Treatment of Synthetic Textile Wastewater Using Ultrasonication as Advanced Oxidation Process

Ayush Singh, Uttamkumar R. Tanwar, Vishal Kumar Sandhwar, Rohit Lade, Shivendu Saxena
Department of Chemical Engineering
Parul Institute of Technology, Vadodara, Gujarat, India,
aayushsingh502@gmail.com, uttamtanwar0603@gmail.com, vishal.sandhwar8850@paruluniversity.ac.in, rohit.lade8921@paruluniversity.ac.in, shivendu.saxena@gmail.com,

Abstract*: *Wastewater crisis is one of the major problems faced by the globe. A due rapid increase in industrialization the quantity of wastewater generation has been increased exponentially. Textile industries contribute a major role in waste generation. A report suggests that textile industries contribute 17 to 20 % wastewater of total wastewater. Congo red which possesses a complex structure is widely used in the textile industry as the anionic dye is used to perform experiments. Congo red solution of 20 ppm was prepared in a lab. Ultrasonic bath of 40 kHz is used to check the efficacy of cavitation effect on decolorization of dye solution at different parameters such as volume, power, and sonication time and pH variation. Significant decolorization was obtained at 50W power and maximum % removal of color was observed at sonication time 180 min. Hydrogen peroxide was also used along with sonication but no significant effect on decolorization was observed.

***Keywords*: Ultrasonication, wastewater treatment, advanced oxidation processes, Congo red.**

(***(Article history: Received: 6 th February 2021 and accepted 20 th March 2021)***

I. INTRODUCTION (*HEADING 1*)

The textile industry is one of the largest water-consuming and water-polluting industries as large amount of dyes is discharged in the waste stream. The textile industry and consequently its wastewater have been increased exponentially due to a rapid increase in demand. If these wastewaters are discharged to the environment without any treatment, these dyes can remain in the environment for an extended period due to their high stability to light and temperature. Dyes are natural or synthetic coloured organic compounds having the property of imparting their colours to other substances [1]. The presence of even very low concentrations of dyes (less than 1 ppm) in the effluent is highly undesirable. Depending on the exposure time and dye concentration, dyes can have acute and/or chronic effects on exposed organisms. They also affect the absorption and reflection of sunlight through water, reduce oxy-gen solubility and threaten the photosynthetic activity of aquatic plants and algae. The effect in a reduction in the oxygen levels interferes with the growth of bacteria such that they become inefficient in biologically degrading impurities in the water and hence the risk for the food chain.

There are various types of dyes used in textile industries which produce a high amount of wastewater. Approximately 10,000 commercially available dyes with over 7×10^5 tonnes of dyestuff are being produced annually across the world today. Synthetic dyes are used widely by various industries such as paper, textile, plastics, paints, food, printing, pharmaceuticals, etc. Colour their products that produce huge amounts of coloured wastewater annually. Amounting to the harmful nature of these effluents the discharge of these coloured effluents into the atmosphere has become a worldwide concern. Congo red is one such dye which is widely used in the textile industry due to its cheap cost and high ability imparting Colour to a substance. Congo red (CR) is a benzidine-based anionic diazo dye known to metabolize to benzidine, a known human carcinogen. Congo red (CR) is lethal to animals and plants and is therefore of potential health, and environmental and ecological concern when it is introduced into the water stream. CR containing effluents must, therefore, be treated efficiently before they are discharged into the bodies of water or the environment. Congo red dye degradation by cavitation is also an option for handling waste [1], [2].

There are different conventional strategies utilized for the treatment of material wastewater. Physical techniques, for example, coagulation-flocculation, and adsorption are utilized for the process. Coagulation technique is utilized for decolourization of wastewater having to scatter Color. This technique has low decolourization proficiency for receptive and tank kinds of Color. This method has confinement of producing resultant sludge. Adsorption is additionally utilized for decolourization of Color [3]. In any case, Adsorption through enacted carbon is considered as viable because of its high limit of concentration uptake per gram. Be that as it may, its trouble in recovery and significant expense constrains its application for decolourization of wastewater [4]. Natural strategy for treatment is additionally utilized for the treatment of material wastewater. There is diverse organic treatment strategy which incorporates Trickling channels, actuated ooze process, anaerobic and so forth biodegradation technique, for example, parasitic decolourization, microbial degradation are utilized in industry for treatment of profluent the same number of microscopic organisms, growths, yeast, green growth can debase distinctive toxin. Be that as it may, natural treatment requires an enormous land region and it is compelled towards the poisonousness of certain synthetic compounds just as diurnal variety and less adaptability in structure and activity. The natural procedures are not compelling in decolourization of material wastewater containing azo colours and numerous business Color are harmful to life form and result in the issue of sludge bulking, rising sludge

