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RESEARCH PAPER

Ultrasound-assisted intensified decolorization of Acid Yellow 17 using different additives with modelling studies

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Abstract
The current study examines Acid Yellow 17 (AY17) degradation utilizing a dual-frequency sonochemical reactor at 4 L capacity. The effects of several factors including pH, ultrasonic power, initial concentration, and combination with oxidants (H_2O_2, Fenton's reagent, and persulfate) on the AY 17 decolorization has been elucidated in details. Only sonication achieved 64.4% AY17 decolorization under optimized conditions of AY17 initial concentration (25 ppm), acidic environment (pH 3), power (250 W), and dual frequency operation. Fenton reagent increased the AY17 decolorization to a maximum extent (100%) compared to US + H_2O_2 and US + KPS combinations when various oxidants were applied. Kinetic investigations for several treatment approaches were also carried out. The Box–Behnken design was also used to model the US + Fenton and US + KPS processes, and the ideal parameters for efficient AY17 decolorization were elucidated. Overall, a novel combination approach has been developed for efficient decolorization of AY 17 for the first time.

Keywords Acid Yellow 17 · Dye degradation · Cavitation · Advanced oxidation processes

Introduction

The adoption of stricter pollution control legislations has led to an increase in interest in the development of advanced methodologies for the treatment of effluents containing dye. The native microbial consortium and aquatic life are all impacted by dye-containing effluents (Sghaier et al. 2019) and hence the treatment of such effluents is an important requirement. Dyes find widespread usage and hence the generation of dye containing effluents is also very common. In addition to industrial usage, dyes are being commonly used in variety of home items like shower gel, shampoo, liquid soap, bubble bath, all-purpose cleaner, and alcohol-based perfumes (Adar 2021). Considering the wide range of usage, the possibility of water contamination with dyes cannot be ruled out and as laws governing discharge of effluents are becoming more stringent, related sectors must come up with cost-effective water treatment methods. Physical, biological, and chemical treatments are the three main treatment options that can be used to treat dye wastewater but they all have processing issues, especially for highly laden effluents (Li et al. 2021). Due to their potential application in the treatment of wastewater in variety of chemical processing sectors, advanced oxidation processes (AOPs) have been the subject of extensive research during the past two decades. Various AOPs have been employed effectively, including ozonation, Fenton- or Fenton-like oxidation, metal oxide photocatalysis, UV/H_2O_2 processes, and ultrasonic radiation (de Souza et al. 2010).

High frequency sonication (US) has gained interest as an AOP for wastewater treatment. Ultrasound generates cavitational effects such as localized hotspots with high temperatures and oxidizing free radicals that can effectively bring about decolorization of wastewater. However, since ultrasound induced decolorization often requires a significant amount of energy, adding additives or oxidants have been also targeted that can yield lower treatment costs by effectively producing a considerably larger loading of hydroxyl radicals (Kodavatiganti et al. 2021).

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The aim of the present study is to investigate the breakdown and mineralization process of Acid Yellow 17 dye using ultrasound-based treatment techniques, specifically using a dual-frequency ultrasonic flow cell. Acid Yellow 17 is a water-soluble, greenish-yellow reactive dye primarily used in printing, soaps, detergent, textile, and cosmetic industries (Ratnamala et al. 2017). AY 17 has mutagenic and tumorigenic effects coupled with harmful effects on the respiratory system. If released into streams without treatment, the potential environmental consequences can be significant (Forgacs et al. 2004). The literature review revealed no studies for ultrasound induced decolorization of AY 17 anda also a limited number of studies on the degradation using oxidative techniques (Khan et al. 2019), including the use of UV light (Bougdour et al. 2018), visible light (Huda et al. 2019), Fenton oxidation (Khan et al. 2018) and solar photocatalysis (Khanna and Shetty 2013).

Khan et al. (2019) studied the oxidative degradation of Acid Yellow 17 dye using the Fenton-like process involving H_2O_2 and Fe^{3+}. The highest level of degradation of AY-17 dye was observed at a pH of 3 within a time frame of 60 min, using the most effective concentrations of AY 17, H_2O_2, and Fe_2^{+}. The study also investigated the impact of various anions as HCO_3^{-}, CO_3^{2-}, Cl^{-}, and SO_4^{2-} on dye degradation. The Fenton-like process was observed to be an effective method for dye degradation, resulting in a maximum degradation of 66% and 83% in natural water samples and standard samples, respectively.

Bougdar et al. (2018) examined the effectiveness of utilizing UV light and iron ions as activators of peroxydisulfate ($S_2O_8^{2-}$ or PDS) for the degradation of reactive yellow 17 (RY17) azo dye. The most effective conditions for the degradation of RY17 were elucidated as concentrations of 10 mg/L for RY17, 0.05 mM for Fe^{2+}, 1 mM for $S_2O_8^{2-}$, and a pH of 3. The removal percentages of RY17 were 63.3%, 81.0%, and 95.4% after 20 min using approaches involving $S_2O_8^{2-}$ /Fe^{2+}, $S_2O_8^{2-}$ /UV and $S_2O_8^{2-}$ /Fe^{2+}/UV respectively confirming that use of $S_2O_8^{2-}$ /Fe^{2+}/UV system is highly effective.

Huda et al. (2019), elucidated a microwave-assisted technique to synthesize Sn_3O_4 nanostructures with a flower-like morphology with subsequent application in photoelectrocatalytic degradation of Acid Yellow 17 dye using visible light. The thin-film Sn_3O_4/TiO_2/Ti electrodes exhibited remarkable efficiency in removing color, achieving a 95% removal within 60 min at pH 2. At a low bias potential, the efficiency improved, achieving 97% color removal and 83% TOC removal. The kinetic rate for the combination was nearly three times higher compared to photocatalysis. The findings indicate that Sn_3O_4/TiO_2/Ti photoelectrodes provide an environmentally friendly approach for treating wastewater with visible light sources.

Khan et al. (2018) examined the degradation of AY 17 using H_2O_2/Fe^{2+} elucidating the effects of various factors, including pH, temperature, H_2O_2 concentration, Fe^{2+} concentration, AY 17 concentration and presence of anions on the degradation of AY 17. The optimal conditions were found to be pH as 3, loading of AY17 and $Fe^{2+} = 0.06$ mM, $[H_2O_2] = 0.9$ mM and treatment time of 60 min yielding 89% degradation using the Fenton oxidation at 25 °C, demonstrating its efficiency.

Khanna and Shetty (2013) investigated the application of $Ag@TiO_2$ core–shell nanoparticles in solar photocatalysis for the treatment of Acid Yellow17 dye-contaminated water. The $Ag@TiO_2$ nanoparticles were synthesized using a streamlined method that involved a single-step process and subsequent calcination. It was reported that these compounds exhibited remarkable efficiency in the solar photocatalysis of AY-17 mainly attributed to distinct photocatalytic properties of the catalyst including the prevention of electron–hole recombination and the ability to absorb visible light. Optimal degradation conditions were determined to be a pH of 3, a dye/catalyst ratio of 1:10 (g/g), and an oxidant concentration of 2 g/L of $(NH_4)_2S_2O_8$. The efficiency of the $Ag@TiO_2$ catalyst remained relatively stable after being reused three times. According to the study, $Ag@TiO_2$ core–shell structured nanoparticles demonstrated a higher level of effectiveness compared to TiO_2 or Ag-doped TiO_2 nanoparticles.

Adar et al. (2021) also focused on the removal of AY 17 dye using adsorption and heterogeneous persulfate (HPS) oxidation systems. The study investigated the impact of various factors, including temperature, pH, persulfate concentration, adsorbent dosage, reaction time, dye concentration, and NaCl concentration, on the removal of color and COD. Based on the findings, it was confirmed that PAC as an adsorbent resulted in a reduction in reaction time for HPS oxidation and the combined process resulted in almost complete color and COD removal.

The originality of the current work is thus established by the fact that no study has ever combined US with other oxidants like H_2O_2, KPS, and Fenton for the case of AY17 dye. The primary goal of the current study is to establish a highly efficient treatment method utilizing ultrasonication and showcase its efficacy by employing a pilot scale ultrasonic reactor that can operate in dual frequency mode. The reactor is combined with oxidants with detailed optimization of operating conditions, resulting in a commercially relevant approach due to its innovative nature and elucidating the specific advantages in the degradation of Acid Yellow 17.

