13], phenol [14], and pesticides [15] as well as for the case of only pyridine [11]. 3MP is an important derivative of pyridine and mostly used in drug manufacturing as intermediates and as a solvent in many industries, justifying the presence selection as model compound for investigation. Literature analysis related to specific pollutant as 3MP revealed that only biodegradation [16] and adsorption [17] have been reported as remediation approaches though the problems with both these approaches are well known. Thus the novelty of the current work dealing with the application of ultrasound for effective degradation of 3MP is clearly established. Ultrasound combination with sulphate based oxidising agent in combination with solar irradiation is also reported for the first time.

Overall the present work has focused on understanding the degradation of 3MP using ultrasound individually first and subsequently in combination with oxidants like PMS, KPS, Fenton reagent and hydrogen peroxide as well as with solar irradiations. The effect of parameters like pH, concentration, time, temperature and power at fixed frequency on degradation of 3MP has been studied initially to optimize the operation of ultrasound. The optimized parameters were then used in the combination approaches where the loading of oxidants was optimized. Identification of intermediates has also been attempted along with proposing a degradation pathway.

2. Experimental methodology

2.1. Materials

3-Methyl pyridine (3MP) was obtained from Sigma-Aldrich [now Merck India], Mumbai and then used for preparing simulated synthetic wastewater based on dissolution of required quantum in distilled water (initially stock solution is prepared and then diluted to get the required different concentrations for the experimentation). All the other chemical reagents including those required for analysis were also procured from Sigma-Aldrich [now Merck India].

2.2. Ultrasonic bath

The degradation study was conducted in 8 L capacity ultrasonic bath reactor operating at frequency of 25 kHz and maximum power rating of 100 W. The ultrasonic bath had dimensions of 300 × 180 × 150 mm and the generator was a separate unit. The control panel provided on the generator had the facility of setting the operational parameters (temperature, power and time). A drainage outlet was also provided at the bottom of the bath so as to allow withdrawal of solution. The simulated effluent was taken in 1 L conical flask which was placed at the centre of bath where maximum cavitation activity is expected based on position of the transducers. The

schematic representation of the experimental setup has been given in Fig. S1. Most experiments were conducted at 100 W power dissipation (except those for understanding the effect of power). The actual utilised power at this supplied power was 20 W as determined using the calorimetric measurements [18].

2.3. Experimental methodology

Initially experiments were performed using only ultrasound to understand the effects of temperature, time, pH and power dissipation. Digital thermocouple was used to monitor temperature of the solution. The pH of 3MP solution was adjusted using 0.1 N aqueous solution of H₂SO₄ or 0.1 N aqueous solution of NaOH as per the requirement. The range of temperature used in the study was 25 to 50 °C whereas pH range selected was from 2 to 10 and initial pollutant concentration range was from 25 mg/L to 100 mg/L. Once the best conditions for ultrasonic degradation were established, all subsequent experimentation for combination approaches were carried out at optimized sonication time of 90 min, power of 100 W, temperature of 45 °C and pH of 9.

Combination of ultrasound with hydrogen peroxide, Fenton reagent, Peroxymono sulphate (PMS) and potassium Persulphate (KPS) at different loadings was studied to establish optimised loading of oxidising agents. Subsequently combination of ultrasound with Fenton reagent, oxidising agents and solar irradiations was also studied to see the intensification benefits for degradation of 3MP. Outdoor experiments were performed under solar irradiations using two magnifying glasses having diameter of 75 mm and focal length of 30 cm applied as concentrators. All the outdoor experiments were performed at light intensity 950 W/m². During the experiments, samples were regularly withdrawn at specific time intervals as 10 min, centrifuged to remove any solid content and considered for further analysis.

2.4. Analyses of pollutant and degradation products

2.4.1. HPLC analyses

The withdrawn samples at specific time intervals during the 3MP degradation studies were analysed using HPLC instrument (Analytical Technologies Pvt. Ltd.) containing Binary Gradient HPLC pump (P-3000 M) with UV detector (single wavelength) having detection range of 200–700 nm and the HPLC column, Cosmosil C-18 (250 mm × 4.6 mm (ID)). Methanol and water (both HPLC grade, 70:30 v/v) mixture at flow rate of 0.8 mL/min was used as mobile phase. Proper cleaning of column before and after analysis of 3MP was carried out using methanol (HPLC grade). The sample volume taken for the analysis was 20 µL with run time of 15.42 min. All samples were measured at detection wavelength of 263 nm.

2.4.2. GCMS analyses

The degradation products were analysed using GC-MS instrument (Shimadzu TQ-8050), with column dimensions of 3 cm × 0.250 mm. For separation of degradation products, the chromatographic conditions applied were injection temperature of 250 °C and helium as the carrier gas at fixed flow rate of 1 mL/min. Both the ion source and the interface were set at fixed temperature of 250 °C. The scan time was 15 min and scan range used in the work was m/z of 10–300. For the analysis, the injection volume taken was 2 µL with split ratio of 1.

3. Results and discussion

3.1. Effect of ultrasonic power on degradation of 3 MP

The degradation experiments were performed at different powers from 25 W to 150 W to understand the effect of power dissipation. Degradation was observed to be enhanced with an increase in power from 25 W to 100 W. Quantitatively the extent of degradation was

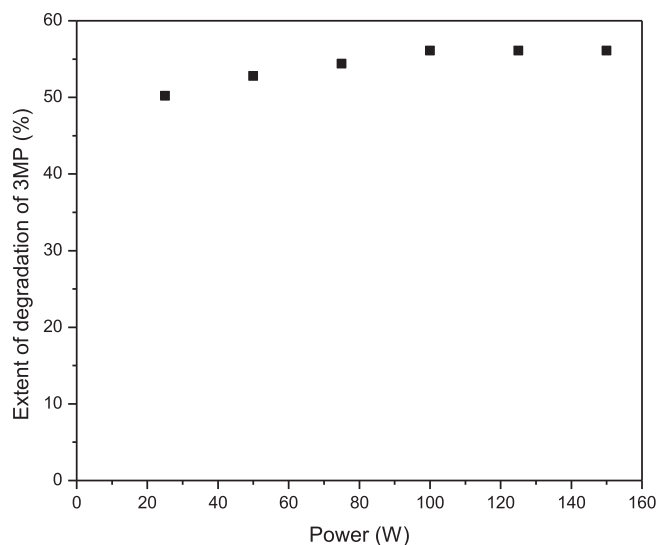


Fig. 1. Effect of Power on extent of degradation of 3MP ($T = 45\text{ }^{\circ}\text{C}$, time = 90 min, $c_i = 100\text{ mg/L}$).

found to be 50.2% at 25 W and it increased to 56.1% at power dissipation of 100 W. At higher power over the range of 25 to 100 W, higher extent of cavitation effects (thus more turbulence and quantum of free radicals generated) is observed leading to enhanced degradation of 3MP. It was also noticed that no significant change in the degradation of 3MP is observed for a subsequent increase in power from 100 W to 150 W (actual value is 56.5%) as per the data shown in Fig. 1. The observed marginal change in the extent of degradation beyond the power of 100 W can be attributed to the cushioning effects due to the formation of large numbers of bubbles that coalesce forming higher size bubbles that collapse inefficiently. Also accumulation of such bubbles near the transducer surface scatter the sound waves throughout the reactor and thus lesser amount of energy is actually utilized in the liquid even at higher supplied power. Considering the obtained results, 100 W was selected as optimised power for further experimental study considering that there is a definite trend in obtaining higher extent of degradation with an increase in power from 25 W till 100 W. Rad et al. [19] reported similar trend of higher degradation of famotidine for an increase in power till optimum value of 150 W. Sivakumar and Pandit [20] reported similar trends of changes in the extent of degradation of rhodamine B with existence of optimum power dissipation depending on the type of ultrasonic reactor. For ultrasonic horn, it was reported that the extent of degradation remained in the range of 80 to 90% for a change in the power intensity from 5 to 25 W/cm^2 . Wang et al. [21] reported that the extent of COD degradation for ammonia landfill leachate increases from about 10% to 18% by increasing power from 50 W to 150 W. It is important to note that though the trends of optimum are same, exact value as well as the extent of changes observed in the extent of degradation/mineralization is different for specific pollutant and hence the detailed investigation presented in the work is justified.