and pin flock. The other strategy for the treatment of material wastewater is advance oxidation process (AOPs) which incorporates ozonation, ultrasonication treatment and so forth [5], [6]. In AOPs essentially hydroxyl radical is created which helps in degradation and decolourization of wastewater. Cavitation through ultrasonication is a decent option for treatment of wastewater since it doesn't produce slime after the procedure, likewise, no poisonous result is framed from it and not at all like natural treatment, it does not require the large region to work. There are two sorts of cavitation in sonication as hydrodynamic and acoustic cavitation.

Hydrodynamic cavitation takes place by the sudden pressure difference in solution. Acoustic cavitation takes place by passing high frequency into the solution [7]. In water sonolysis comprising hydrophilic compounds such as textile dye, hydroxyl radical is only generated by water fragmentation in the collapsing bubbles, and destruction of oxidative dye is possible if radicals are effectively dragged into the bulk solution. The efficiency of $^{\bullet}OH$ diffusion depends on system parameters such as reaction time, frequency, presence of cavitation nuclei and ambient condition[8]–[10]. Acoustic cavitation is passing frequency greater than 20 kHz into the aqueous medium. Here a frequency of 40 kHz is passed through the effluent. In the present study, an attempt has been made to employ ultrasonic cavitation for degradation/decolorization of Congo red dye which is widely used in the textile industry and to observe the effect of initial concentration, reaction time and volume of effluent on decolorization.

II. MATERIALS AND METHODS

A. *Materials*

Congo red dye (CR) (C I Number 22120; 696.68 g/mol) dye of company Mayur dye chem was obtained. The stock solution of Congo red was prepared in distilled water. For experimental run hydrochloric acid (HCl) of 37% w/v and sodium hydroxide (NaOH) of 4%, w/v from Aditya Birla Chemicals India was used. Hydrogen peroxide (H_2O_2) of 6% w/v was also used as an oxidizing agent. Ultrasonic bath with a capacity of 600ml, frequency 40 kHz and operating power of 30 W, 50 W of DADI model was used. Phenolphthalein indicator of 1% w/v is used in the titration process.

B. *Experimental setup*

The experimental setup shown in Fig 1 & 2, for treatment of synthetic wastewater treatment was prepared using 1 collection tank, sonication unit, water pump, filter unit and tank for treated water. Initially, plywood is used for the base of the setup and a stand is made on which wastewater collection tank is placed then a pipe is connected to tank through which waste sample supplied to sonication tank, then treatment of solution is done in sonication unit. A pump is connected in sonication unit such that treated water is sent to filter unit which consist layer of pebbles, fine sand and activated carbon and finally, the treated water is obtained in final collection tank after filtration.

C. *Experimental Methodology*

Initially, the stock solution was prepared using Congo red dye and water as shown in Fig. 3. Stock solution of 1000 ppm was prepared by mixing 1 gm of Congo red dye in 1000 ml water then samples of 20 ppm are prepared from stock solution. The pH of the samples is measured using pH meter, which is around of 5.6. Ultrasonic bath of DADI model is used with a working volume of 500 ml. Effect of acoustic cavitation is observed on the Congo red solution and treated water was obtained in the beaker.