Materials and methods

Materials

Experiments were carried out using Acid Yellow 17 dye. Table 1 presents the structure of the dye and the physicochemical characteristics of the dye. The chemicals obtained from Himedia include ferrous sulphate heptahydrate, hydrogen peroxide (30% W/V), sulphuric acid, sodium hydroxide, potassium persulfate, silver sulphate, mercuric sulphate, and ammonium ferrous sulphate. A solution of AY17 with a concentration of 1000 parts per million (ppm) was prepared using deionized (DI) water. The solution was then diluted to the desired concentration for the study. The experiments utilized DI water obtained from the laboratory's Millipore Milli-Q Gradient water purification unit for solution preparation. The pH of the solution was adjusted using 1M H_2SO_4 and 1M NaOH solutions as per the requirement with both the solutions being freshly prepared in the laboratory.

Reactor set-up

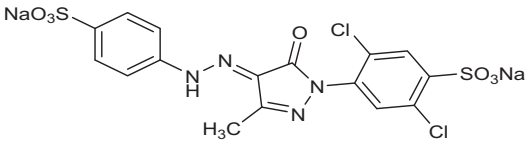
A dual-frequency ultrasonic reactor (10 L capacity with 20 × 20 × 25 cm as the geometric dimensions) made of stainless steel was applied in the current investigation. The ultrasonic reactor was equipped with 5 transducers on every side, resulting in a total of 20 transducers for the entire reactor. The ultrasonic reactor is equipped with two operating sets with one at frequency of 22 kHz and second at a frequency of 44 kHz. During operation in single frequency mode, the ultrasonic reactor utilized transducers of 22 or 44 kHz frequency, which operated independently on the opposing sides of the reactor. In the case of dual frequency mode, all transducers were fully functional operating at 22 and 44 kHz (Momin and Gogate 2024). A temperature of 30 °C (ambient conditions) was maintained constant by consistently circulating cold water through the cooling coil assembly so as to counter any heat dissipation with the use of ultrasound.

Methodology

The reactor assembly was meticulously cleaned with alkali and water until the pH approached neutral before each experiment. For each experimental run, a 4 L volume of AY17 dye was utilized as an aqueous solution with a concentration of 25 ppm (unless stated otherwise). The trials were conducted for 210 min, following the optimization results from previous studies. Samples were collected at 10-min intervals. Effect of pH was studied at different pH values (2, 3, 4, 6, 8 and 10) under fixed operating parameters, including dual frequency, 200 W of power dissipation, 25 ppm as AY17 concentration initially, 30 °C of temperature, and 210 min of sonication time. To explore the influence of power on the decolorization of AY17, experiments were carried out using varying powers (100 W, 1500 W, 200 W, 250 W, and 300 W). The impact of initial concentration on decolorization of Acid Yellow 17 was studied using a range of initial concentrations, including 25, 50, 100, and 200 ppm. The study examined the impact of hydrogen peroxide (H_2O_2) (ranging from 25 to 500 ppm), at constant initial dye concentrations (25 ppm). To understand the role of oxidant loading in Fenton process, Fe^{2+} concentration was varied from 1 to 15 ppm, while keeping the H_2O_2 loading at its optimal level of 100 ppm (determined in the previous set of experiments). Effect of KPS loading was examined by adjusting the KPS loading from 5 to 30 ppm. The combined effect of Fe^{2+} and KPS was also explored by varying Fe^{2+} loading (1–5 ppm) while keeping the KPS loading constant at 20 ppm. All the experiments involving oxidants were conducted at an initial pH of 3, a temperature of 30 °C, and a dye concentration of 25 ppm.

Conventional experiments were also performed in the same reactor assembly at 30 °C, utilizing a stirrer at constant stirring speed of 300 rpm without ultrasound for

Table 1 Properties of the AY17

Name	:	Acid Yellow 17
Structure	:	
C.I. No		18965CAS 6359-98-4,551.29
IUPAC Name	:	Disodium 2, 5-dichloro-4-(5-hydroxy-3-methyl-4-(sulphophenylazo)pyrazol-1-yl) benzenesulphonate
Molecular formula	:	$C_{16}H_{12}Cl_2N_4NaO_7S_2^+$
Molecular weight	:	530.3

comparative analysis. The dye solution was treated with precise concentrations of oxidizing agents, including hydrogen peroxide, ferrous sulphate, and potassium persulfate. The effectiveness of combining ultrasound treatment with chemical oxidants was finally tested. The Box–Behnken design (BBD) of response surface methods was employed to estimate and optimize the degree of coupled oxidative decolorization.

Analysis

UV–Visible spectrophotometer (UV-1900 model, Shimadzu Corporation Analytical and Measuring Instruments Division, Japan) determined AY17 dye concentration with measurements at 402 nm absorbance. The equation used to calculate dye decolorization (%) is:

$$\textit{Extent of Decolorization}(\%) = \frac{C_0 - C}{C_0} \times 100 \quad (1)$$

where, C_0 = Initial concentration of AY17dye (mg/L), C = Concentration of AY17 at different time intervals (mg/L).

The extent of dye mineralization was analyzed using COD measurements. For this analysis, the withdrawn samples were quenched with sodium hydroxide before COD analysis to remove residual oxidants. COD was measured using a COD digester (model: HI 839,800) supplied by Hanna Equipment Pvt. Ltd. (Mumbai, India) following the standard protocol, ISO 6060:1989. The process involved digestion at 150 °C for 2 h and titration against ferrous ammonium sulfate.

BBD modelling

For the purpose of modelling the coupled oxidative AY17 decolorization, the Box–Behnken rotatable design was used. Using Design-Expert 12® software, statistical analysis and model construction were carried out. To minimize error, an experimental matrix with chosen process parameters was generated using BBD design and run in random sequence. Table 2 displays the experimental AY17 decolorization (response) data, which was subsequently analysed for different models like linear, 2FI, cubic, and quadratic models (Eq. 2):

$$\text{AY17 Removal}\ (\%) = \beta_0 + \sum_{i=1}^{k} \beta_i X_i + \sum_{j=1}^{k} \beta_j X_j^2 + \sum_{i<j}^{k} \beta_{ij} X_{ij} + \cdots \quad (2)$$

where AY17 Removal is the AY17 decolorization (predicted response), i, j, and ij are the regression model coefficients, k is the number of independent variables, and Xi is the linear coefficient of the ith parameter and Xj is the quadratic coefficient of the jth parameter (Sivamani et al. 2022). To determine the viability of the developed model, statistical analyses like ANOVA, and T-test were also conducted.

Table 2 BBD matrix with real and predicted values

US time (5–30 min)	Fe^{2+} dosage (1–5 ppm)	H_2O_2 dosage (50–150 ppm)	KPS dosage (10–30 ppm)	US + Fenton		US + Fe^{2+} + KPS	
				$\%R_{act}$	$\%R_{pred}$	$\%R_{act}$	$\%R_{pred}$
5	1	100	20	49.7	49.42	43.4	43.29
30	1	100	20	91.7	90.6	83.9	83.09
5	5	100	20	59.6	60.7	53.2	54.01
30	5	100	20	58.7	58.97	51.7	51.81
5	3	50	10	65.3	64.64	59.4	58.76
30	3	50	10	88.3	88.46	80.9	80.96
5	3	150	30	85.2	85.04	78.2	78.14
30	3	150	30	100	100	100	93.54
17.5	1	50	10	54.7	55.64	48.5	49.25
17.5	5	50	10	56.7	56.26	50.4	50.23
17.5	1	150	30	82.3	82.74	76.3	76.48
17.5	5	150	30	62.7	61.76	55.7	54.95
17.5	3	100	20	99.6	99.66	94.4	90.52
17.5	3	100	20	99.8	99.66	94.7	90.52
17.5	3	100	20	100	99.66	94.2	90.52
17.5	3	100	20	99.7	99.66	94.9	90.52
17.5	3	100	20	99.2	99.66	94.4	90.52

Results and discussion

Effect of pH

Although acidic pH condition is optimal for the majority of azo dye degradation, the variation in the extent of degradation is pollutant-dependent and also many a times, the optimum value also differs making it important to study the effect of pH. Different pH values, including 2, 3, 4, 6, 8 and 10, were applied in this investigation under fixed operating parameters, including dual frequency mode, 200 W of power dissipation, 25 ppm as AY17 concentration at the start, 30 °C as temperature, and 210 min of time. According to the data shown in Fig. 1, the decolorization values obtained at various pH levels of 2, 3, 4, 6, 8 and 10 were 66.6%, 64.4%, 56.9%, 43.6%, 13.8 and 10.8%, respectively. According to the integral analysis method for determining kinetics, the determined rate constants were 0.003, 0.0028, 0.0032, 0.0019, 0.0007, and 0.0005 min^{-1} at same sequence of values of pH. Under acidic pH circumstances, decolorization was seen to occur quite quickly, though too strong a pH as 2 had only a minimal impact compared to pH of 3. Acidic circumstances favor the production of hydroxyl radicals and their ability for oxidation (Kanthale et al. 2008). Similarly, an acidic pH may speed up the protonation of azo molecules, by imparting a hydrophobic end to them, therefore facilitating their presence near the cavity interface, where there is highest concentration of hydroxyl radicals (Kodavatiganti et al. 2021). An alkaline environment on the other hand promotes the recombination reaction of the generated hydroxyl radicals, leading to the production of hydrogen peroxide; as a result, fewer hydroxyl radicals will be used for the pollutant oxidation reaction in the liquid zone, resulting in a generally lesser degree of decolorization. The level of decolorization was found to be 64.4%, at the optimal pH of 3 determined in this work. The best pH of 3 was chosen since, at pH 2, there is little to no improvement, indicating that such a modification is not practical for commercial use. Wang et al. (Wang et al. 2005) reported comparable findings regarding methyl orange, indicating that a pH of 3.5 resulted in a degradation of 10%, while a neutral pH of 7 yielded a degradation rate of 7%. It is clear that variation in degradation and optimal pH are different elucidating the importance of the current work.