3.2. Effect pH on ultrasonic degradation of 3 MP

Degradation of 3MP was also studied at varying pH from 2 to 10 at fixed treatment time of 90 min, power dissipation of 100 W and temperature of $45\text{ }^{\circ}\text{C}$. The obtained results are depicted in Fig. 2. The extent of ultrasound assisted degradation of 3MP solution with initial concentration of 100 mg/L increased with an increase in pH from 2 to 9 and then marginally changed for further increase in pH to 10. As the pH increased from 2 to 9, the degradation extent progressively increased from 18.2% to 56.1%. The pKa value of 3MP is 5.63 indicating that it is basic in nature. 3MP contains N atom which is more electronegative than sp^2 hybridised C molecule. In strongly acidic condition, stable

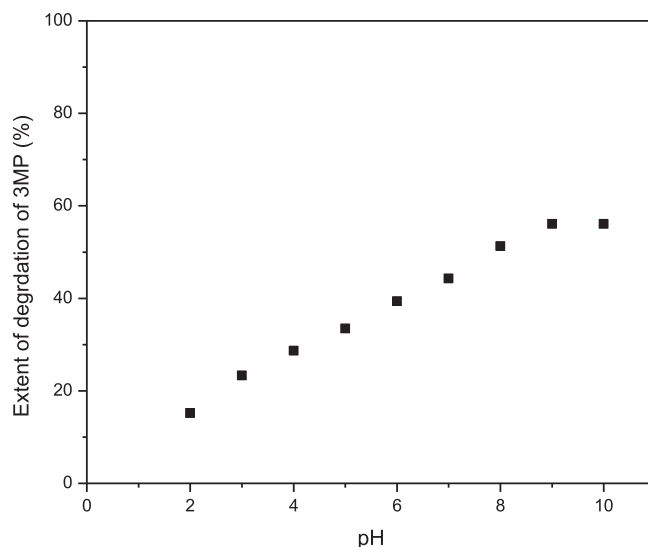


Fig. 2. Effect of pH on extent of degradation of 3MP ($T = 45\text{ }^{\circ}\text{C}$, time = 90 min, $c_i = 100\text{ mg/L}$, power = 100 W).

pyridium salt predominately exists in the solution [11] which undergoes oxidation at lower rates as compared to the form in alkaline conditions. It is clearly seen from the obtained results that the degradation is significantly higher in alkaline conditions while rate of degradation decreased in acidic conditions. As further increase in pH beyond 9 resulted in no effect on the extent of degradation, pH of 9 was established as best pH for degradation of 3MP. Though most of the sonochemical degradation has been reported to favour under acidic conditions, some examples of beneficial results at alkaline conditions (though with different value of best operating pH) can be seen for the nitro or amino compounds. For example, Wang et al. [21] reported that the degradation of ammonia-nitrogen from leachate enhanced from 10.24% to 98.3% with an increase in pH value from 3 to 11. Similar observation was also demonstrated by Elsayed [11] for degradation of pyridine from wastewater with maximum degradation being observed at pH of 8.5. He et al. [22] demonstrated similar results for degradation of p-aminophenol with maximum degradation of 98% being reported at pH of 12. Considering the results obtained in the current work, pH of 9 was established as best treatment condition and used for the subsequent experiments.

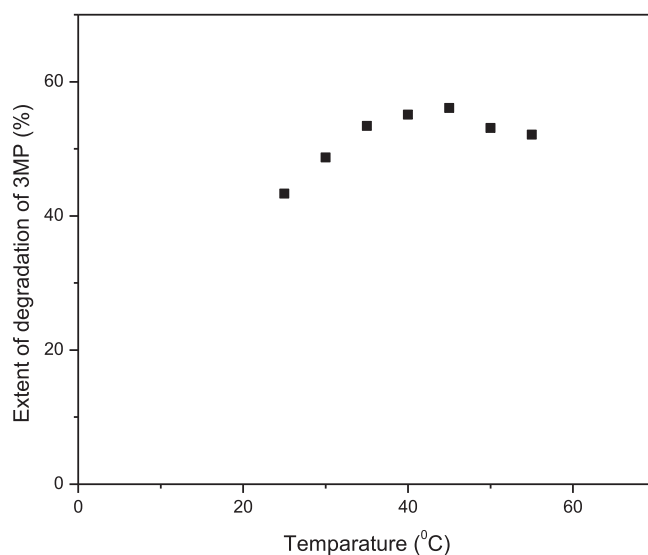


Fig. 3. Effect of Temperature on extent of degradation of 3MP (pH = 9, time = 90 min, $c_i = 100\text{ mg/L}$, power = 100 W).

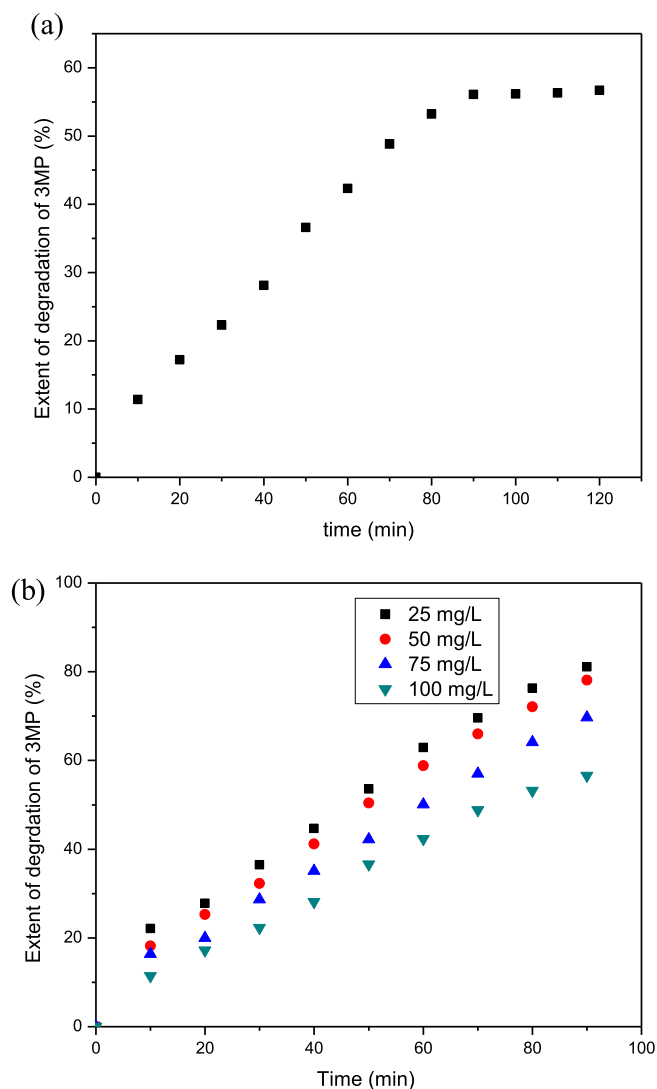


Fig. 4. a) Effect of contact time at 100 mg/L as fixed initial concentration on the extent of degradation of 3MP ($T = 45\text{ }^{\circ}\text{C}$, $\text{pH} = 9$, power = 100 W) b) Effect of initial concentrations on the extent of degradation of 3MP ($T = 45\text{ }^{\circ}\text{C}$, $\text{pH} = 9$, power = 100 W).

3.3. Effect of temperature on ultrasonic degradation of 3 MP

The study of ultrasound induced degradation was performed at different temperatures ($25\text{ }^{\circ}\text{C}$ to $55\text{ }^{\circ}\text{C}$) with usage of coolant or the heating medium to control the temperature as required. Considering the typical application of wastewater treatment at ambient conditions or with some minor increase in the temperature, the range of temperature has been decided in the current work. In actual application, using too high temperature would not be economical since the typical discharge requirement is again at ambient conditions. The degradation experiments were conducted under conditions of 100 mg/L as initial concentration of 3MP solution, optimised pH as 9, power dissipation as 100 W and treatment time of 90 min. The obtained results for the extent of degradation of 3MP are shown in Fig. 3, where it can be seen that the extent of ultrasonic degradation of 3MP increased from 40.1% to 56.1% for an increase in temperature from $25\text{ }^{\circ}\text{C}$ to $45\text{ }^{\circ}\text{C}$ whereas the extent of degradation reduced marginally to values of 54.1% and 53.1% after increasing temperature further to $50\text{ }^{\circ}\text{C}$ and $55\text{ }^{\circ}\text{C}$ respectively. It can be thus said that best results are obtained at operating temperature of $45\text{ }^{\circ}\text{C}$. The obtained results can be explained on basis of counteracting effects of enhanced kinetics and reduced cavitation effects with an