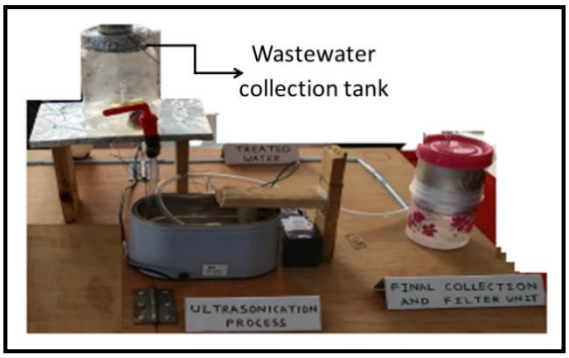

Fig. 1: Experimental setup

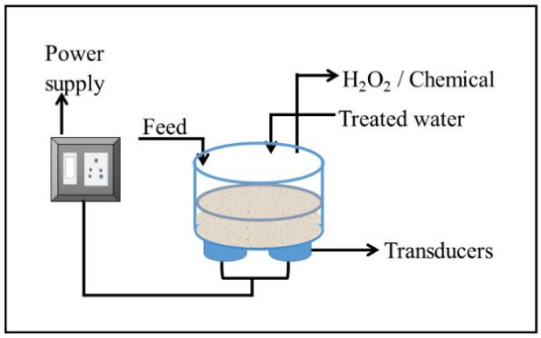

Fig. 2: Schematic diagram of experimental setup

Fig. 3 stock solution and sample of 20 ppm of CR dye

a) Acoustic Cavitation

Initially, 100 ml of Congo red solution was taken in an ultrasonic bath for a treatment time of 10 minutes to observe concentration change. A frequency of 40 kHz was passed through the solution with a power of 30 & 50 W due which the cavitation process takes place in solution. Cavitation generation which takes place by passing high frequency (>16 KHz) in solution is known as acoustic Cavitation. In the cavitation process, high temperature around ~5000k is generated for Pico seconds and high pressure of ~1000 bar is also generated due to which effective degradation takes place. In experiment hydrogen peroxide was used as an additive to generate higher $^{\bullet}OH$ radicals in the solution.

Samples were taken at an interval time of 30 minutes; the last sample was taken a time of 210 minutes. Several experiments were conducted on different parameter as A. Effect of pH B. volume vs. time C. effect of concentration of different power outage D. concentration vs. time. Different results were obtained from these experiments.

b) Analytical procedure

Initially, pH measurement was using a pH meter. The concentration of the solution after the treatment was measured by titration method. Titration equipment was used in the lab and concentration calculation was done using the basic formula of $N_1V_1 = N_2V_2$. Normality of the treated sample is first calculated using this formula then the value of normality is multiplied by 1000 to obtain a concentration in mg/lt. For sample collection the Congo red solution was treated in sonicator at a time interval of 30 minutes then the sample was collected after that pH measurement was done. This sample collected was then titrated with sodium hydroxide of 0.1N because after treatment pH of the treated solution was 6. Concentration vs. % removal graph is plotted.

III. Result and Discussion

A. *Effect of sonication on different volume of solution.*

First we examine the effect of sonication on different volume. For this, four different volumes such as 50, 100, 150, and 200 were used at fixed parameters i.e. constant power, constant time, and constant concentration. Fig. 4 represent the effect of volume variation on CR removal using ultrasonication. However, the data of this experiment is given in Table 1. It is observed from the figure that with increase in volume from 50 to 100 ml the removal of CR dye increases whereas further increase in volume from 100 ml to 200 ml, the removal of CR dye decreases. At low volume of sample, the effect of sonication is not that effective. It may be due to the formation of cavity cloud, which decreases the efficacy of hydroxyl radicals to degrade the dye molecules. Similarly, at higher volume, the generation of hydroxyl radicals in per unit volume as compared to 100 ml may be less, which reduces the efficacy of ultrasonication to degrade CR molecule. According to experimental data of treatment based on volume variation a significant change in % removal was observed in 100 ml sample, therefor the optimum volume for treatment of solution is taken as 100 ml.