Effect of US power

In order to study the impact of power dissipation on the decolorization of AY17, a series of tests were conducted at a consistent dual frequency operation while adjusting the power levels over the range of 100–300 W. Decolorization percentages at 100 W, 150 W, 200 W, 250 W, and 300 W were 43.6% 50.7%, 57.3%, 64.4%, and 67.4%, respectively (Fig. 2). The decolourisation process was determined to follow first order kinetics, and the obtained rate constants were 0.0022 min^{-1}, 0.0024 min^{-1}, 0.0028 min^{-1}, 0.0032 min^{-1}, and 0.003 min^{-1} for power dissipation levels of 100 W, 150 W, 200 W, 250 W, and 300 W, respectively. It is clearly elucidated that decolorization increased as power dissipation increased till 250 W, at which point 64.4% decolorization was observed with rate constant as 0.0032 min^{-1}. The observed decolorization increase till optimum of 250 W can be attributed to greater sonic intensity (Karnjkar et al. 2015), which leads to increased bubble activity in terms of both

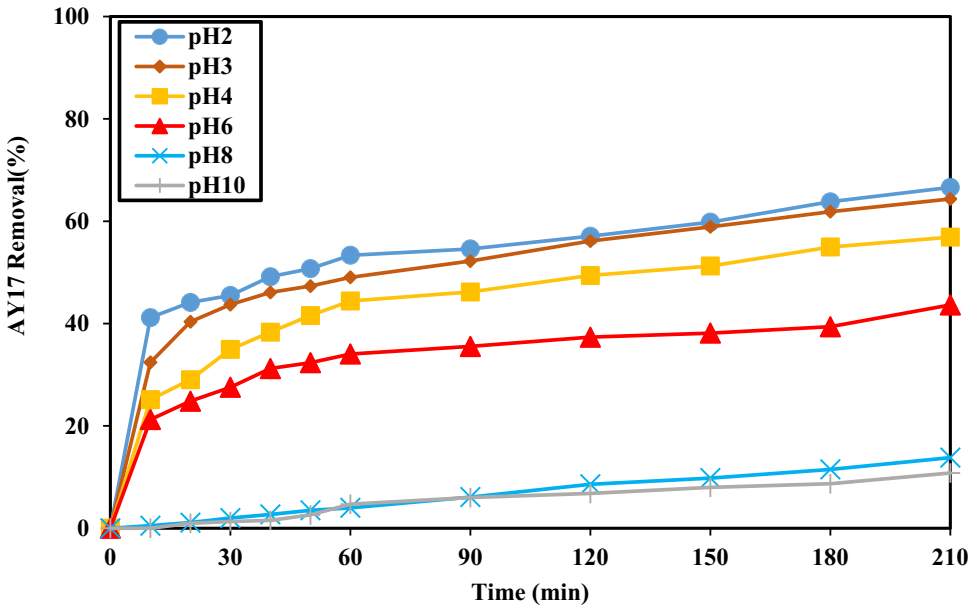


Fig. 1 Effects of solution pH on AY 17 removal (process conditions: temperature: 30 °C, 250 W, 25 mg/L AY17 concentration, dual frequency)

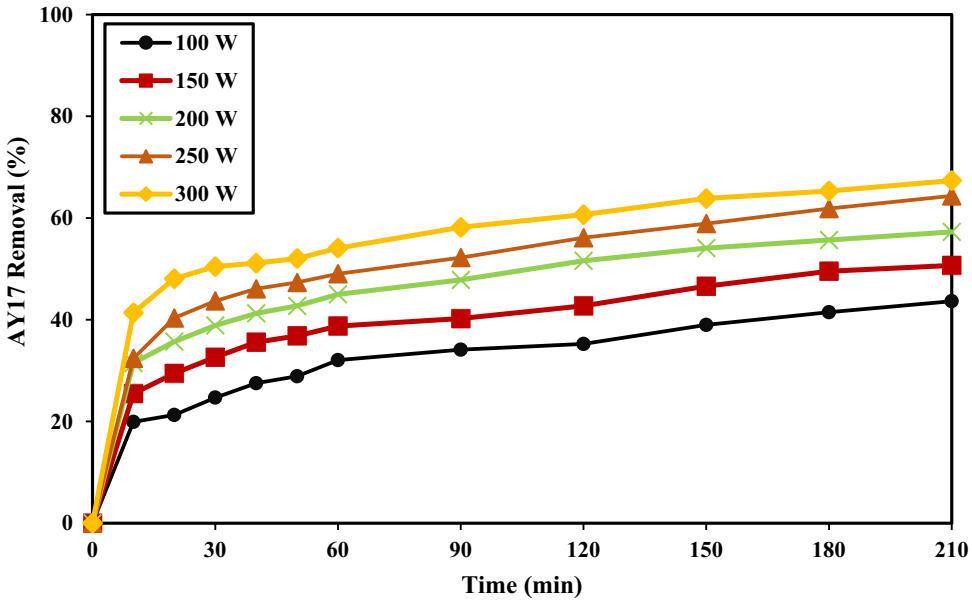


Fig. 2 Effects of US power dissipation on AY 17 removal (process conditions: temperature: 30 °C, pH: 3, 25 mg/L AY17 concentration, dual frequency)

the number and collapse intensity of the bubbles, ultimately resulting in a greater quantum of hydroxyl radicals (Bagal and Gogate 2013). Beyond the recognized 250 W as optimum power dissipation, excessive cavitation events result in cushioning collapse and subsequently lower intensity (Karnjkar et al. 2015), which explains the lower decolorization efficiency seen at 300 W, the greatest power examined in the work. Based on the findings, 250 W was chosen as the best power for the subsequent studies involving the use of oxidants. Gote et al. (2023) studied the influence of power on the degradation of Chrysoidine R dye, examined within the power range of 80–120 W. The lowest degradation observed was 27.03% at a power level of 80 W, with an increase noted at higher power levels with actual values as 42.5% and 45.6% at power levels of 100 W and 120 W, respectively meaning that no optimum power could be seen in their study. The range of power investigated and the type of pollutant affects the trends again demonstrating the importance of the present study.

Effect of initial concentration

The decolorization of Acid Yellow 17 was also studied over a range of initial concentrations, including 25, 50, 100, and 200 ppm, to examine the impact of initial concentration. The experiments were conducted at a temperature of 30 °C, with an optimized power of 250 W, an optimized initial pH of 3, and a dual frequency mode. The obtained extent of decolorization at different initial concentrations in the same sequence were 64.4%, 45.6%, 34.8%, and 23.6% with a corresponding first-order rate constants as 0.0032 min^{-1}, 0.003 min^{-1}, 0.0021 min^{-1}, and 0.0014 min^{-1}. The decolorization process was found to be more noticeable when the initial dye concentrations were lower, as also depicted in Fig. 3. At higher dye concentrations, fixed quantum of free radicals is not able to react with the dye molecules effectively resulting in lower extents of decolorization. In acidic circumstances, the hydrophobic component is more likely to be found at the cavity's surface, allowing for better contact with reactive radicals. The decrease in reactivity with the •OH radicals, and hence the decrease in decolorization, might be attributed to the presence of more pollutants in the surrounding media. Due to the increasing concentration, these pollutants are unable to interact with the hydroxyl radicals on the cavity's surface before self-quenching occurs. Existing research also demonstrate similar tendencies in the impact of initial concentration. Momin and Gogate (Momin and Gogate 2024) found that the degradation of Procion brilliant yellow H-E6G using cavitation decreased from 19.1 to 6.8% as the concentration varied from 15 to 30 ppm. Wang et al. (2011) investigated the degradation of reactive brilliant red K-2BP via cavitation and observed a reduction in degradation from 94.2 to 24.7% as the concentration varied from 10 to 50 mg/L, indicating that the optimal initial dye concentration as 10 mg/L.

