



## Degradation of Reactive Red 120 dye using hydrodynamic cavitation

Virendra Kumar Saharan, Mandar P. Badve, Aniruddha B. Pandit\*

Chemical Engineering Department, Institute of Chemical Technology, Mumbai 400019, India

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### ABSTRACT

In the present work, degradation of Reactive Red 120 dye (RR120) has been carried out using hydrodynamic cavitation (HC) one of the upcoming advance oxidation techniques (AOPs). The effect of various operating parameters such as inlet fluid pressure, cavitation number, solution pH and addition of  $H_2O_2$  as a supplementary oxidizing agent on the degradation rates were studied. The cavitation device used in this study has been optimized in terms of inlet fluid pressure and cavitation number. The photographic study was carried out to analyze the cavity behavior inside a transparent venturi. The degradation of RR120 was found to be dependent on the solution pH and higher degradation was achieved in acidic medium and addition of  $H_2O_2$  further enhances the degradation rate.

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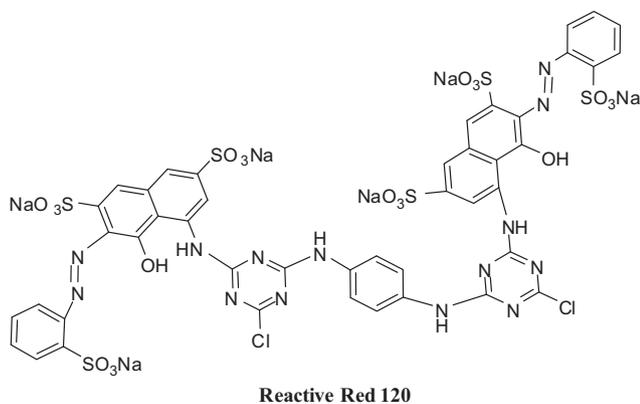
### 1. Introduction

Waste water from the textile industry containing dyes causes serious environmental problem due to their intense color and potential toxicity. About 10–20% of the total dyestuff used in the dyeing process is released into the environment [1,2]. The waste water containing colored solution is the source of aesthetic pollution, eutrophication, and perturbations in aquatic life essentially due to their organic nature. Among all types of dye used in the textile and paper industry around 50–70% dyes are of Azo class [2–5]. These dyes are resistant to degradation by biological treatment methods and in fact introduce toxicity to the microbes and can be converted to hazardous by-products through oxidation, hydrolysis, or other chemical reactions taking place in the wastewater itself [1]. So these effluents need to be treated before their discharge into the environment. In the past few years many researchers have tried different methods for the degradation of textile dyes. These include carbon bed adsorption, biological methods, oxidation using chlorination and ozonation, electrochemical methods, membrane processes and other advanced oxidation techniques [6,7]. In last decade a new technology called as hydrodynamic cavitation (HC) has been extensively studied by many researchers in the area of waste water treatment because this technique is energy efficient and also easy to scale up to industrial scale [8–11]. In hydrodynamic cavitation, cavities are formed by passing the liquid through the constriction/geometry provided in line such as venturi, orifice plate. When the pressure at the throat or vena-contracta of the

constriction falls below the vapor pressure of the liquid, the liquid flashes, generating number of cavities that subsequently collapse when the pressure recovers downstream of the mechanical constriction. The effects of cavity collapse are in terms of creation of hot spots, releasing highly reactive free radicals, surface cleaning and/or erosion, and enhancement in local transport (heat, mass and momentum) rates. The collapse of bubbles, generates localized “hot spots” with transient temperature of the order of 10,000 K, and pressures of about 1000 atm [12]. Under such extreme conditions water molecules are dissociated into  $OH^\bullet$  and  $H^\bullet$  radicals. These  $OH^\bullet$  radicals then diffuse into the bulk liquid medium where they react with organic pollutants and oxidize/mineralize them. The two main mechanisms for the degradation of pollutants using hydrodynamic cavitation are the thermal decomposition/pyrolysis of the volatile pollutant molecules entrapped inside the cavity during the collapse of the cavity and secondly, the reaction of  $OH^\bullet$  radicals with the pollutant occurring at the cavity–water interface. In the case of non volatile pollutant the main mechanism for the degradation of pollutants will be the attack of hydroxyl radicals on the pollutant molecules at the cavity–water interface and in the bulk fluid medium. The mechanical effects are also significant. In some cases the intensity of shockwaves generated by the collapsing cavity can break molecular bonds, especially the complex large molecular weight compounds. The broken down intermediates are more amenable to  $OH^\bullet$  attack as well as biological oxidation, which can further enhance the rate of oxidation/mineralization of the pollutants.

In the present work the degradation of Reactive Red 120 dye (RR120) has been carried out using self designed hydrodynamic cavitation set-up and also the effect of solution pH and addition of  $H_2O_2$  on the degradation rate has been studied. In this study,

\* Corresponding author. Tel.: +91 22 3361 2012; fax: +91 22 3361 1020.  
E-mail address: [ab.pandit@ictmumbai.edu.in](mailto:ab.pandit@ictmumbai.edu.in) (A.B. Pandit).



**Fig. 1.** Molecular structure of Reactive Red 120.

two important operating parameters (inlet pressure and cavitation number) for a cavitation device have been optimized in order to get maximum cavitation effects. The photographic study was also carried out to observe the cavity behavior inside the cavitation device (venturi), which offers a plausible explanation to the observation of the optimum operating conditions.