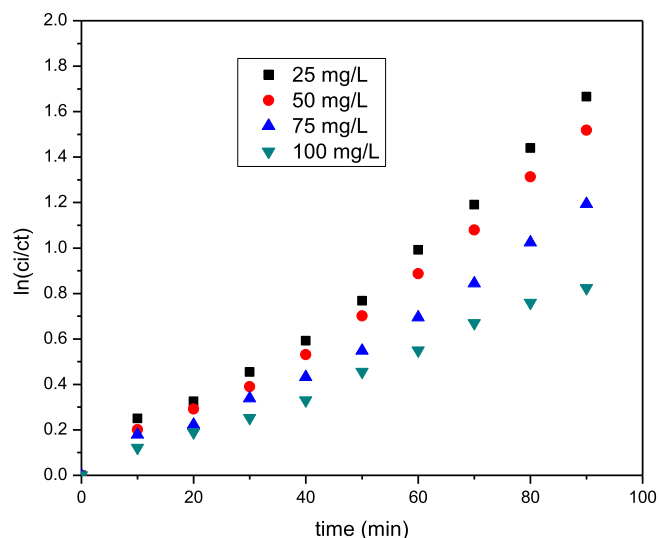


Fig. 5. Kinetic fitting for Degradation of 3MP ($T = 45\text{ }^{\circ}\text{C}$, $\text{pH} = 9$, power = 100 W).

increase in the temperature. Till an optimum temperature observed as $45\text{ }^{\circ}\text{C}$, the kinetic effects are more dominating [14] whereas for increase beyond $45\text{ }^{\circ}\text{C}$, lower generation of hydroxyl radicals due to lower intensity of cavitation seem to be controlling. At temperatures above $45\text{ }^{\circ}\text{C}$, the vapour content in bubbles is significantly higher due to higher vapour pressure of liquid providing a cushioned collapse of the bubbles and resulting in a decrease in the released energy at the time of collapse, consequently reducing the free radical formation [23]. Credence to the observed trends for effect of temperature, though with different ranges of temperature and value of optimum, can also be obtained by comparing the trends with literature results. Golash and Gogate [24] investigated degradation of dichlorvos using ultrasound over temperature range of $15\text{ }^{\circ}\text{C}$ to $45\text{ }^{\circ}\text{C}$. It was reported that increasing temperature from $15\text{ }^{\circ}\text{C}$ to $30\text{ }^{\circ}\text{C}$ was favourable for the extent of degradation and a reduction in degradation was observed for further increase in temperature to $45\text{ }^{\circ}\text{C}$. Shriwas and Gogate [25] studied the effect of temperature on degradation of 2,4,6-trichlorophenol and reported an increase in degradation from 14% to 43% for an increase in the temperature from $25\text{ }^{\circ}\text{C}$ to $40\text{ }^{\circ}\text{C}$. Elsayed [26] also reported that degradation increased with an increase in temperature from $20\text{ }^{\circ}\text{C}$ to $40\text{ }^{\circ}\text{C}$. It must be understood that the effect of temperature for sonochemical degradation cannot be generalized and the existence of optimum or a continuous increase as well as the value of optimum depends upon the type of pollutant, and interaction between free radicals and pollutants, gas solubility, static pressure etc. Thus it is recommended that the trends must be established for the specific system in question highlighting the importance of the current work.

3.4. Effect of time and initial concentration on ultrasonic degradation of 3MP

The degradation of 3MP was also studied using different initial concentrations of 3MP (over the range of 25 mg/L to 100 mg/L) at varying time. Fig. 4(a) shows the results obtained for degradation at fixed initial concentration of 3MP as 100 mg/L in terms of kinetic profile i.e. change with respect to the treatment times. It can be seen that the degradation increases with time dominantly over the initial time period and after 90 min, no substantial increase in rate of degradation was observed (the actual values are 56.3% at 100 min and 56.5% at 120 min). One of the reasons for the observed dominant saturation after 90 min can be that the intermediates formed from the initial degradation of 3MP react predominantly with the generated hydroxyl radicals leading to continued mineralization though this was

Table 1

Effect of different initial concentrations on extent of degradation of 3MP and first order rate constant.

Only US, $c_i = 100$ mg/L Time = 90 min, pH = 9, power = 100 W and Temperature = 45 °C			
concentration	Extent of degradation	Rate constant (min^{-1})	R^2
25 mg/L	81.1	0.0178	0.98
50 mg/L	76.1	0.0162	0.98
75 mg/L	69.7	0.0127	0.98
100 mg/L	56.1	0.0099	0.99

not confirmed in the study. It is important to note that the results are indeed reproducible and also match with the earlier literature. Shriwas and Gogate [25] reported that the extent of degradation 2, 4, 6-trichlorophenol was only around 30% at optimised treatment time of 150 min using only US and any increase in treatment time beyond 150 min didn't yield any improvement in the extent of degradation. Considering the observed trends, further degradation studies for understanding the effect of operating conditions and combinations were carried out for 90 min as the fixed treatment time.

It has been also observed from the data shown in Fig. 4(b) that as the initial concentration of 3MP increases from 25 to 100 mg/L, the extent of degradation reduced from 71.1% to 56.1% in 90 min of treatment. It must be understood that even though the extent of degradation expressed in % decreases at higher concentration, the amount of 3MP degraded expressed in terms of mass or moles of 3MP was higher. The amount of 3MP degraded at 100 mg/L solution was almost two times and the amount of 3MP degraded at 50 mg/L almost three times as compared to the amount of 3MP degraded at 25 mg/L as the initial concentration. The decrease in the rate of degradation of 3MP observed at higher initial concentration is attributed to the fact that higher concentration leads to reduced cavitation activity and also the production of free radicals is limited [27]. Elsayed [26] reported similar results for the extent of degradation of pyridine using ultrasound where the decrease in extent of degradation was observed from 52% to 15% as the pyridine loading increased from 10 mg/L to 100 mg/L. Pradhan and Gogate [28] reported similar observation for degradation of p-nitrophenol, where the use of 0.5% solution (w/v) resulted in 48.3% degradation and 1% p-nitrophenol solution (w/v) resulted in lower degradation as 42.3%. Again the actual changes in the extent of degradation are specific to the pollutant elucidating the need for detailed

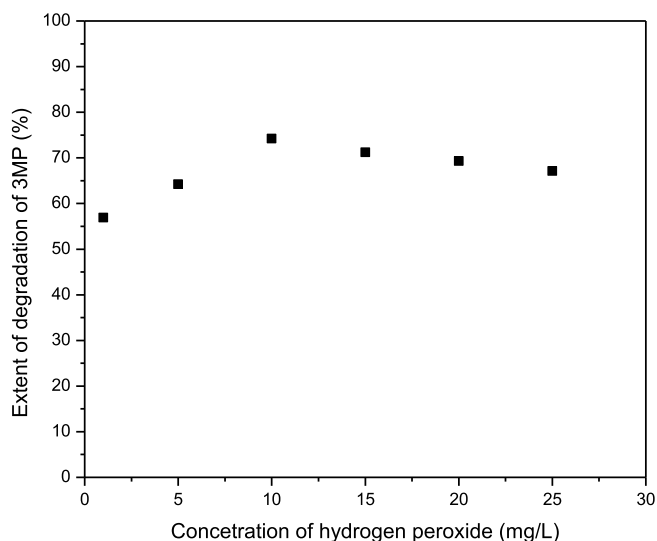


Fig. 6. Effect of addition of H_2O_2 on extent of degradation of 3MP using ultrasound ($T = 45$ °C, $t = 90$ min, power = 100 W, pH = 9, $c_i = 100$ mg/L).