Effect hydrogen peroxide loading

The study initially examined the impact of hydrogen peroxide (H_2O_2) individually (without ultrasound) under constant initial dye concentration (25 ppm) and varying H_2O_2 loadings (ranging from 25 to 500 ppm). The extent of decolorization observed at different loadings of H_2O_2 as 25, 50, 100, 200, and 500 ppm were 66.5%, 61.6%, 70.6%, 60.1%, and 57.9% respectively with kinetic rate constants as 0.0037 min^{-1}, 0.0033 min^{-1}, 0.0041 min^{-1}, 0.003 min^{-1}, and

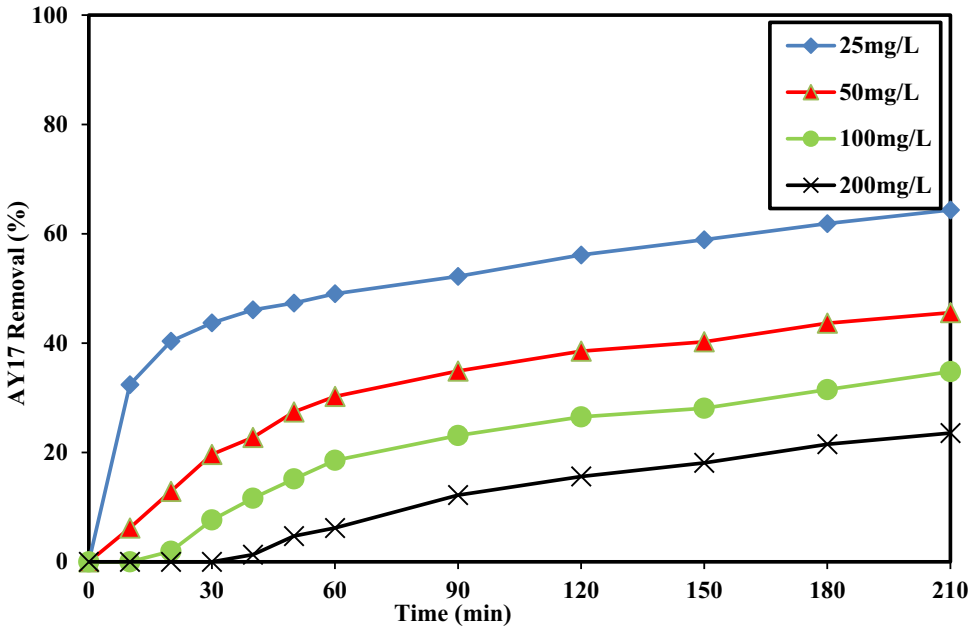


Fig. 3 Effects of initial dye concentration on AY 17 removal (process conditions: temperature: 30 °C, pH:3, 250 W, dual frequency)

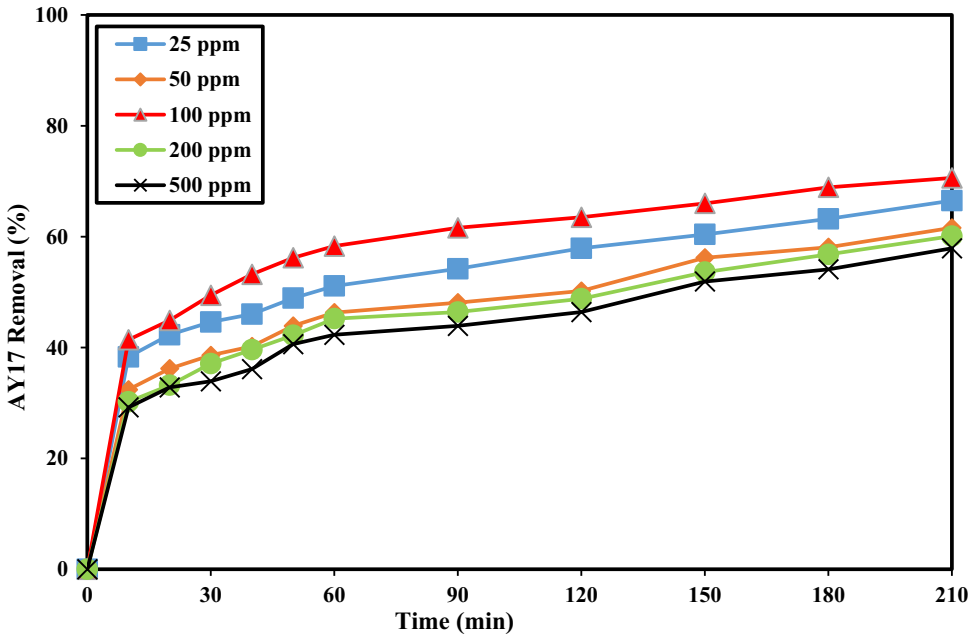


Fig. 4 Effect of H_2O_2 dosage on AY 17 removal using only hydrogen peroxide oxidation (process conditions: temperature: 30 °C, pH:3)

0.0028 min^{-1} as shown in Fig. 4. It was found that at a concentration of 100 ppm of H_2O_2, the decolorization reached its maximum at approximately 70.6%. Further increasing the H_2O_2 loading led to a decrease in decolorization.

Further experiments involved testing different concentrations of H_2O_2, ranging from 25 to 500 ppm, along with ultrasound. The initial pH was set at 3, and the starting concentration of AY17 was 25 ppm. The purpose was to investigate the effectiveness of combining $H2O_2$ with ultrasound for the decolorization of AY17. The extent of decolorization observed at different loadings of H_2O_2, specifically as 25, 50, 100, 200, and 500 ppm were 82.1%, 88.5%, 100%, 87.8%, and 84.8% as shown in Fig. 5. Additionally, the kinetic rate constants for these loadings in the same sequence were 0.1217 min^{-1}, 0.1356 min^{-1}, 0.1612 min^{-1}, 0.1102 min^{-1}, and 0.0037 min^{-1}. It was determined that the optimal loading of H_2O_2 was 100 ppm, which resulted in complete decolorization. The addition of H_2O_2 to the reactor intensified the decolorization process due to the increased formation of hydroxyl radicals (Neppolian et al. 2002). The processes were found to be mutually beneficial as ultrasound assists in the dissociation of peroxide, resulting in

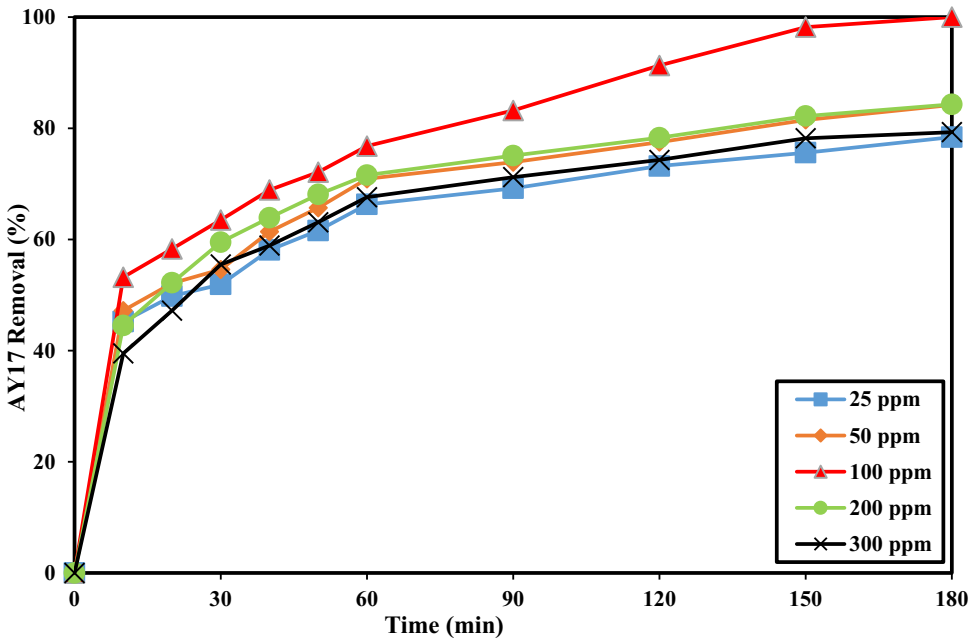


Fig. 5 Effect of H_2O_2 dosage on AY 17 removal using combined ultrasound + H_2O_2 approach (process conditions: temperature: 30 °C, pH:3, 250 W, dual frequency)