## 2. Materials and methods

### 2.1. Materials

Reactive Red 120 dye (molecular weight: 1470 g/mol; molecular formula:  $C_{44}H_{24}Cl_2N_{14}Na_6O_{20}S_6$ ) was a gift sample from ATUL Limited India, and hydrogen peroxide was purchased from S.D. Fine Chemicals (India). The chemical structure of Reactive Red 120 dye is shown in Fig. 1. The experiments were carried out within the temperature range of 30–35°C. All the solutions were prepared with tap water as a dissolution medium. The concentration of dye was

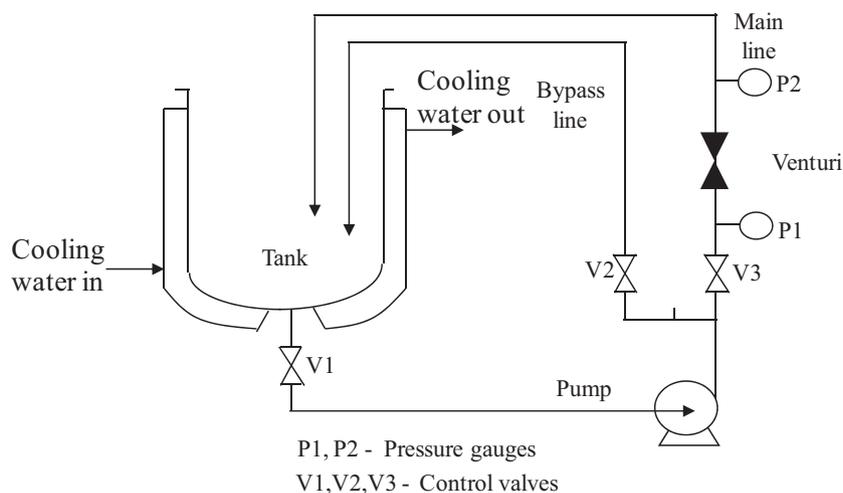
kept constant in all the cases at 34  $\mu$ M (50 ppm). The concentration range of  $H_2O_2$  was kept in the range of 0–3400  $\mu$ M and added externally.

### 2.2. Hydrodynamic cavitation reactor

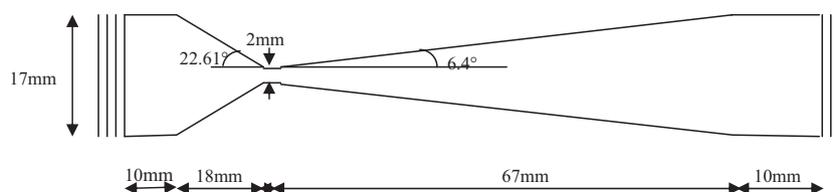
The experimental setup is shown in Fig. 2. The setup includes a holding tank of 15 l volume, a positive displacement pump of power rating 1.1 kW, control valves (V1, V2, and V3), and flanges to accommodate the cavitating device in the main line and a bypass line to control the flow through the main line. The suction side of the pump is connected to the bottom of the tank and the discharge from the pump branches into two lines; the main line and a bypass line. The main line consists of a flange which houses the cavitating device which can be either orifice or a venturi. The main line flow rate was adjusted by changing the number of piston strokes per unit time of the pump, which affects the total flow generated. Additionally, a valve is also provided in the bypass line to control the liquid flow through the main line. Both the mainline and bypass line terminate well inside the tank below the liquid level to avoid any induction of air into the liquid due to the falling liquid jet. Fig. 3 shows one of the cavitating device (venturi) used in this work. Two different types of materials were used in the fabrication of venturi. A transparent venturi made-up from acrylic was used for the photographic study and a metal venturi made-up from brass was used for the rest of the experiments.

### 2.3. Experimental and analytical methods

Hydrodynamic cavitation based degradation of RR120 was carried out at different conditions using fixed solution volume of 6 l and for a constant circulation time of 3 h. The initial concentration of RR120 was kept constant in all the cases at 34  $\mu$ M (50 ppm). The temperature of the solution during experiments was kept constant in all the cases at about 35°C and was maintained by circulating



**Fig. 2.** Schematic representation of hydrodynamic cavitation reactor set-up.



**Fig. 3.** Schematic of venturi.

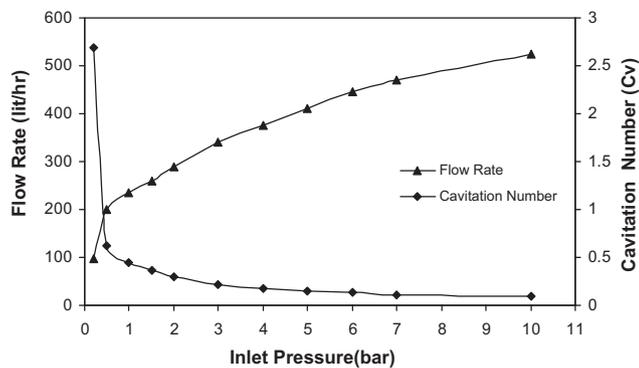


Fig. 4. Effect of inlet pressure on the main line flow rate and cavitation number ( $C_v$ ).

cooling water through the jacket provided to the holding tank. The photographs were taken using digital camera (Canon EOS 1000D model). The shutter speed was kept 1/2600 s as it was found to be adequate to capture the fast moving cavity and also gave adequate illumination. The absorbance of RR120 was monitored using UV-Spectrophotometer (Shimadzu-1800) and then the concentration of dye was calculated by analyzing the absorbance of dye solution at the wavelength of 513 nm. The complete mineralization was analyzed by measuring the Total Organic Carbon (TOC) content of dye solution using TOC analyzer (ANATOC II, SGE International Pty Ltd., Australia).