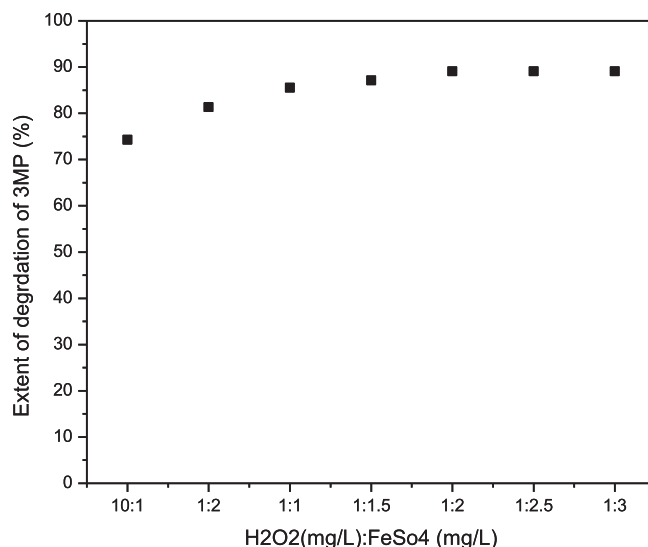


Fig. 7. Effect of addition of Fenton's reagent on extent of degradation of 3MP using ultrasound ($T = 45$ °C, $t = 90$ min, power = 100 W, pH = 9, $c_i = 100$ mg/L, H_2O_2 loading = 10 mg/L).

study as presented in the work.

Another important point to be noted from the trends represented in Fig. 4b is that over the initial 10 min, the rate of degradation is quite high for all the concentrations which subsequently lowers down and gives the true kinetic variation with the time of treatment. The initial higher degradation rate observed in the present study can be attributed to the presence of dissolved gases initially which are removed by the action of ultrasound subsequently giving somewhat slower rate of degradation.

Integral analysis was also followed to establish the kinetic rate constant. For the assumed first order mechanism, the change in concentration of 3MP is governed by following equation:

$$\ln \frac{c_i}{c_t} = kt$$

where, c_i and c_t are the initial concentration of 3MP and concentration at time t respectively, t is the sonication time and k is the rate constant. For the kinetic analysis, the graph of $\ln \frac{c_i}{c_t}$ vs t was plotted at different initial concentrations as illustrated in Fig. 5. The obtained values of the kinetic rate constant and the regression coefficient, R^2 are represented in Table 1. It can be concluded based on the obtained R^2 values (almost equal to 0.98 for all initial concentrations) that degradation of 3MP can be well represented by first order kinetics. It was also observed that rate constant values decreased from 0.0178 min^{-1} to 0.0099 min^{-1} with an increasing concentration from 25 mg/L to 100 mg/L, similar to the trend observed for the change in extent of degradation of 3MP. The kinetic analysis established in the work allows establishing the important design related information possibly required for scale up in

Table 2

Comparison of processes based on US/ H_2O_2 /Fenton in terms of degradation of 3MP and first order rate constant.

$c_i = 100$ mg/L, time = 90 min, pH = 9, power = 100 W, H_2O_2 loading = 10 mg/L, FeSO_4 loading = 20 mg/L and Temperature = 45 °C			
Scheme	Extent of degradation (%)	Rate constant (min^{-1})	R^2
Only H_2O_2	17.51	0.0020	0.99
Only Fenton	24.8	0.0030	0.99
US Only	56.1	0.0099	0.99
US/ H_2O_2	74.1	0.0143	0.99
US/Fenton	89.2	0.0220	0.97

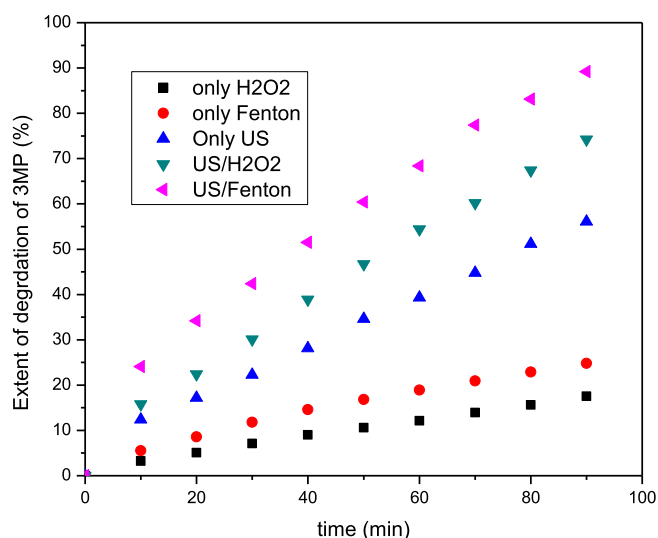


Fig. 8. Comparison of different combination approaches based on Ultrasound with H_2O_2 /Fenton applied for degradation of 3MP ($T = 45^\circ\text{C}$, $t = 90$ min, $\text{pH} = 9$, $c_i = 100$ mg/L, power = 100 W, H_2O_2 loading = 10 mg/L, FeSO_4 loading = 20 mg/L).

terms of the capacity of the required sonochemical reactor or the residence time. It is important to note that though the extent of degradation and kinetic rate constant were higher at lower concentration as 25 mg/L, combination experiments were performed at 100 mg/L as the selected initial concentration. Typically the concentrations of pyridine and its derivatives are in the range of 20 to 200 mg/L and also during emergency spillage the concentration increases to 1000 mg/L. As an adequate representation of these generally observed concentrations, experiments were performed at initial concentration as 100 mg/L.

3.5. Degradation of 3MP using combination approach of ultrasound and hydrogen peroxide

3MP degradation was also investigated using addition of hydrogen peroxide as oxidising agent during the sonochemical treatment with an objective to intensify the degradation. In addition to the fact that H_2O_2 has excellent oxidising capability, it also acts as a good source of hydroxyl radicals in the presence of ultrasound based on the dissociation of H_2O_2 . The degradation of 3MP solution of 100 mg/L as initial strength was investigated at different H_2O_2 loadings from 1 mg/L to 25 mg/L at optimised conditions of sonochemical degradation. It has been observed that the degradation efficiency increased with an increase in the H_2O_2 loading with maximum extent of degradation observed as 74.2% at 10 mg/L dosage of H_2O_2 (addition of 0.25 mL of the commercial 30% w/v grade of H_2O_2). With a subsequent increase in H_2O_2 loading to 25 mg/L, the extent of degradation decreased to 68.2% as per the trends shown in Fig. 6. The initial increase in the extent of degradation till oxidant loading of 10 mg/L (0.25 mL as the actual added volume) is attributed to the enhanced formation of hydroxyl radicals and lower quantum of the residual hydrogen peroxide in the solution. Beyond the optimum loading, the additional H_2O_2 remains unutilised in solution which leads to scavenging action on hydroxyl radicals [29]. Based on the obtained results, it is clearly established that the adequate dose of hydrogen peroxide for intensified degradation of 3MP is 10 mg/L. Further studies were conducted by keeping 10 mg/L (0.25 mL as the actual volume) as the optimised loading of H_2O_2 . The optimised loading of hydrogen peroxide depends upon the type of pollutants and the reactivity with hydroxyl radicals, thus making detailed study always important for specific pollutant.

H_2O_2 is a strong oxidising agent and hence has some oxidation

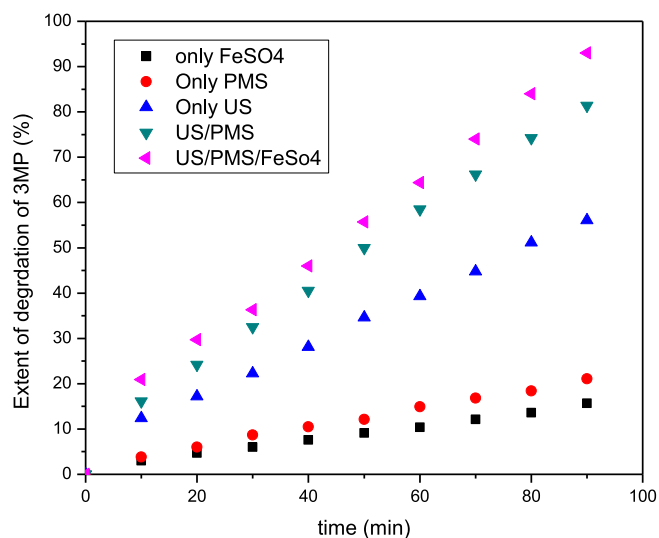
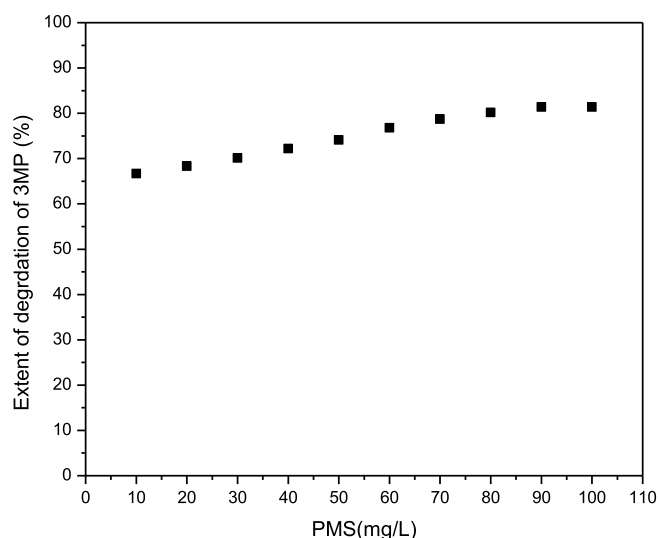


Fig. 9. Effect of addition of PMS on extent of degradation of 3MP using ultrasound ($T = 45^\circ\text{C}$, $t = 90$ min, $\text{pH} = 9$, $c_i = 100$ mg/L, power = 100 W).