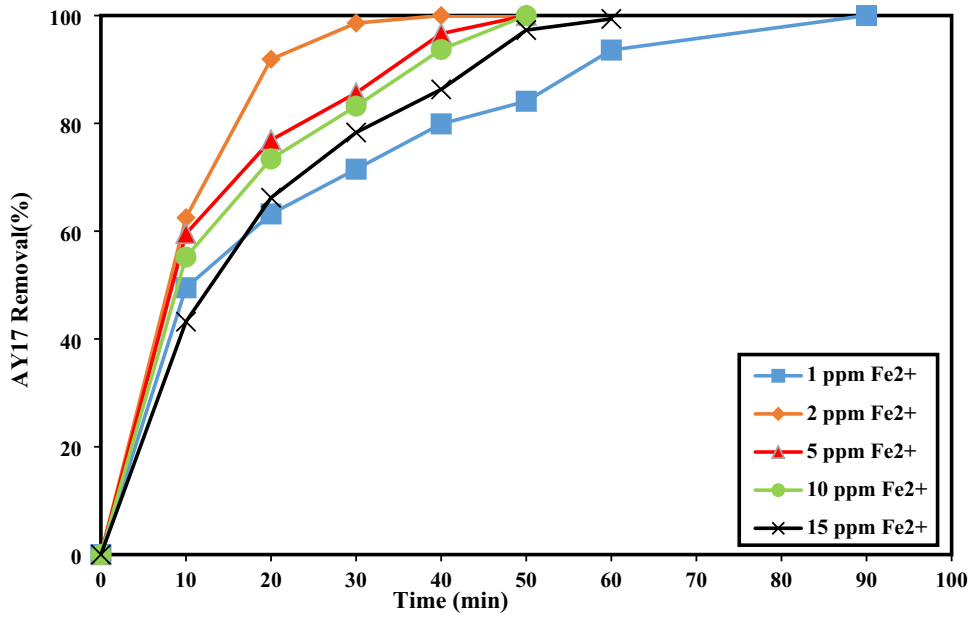


Fig. 6 Effect of Fenton reagent dosage on AY 17 removal using only Fenton (process conditions: temperature: 30 °C, pH:3)

an enhanced production of hydroxyl radicals. The decrease in decolorization beyond the optimal H_2O_2 loading may be related to enhanced hydroxyl radical scavenging by larger residual H_2O_2 concentrations. Similar findings on optimum H_2O_2 loading were reported in the literature. Merouani et al. (2010) found that applying hydrogen peroxide at 100 mg/L elucidated as optimum with study over the range of 50–1000 mg/L accelerated sonochemical degradation of Rhodamine B present in an aqueous phase at loading of 5 mg/L. Adding H_2O_2 at optimal loadings boosted dye degradation by decomposing it into hydroxyl radicals due to the action of ultrasound, resulting in a faster degradation. The importance of the current work is clear based on the first study to depict the trend of optimal H_2O_2 loading for the specific pollutant AY17 and considering the fact that optimum loading cannot be generalized.

Effect of Fenton's reagent loading

The Fe^{2+} concentration was varied from 1 to 15 ppm, while keeping the H_2O_2 loading at its optimal level of 100 ppm, as determined in the previous experiments. Initially the experiments were performed at an initial pH of 3, a temperature of 30 °C, and a dye concentration of 25 ppm without using

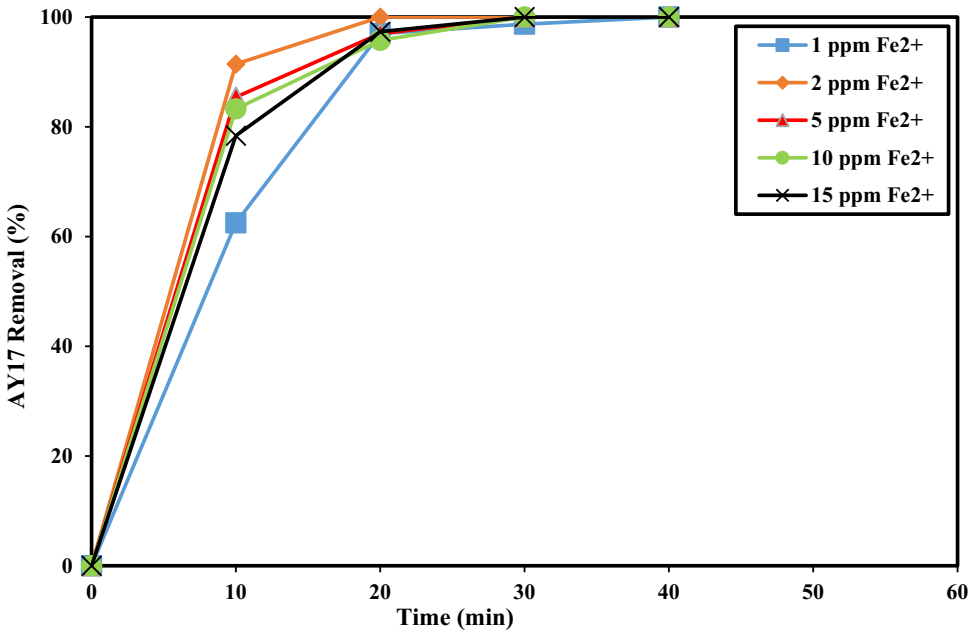


Fig. 7 Effect of Fenton reagent dosage on AY 17 removal using combined ultrasound + Fenton approach (process conditions: temperature: 30 °C, pH:3, 250 W, Dual frequency)

ultrasound. The purpose of these experiments was to investigate the impact of the Fenton reagent alone. The degradation was close to 100% for all loadings of Fe^{2+} as 2, 5, 10, 15, and 20 ppm, as shown in Fig. 6 but it can be said that the most effective decolorization of dye based on requirement of lower time occurred when using 2 ppm of Fe^{2+} and 100 ppm of H_2O_2. The decolorization efficiency showed a slight decline for Fe^{2+} dosages of 10 ppm and 15 ppm. Using higher concentrations of the Fenton reagent can hinder the process of decolorization and limit the interaction between the pollutant and reactive radicals as well as generate sludge creating additional disposal issues. There have been multiple documented instances of this effect in the literature (Cetinkaya et al. 2018).

Further the use of Fenton reagent was studied in the presence of the ultrasound with the Fe^{2+} loading adjusted from 1 to 15 ppm, while maintaining optimal H_2O_2 loading at 100 ppm. The experiment was conducted at a starting pH of 3, a temperature of 30 °C, and specific power 250 W and dual frequency mode. The aim was to investigate the impact of adding the Fenton reagent in combination with ultrasound and it was demonstrated that the decolorization achieved

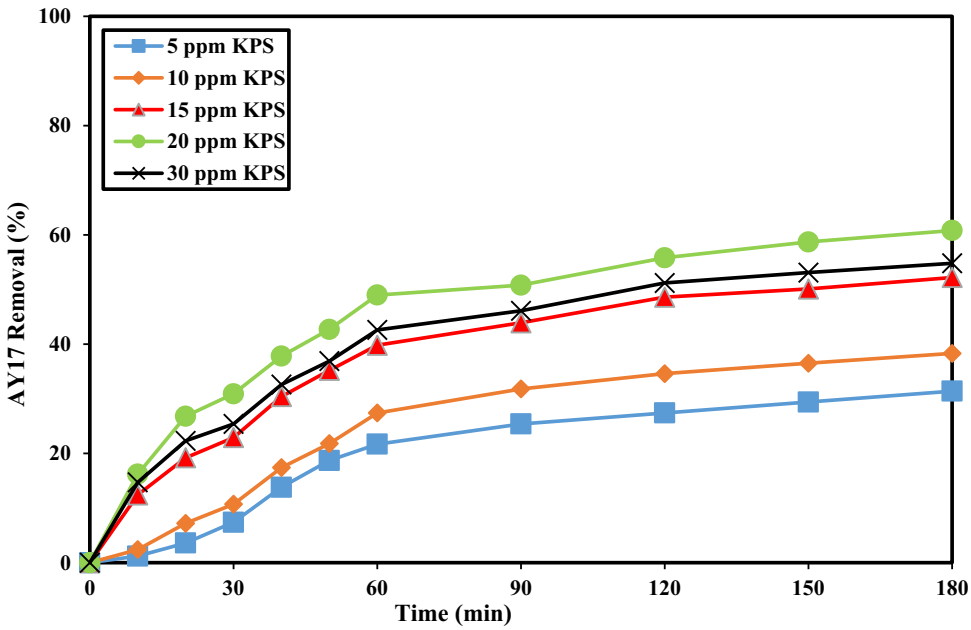


Fig. 8 Effect of KPS dosage on AY 17 removal using only KPS oxidation (process conditions: temperature: 30 °C, pH:3)

