

Ultrasonic Intensification of the Chemical Degradation of Methyl Violet: An experimental Study

N.P. Dhanalakshmi and R. Nagarajan

Abstract—The sonochemical decolorization and degradation of azo dye Methyl violet using Fenton's reagent in the presence of a high-frequency acoustic field has been investigated. Dyeing and textile effluents are the major sources of azo dyes, and are most troublesome among industrial wastewaters, causing imbalance in the eco-system. The effect of various operating conditions (initial concentration of dye, liquid-phase temperature, ultrasonic power and frequency and process time) on sonochemical degradation was investigated. Conversion was found to increase with increase in initial concentration, temperature, power level and frequency. Both horn-type and tank-type sonicators were used, at various power levels (250W, 400W and 500W) for frequencies ranging from 20 kHz - 1000 kHz. A 'Process Intensification' parameter PI, was defined to quantify the enhancement of the degradation reaction by ultrasound when compared to control (i.e., without ultrasound). The present work clearly demonstrates that a high-frequency ultrasonic bath can be used to achieve higher process throughput and energy efficiency at a larger scale of operation.

Keywords—Fenton oxidation, process intensification, sonochemical degradation of MV, ultrasonic frequency

I. INTRODUCTION

ULTRASOUND (US) is a sound pitched above human hearing at frequencies greater than 16 kHz or 16,000 cycles per second, and is typically associated with the frequency range of 20 kHz to 1 MHz. It influences many chemical reactions in a variety of reacting systems. It has successfully increased reactant conversion (e.g., reactivity of metal powders by 100,000 times), initiated various chemical reactions by generating free chemical ions (radicals), improved process yield and changed the reaction pathway in biological, chemical, and electrochemical systems.

Low-intensity, high frequency ultrasound does not alter the state of the medium through which it travels, and is commonly used for nondestructive evaluation and medical diagnosis. However, high-intensity, low-frequency ultrasound does alter the state of the medium, and is the type of ultrasound typically used for sonochemical applications.

The chemical and mechanical effects of ultrasound are caused by cavitation bubbles which are generated during the rarefaction, or negative pressure, period of sound waves.

During the negative-pressure cycle, the liquid is pulled apart at sites containing some gaseous impurity (nucleation sites), forming a void/cavity. Nucleation sites are also known as "weak spots" in the fluid. When the gases and vapors trapped in the cavity are compressed, a local "hot spot" is created which reaches a temperature and pressure in excess of 5000 K and 500 atm during implosion. Even though the temperature is extraordinarily high, the local "hot spot" region itself is so small that the heat dissipates quickly. Thus, at any given time, the bulk liquid remains near ambient temperature. This local heat from implosion decomposes water into extremely reactive hydrogen atoms and hydroxyl radicals. However, during the quick-cooling phase, H⁺ and OH⁻ radicals recombine to form hydrogen peroxide and molecular hydrogen. Some other compounds may be added to the system irradiated with US, and cause a wide range of secondary reactions can occur. Most of the organic compounds are degraded in this environment.

Here, the chemical of interest for our research was methyl violet (MV) dye, and reaction was carried out in a homogenous batch system. These dyes are mixtures of tetramethyl, pentamethyl and hexamethyl pararosanilins. They are mainly used in textile dyeing to obtain purple and also give deep violet colors, especially in printing inks and paints. These colored dyes from industrial effluent are highly polluted by suspended solids (ss), high Chemical Oxygen Demand (COD) and Biochemical Oxygen Demand (BOD) values, heat, acidity, basicity and other soluble substances. These dyes, even in small amounts are highly visible and toxic to the aquatic environment, as dyes absorb and reflect sunlight, thereby affecting bacterial growth and photosynthesis in aquatic environments.

Traditional chemical and physical processes, such as elimination by adsorption on activated carbon, coagulation by chemical agents, oxidation by ozone or hypochlorite, or electrochemical methods are not cost-effective. Recently, solid wastes such as; banana stalk, beer brewery discharge, agricultural waste, passion fruit, fly ash, etc., are being used as low-cost absorbents [1]. These methods do not eliminate the colors completely, sometimes are expensive and usually cause other waste pollutants as secondary products. Therefore, the purification of colored water discharges remains a problem for many industries, and it is necessary to develop new technologies to treat these waters. Among several physico-chemical processes, Fenton's oxidation is one of the oldest advanced oxidation processes which continues to be used successfully, as it is comparatively cheap, of low toxicity, and