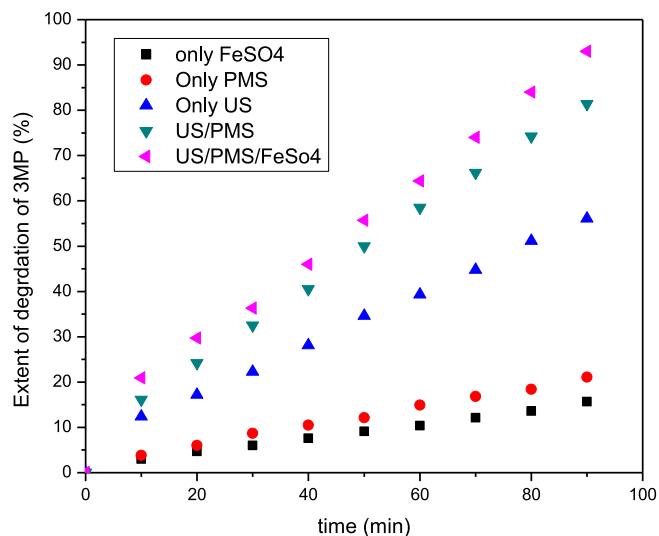


Fig. 10. Comparison of different combination approaches based on Ultrasound and PMS applied for degradation of 3MP ($T = 45^\circ\text{C}$, $t = 90$ min, $\text{pH} = 9$, $c_i = 100$ mg/L, power = 100 W, $\text{FeSO}_4 = 20$ mg/L, PMS = 80 mg/L).

Table 3

Comparison of processes based on US/FeSO₄/PMS in terms of degradation of 3MP and first order rate constant.

$c_i = 100$ mg/L, time = 90 min, pH = 9, power = 100 W, FeSO ₄ = 20 mg/L, PMS = 80 mg/L and Temperature = 45 °C,			
Scheme	Extent of degradation (%)	Rate constant (min ⁻¹)	R ²
Only PMS	21.10	0.0024	0.99
Only FeSO ₄	15.70	0.0011	0.99
US Only	56.1	0.0099	0.99
US/PMS	81.4	0.0196	0.97
US/PMS/FeSO ₄	92.1	0.0257	0.95

capacity without the use of ultrasound. Experiments were conducted with optimised loading of H₂O₂ without using ultrasonic irradiation and it was observed that the extent of degradation was only 17% without ultrasound, clearly confirming the role of ultrasound in the expected dissociation of added H₂O₂.

Comparison of the obtained trends for combination of ultrasound and hydrogen peroxide with the literature has now been presented to understand if similar trends in terms of qualitative and quantitative variation are observed. Mishra and Gogate [30] studied the combination of ultrasound with hydrogen peroxide for degradation of rhodamine B over the hydrogen peroxide loading range of 200 mg/L to 800 mg/L. It was reported that the extent of degradation increases from 32% to 45% with an increase in H₂O₂ loading from 200 mg/L to 500 mg/L. A subsequent increase in loading from 500 mg/L to 800 mg/L resulted in a reduction in the extent of degradation to 38%. Shriwas and Gogate [31] reported that the extent of degradation of methyl Parathion enhanced by increasing H₂O₂ loading from 60 mg/L to 200 mg/L but a further increase in loading resulted in a decrease in the extent of degradation. Bhirud et al. [32] investigated degradation of formic acid and reported that extent of degradation enhanced with addition of 0.5 mL/L of H₂O₂ and further increase in dose of H₂O₂ to 1 mL/L yielded reduced extent of degradation for fixed 100 mg/L as the initial concentration of formic acid solution. The comparison clearly enabled the importance of the current work as the optimum loading values are different depending on the specific pollutant and no studies are reported earlier for the 3MP.

3.6. Degradation of 3MP using combined approach of ultrasound and Fenton chemistry

Combination approach of ultrasound and Fenton's reagent for degradation of 3MP was studied at different loading of FeSO₄ keeping loading of H₂O₂ fixed at 10 mg/L established as optimum in the study associated to understanding the effect of loading of H₂O₂. The objective of using the combination was to provide continuous supply of hydroxyl radicals based on the inter-conversion of the Fe⁺² ions (ferrous ions) into Fe⁺³ (Ferric ions) and back into Fe⁺² ions (ferrous ions) by breakage of the formed complex under the action of ultrasound [33]. The obtained results at different ratios of H₂O₂:FeSO₄ are depicted in Fig. 7, where it can be seen that the extent of degradation increases from 74.2% to 89.2% with an increase in FeSO₄ loading from 1 mg/L to 20 mg/L at fixed H₂O₂ loading as 10 mg/L. It can be easily understood from the obtained results that combination approach is effective and enhanced degradation of 3MP is obtained as compared to individual approach or that with the combination of only H₂O₂ and also the degradation is favoured with an increase in concentration of ferrous ions at optimised conditions. It is also interesting to note that subsequent increase in FeSO₄ loading to 25 mg/L and 30 mg/L was not favourable as the extent of degradation did not change significantly (actual value of around 89.5%) and hence it was established that 20 mg/L FeSO₄ loading is the desired optimum loading for fixed 10 mg/L of H₂O₂ to

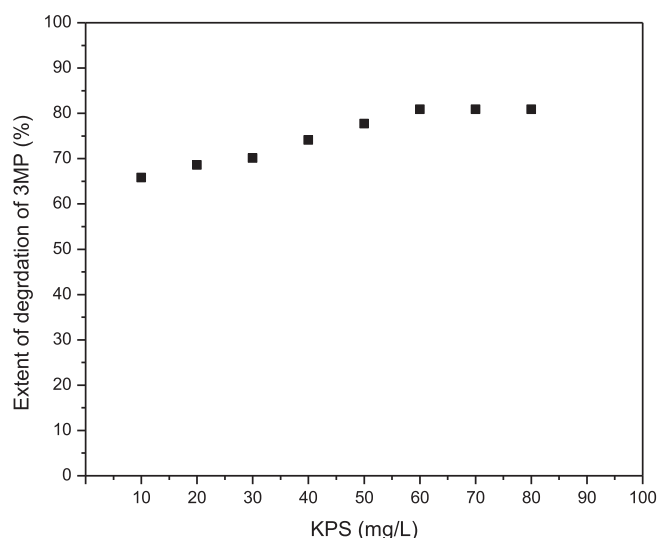


Fig. 11. Effect of addition of KPS on extent of degradation of 3MP using ultrasound (T = 45 °C, t = 90 min, pH = 9, c_i = 100 mg/L, power = 100 W).

achieve maximum degradation of 3MP in an effective manner. It can be also noted from the Table 2 that the rate constant for combined approach of US/Fenton was much higher compared to only US and only Fenton.

It is worthwhile to compare the obtained trends in the present work with literature. Golash and Gogate [24] reported that the extent of degradation of dichlorvos enhanced from 77.1% to 100% by increasing H₂O₂:FeSO₄ loading from 1:0.5 to 1:3. Elsayed [26] also reported that extent of degradation enhanced from 37.1 to 71.1% with an increase in H₂O₂:FeSO₄ ratio from 100:1 to 100:10. Similar trends were also reported by Linga et al. [34] confirming enhanced degradation of 2-chlorophenol for the Fenton combination with ultrasound at higher FeSO₄ loadings. Again the quantitative changes in the extent of degradation with loadings of Fenton's reagent are different making the current study novel.