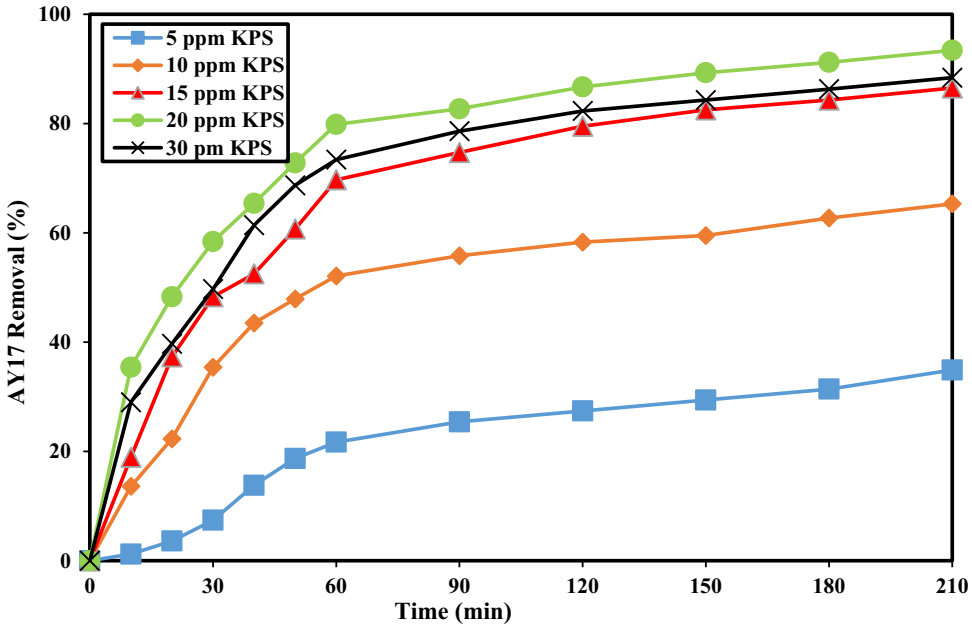


Fig. 9 Effect of KPS dosage on AY 17 removal using combined Ultrasound + KPS approach (process conditions: temperature: 30 °C, pH:3, 250 W, dual frequency)

nearly 100% effectiveness, as shown in Fig. 7. When the Fe^{2+} loading was set at 2 ppm and the H_2O_2 concentration was 100 ppm, the dye solution achieved complete decolorization in minimum time. One possible explanation for the absence of a notable impact of ultrasound (US) when combined with Fenton reagent could be the considerably higher efficacy of Fenton reagent alone in degrading AY17 dye. When Fenton's reagent is applied with a lower load or in the case of compounds with limited reactivity to Fenton's reagent, ultrasound is expected to play a prominent role. The hypothesis is best understood through a comparison with the literature, as the optimal loading and positive benefits of using ultrasound is typically depending upon the system. Song et al. (2009) examined the utilization of US in conjunction with Fenton chemistry for the degradation of acid red 88 dye. The authors reported that the optimal ratio of H_2O_2/Fe^{2+} was 18 resulting in a much higher dye degradation of 98.6% compared to the use of only Fenton.

Effect of persulfate loading

Similar to other oxidants, use of persulfate was studied as individual operation without using ultrasound first with the KPS loading adjusted from 5 to 30 ppm under

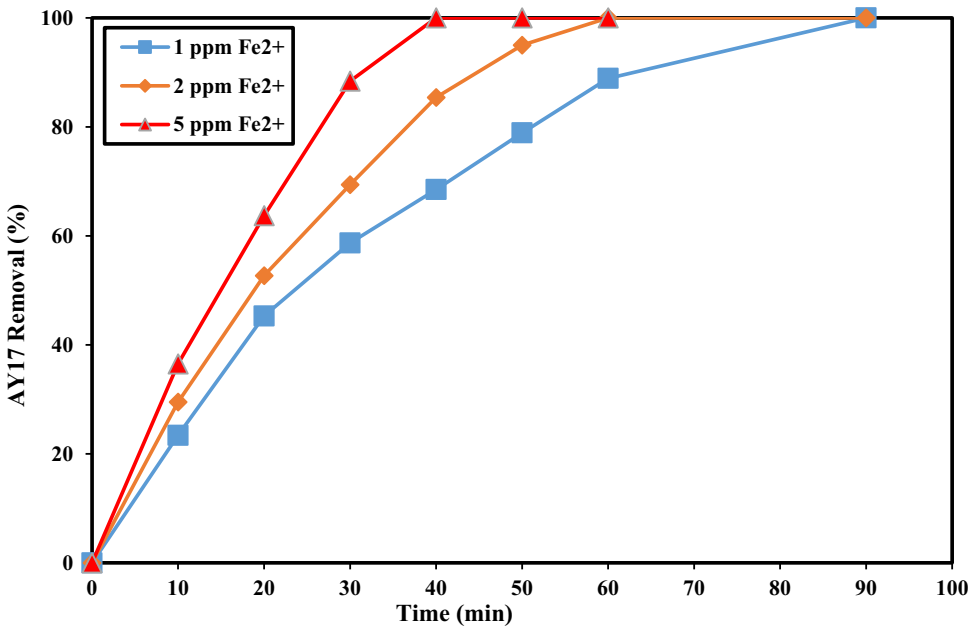


Fig. 10 Effect of KPS + Fe^{2+} dosage using combined oxidants without ultrasound (process conditions: temperature: 30 °C, pH:3)

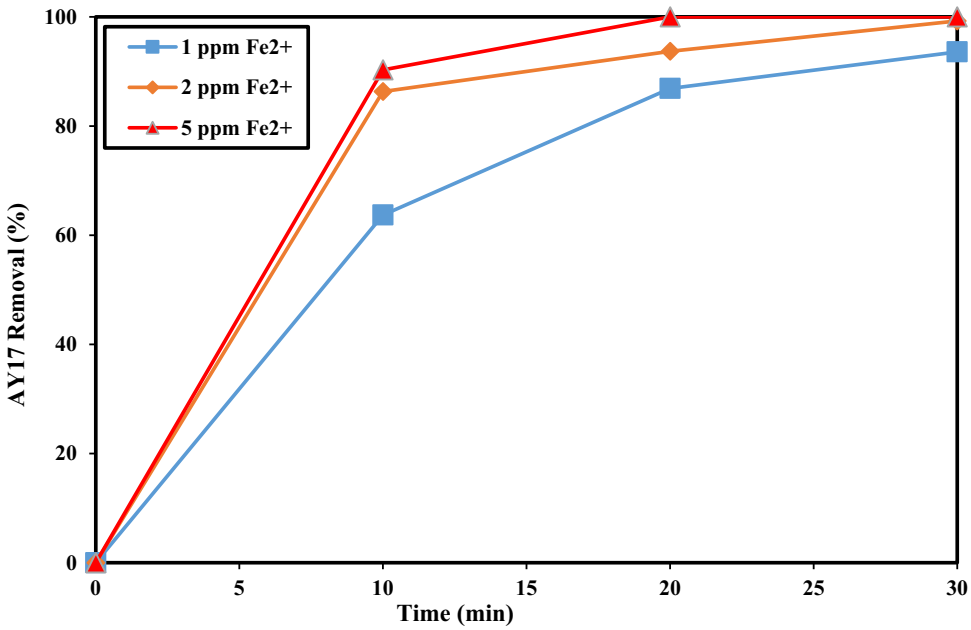


Fig. 11 Effect KPS + Fe^{2+} dosage using combined oxidants with ultrasound (process conditions: temperature: 30 °C, pH:3, 250 W, Dual frequency)

specific conditions of an initial pH of 3, a temperature of 30 °C, and an initial dye concentration of 25 ppm in order to evaluate the effect of only KPS. The decolorization extent obtained at different concentrations of KPS as 5, 10, 15, 20, and 30 ppm was 34.9%, 39.9%, 53.9%, 62.7%, and 55.8%, respectively. At 20 ppm of KPS, the highest amount of dye decolorization was achieved, and it further decreased as the oxidant concentration was raised (Fig. 8).