### 3. Results and discussion

#### 3.1. Hydraulic characteristics

The hydraulic characteristics of the cavitating device (venturi) has been studied by measuring the main line flow rate and by using a dimensionless parameter called as cavitation number ( $C_v$ ). The inlet pressure to the venturi as well as flow through the main line was adjusted by changing the number of piston strokes per unit time. The cavitation number is a dimensionless number used to characterize the condition of cavitation in hydraulic devices [12,13]. The cavitation number is defined as

$$C_v = \left( \frac{p_2 - p_v}{(1/2)\rho v_o^2} \right) \quad (1)$$

where  $p_2$  is the fully recovered downstream pressure,  $p_v$  is the vapor pressure of the liquid,  $v_o$  is the velocity at the throat of the cavitating constriction which can be calculated by knowing the main line flow rate and diameter of the venturi or orifice. Under ideal condition cavities are generated at a condition  $C_v \leq 1$  but in many cases cavities are known to get generated at a value of  $C_v$  greater than one due to the presence of some dissolved gases and suspended particles which provide additional nuclei for the cavities to form [13]. The cavitation number at which first cavity appears is called cavity inception number ( $C_{vi}$ ). Fig. 4 shows the effect of the pump discharge pressure (venturi inlet pressure) on the main line flow rate and cavitation number. The liquid flow rate through the main line increases with an increase in the pump discharge pressure. It was found that cavitation number decreases with an increase in inlet pressure to the venturi. An increase in the discharge pressure increases the flow through the main line, the velocity at the throat of the venturi also increases, which subsequently reduces the cavitation number as per the definition of  $C_v$ . The number of cavities generated increases with a decrease in cavitation number i.e. with an increase in the liquid velocity. Yan and Thorpe [14] reported the cavitation number for the inception of

cavity for different orifice sizes. They observed that for a given size orifice, the cavitation inception number remains constant within a experimental error for a specified liquid. The cavitation inception number does not change with the liquid velocity and is a constant for a given orifice size and is found to be increasing with an increasing size and dimension of the orifice. Moholkar and Pandit [15] have discussed this observation in terms of increased turbulent fluctuating velocity magnitude and its variation with the orifice dimensions.

#### 3.2. Photographic analysis of cavitating device

To study the cavitation behavior inside a cavitating device (venturi) photographs were taken at different venturi inlet pressures (Fig. 5a–f). The inlet pressure to the venturi was gradually increased from the lowest possible inlet pressure until some very small bubbles (cavities) could be seen intermittently. These bubbles seemed to form at the throat of venturi and were seen at the edge (perimeter) of the venturi and just downstream of the throat of venturi. This condition was defined as cavitation inception, i.e. the first cavitation bubble formation (Fig. 5a,  $C_v = 0.45$ ). It was observed that with an increase in the venturi inlet pressure (reduction in  $C_v$ ) the number density of cavities increases. As the venturi inlet pressure increases cavitation number decreases and with the decrease in cavitation number more number of cavities are formed (Fig. 5a–c). Initially at lower pressure the number density of cavities are low and these cavities behave as individual cavities and they collapse as soon as they come out on the downstream of the venturi. No cavity cloud was observed up to 5 bar venturi inlet pressure ( $C_v = 0.15$ ) as till this value of the inlet pressure the volume fraction occupied by the cavity is quite low and each cavity tends to behave individually. At the operating condition of inlet pressure of higher than 5 bar, number density of cavities becomes so high that entire downstream area is filled with cavities and these cavities then start coalescing with each other and form a cavity cloud (Fig. 5d–f). The first clear cavity cloud was observed at 6 bar pressure ( $C_v = 0.13$ ) and with further increase in inlet pressure almost entire downstream area is filled with cavity cloud. The condition of cavity cloud formation is called choked cavitation [16]. Once choking occurs, a thick vaporous cavity cloud is detected throughout the downstream of the venturi and length of the cavitation cloud zone extends further downstream from the throat of the venturi with further increase in pressure. Yan and Thorpe [14] have shown both experimental and theoretical aspects of this flow regime transitions caused by cavitation when water is passing through an orifice. They have shown that how the transition occurs from single-phase to two-phase bubbly flow (cavitation inception) and then from two-phase bubbly flow (cavitation inception) to two-phase annular jet (central liquid core covered by annular vapor cloud) flow (choked cavitation). They have calculated the cavitation inception number experimentally and have shown that the cavitation number at inception is independent of the liquid velocity but strongly dependent on the size and shape of the geometry. Hence cavitation inception number does not change with the liquid velocity and is a constant for a given orifice plate. They have also explained that the minimum pressure at which cavitation inception occurs was found to be well above the vapor pressure and the formation of the small bubbles (cavities) at cavitation inception number is due to desorption of gas upon pressure reduction. Yan and Thorpe have also developed a correlation for the cavitation number at which choked cavitation occurs and found good agreement between experimental and theoretical value. The cavitation number at the choked cavitation is a function of the ratio of orifice diameter to the pipe diameter only. They have measured the pressure at the vena contracta and found out that choked cavitation occurs when the minimum pressure (pressure at the throat or vena contracta) approaches the vapor pressure