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easy to handle as a reagent (Fe^{2+} and H_2O_2) with simple technology that makes Fenton treatment of particular interest [2]. Fenton's reagent, a mixture of hydrogen peroxide and ferrous iron, is effective for color, COD and TOC (total organic carbon content) removal from dye effluent. In Fenton system, the free radicals generated are considered as dominant species with the potential ability to oxidize almost all organic contaminants in aqueous solution into carbon dioxide and water. For the decolorization of azo dye, destruction of dye to mineral state is not necessary since the removal of color is associated with the breaking of the chromophores, i.e., conjugated unsaturated bond ($-\text{N}=\text{N}-$) in molecules. However, the end products formed are of concern due to their toxicity. The main aim of the present study was to evaluate enhancement of Fenton's oxidation process to achieve complete decolorization of azo dye by using ultrasound. The process intensification due to ultrasound is defined by the parameter, Process Intensification (PI), and is given by

$$\text{Process Intensification (PI)} = \frac{\text{Key process metric with ultrasound}}{\text{Key process metric without ultrasound}} \quad (1)$$

In the case of decolorization,

$$\text{PI}_{\text{DA}\%} = \frac{\text{DA \% with ultrasound}}{\text{DA \% without ultrasound}} \quad (2)$$

where

$$\text{Decolorization Activity (DA)} = \frac{A_i - A_f}{A_i} \times 100 \quad (3)$$

and A_i = Initial absorbance & A_f = final absorbance .

US process results in mineralization of solute without producing sludge or some other material that must then be discarded, and this constitutes a major advantage of this process. Literature shows that publications in the field of sonochemical reactions have increased significantly in the past two decades. Chang-qi et al. [1] investigated the degradation of methyl orange using ultrasound and Fenton reagent, and found that hydroxyl radical pathway was the major reaction mechanism for degradation. Kenji et al. [3] studied the decolorization of azo dyes (Reactive red 22 and methyl orange) using 200 kHz. They also proposed Langmuir-Hinshelwood mechanism for rate kinetics at bubble interface. Chafia et al. [4] investigated the degradation of MV using Fenton process alone and found the optimum condition for the reaction as pH 3, concentration of H_2O_2 of 2.1 mM and ferrous ion and dye concentration of 0.06 mM at 300C. Gogate et al. [5] analyzed the degradation of formic acid using US. He observed that high-frequency irradiation gives more beneficial degradation than low-frequency, which was also reviewed in their earlier work. Wang et al. [6] studied the degradation of methyl violet using 20 kHz ultrasound, and found that reaction temperature, concentration of dye and pH of the medium are the primary parameters. Little et al. [7] investigated the degradation of phenanthrene (PAH) using 30 kHz probe-type and achieved nearly 88% reduction and also observed no higher order resulting in hazardous products.

In this study, both US and Fenton's reagents were used in

combination to achieve complete decolorization of methyl violet. Both horn-type and tank-type sonicators at various power levels (250W, 400W and 500W) and frequencies ranging from 20-1000 kHz were investigated. The control experiments were performed at room temperature without US. The temperature effect on degradation of methyl violet was studied for constant bath temperature (30, 40, 50, 60 and 800C). A parametric study on process intensification (PI DA %) was conducted.

II. EXPERIMENTAL AND ANALYTICAL

A. Materials

Methyl violet dye ($\text{C}_{24}\text{H}_{28}\text{N}_3\text{Cl}$), and Fenton's reagent, hydrogen peroxide of 30 % grade, 0.1 N H_2SO_4 and sodium hydroxide of 1 N were used. All other reagents were commercially-available analytical grade. All the makeup solution was prepared using distilled water for this study. MV has methyl groups attached to the amine functional groups, and are soluble in water, ethanol, diethylene glycol and dipropylene glycol.

B. Ultrasonic system and experiment

The degradation experiments were conducted in both ultrasonic tank-type (cylindrical jacketed stainless-steel reactor equipped with in-built piezoelectric transducer placed at the rectangular bottom and an external generator) and probe-type ultrasonic horn directly inserted into the reaction vessel. The reactions were conducted under atmospheric conditions. The frequency ranges used in tank-type are from 25 kHz-1 MHz and at various power levels (250, 400 and 500W), and in horn-type, 20 kHz was used at various power levels. Fig. 1 and Fig. 2 show diagrams of the experimental apparatus.