It is important to compare different processes based on ultrasound, hydrogen peroxide and FeSO₄. As depicted in Fig. 8 and Table 2 for different combination approaches, it has been observed that the extent of degradation using US with oxidising agents gives improved

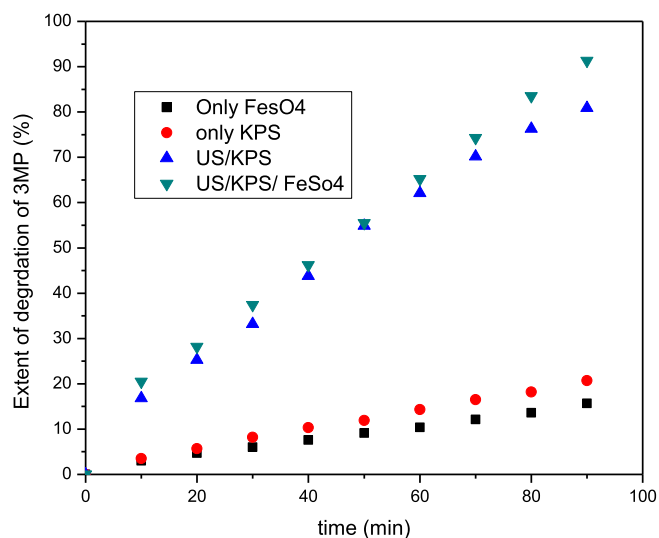


Fig. 12. Comparison of different combination approaches based on Ultrasound and KPS applied for degradation of 3MP (T = 45 °C, t = 90 min, pH = 9, c_i = 100 mg/L, power = 100 W, FeSO₄ = 20 mg/L, KPS = 60 mg/L).

Table 4

Comparison of processes based on US/FeSO₄/KPS in terms of degradation of 3MP and first order rate constant.

$c_i = 100$ mg/L, time = 90 min, pH = 9, power = 100 W, FeSO₄ = 20 mg/L, KPS = 60 mg/L and Temperature = 45 °C

Scheme	Extent of degradation (%)	Rate constant (min ⁻¹)	R ²
Only KPS	20.6	0.0022	0.99
Only FeSO ₄	15.70	0.0011	0.99
US Only	56.1	0.0099	0.99
US/KPS	80.9	0.0187	0.99
US/KPS/FeSO ₄	92.1	0.0243	0.96

performance compared with the degradation using only US and only oxidising agents. It can be also noted from the Table 2 that rate constant for different combined approaches were higher as compared to the individual approaches. Careful observation of the presented data in Fig. 8 also revealed that initial higher degradation rate is observed for the approaches involving ultrasound which can be attributed to the presence of dissolved gases initially which are removed by the action of ultrasound subsequently giving somewhat slower rate of degradation. This is also confirmed based on the fact that initial higher rates are only seen for the approaches involving ultrasound and not for approaches involving only oxidants. It is also clearly established that US/Fenton approach is better as compared to US/H₂O₂ or any other individual approaches compared here.

3.7. Degradation of 3MP using ultrasound and peroxymonosulphate (PMS)

3MP degradation was also studied using combination of ultrasound with peroxymonosulphate (PMS) at different concentrations. Considering the fact that no study has been reported on the degradation of pyridine or its derivatives using sulphate based oxidizing agents, importance of the presented study is established. The obtained results for the extent of degradation of 3MP solution has been depicted in Fig. 9 at different loadings of PMS over the range of 5 mg/L to 100 mg/L under optimised operating conditions of 100 W as power dissipation, pH of 9, temperature of 45 °C and treatment time of 90 min. The extent of degradation of 3MP was observed to increase from 61.5% to 81.4% due to an increase in the PMS loading from 5 to 80 mg/L. The observed first order rate constant was also the maximum at 0.196 min⁻¹ at the loading of PMS as 80 mg/L. Typically, an increase in the PMS loading from 5 to 80 mg/L leads to increase in the free radicals which resulted in enhanced degradation of 3MP. Subsequent increase in PMS loading to 100 mg/L did not produce a significant change in the extent of degradation, establishing 80 mg/L as the optimum.

More and Gogate [35] also reported similar trends for the effect of

Table 5

Comparison of processes based on US and Solar irradiation with different combinations of oxidising agents in terms of degradation of 3MP and first order rate constant.

$c_i = 100$ mg/L, time = 90 min, pH = 9, power = 100 W, H₂O₂ loading = 10 mg/L, FeSO₄ = 20 mg/L, KPS = 60 mg/L, PMS = 80 mg/L and Temperature = 45 °C

Scheme	Extent of degradation (%)	Rate constant (min ⁻¹)	R ²
Only Solar	12.60	0.0010	0.99
US Only	56.1	0.0099	0.99
US/H ₂ O ₂ /Solar	84.1	0.020	0.97
US/Fenton/Solar	95.1	0.030	0.97
US/PMS/Solar	93.3	0.028	0.95
US/PMS/FeSO ₄ /Solar	97.4	0.0379	0.96
US/KPS/Solar	93.1	0.0261	0.96
US/KPS/FeSO ₄ /solar	94.36	0.0286	0.96

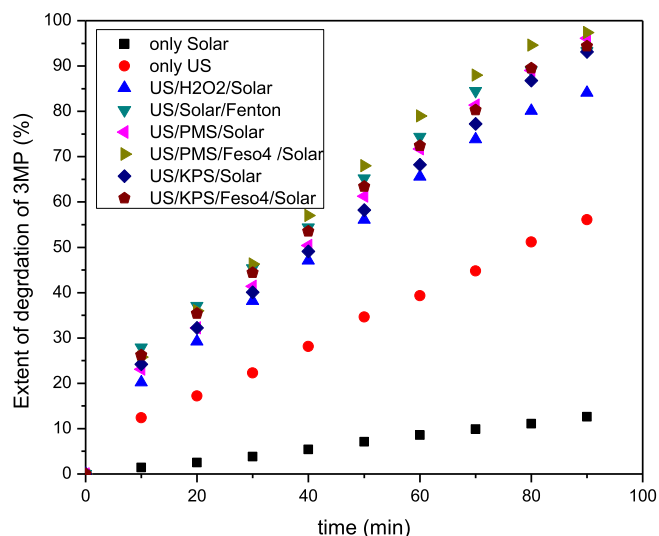
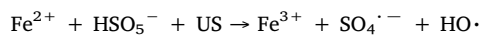


Fig. 13. Comparison of different combination approaches based on Ultrasound and Solar with different oxidising agents applied for degradation of 3MP (T = 45 °C, t = 90 min, pH = 9, c_i = 100 mg/L, power = 100 W, H₂O₂ loading = 10 mg/L, FeSO₄ = 20 mg/L, KPS = 60 mg/L, PMS = 80 mg/L).

addition of PMS for degumming of soybean oil. It was reported that increasing the PMS dose from 0.6 g/L to 2 g/L resulted in an increase in the extent of degumming to 95.1%, but further increase in the PMS dose to 5 g/L resulted in not much change in the extent of degumming. Lu et al. [36] reported similar trends for the degradation of atrazine with an increase in observed degradation from 28.90% to 58.77% with an increase in PMS concentration from 50 μmol/L to 400 μmol/L. Subsequently, not much change in the extent of degradation was observed with further increase in the loading of PMS. It is important to note that beyond the optimum only marginal effects are seen in the current work and also two cited examples above though this cannot be generalized and strongly negative results are reported in the literature [37]. It can be thus said that the actual optimum dosage of PMS will be specific to the system and needs to be established as per the methodology depicted in the current work.

3.8. Degradation of 3MP using hybrid approach of ultrasound/PMS/FeSO₄

The hybrid approach of Ultrasound/PMS/FeSO₄ was applied for studying the 3MP degradation at optimised loading of PMS (80 mg/L) and FeSO₄ (20 mg/L) established in the study involving individual oxidants. The decomposition of PMS in the presence of FeSO₄ and ultrasound (US) takes place by following reaction:



The generation of additional radicals is expected to be beneficial for pollutant degradation. As per the obtained results, it was observed that the FeSO₄ addition increased the extent degradation of 3MP to 92.1% (data shown in Fig. 10) with a higher first order rate constant as 0.0257 min⁻¹ (data shown in Table 3) as compared to combination of US with PMS. FeSO₄ also acts as activator to PMS which results in the generation of higher quantum of SO₄^{·-}, which enhances the degradation of 3MP. Similar trends were also reported by Liu et al. [38] for the approach of PMS/FeSO₄ applied for sonochemical degradation of azo dye with maximum extent of degradation as 90% observed for the hybrid approach. Brienza et al. [39] also reported similar trends for degradation of β-esteradiol using photocatalytic oxidation in the presence of PMS/FeSO₄ as oxidizing agents. Again the quantitative differences in the observed increase direct the need for the detailed study for the specific combination of oxidants, activation approach and pollutants.