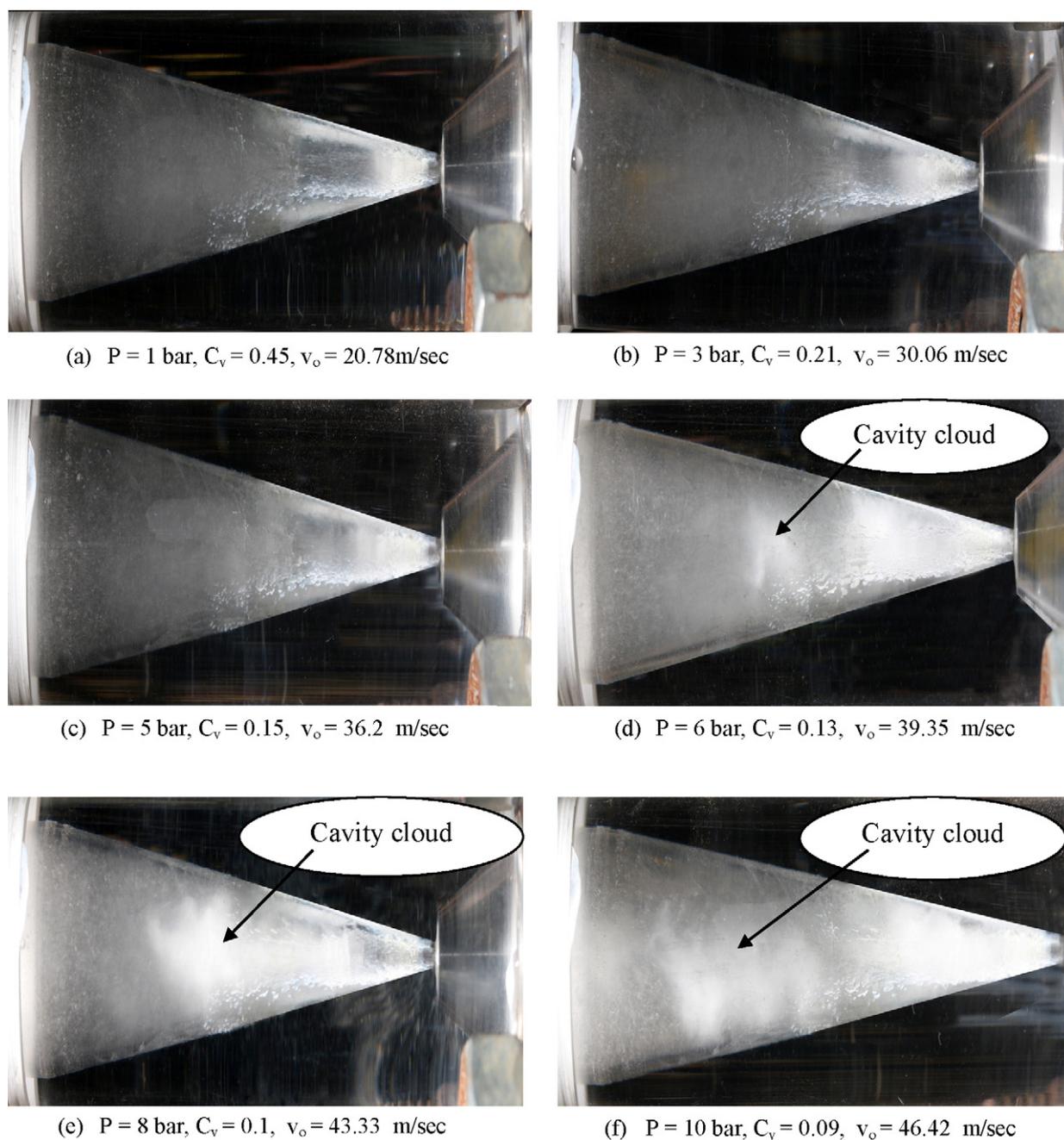


Fig. 5. Photographs showing the development of cavities downstream of the venturi.

and vaporization of the liquid becomes dominant at choked cavitation.

### 3.3. Dye degradation kinetics

In the case of hydrodynamic cavitation, the degradation of dye is due to the oxidation of dye molecules by  $\text{OH}^\bullet$  radical attack and/or by the thermal decomposition of dye molecules entrapped inside the collapsing cavity. As mentioned earlier, in the case of non volatile compound the main mechanism for the destruction of pollutant is the attack of  $\text{OH}^\bullet$  radicals on the pollutant molecules and most investigators [17–21] have observed that it follows the first order kinetics.

To correlate the observed data, pseudo first order kinetics was assumed and rate constants for the decolorisation as well as for the

mineralization process were calculated using the following equation.

$$\ln\left(\frac{C_0}{C}\right) = k \times t \quad (2)$$

where  $C$  is the concentration of dye in mol/l,  $k$  is the rate constant ( $\text{min}^{-1}$ ) and  $t$  is the time in minutes.

Fig. 6 shows the plot of  $\ln(C_0/C)$  vs time ( $t$ ). The plot of  $\ln(C_0/C)$  vs time ( $t$ ) is a straight line passing through the origin, which confirms that the degradation of RR120 using hydrodynamic cavitation showing a first order reaction kinetics.

### 3.4. Effect of inlet pressure

The venturi inlet pressure affects the cavitation condition inside the cavitating device. The number of cavities being

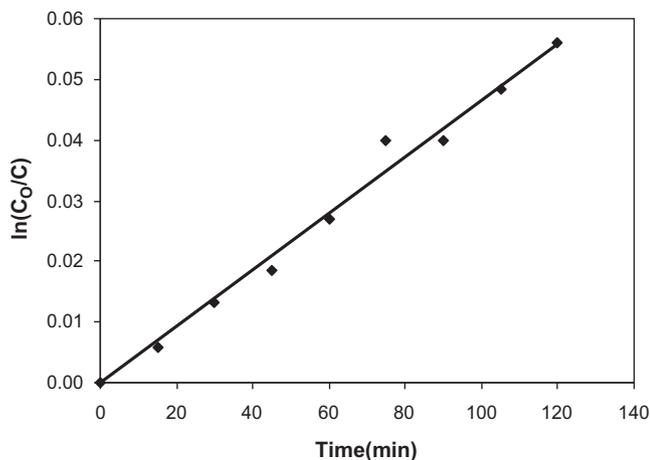


Fig. 6. First order degradation of RR120 (conditions: volume of solution: 6l, inlet pressure: 3 bar, initial concentration: 34  $\mu$ M, pH of solution: 7.3).

generated and the cavitation intensity (collapse pressure magnitude) depends very much on the inlet pressure. To study the effect of the venturi inlet pressure on the degradation of RR120, experiments were carried out at different inlet pressure ranging from 3 to 10 bar. The initial concentration of dye and pH was adjusted at 34  $\mu$ M and 7.3 respectively. Fig. 7 shows the effect of inlet pressure on the degradation rate of RR120. It was observed that the degradation rate increases with an increase in the inlet pressure reaching a maximum (5 bar) and then drops. The local energy dissipation rate and the intensity of turbulence increase with an increase in the inlet pressure, thereby increasing the collapse intensity. The increase in cavitation intensity results into increased degradation rate of dye. The reduction in degradation rate beyond 5 bar inlet pressure can be attributed to the condition of choked cavitation as discussed earlier. As the pressure increases, more number of cavities are formed resulting into the formation of vapor cloud, thereby decreasing the collapse pressure or intensity of the cavitation collapse event and hence the extent of the degradation of the dye. The photographic study of venturi also depicts a similar trend that at a operating condition of pressure higher than 5 bar, choked cavitation occurs (see Fig. 5c–f) which is also in accordance with the optimum (highest degradation kinetic rate constant) found by experimental analysis. Sawant et al. [16] have studied the effect of hydrodynamic cavitation on killing of zooplankton. They have observed that at choked cavitation number condition, very large numbers of cavities are generated. Such a large number of cavities tend to damp the energy