Fig.1 US probe

Fig.2 US tank

Initially, the water in the ultrasonic tank was degassed to remove the small suspended gas bubbles and dissolved gases. Methyl violet of 12 mg was added to 400 ml of distilled water in a 1000 ml beaker, and was homogenized in an ultrasonic bath for half an hour for good dissolution. The dye oxidant, Fenton's reagent, consists of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and H_2O_2 (30% v/v) prepared by dissolving equivalent amount (10 mg) of weighed FeSO_4 in 10 ml of distilled water, 100 ml of H_2O_2 was measured and kept aside. After dissolution, 3 ml of 0.1 N H_2SO_4 was added to maintain optimum pH of 3. At the start of the reaction, all the reactants are mixed simultaneously and irradiated continuously with US for 150 minutes. The kinetics of oxidation by US were followed by taking samples at regular intervals from 0-150 minutes, and analyzing using UV-Vis

Spectrophotometer (580 nm). The residual concentration of dye was deducted from calibration curve at wavelength of maximum absorbance (580-581 nm). The cells used were 1cm thick quartz. The same procedure was followed to study the kinetics of dye degradation for various frequencies (25, 40, 58, 68, 132, 58 + 192, 430, 470 kHz and 1 MHz) and at different power levels (250,400 and 500W). All the experiments have been done in duplicate and the shown data are averaged values between the trials.

C. Analytical procedures

The pH was measured using pH meter at regular intervals to ensure the optimum pH of 3. The UV-Vis spectra of MV solution were recorded from 400 nm to 650 nm using a spectrophotometer, showing maximum absorbance wavelength at 581 nm. The calibration curve obtained for different known concentrations of dye and their corresponding peak absorbances at wavelength of maximum absorbance (580-581 nm) was plotted. Thus, the concentration of MV with time can be determined by measuring the absorption intensity, and hence, concentrations from the calibration curve.

III. RESULTS AND DISCUSSION

A. Degradation characteristics: Effect of ultrasonic irradiation time

Fig. 3 shows the changes in the absorption spectra of Methylviolet degradation process under sonication. From the spectrum, it is clear that the color of the dye solution slowly fades with irradiation time. The absorption intensity at 581 nm is 2.0 initially, but it reaches 0.029 after 150 min sonication with 20 kHz probe. Also, it was observed that the solution turns pale/ transparent, confirming that azo bonds ($-N=N-$) are destroyed.

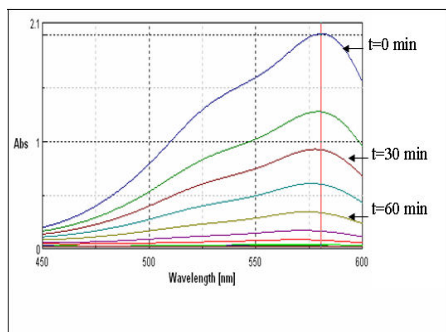


Fig. 3 Absorption spectrum of MV

B. Effect of Fenton's reagent

From Fig. 4, no decrease in concentration is evident for sonication without Fenton's reagent, whereas in presence of Fenton's reagent, the dye degradation is almost complete. This implies that in the presence of oxidizing agent, sufficient hydroxyl radicals are generated to decompose the dye. Since stirring or agitation is commonly used in waste water treatment,

stirring with Fenton reagent was experimented with at various rpm at room temperature, and used as a benchmark for comparison. The results show that degradation associated with stirring provides only slight improvement compared to control without stirrer.

These data validate the application of sonication in conjunction with Fenton's reagent, and this experiment was conducted at 25 kHz, 500W power. From the results, it is obvious that 'US+ Fenton's reagent' enhances the decolorization. This provides the incentive for further studies at various ultrasonic field settings to optimize the operating conditions.