The same range of loading of KPS as 5, 10, 15, 20, and 30 ppm was also used for study in the presence of ultrasound under optimized conditions. The percentage of dye decolorization aided by sonochemical treatment was 34.9%, 65.3%, 86.5%, 93.4%, and 88.4% for KPS loadings of 5, 10, 15, 20, and 30 ppm, respectively (Fig. 9). The highest level of dye decolorization was again observed at a concentration of 20 ppm of KPS. Observations indicated a lower decolorization when the KPS loading increased further from 20 to 30 ppm likely due to the presence of an excess of $S_2O_8^{2-}$ ions that scavenge the reactive $SO_4^{\bullet-}$ radicals (Bougdour et al. 2018). In addition, the degradation efficiency was found to be low due to the absence of the required conditions for persulfate activation in the individual KPS method. When considering the KPS combination with ultrasound, it is worth noting that ultrasound can induce the activation of persulfate, which leads to a more effective decolorization process due to the increased formation of free radicals. It is worth mentioning that the impact of persulfate when used in conjunction with ultrasound was comparatively weaker than

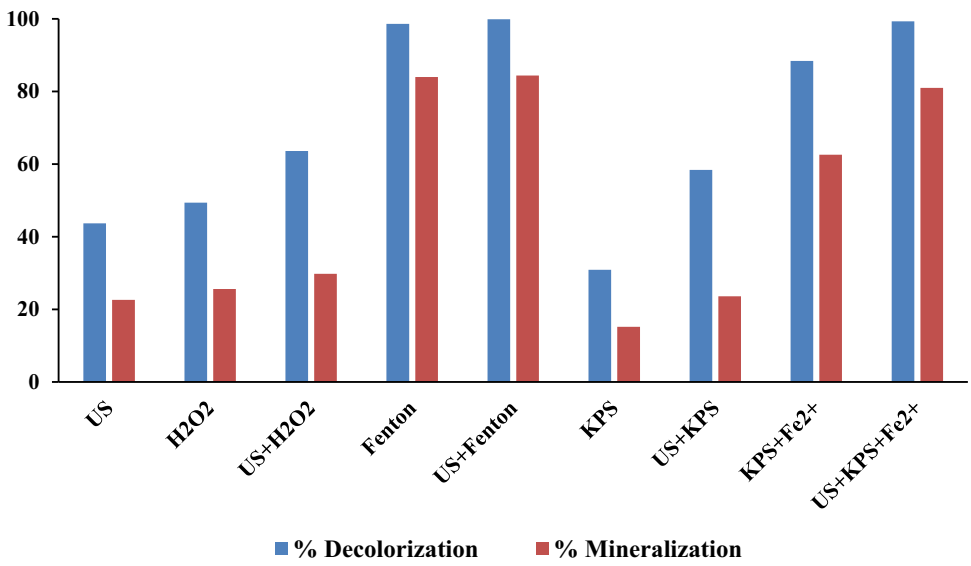


Fig. 12 Comparison of decolorization and mineralization of AV-7 dye using various treatment schemes

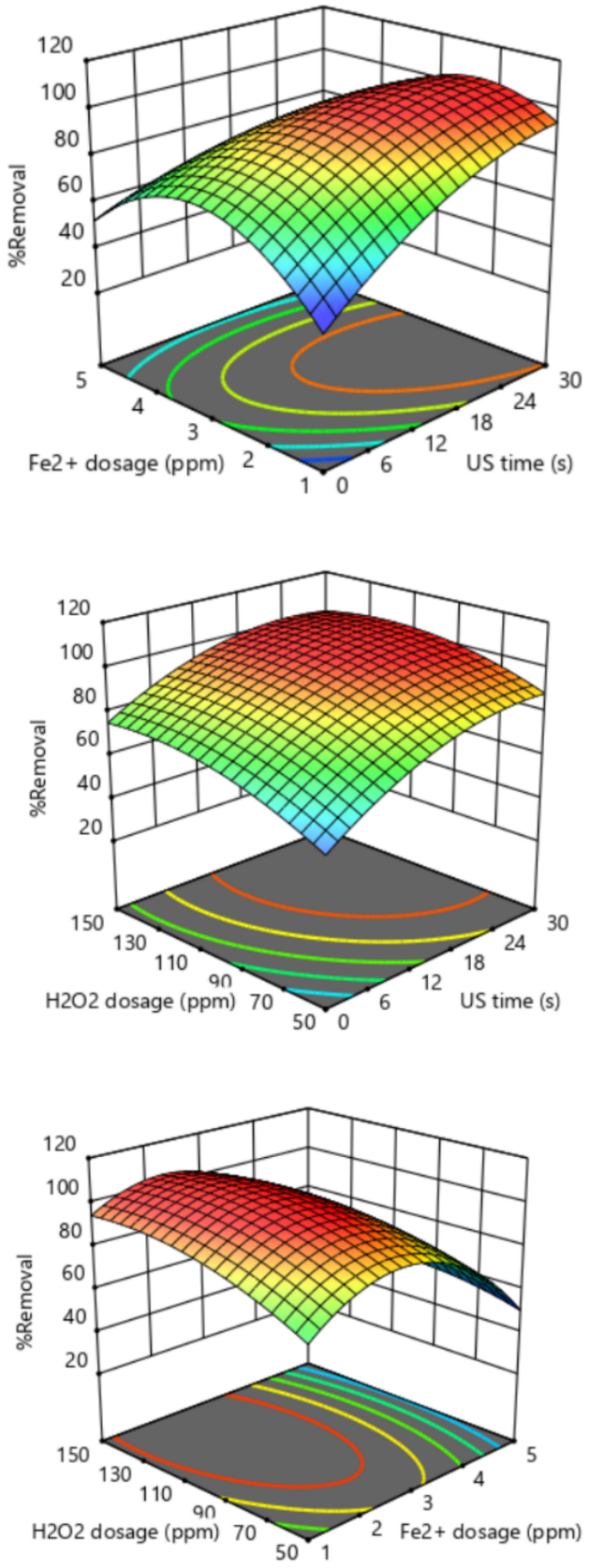


Fig. 13 3D plots for effect of operating parameters in ultrasound assisted Fenton process

the combined effect of ultrasound with Fenton or hydrogen peroxide. The results indicated that, unlike the hydroxyl-based enhancement observed in the US + Fenton process, the sulfate radicals formed by the activation of persulfate by ultrasound are not highly effective in degrading AY17 dye.

Effect of persulfate and ferrous sulphate combination

In this specific combination of oxidants, the Fe^{2+} loading was varied from 1 to 5 ppm while keeping the KPS loading constant at 20 ppm. The experiment was conducted at a starting pH of 3, a temperature of 30 °C, and an initial dye concentration of 25 ppm. The purpose of this study was to assess the impact of the KPS + $FeSO_4$ combination. After 30 min, all of the color associated with the Fe^{2+} loading was completely removed as per the quantified decolorization as shown in Fig. 10. The presence of Fe^{2+} had a significant impact on the effectiveness of AY17 degradation due to significant activation effects on KPS and also due to the formation of multiple oxidizing species.

In the case of combination with ultrasound as well, Fe^{2+} loading was varied from 1 to 5 ppm, while maintaining a constant KPS loading of 20 ppm. The starting pH was set at 3, the initial temperature at 30 °C, and the initial dye concentration at 25 ppm. These adjustments were made to assess the impact of combining KPS with $FeSO_4$ and ultrasound. According to the data presented in Fig. 11, it can be observed that the decolorization achieved through sonochemical treatment combined with KPS was 100% for best Fe^{2+} loadings of 5 ppm within a time frame of 20 min, which is lower than required 40 min for without ultrasound. The generation of free radicals through the combination of KPS and ultrasound was enhanced by the addition of $FeSO_4$. The presence of a substantial amount of Fe^{2+} in the Fe^{2+}/KPS system greatly enhances the effectiveness of AY17 degradation attributed to the fact that Fe^{2+} has the ability to activate PS molecules, leading to the production of $SO4^{\bullet-}$ radicals in the solution. The efficiency is enhanced when ultrasound is present leading to much faster decolorization.