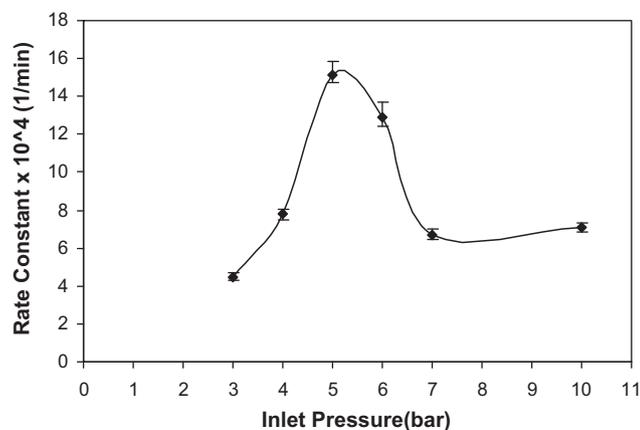


Fig. 7. Effect of inlet pressure on degradation rate of RR120 (conditions: volume of solution: 6l, initial concentration: 34  $\mu$ M, pH of solution: 7.3).

released by the neighboring cavity collapse. Thus, the net energy available for cell disruption decreases and the zooplankton killing rate reduces. Hence cavitation device should always be operated at a cavitation number higher than choked cavitation number as it generates maximum cavitation intensity and cavities collapse individually, giving the most effective energy utilization.

Senthilkumar and Pandit [22] have also shown that with an increase in the venturi inlet pressure the pressure drop across the venturi also increases, resulting in an increase in the cluster collapse pressure. They have also found that the cluster collapse pressure or the cavitation intensity increase with an increase in the inlet pressure reaching to the maximum and then decreases for the reason specified above. The observation earlier reported in Fig. 8 is consistent with the above discussion and earlier similar observations.

### 3.5. Effect of cavitation number ( $C_v$ )

Fig. 8 shows the effect of cavitation number on degradation of RR120. It was observed that the rate of degradation increases with a reduction in cavitation number, reaches a maximum and then drops. The maximum degradation rate was achieved at a cavitation number of 0.15 (achieved at an operating pressure of 5 bar). As the cavitation number decreases, more number of cavities are generated [23]. The increase in the number of cavitation collapse pressure pulses and  $\text{OH}^\bullet$  radicals thus generated also increase, resulting into an increased degradation rate. The degradation rate decreases with further decrease in cavitation number ( $C_v < 0.15$ ). This may be because of reduced cavitation intensity due to excess numbers of cavities inside the venturi at very low cavitation number. Once the cavitation device is completely filled with a lot of cavities (choked cavitation) these cavities start coalescing to form a larger cavitation bubble (cavity cloud). These larger bubbles escape the liquid without collapsing or result into an incomplete collapse, thus reducing the cavitation yield (reduced degradation rate after  $C_v < 0.15$ ) in terms of the reduced generation of  $\text{OH}^\bullet$  radicals. Where, the cavitation yield can be defined as number of molecules degraded per unit energy dissipated. Senthilkumar et al. [24] have carried out decomposition of aqueous KI solution using hydrodynamic cavitation. They have shown that iodine liberation increases with a decrease in cavitation number, reaches to the maximum and then drops. The optimum cavitation number found in their work was in the range of 0.15–0.25 for all the orifice plates studied in their work, which is similar to the optimum found in our work using venturi.

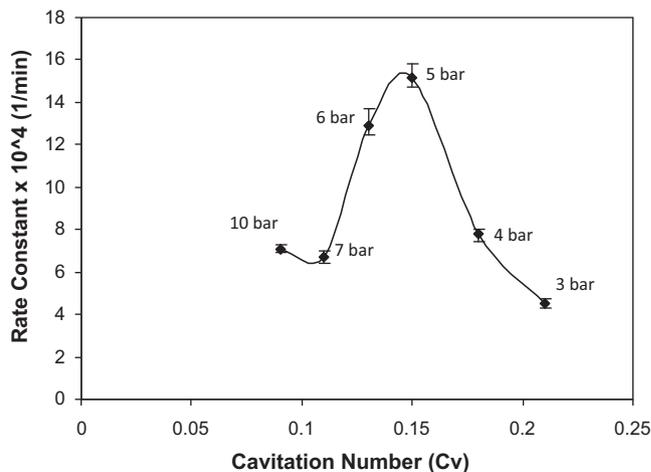
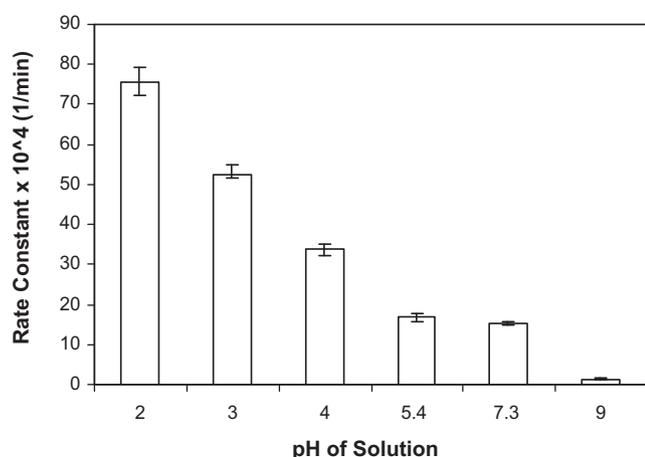


Fig. 8. Effect of cavitation number on degradation rate of RR120 (conditions: volume of solution: 6l, initial concentration: 34  $\mu$ M, pH of solution: 7.3).