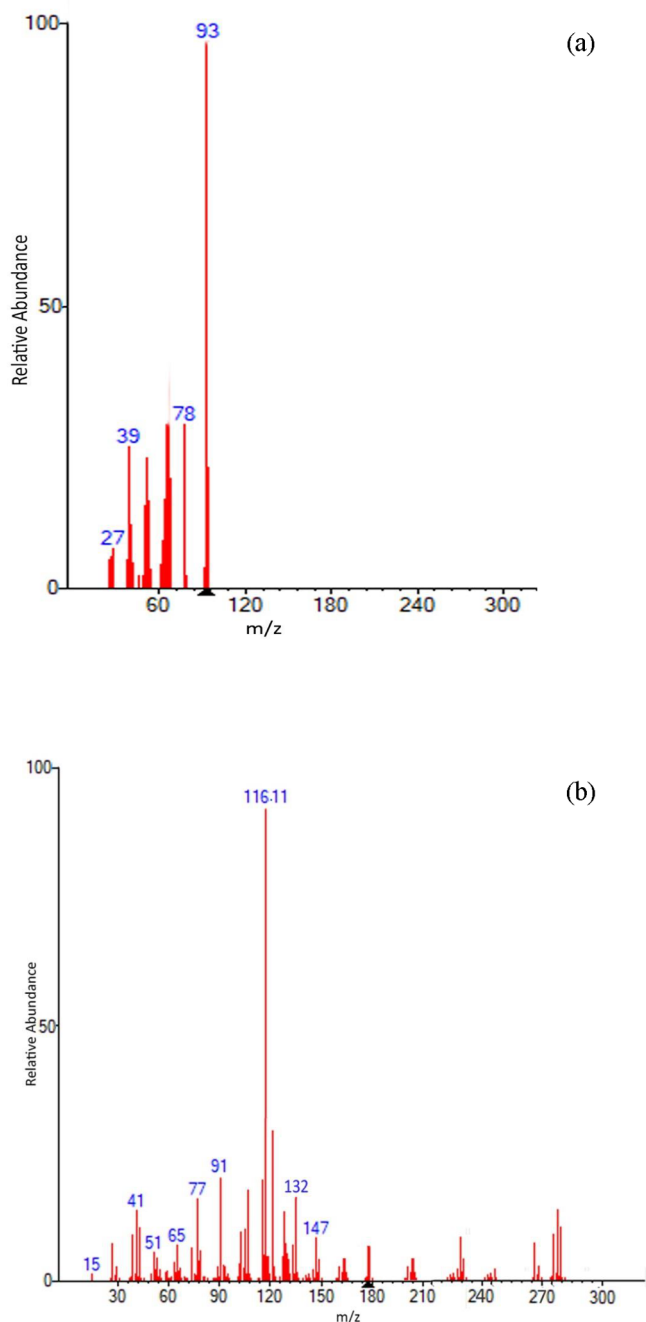


Fig. 14. GC-MS analysis of 3MP solution, a) before degradation b) after degradation.

The comparison of different approaches involving ultrasound, PMS and FeSO_4 is depicted in Fig. 10 and Table 3, where it is seen that the extent of degradation using US combined with oxidising agents gives improved performance compared when the degradation is carried out by using only US and only with different oxidising agents. It can be also noted that rate constant was maximum for US/PMS/ FeSO_4 approach ($k = 0.0257 \text{ min}^{-1}$) with maximum extent of degradation compared to other combinations involving PMS or the individual approaches.

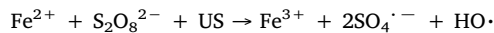
3.9. Degradation of 3MP using ultrasound and potassium sulphate (KPS)

3MP degradation studies were also performed using potassium sulphate (KPS) as oxidant at different initial concentrations over the range of from 5 mg/L to 100 mg/L combined with ultrasound.

Experiments were performed using 100 mg/L of 3 MP solution at optimised conditions of 100 W as the power dissipation, pH of 9, temperature of 45°C and treatment time of 90 min. The obtained results for US/KPS system are shown in Fig. 11 where it is seen that 3MP degradation increased from 60.5% to 80.9% for a change in KPS loading from 5 to 60 mg/L. The observed kinetic rate constant at KPS loading of 60 mg/L was 0.0187 min^{-1} . The combination of US/KPS also generates $\text{SO}_4^{\cdot-}$ radicals driving enhanced degradation of 3MP. An increase in KPS loading from 5 to 60 mg/L led to increase in free radical quantum which resulted in enhanced degradation of 3MP. For subsequent increase in KPS loading to 100 mg/L, extent of degradation remained unchanged and hence 60 mg/L as the KPS loading was established as appropriate to be used for further experiments. Similar trends were also reported by Gokulakrishnan et al. [40] who investigated the degradation of dye using KPS combined with ultrasound. The rate of degradation was reported to extensively increase with addition of KPS for methyl green dye degradation. Prajapat and Gogate [41] reported that the degradation of guar gum enhanced from 24.18% (only US) to 98.27% (combination of US and KPS at loading of 0.1%). Though the use of KPS is seen to give beneficial effects in the compared cases, the extent of increase and the optimum loading are dependent on the specific pollutant and mode of activation. This observation clearly directs the need of detailed investigations also confirming the utility of the presented work.

3.10. Degradation of 3 MP using hybrid approach of ultrasound/KPS/ FeSO_4

The degradation of 3MP using the hybrid approach of ultrasound/KPS/ FeSO_4 has also been studied at optimised loading of KPS (60 mg/L) and FeSO_4 (20 mg/L) established in the study involving individual oxidants. The decomposition of KPS in the presence of FeSO_4 and ultrasound takes place by following reaction:



The results presented in Fig. 12 establish that FeSO_4 addition increases the extent degradation of 3MP to 91.3% with first order rate constant of 0.0243 min^{-1} as per data shown in Table 4. Similar to the mechanism mentioned for PMS earlier, FeSO_4 acts as activator of KPS yielding more $\text{SO}_4^{\cdot-}$ and $\text{HO}\cdot$ radicals which enhance the degradation of 3MP. Zou et al. [42] also reported that the degradation of antibiotic, sulfadiazine, by using only US was 50%, which enhanced to 90% with hybrid approach of US/KPS/ FeSO_4 .

The comparison of different approaches involving ultrasound, KPS and FeSO_4 depicted in Fig. 12 and Table 4 demonstrate that the extent of degradation using ultrasound with oxidising agents gives improved performance compared when the degradation is carried out using only US or only oxidising agents. The rate constant was found to be maximum for US/KPS/ FeSO_4 ($k = 0.0243 \text{ min}^{-1}$) combination coupled with maximum extent of degradation compared to other approaches based on KPS or FeSO_4 .

3.11. Degradation of 3MP using ultrasound in combination with solar irradiation and oxidants

Effect of using solar irradiation combined with ultrasound and oxidants on the degradation of 3MP was studied at optimum operating conditions and optimised loading of oxidising agents established using the earlier studies. Solar irradiation is a useful alternative to UV light that can help in reducing the cost associated with the treatment. Experiments were performed using reflectors to analyse the effect of solar irradiation on 3MP degradation. Degradation experiments were performed under constant level of solar irradiation with intensity of 950 W/m^2 . Experiments were also performed under solar irradiation only without the use of ultrasound and oxidising agents. Use of only

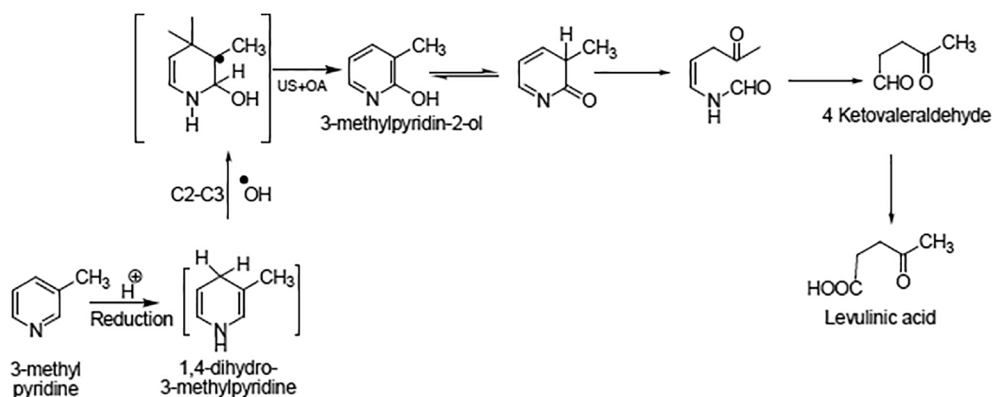


Fig. 15. Proposed pathway for degradation of 3MP.