B. *Effect of initial dye concentration*

The effect of initial dye concentrations on the sonolytic degradation rate of Congo red was investigated at temperature 25°C and pH 5.6 of aqueous media. In order to understand the effect of sonication time on CR removal from dye solution, the 100 ml of 20 ppm solution was subjected to ultrasonication at different time interval in the range of 30 to 210 minutes. Fig. 5 shows the initial concentration vs. percentage (%) removal. The data observed between the residual concentration and % CR removal with respect to sonication time is presented in Table 2. It is observed that maximum content removal was done at sonication time 180 min. There was a significant increase in content removal in the range of 30 to 120 minutes. The energy input required here for more content removal is not much efficient. However, further research work is required to optimize the process so that in less sonication time maximum removal can be obtained. It is evident from the figure that there is slightly increase in percentage (%) CR removal after 150 min. As we can observe from the figure that after 180 minutes the graph seems to be in steady state and there is no significant change in % CR removal. Therefore 180 minutes are optimum time for the treatment and used for further experiment. A similar type of result was obtained in experiments mentioned in research paper by Mardikar et al. [10]. According to their work, with increasing initial concentration the degradation rate is decreases constantly i.e. more initial concentration can decrease the degradation rate of a solution.

TABLE **1** Effect of volume variation on CR removal

Volume (ml)	Residual concentration(mg/l)	% Removal
50	15.9	20.5
100	10.4	48
150	11.1	44.5
200	12.4	38

(Experimental conditions: initial pH = 5.6, Sonication Time = 180 min, Initial concentration=20 mg/l)

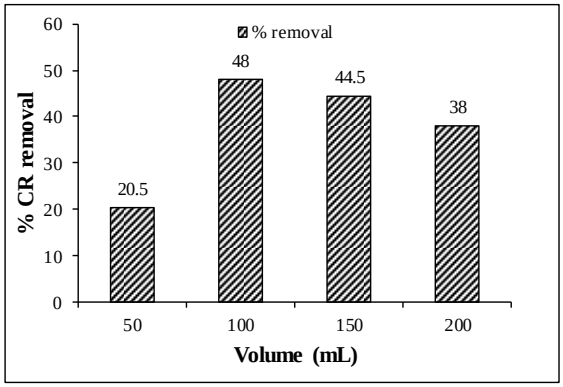

Fig. 4 Effect of volume on % CR removal

TABLE **2.** Effect of sonication time on degradation of CR

Sonication time (min)	Residual concentration (mg/L)	% Removal
0	20	0
30	18.6	7
60	15.4	23
90	12.2	39
120	9.8	51
150	7.2	64
180	6.1	69.5
210	6.0	70

(Experimental conditions: initial pH =5.6, Volume = 100ml, Time interval = 30 min. interval, Initial concentration = 20mg/l.)

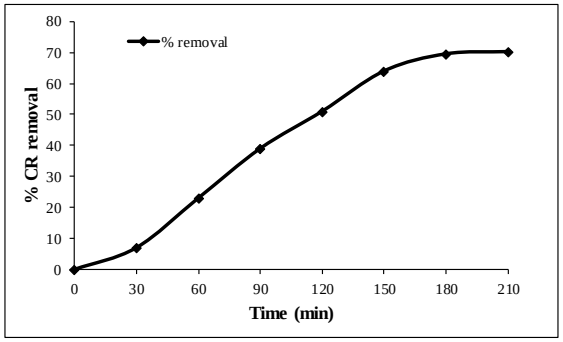

Fig.5 Initial concentration vs. % Removal

Fig. 6 Samples before and after treatment

TABLE 3 Effect of power variation

Power (W)	Residual Concentration (mg/l)	% Removal
30	8.6	57
50	7.2	64

(Experimental conditions: initial pH = 5.6, Volume = 100ml, sonication Time = 180 min. initial concentration = 20 mg/l.)

C. Effect on concentration of different power output

To determine the effect of different power output, two power output were used 30W and 50W in this study. For power variation, we fix three parameters i.e. fixed volume, fixed concentration, and fixed time. Table 3 shows the observed data for both power output and 180 minutes treatment time. As per treatment the final concentrations obtained at 30W is 8.6 mg/lit and at 50W is 7.2 mg/lit. It is observed from the obtained result that with increasing power output percentages (%) removal of CR increases. Maximum 64% removal of CR from dye solution was observed at 50W power output. According to Hossein et al. [1], the expanded number of air bubbles and intense conditions in the cavitation procedure at high power improve the impact on a surface level and mass exchange. Therefore, power output is also a key factor for degradation of congo red solution.