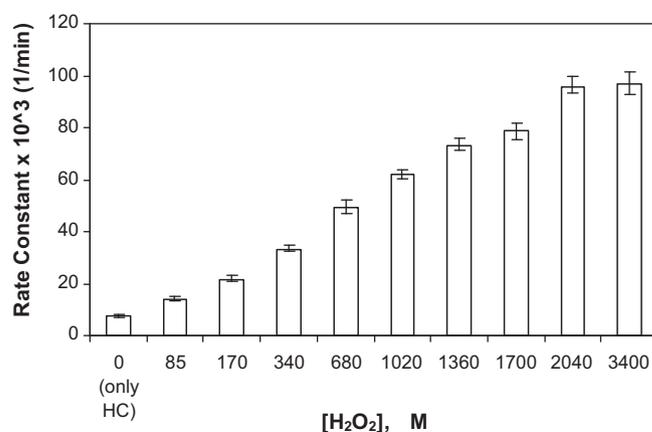
**Fig. 9.** Effect of solution pH on degradation rate of RR120 (conditions: volume of solution: 6 l, initial concentration: 34  $\mu$ M, inlet pressure: 5 bar).

### 3.6. Effect of pH

The effect of medium pH was investigated by carrying out experiments at different pH in the range of 2–11. All the experiments were carried out at 5 bar venturi inlet pressure and 34  $\mu$ M initial dye concentration. Fig. 9 shows the effect of pH on the degradation rate of RR120. The results indicate that the rate of degradation increases with a decrease in solution pH i.e. acidic medium is more favorable for the degradation of dye. Much lower degradation rate was observed at pH 10.0. About 60% decolorisation and 28% reduction in TOC was obtained in 3 h at pH 2.0 using HC operating at 5 bar pressure. The enhancement in the degradation rate at lower pH can be attributed to the fact that dye molecule is present in the molecular state at lower pH. In its molecular state, dye molecule becomes more hydrophobic, and hence can easily locate or prefer to be at the gas–water interface of the collapsing cavities. At the interface of cavities, the dye molecule is then subjected to the direct attack of OH $\cdot$  radicals, resulting into increased degradation rate. Whereas in the basic medium (pH > 7.0) the dye molecules get ionized and become hydrophilic in nature, thereby remain in the bulk liquid. Due to the recombination of OH $\cdot$  radicals, only a small fraction of the generated OH $\cdot$  radicals diffuse into the bulk resulting into lower concentration of OH $\cdot$  radicals being used and made available for the oxidation of the dye as only about 10% of the OH $\cdot$  radicals generated in the cavity can diffuse into the bulk solution [25]. This causes a reduction in the rate of degradation. Ince and Guyer [26] have studied the effect and hence the subsequent impacts of pH and molecular structure on ultrasonic degradation of azo dyes. They have explained that the acceleration in decolorisation of dye by acidification is due to neutralization of the dyes upon protonation of negatively charged SO $_3^-$  sites, and the hydrophobic enrichment of the molecules to enhance their reactivity under ultrasonic cavitation. While percentage reduction in decolorisation under alkaline conditions is a consequence of ionization of the dyes by hydrogen loss from protonated sites and naphthol–OH, resulting in enhanced hydrophilic character to the dye, which does not accumulate at the cavity–water interface and hence is not affected significantly by the cavitation event.

### 3.7. Effect of H $_2$ O $_2$

In the case of hydrodynamic cavitation based degradation of dye, the controlling mechanism is the free radical attack. The use of H $_2$ O $_2$  should enhance the degradation rate due to the generation of additional free radicals. Fig. 10 shows the effect of the addition of H $_2$ O $_2$  on the degradation rate of RR120. Different molar ratios

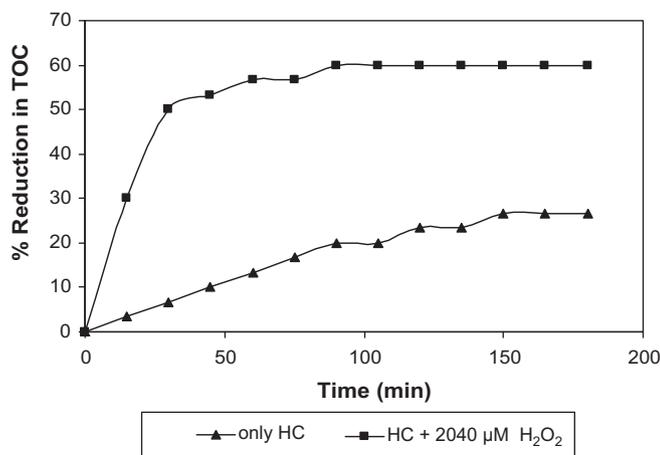


**Fig. 10.** Effect of H $_2$ O $_2$  addition on degradation rate of RR120 (conditions: volume of solution: 6 l, initial concentration: 34  $\mu$ M, pH of solution: 2.0, inlet pressure: 5 bar).