Table 6

Comparison of different schemes of operations at optimized conditions in terms of extent of degradation of 3MP, Energy efficiency and Synergetic Index.

Schemes	Extent of degradation (%)	First order Rate constant (min^{-1})	Energy efficiency (mg/J)	Synergetic Index
Only US	56.1	0.0099	1.108×10^{-04}	–
Only H_2O_2	17.51	0.0020	–	–
Only Fenton	24.8	0.0030	–	–
Only PMS	21.1	0.0024	–	–
Only KPS	20.6	0.0022	–	–
Only FeSO_4	15.70	0.0011	–	–
Only Solar	12.60	0.0010	–	–
US/Solar	61.2	0.0100	1.200×10^{-04}	0.92
US/ H_2O_2	74.1	0.0143	1.400×10^{-04}	1.20
US/Fenton	89.2	0.0220	1.760×10^{-04}	1.70
US/PMS	81.4	0.0196	1.600×10^{-04}	1.55
US/PMS/ FeSO_4	92.1	0.0257	1.810×10^{-04}	1.96
US/KPS	80.9	0.0187	1.590×10^{-04}	1.50
US/KPS/ FeSO_4	91.3	0.0243	1.8000×10^{-04}	1.86
US/ H_2O_2 /Solar	84.1	0.0200	1.660×10^{-04}	1.59
US/Fenton/Solar	95.1	0.0300	1.870×10^{-04}	2.16
US + PMS + Solar	93.3	0.0280	1.840×10^{-04}	2.10
US/PMS/ FeSO_4 /Solar	97.4	0.0379	1.920×10^{-04}	2.70
US/KPS/Solar	93.1	0.0261	1.839×10^{-04}	2.02
US/KPS/ FeSO_4 /Solar	94.4	0.0286	1.8600×10^{-04}	2.14

solar irradiation resulted in only 12.60% degradation based on the oxidation capacity induced by solar irradiations itself. The obtained results for the subsequent studies involving different combinations under solar irradiation are presented in Table 5 and Fig. 13. It was clearly seen that the extent of degradation and first order rate constant of 3MP using US and oxidising agent in the presence of irradiations is enhanced for each combination compared to experiments performed in the absence of solar irradiation. The quantum of free radicals produced is enhanced in the presence of solar irradiations as it provides activation effects on the oxidants which leads to faster and enhanced degradation of pollutant. The combination of US/PMS/ FeSO_4 in the presence of solar irradiation remained the most effective treatment giving maximum degradation of 97.4% and rate constant of 0.0379 min^{-1} .

Patil and Gogate [43] investigated ultrasound assisted degradation of dichlorvos in various combinations with solar irradiation and reported similar higher efficacy with almost 100% degradation. Brienza et al. [39] also reported that degradation of estradiol using photo-Fenton method was faster compared to only Fenton due to enhanced activation of oxidising agents by the solar irradiations leading to enhanced sulphate radical formation and subsequent attack on the pollutants. The current work has clearly established that use of solar irradiations presents a useful approach of intensifying the degradation process and the reported results have a very good commercial

importance.

4. Analysis of intermediates in the degradation of 3MP

The sample of 3MP solution obtained after treatment using combined approach of US/PMS/ FeSO_4 in the presence of solar irradiations, where maximum degradation is achieved, was analysed using the GC-MS technique. The obtained chromatograms for the GC-MS analysis of 3MP before and after degradation is represented in Fig. 14. The prominent peak detected at retention time of 4.11 min at m/z , 93 as shown in Fig. 14(a), confirmed the presence of 3MP (molar mass of 3MP = 93). In Fig. 14(b), prominent peaks detected at mass spectrum of m/z , 116.11 at retention time of 11.813, confirmed the presence of Levulinic acid. The observed intermediates depicted in Fig. 14 allowed establishing some insights into the degradation pathways. It is observed that degradation process is initiated with formation of reductive intermediate as 1,4, dihydro, 3-methyl pyridine due to the C₂-C₃ ring cleavages induced by the use of US and oxidising agents, which subsequently is converted to levulinic acid. The proposed cleavage pathway (Fig. 15) is matching to the pathway suggested by Lee et al. [44] for aerobic degradation of 3MP. Similar degradation pathway was also suggested for microbial degradation by Watson and Cain [45]. It is also important to understand that the identified degradation products are nontoxic and almost complete mineralization of toxic compound can be obtained at the end of the treatment confirming the efficacy of the applied combination treatment technique in the present work.

5. Energy efficiency and synergetic index

The obtained data for the energy efficiency and synergetic index for different treatment approaches is represented in Table 6. It can be clearly seen that combination of US and oxidising agents resulted in enhanced energy efficiency and synergetic index of greater than 1 is obtained for all the combination approaches. The improvement in synergetic index and energy efficiency was also clearly observed based on the calculated data for the introduction of solar irradiation in combination with different oxidising species compared to the same combinations without solar irradiations as shown in Table 6. Overall the best treatment approach for degradation of 3MP was the combination of US/PMS/ FeSO_4 /Solar irradiation that resulted in maximum extent of degradation (97.4%), with maximum energy efficiency ($1.920 \times 10^{-04} \text{ mg/L}$) and highest synergetic index value (2.70).

6. Conclusions

The present study has clearly demonstrated an efficient approach for intensified sonochemical degradation of 3-Methylpyridine (3MP). The comprehensive study related to effect of different operating parameters and use of oxidising agents has established the best treatment

conditions as pH of 9, time of 90 min, power dissipation of 100 W and temperature of 45 °C. It is also demonstrated that the degradation of 3MP follows first order kinetics mechanism. Degradation of 3MP was favoured by the use of different oxidising species like hydrogen peroxide, Fenton's reagent, peroxymono sulphate (PMS) and potassium persulphate (KPS). Application of solar irradiations also intensified the treatment based on the activation effects on the oxidants. Combined approach of US//PMS/FeSO₄/Solar irradiation was established as the best protocol compared to all other combination approaches or the individual treatment options establishing maximum degradation as 97.4% with highest energy efficiency as 1.924×10^{-4} mg/J and synergetic index as 2.70. GC-MS analysis allowed establishing formation of non-toxic product as Levulinic acid. Overall the work has established for the first time utility of ultrasound based treatment for effective remediation of 3MP present as the toxic pollutant in wastewater.

CRediT authorship contribution statement

Gaurav B. Daware: Methodology, Validation, Investigation,

Appendix A

Treatment time for each batch = 90 min (5400 sec),

Volume of solution = 1600 mL (two flasks were kept in sonicator each containing 800 mL of 3MP solution)

Initial 3MP concentration = 100 mg/L and after degradation, the concentration reduced to 43.9 mg/L for the case of only ultrasound.

Amount of 3MP degraded after 5400 sec = 56.1 mg/L

Power consumption by bath sonicator = 100 W.

Power utilized for stirring = 50 W

Total Power utilized = 150 W

Power dissipated per unit volume = $150/1.6 = 93.75$ W/L

Power consumed = $93.75 \times 5400 = 506250$ J/L

Energy efficiency = (the amount of 3MP degraded/power consumed (J))

= $56.1/506250 = 1.108 \times 10^{-4}$ mg/J.

Appendix B

Synergetic index (*f*)

Combination of US + Hydrogen peroxide

Rate constant for only US (K_{US}) = 0.0099 min^{-1}

Rate constant for Hydrogen peroxide ($k_{H_2O_2}$) = 0.0029 min^{-1}

Rate constant for combined US and Hydrogen peroxide scheme $k_{(US/H_2O_2)} = 0.0143 \text{ min}^{-1}$

$$f = \frac{k_{(US/H_2O_2)}}{K_{US} + k_{H_2O_2}}$$

$$f = \frac{0.0143}{(0.0099 + 0.0029)}$$

$$f = 1.20$$

Appendix C. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.ultsonch.2020.105120>.

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Writing - original draft. **Parag R. Gogate:** Conceptualization, Validation, Writing - review & editing, Supervision, Funding acquisition.

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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