D. Effect of pH

In general, it is observed that the pH values markedly influence the degradation of organic pollutants. In this article, the effect of the initial pH values of the aqueous solution on the sono-chemical degradation rate of Congo red was investigated at different pH in the range of 2.0 - 12.0 with initial dye concentration 20 mg/L and temperature 25±2°C as shown in Table 4. The results we observed, indicate that the ultrasonic degradation rate constants in acidic water (pH 2.0-3.0) and higher than those obtained in neutral aqueous solutions (pH 6.0- 8.0), and much higher in basic medium (10.0-12.0). According to Mardikar et al. [2], both high acidic and high basic conditions are favorable to ultrasonic degradation of Congo red. Fig 7 shows the graph between pH & % CR Removal. It is observed from the graph that for higher acidic and basic condition the % removal of CR is more effective compared to moderate pH value.

TABLE 4 Effect of pH

pH	Residual Concentration	% Removal
2	12.4	38
4	11.2	44
6	16.9	15.5
8	15.6	22
10	11.8	41
12	10.2	49

(Experimental conditions: volume = 100 ml, sonication time = 180 min. for each pH value, initial concentration = 20 mg/l.)

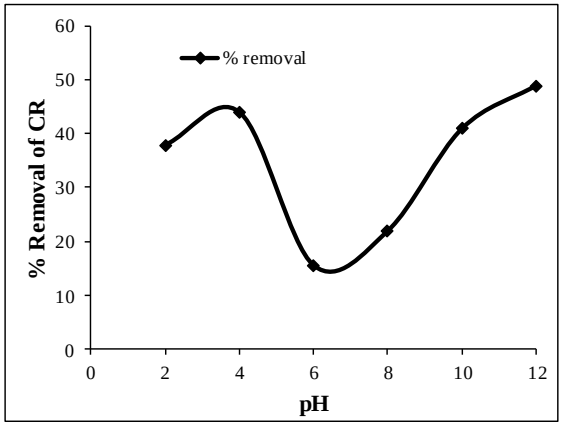

Fig 7: Graph between pH & % CR Removal

IV. Conclusion

In this paper, we studied the cavitation effect on Congo red solution of 20 ppm. In this work, acoustic cavitation is generated by sonicator of 40 KHz frequency. It is observed that the maximum decolorization of 69.5% was obtained at sonication time 180 min. Moreover, experiment on two different outputs were conducted. It is observed from this experiment that more power output gives more decolorization. Volume variation experiments were

conducted on four different volumes. It is observed that low volume treatment gives the high treatment efficiency conducted on different pH. Moreover, both high acidic and high basic conditions are favorable for ultrasonication degradation of Congo red dye. However for making process economically effective further research and optimization is needed. Further research can be conducted for higher volume of effluent.

ACKNOWLEDGMENT

The authors are thankful to Parul Institute of Technology, Vadodara, Gujarat, India, for providing conception.

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AUTHOR PROFILE

	**Ayush Singh** Student, Department of Chemical Engineering, Parul Institute of Technology, Parul University, Vadodara, India Specialization: Chemical Engineering B.Tech. in Chemical Engineering
	**Uttamkumar R. Tanwar** Student, Department of Chemical Engineering, Parul Institute of Technology, Parul University, Vadodara, India Specialization: Chemical Engineering B.Tech. in Chemical Engineering
	**Dr. Vishal Sandhwar** Assistant Professor, Department of Chemical Engineering, Parul Institute of Technology, Parul University, Vadodara, India Specialization: Chemical Engineering Experience:2.5 years 7 SCI publications B.Tech., M.Tech., Ph.D. in Chemical Engineering
	**Dr. Rohit Lade** Assistant Professor, Department of Chemical Engineering, Parul Institute of Technology, Parul University, Vadodara, India. Specialization: Chemical Engineering Experience:1.5 years 5 SCI publications B.Tech., M.Tech., Ph.D. in Chemical Engineering
	**Dr. Shivendu Saxena** Assistant Professor, Department of Chemical Engineering, Parul Institute of Technology, Parul University, Vadodara, India. Specialization: Chemical Engineering Experience:3 years 4 SCI publications B. Tech., M. Tech., Ph.D. in Chemical Engineering