of dye to H $_2$ O $_2$  concentration were selected ranging from 2.5 times to 100 times. All the experiments were carried out at 5 bar venturi inlet pressure and 34  $\mu$ M initial dye concentration and at pH 2 for a fixed time (180 min) of operation. It was observed that the degradation rate of dye increases with an increase in the concentration of H $_2$ O $_2$ . Almost 100% decolorisation and 60% reduction in TOC was obtained at 2040  $\mu$ M concentration of added H $_2$ O $_2$  (ratio of 1:60) as compared to only 60% reduction in color and 28% reduction in TOC in case of no H $_2$ O $_2$  (HC only). There was no further enhancement in the rate of degradation of dye after 2040  $\mu$ M concentration of added H $_2$ O $_2$  and also no improvement in percentage reduction of TOC was observed after 2040  $\mu$ M concentration of H $_2$ O $_2$ . Thus, the optimum concentration of hydrogen peroxide can be considered as 2040  $\mu$ M, which gives a molar ratio of 60:1 (H $_2$ O $_2$ :dye concentration). The addition of H $_2$ O $_2$  provides the additional OH $\cdot$  radicals for the oxidation of dye molecules, which causes increase in degradation rate. The scavenging of the OH $\cdot$  radicals is continuously taking place during the treatment time by H $_2$ O $_2$  itself and due to the presence of other scavenging species such as oxygen, SO $_4^{2-}$  ions and due to recombination of OH $\cdot$  radicals. Therefore, the combined effect of HC and H $_2$ O $_2$  will be very much dependent on the utilization of the generated free radicals by the dye molecules. It was also observed that only 13.15% decolorisation takes place in 3 h with normal stirring (no HC) and with the addition of 2040  $\mu$ M H $_2$ O $_2$ . Thus, the combination of HC and H $_2$ O $_2$  gives better result as compared to individual operation of these advanced oxidation process, since hydrodynamic cavitation enhances the micro mixing and thereby increases the effective utilization of OH $\cdot$  radicals by pollutant molecule. Teo et al. [27] have also reported a similar conclusion about the effect of H $_2$ O $_2$  on the degradation of p-chlorophenol using ultrasound. They have reported that the degradation rate increases with an increase in the hydrogen peroxide concentration reaching to the maximum at 20 mM concentration of H $_2$ O $_2$  for an initial concentration of 0.4 mM (giving an optimum molar ratio of 50:1) which is very similar to the optimum found in this work.

### 3.8. Mineralization study

The final products from the oxidation of dye are some intermediates, CO $_2$  and H $_2$ O. These intermediates are expected to be aromatic compounds which also accounts for the TOC of the solution. Zhang et al. [28] have carried out study on the decomposition pathway and reaction intermediate formation of the Reactive Red 120 dye during ozonation. They have found that various aromatic compounds are formed such as phenol,



**Fig. 11.** % Reduction in TOC as a function of time at different optimized conditions (conditions: volume of solution: 6 l, initial concentration: 34  $\mu\text{M}$ , pH of solution: 2.0, inlet pressure: 5 bar).

1,2-dihydroxysulfoebene, 1-hydroxysulfoebene, 4,6-diamino-1,3,5-triazine-2-ol, 2,4-diamino-6-chloride-1,3,5-triazine and 2,4-hydroxy-6-chloride-1,3,5-triazine. Therefore the measurement of dye concentration spectrophotometrically does not guarantee the complete mineralization of dye as it only gives the reduction in color. Mineralization is the complete oxidation of dye molecule into  $\text{CO}_2$  and  $\text{H}_2\text{O}$ . So, in order to observe the complete mineralization of dye, TOC was measured at different optimized parameters. Fig. 11 shows the percentage reduction in TOC with respect to time for the dye solution treated by HC alone and by HC +  $\text{H}_2\text{O}_2$ . It was found that TOC reduced by 28% of the original while 60% decolorisation was observed when the degradation was carried out with hydrodynamic cavitation alone. The addition of  $\text{H}_2\text{O}_2$  enhances the TOC removal, around 60% TOC (100% decolorisation) is reduced by the addition of 2040  $\mu\text{M}$  of  $\text{H}_2\text{O}_2$  in combination of HC at pH 2.0. It was also observed that the decolorisation of dye is a relatively faster process as compared to the mineralization process. The rate constant for the decolorisation and mineralization (i.e. TOC reduction) processes was found to be  $7.54 \times 10^{-3} \text{ min}^{-1}$  and  $2.5 \times 10^{-3} \text{ min}^{-1}$  respectively when the degradation was carried out in hydrodynamic cavitation alone and it increases to  $95.5 \times 10^{-3} \text{ min}^{-1}$  and  $14.3 \times 10^{-3} \text{ min}^{-1}$  with the addition of 2040  $\mu\text{M}$  of  $\text{H}_2\text{O}_2$ . Almost 100% decolorisation is achieved within 15 min, whereas 60% reduction in TOC was observed after 90 min with the addition of 2040  $\mu\text{M}$  of  $\text{H}_2\text{O}_2$  in the case of HC. Madhavan et al. [4] have also observed that TOC removal rate was much less than that of the decolorisation process under the same experimental conditions due to the formation of more stable intermediates in the process of decolorisation.

#### 4. Conclusions

In this work the degradation of Reactive Red 120 dye was carried out using hydrodynamic cavitation. Effects of different process variables such as inlet pressure, cavitation number, solution pH and addition of  $\text{H}_2\text{O}_2$  on the degradation kinetics were studied. The following important conclusions can be drawn from the present work.

1. The rate of degradation was found to be dependent on the venturi inlet pressure and cavitation number. Inlet pressure and the cavitation number are the two important operating parameters in the case of hydrodynamic cavitation which affects the cavitation condition inside the venturi, hence the degradation rate of the dye. The photographic study shows that at an operating venturi inlet pressure higher than 5 bar, choked cavitation occurs

which results into reduced cavitation yield and hence cavitation device should be operated at a cavitation number higher than choked cavitation to get the maximum effect.

2. The degradation of RR120 was found to be pH dependent and acidic medium was found to be favorable for the higher degradation. It was found that operating pH, state of molecule (whether molecular or ionic) and nature (hydrophobic and hydrophilic) are the important parameters which ultimately decide the efficient degradation of pollutants.
3. The addition of  $\text{H}_2\text{O}_2$  enhances the degradation rate due to additional hydroxyl radicals available for the oxidation of dye and shows a synergy. However, this has also an optimum concentration of  $\text{H}_2\text{O}_2$  beyond which, no further enhancement was observed.