Comparison of extent of mineralization in various approaches

The COD measurements were carried out using carefully calibrated amounts of oxidants in the specific methodology. The experimental parameters were set as pH of 3, dual frequency mode, 250 W as the power, treatment time of 60 min, and an initial dye concentration of 50 ppm. A higher initial concentration was selected to ensure the COD values could be measured accurately. Fig. 12 depicts the outcomes of COD reduction achieved and it can be clearly seen that the mineralization achieved by the US + Fenton

Table 3 Model summary statistics for US combined with Fenton process

Source	Sequential p-value	Lack of Fit p-value	Adjusted R^2	Predicted R^2	Recommendation
Linear	0.2742	< 0.0001	0.0775	− 0.2484	–
2FI	0.6896	< 0.0001	− 0.0424	− 1.0147	–
Quadratic	< 0.0001	0.0063	0.9977	0.9850	Suggested
Cubic	0.0063	–	0.9998	–	Aliased

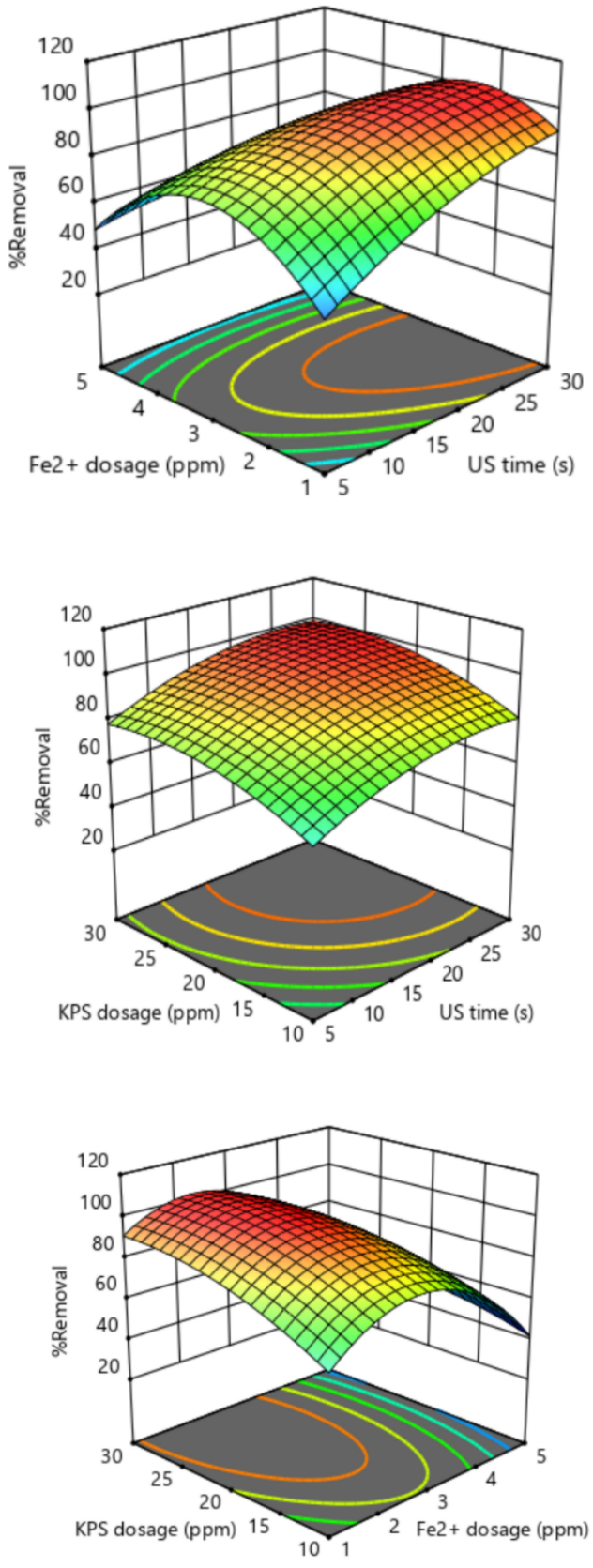


Fig.14 3D plots for effect of operating parameters in ultrasound assisted KPS + Fe^{2+} process

Table 4 Model summary statistics for US combined with KPS + Fe^{2+} process

Source	Sequential p-value	Lack of Fit p-value	Adjusted R^2	Predicted R^2	Recommendation
Linear	0.2615	< 0.0001	0.0854	− 0.2397	–
2FI	0.7305	< 0.0001	− 0.0508	− 1.0614	–
Quadratic	< 0.0001	0.0034	0.9975	0.9831	Suggested
Cubic	0.0034	–	0.9998	–	Aliased

oxidation process was the highest, reaching an impressive level of 84.4%. When comparing the other treatment strategies, it was observed that the US + H_2O_2 and US + KPS approaches yielded much reduced levels of mineralization, specifically at 29.8% and 23.6% respectively. After evaluating different approaches under optimal operating conditions, it is evident that the combined US and Fenton treatment is the most efficient method for achieving decolorization and mineralization. The results demonstrate a remarkable almost 100% decolorization and 84.4% mineralization in the degradation of AY17 dye. The research findings suggest that the combination of sonication and Fenton oxidation is a highly effective treatment method for the removal of the AY17 dye, outperforming other approaches. The degradation rate is enhanced in the US + Fenton process because of the more direct formation of hydroxyl radicals setting the stage for the process intensification of the AY17 dye degradation. Based on the obtained data, it was also concluded that there was a notable decrease in COD values within the first hour, followed by a gradual decline in the rate (Cetinkaya et al. 2018) which is a possible indication for a first order behaviour and feasibility of continuous operation depending on the required treatment levels.

BBD modelling for design equations for dye degradation extent

The AY17 decolorization multivariate regression analysis involved the examination of linear, 2FI, cubic, and quadratic polynomial models. Regression analysis outputs included calculations of ANOVA, Fisher F-test, Student's t-test, p-values, and other statistical parameters. The expected AY17 elimination was estimated based on the fitted model and provided in Table 2. To evaluate the suitability of the quadratic equations that were developed, the residuals were also graphed against a normal percentage likelihood. The results indicated a high level of agreement between the projected and observed values, as evidenced by the data points closely aligning with the straight line on the normal probability plots. The AY17 elimination anticipated by the quadratic equations was well correlated with the experimental findings.

Results for Modelling of US Fenton process

Figure 13 shows the 3D response surfaces of US Fenton process that were built to assess the ideal values. The model summary statistics of the US Fenton process for the AY17 decolourization are shown in Table 3. It showed that the R^2 values were reasonably higher and the lack of fit of the built model was not substantial. In actual factors, the created BBD model equation is as follows:

$$\begin{aligned}\text{AY17 Removal}(\%) = {} & -74.95 + 3.98\ \text{US Time} \\ & + 51.86\ Fe^{2+}\ \text{dosage} + 1.01\ H_2O_2\ \text{dosage} \\ & -0.429\ \text{US time} * Fe^{2+}\ \text{dosage} \\ & -0.003\ \text{Us time} * H_2O_2\ \text{dosage} \\ & -0.054\ Fe^{2+}\ \text{dosage} * H_2O_2\ \text{dosage} \\ & -0.045\ \text{Us time}^2 - 6.916\ Fe^{2+}\ \text{dosage} \\ & -0.032\ H_2O_2\ \text{dosage} \end{aligned} \quad (3)$$

Results for BBD modelling of US + KPS + Fe^{2+} process

Figure 14 shows the 3D response surfaces of US /KPS+Fe^{2+} process that were built to assess the ideal values. The model summary statistics of the US/KPS+Fe^{2+} process for the AY17 decolourization are shown in Table 4. It showed that the R^2 values were reasonably higher and the lack of fit of the built model was not substantial. In actual factors, the created BBD model equation is as follows:

$$\begin{aligned}\text{AY17 Removal}(\%) = {} & -79.026 + 3.70\ \text{US Time} \\ & + 54.18\ Fe^{2+}\ \text{dosage} + 4.76\ \text{KPS dosage} \\ & -0.420\ \text{US time} * Fe^{2+}\ \text{dosage} \\ & -0.0006\ \text{Us time} * \text{KPS dosage} \\ & -0.281\ Fe^{2+}\ \text{dosage} * \text{KPS dosage} \\ & -0.046\ \text{Us time}^2 - 7.296\ Fe^{2+}\ \text{dosage}^2 \\ & -0.076\ \text{KPS dosage}^2 \end{aligned} \quad (4)$$

Conclusions

AY17 dye was successfully removed utilizing ultrasound with higher removal seen when combined with oxidants for decolorization. Maximum extent of decolorization (64.4%) for individual ultrasound was reported when employing solely ultrasound under acidic circumstances (pH of 3), dual frequency mode of operation and best power dissipation of 250 W. It was also concluded that the effectiveness of persulfate and ultrasound in enhancing decolorization or mineralization is limited compared to the Fenton, indicating that sulfate radicals exhibit low reactivity towards AY17 in the applied acidic conditions. The most efficient technique for removing AY17 dye (achieving nearly 100% decolorization) consist of using Fenton reagent in combination with ultrasonic irradiation at the optimal level. The US + Fenton combination was also determined to be the most effective mineralization strategy for AY17 thereby showing significant promise for commercial applications.

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Data availability Data will be made available by the corresponding author on request.

Declarations

Conflict of interest Authors declare no conflict of interest or funding that could have influenced the outcomes of the work.

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