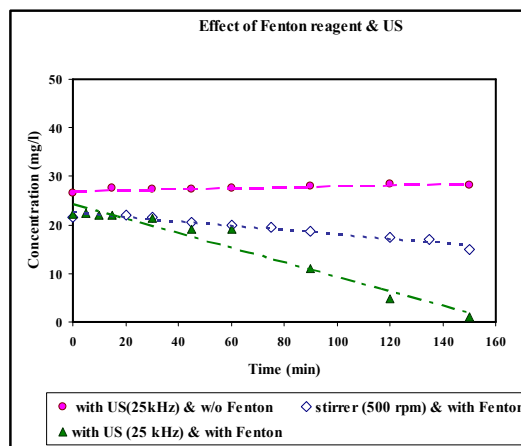


Fig.4 Effect of Fenton's reagent

C. Effect of temperature

The reaction between H_2O_2 and Fe^{2+} is seen to be affected by the temperature, and hence, the kinetics of dye degradation. Experiments were conducted for temperatures of $30^\circ C$ and $80^\circ C$. Fig. 5 illustrates that temperature has a significant effect on reaction rate. The initial 60 min of reaction show nearly the same kinetics for $30-60^\circ C$, but after an hour, the reaction yield is high at higher temperature as cited in [4]. Also, at $80^\circ C$, the decolorization activity is high from the initial period of the reaction, i.e., DA % is linear with time. Hence, for waste-water treatment, 65 % of decolorization can be achieved using $40-50^\circ C$, which may be considered as reasonable temperature range for dye degradation. Elevated temperature does enhance the degradation reaction. This implies that temperature rise during sonication will be an advantage for this kind of reaction. Further increase in temperature was not attempted, since published work [4] indicates that at relatively high temperatures, low yield may result due to the decomposition of H_2O_2 [$2H_2O_2 \rightarrow 2H_2O + O_2$]. As temperature associated with sonication varies with time, the reaction kinetics too vary accordingly.

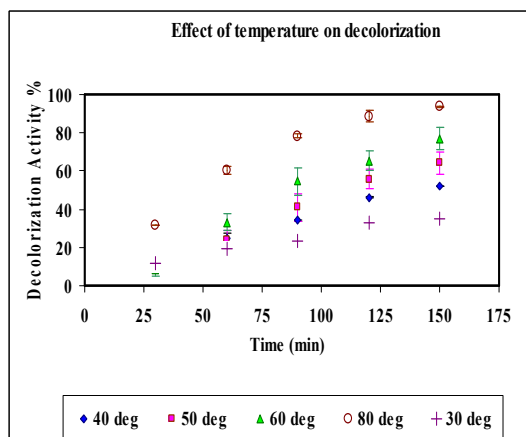


Fig. 5 Temperature effect on degradation of MV

D. Effect of power level

From Fig. 6, it is clear that higher the power, higher is the decolorization activity and hence the PIDA%. The enhanced degradation rate with increase in applied ultrasonic power (250, 400 and 500W) is due to the fact that the number of collapsing cavities increases with increase in power levels, thereby increasing the cavitation activity. There also exists a local high concentration of OH radicals at the interface of the collapsing bubble, which enhances the oxidative decomposition of dye at that region.

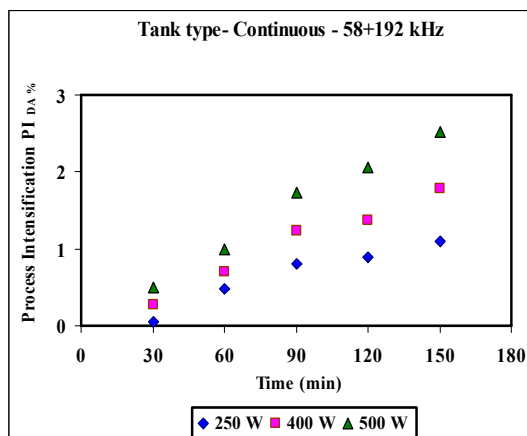


Fig. 6 Effect of power level on MV degradation

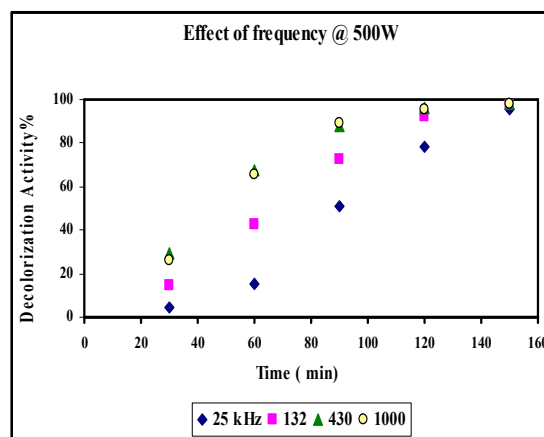


Fig.7 Effect of frequency on MV degradation

E. Effect of frequency

From Fig. 7, as frequency increases, the rate of decolorization is seen to increase and almost reach completion. Although the effect of frequency is a complex one associated with bubble formation and bubble dynamics, it is generally believed that higher frequency US may actually increase the number of free radicals in the system; even though the cavitation is less violent, there are more streaming events (due to higher number density of bubbles) and thus more opportunities for free radicals to be generated and transported, which contribute to an increase in degradation rate.

F. Effect of operation mode

Experiments were conducted in different modes in probe-type sonicator, i.e., continuous mode and pulsed mode (5min ON / 5 min OFF) for different input powers. The results shown in Fig. 8 indicate that decolorization is higher for pulsed mode than continuous for 250 and 400 W input power. Therefore, from an economical as well as effectiveness point of view, pulsed mode at low power will yield higher and more complete decolorization of dye at half the power. Higher degradation can be achieved at shorter duration, which is highly attractive for industrial applications.