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#### References

- [1] U.G. Akpan, B.H. Hameed, Parameters affecting the photocatalytic degradation of dyes using  $\text{TiO}_2$ -based photocatalysts: a review, *J. Hazard. Mater.* 170 (2009) 520–529.
- [2] I.-H. Cho, K.-D. Zoh, Photocatalytic degradation of azo dye (Reactive Red 120) in  $\text{TiO}_2/\text{UV}$  system: optimization and modeling using a response surface methodology (RSM) based on the central composite design, *Dyes Pigments* 75 (2007) 533–543.
- [3] V.K. Saharan, A.B. Pandit, P.S. SatishKumar, S. Anandan, Hydrodynamic cavitation as an advanced oxidation technique for the degradation of Acid Red 88 dye, *Ind. Eng. Chem. Res.* (2011), doi:10.1021/ie200249k.
- [4] J. Madhavan, F. Grieser, M. Ashokkumar, Degradation of Orange-G by advanced oxidation processes, *Ultrason. Sonochem.* 17 (2010) 338–343.
- [5] Y.-L. Song, J.-T. Li, H. Chen, Degradation of C.I. Acid Red 88 aqueous solution by combination of Fenton's reagent and ultrasound irradiation, *J. Chem. Technol. Biotechnol.* 84 (2009) 578–583.
- [6] X. Wang, Z. Yao, J. Wang, W. Guo, G. Li, Degradation of reactive brilliant red in aqueous solution by ultrasonic cavitation, *Ultrason. Sonochem.* 15 (2008) 43–48.
- [7] M.A. Rauf, S.S. Ashraf, Fundamental principles and application of heterogeneous photocatalytic degradation of dyes in solution, *Chem. Eng. J.* 151 (2009) 10–18.
- [8] X.K. Wang, J. Wang, P. Guo, W. Guo, C. Wang, Degradation of rhodamine B in aqueous solution by swirling jet induced cavitation combined with  $\text{H}_2\text{O}_2$ , *J. Hazard. Mater.* 169 (2009) 486–491.
- [9] P. Braeutigam, Z.-L. Wu, A. Stark, B. Ondruschka, Degradation of BTEX in aqueous solution by hydrodynamic cavitation, *Chem. Eng. Technol.* 32 (2009) 745–753.
- [10] M. Sivakumar, A.B. Pandit, Waste water treatment: a novel energy efficient hydrodynamic cavitation technique, *Ultrason. Sonochem.* 9 (2002) 123–131.
- [11] A.G. Chakinala, P.R. Gogate, A.E. Burgess, D.H. Bremner, Treatment of industrial waste water effluents using hydrodynamic cavitation and the advanced Fenton process, *Ultrason. Sonochem.* 15 (2008) 49–54.
- [12] D.V. Pinjari, A.B. Pandit, Cavitation milling of natural cellulose to nanofibrils, *Ultrason. Sonochem.* 17 (2010) 845–852.
- [13] Y.T. Shah, A.B. Pandit, V.S. Moholkar, *Cavitation Reaction Engineering*, Kluwer Academic/Plenum Publishers, New York, 1999.
- [14] Y. Yan, R.B. Thorpe, Flow regime transitions due to cavitation in the flow through an orifice, *Int. J. Multiphase Flow* 16 (1990) 1023–1045.
- [15] V.S. Moholkar, A.B. Pandit, Bubble behavior in hydrodynamic cavitation: effect of turbulence, *AIChE J.* 43 (1997) 1641–1648.
- [16] S.S. Sawant, A.C. Anil, V. Krishnamurthy, C. Gaonkar, J. Kolwalkar, L. Khandeparker, D. Desai, A.V. Mahulkar, V.V. Ranade, A.B. Pandit, Effect of hydrodynamic cavitation on zooplankton: a tool for disinfection, *Biochem. Eng. J.* 42 (2008) 320–328.
- [17] J.-G. Lin, C.-N. Chang, J.-R. Wu, Y.-S. Ma, Enhancement of 2-chlorophenol with ultrasound/ $\text{H}_2\text{O}_2$  process, *Water Sci. Technol.* 34 (1996) 41–48.
- [18] N.N. Mahamuni, Y.G. Adewuyi, Advanced oxidation processes (AOPs) involving ultrasound for waste water treatment: a review with emphasis on cost estimation, *Ultrason. Sonochem.* 17 (2010) 990–1003.
- [19] Ş. Gül, Ö. Özcan-Yıldırım, Degradation of Reactive Red 194 and Reactive Yellow 145 azo dyes by  $\text{O}_3$  and  $\text{H}_2\text{O}_2/\text{UV-C}$  processes, *Chem. Eng. J.* 155 (2009) 684–690.
- [20] C.-H. Wu, Effects of operational parameters on the decolorisation of C.I. Reactive Red 198 in UV/ $\text{TiO}_2$ -based systems, *Dyes Pigments* 77 (2008) 31–38.
- [21] Y.G. Adewuyi, Sonochemistry: environmental science and engineering applications, *Ind. Eng. Chem. Res.* 40 (2001) 4681–4715.
- [22] P. Senthilkumar, A.B. Pandit, Modeling hydrodynamic cavitation, *Chem. Technol.* 22 (1999) 1017–1026.

- [23] N.P. Vichare, P.R. Gogate, A.B. Pandit, Optimization of hydrodynamic cavitation using a model reaction, *Chem. Eng. Technol.* 23 (2000) 683–690.
- [24] P. Senthilkumar, M. Sivakumar, A.B. Pandit, Experimental quantification of chemical effects of hydrodynamic cavitation, *Chem. Eng. Sci.* 55 (2000) 1633–1639.
- [25] M. Goel, H. Hongqiang, A.S. Mujumdar, M.B. Ray, Sonochemical decomposition of volatile and non-volatile organic compounds – a comparative study, *Water Res.* 38 (2004) 4247–4261.
- [26] N.H. Ince, G.T. Guyer, Impacts of pH and molecular structure on ultrasonic degradation of azo dyes, *Ultrasonics* 42 (2004) 591–596.
- [27] K.C. Teo, Y. Xu, C. Yang, Sonochemical degradation for toxic halogenated organic compounds, *Ultrason. Sonochem.* 8 (2001) 241–246.
- [28] F. Zhang, A. Yediler, X. Liang, Decomposition pathways and reaction intermediate formation of the purified, hydrolyzed azo reactive dye C.I. Reactive Red 120 during ozonation, *Chemosphere* 67 (2007) 712–717.