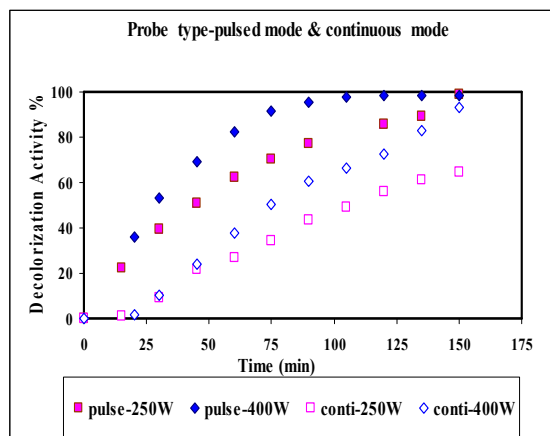


Fig. 8 Comparison between continuous and pulse mode at 20 kHz

G. Effect of tank and probe type

In general, probe-type sonicators have high localized intensity compared to tank-type and hence, greater localized effect as depicted in Fig. 9. The tank-type DA% is lower than probe-type for all input powers. Also, the 500W (higher power) of tank-type and 250 W (lower power) of probe-type show merged values for initial 30 minutes of reaction. However, after 90 mins, DA% of tank-type reaches higher value and coincides with probe-type 500W (higher power) at 150 mins. As the tank-type sonicators can process more volume of dye solution, nearly 10 times more than that of probe-type, it is more economical to use tank-type from practical point of view.

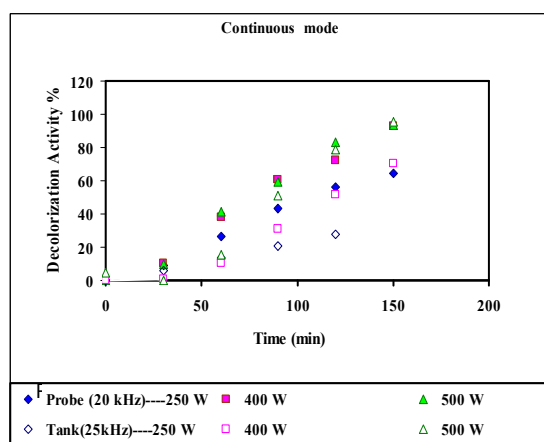


Fig. 9 Comparison between probe and tank type sonication

H. Repeatability

The experiments were repeated to build confidence on repeatability and reproducibility of the measurements. Each experiment was duplicated, and the average value plotted as the data. The spread in measured data is less than 5 %, which can be considered acceptable. A typical dual-frequency error bar chart is shown in Fig. 10.

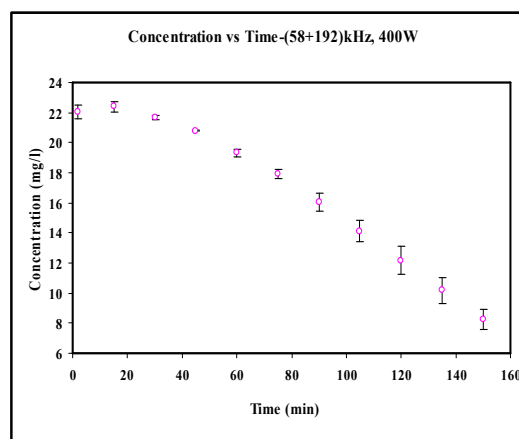


Fig. 10 Repeatability for dual frequency

IV. CONCLUSION

Dye degradation process is intensified in the reinforcing presence of oxidizing agent and ultrasound, resulting in complete decomposition of dye in less time compared to control and benchmark of mechanical agitation. MV degradation is temperature-dependent, and as temperature increases, reaction proceeds faster. The temperature-rise associated with sonication is therefore beneficial. In both tank-type and probe-type sonicators, for a given frequency, increase in power level increases the decomposition rate. This is due to an increase in the number density of cavitation bubbles and in associated implosion intensity. The associated rise in reaction rates of hydroxyl ion and dye at the bubble interface results in an enhancement of degradation. Higher frequencies also enhance sonochemical degradation as number density of bubbles formed increases. This, in turn, generates more hydroxyl radicals which help in azo decomposition. In probe-type, pulsed mode of operation proves to be more cost-effective than continuous. Though probe-type sonicator is more intense and effective in degradation, tank-type is preferred from scalability point of view as the volume treated per batch can be ten times higher compared to probe-type. Based on these initial results, ultrasonic intensification of dye degradation is worthy of further study, particularly with regard to scale-up.

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