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Decolorisation of Reactive Red 120 by hydrodynamic cavitation

Litesh V. Malade[a]*, Umesh B. Deshannavar[b]

[a]D. Y. Patil College of Engg and Tech., Kasaba Bawada, Kolhapur 416006, India.
[b]KLE Dr. M. S. Sheshgiri College of Engg. and Tech, Belgaum 590008, India.

Abstract

Decolorisation of reactive red 120 (RR120), was investigated using hydrodynamic cavitation (HC). Present works mainly study effect of various geometrical parameters of orifice plates on decolorisation of RR120 in aqueous solution. For this purpose seven orifice plates having different diameter and number of holes were used in present study. After optimizing orifice geometry effect of operating conditions such as operating pressure, initial concentration of dye in liquid, initial temperature of liquid, operating pH and addition of oxidizing agent (H_2O_2) on percentage decolorisation of RR120 have been investigated and optimum conditions were determined. Kinetic analysis suggests decolorisation of RR120 using hydrodynamic cavitation follow first order kinetics. Almost 74% decolorisation was obtained by using HC alone with orifice plate 2 at 3.5 kg/cm^2, 30^{o}C, pH of 2 & 10 mgl^{-1} of dye concentration in aqueous solution. After adding oxidizing agent H_2O_2 decolorisation rate increases to 97.5% at optimum concentration of 120 mgl^{-1} of H_2O_2.

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Keywords: Hydrodynamic cavitation; Reactive Red 120; Decolorisation; Orifice plate geometry; Hydrogen Peroxide

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1. Introduction

Textiles industry consumes most of the dye, due to high demand for polyester and cotton in the world [1]. About 10–20% of this dye is lost in the dyeing process and released to wastewater body [2, 3]. Due to high stability these dyes will remain in water bodies for the extended period of time disturbing natural growth activity of aquatic life and also have harmful effects on exposed organisms [3-6]. Reactive dyes are mainly used in the textile industries due to their good stability during washing [7-9]. Unfortunately due to their high solubility, 50% of reactive dye

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* Corresponding author. Tel.: +91-231-2601431; fax: +91-231-2601432.
E-mail address: litesh.m@gmail.com

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remains in effluent [10-11]. Conventional methods like physical, chemical and biological are non destructive and convert organic load from primary waste (liquid) to secondary waste (solid) creating problem of sludge disposal [12-17]. Advanced oxidation processes (AOP) mainly produce highly reactive hydroxyl radical in aqueous phase which oxidizes organic pollutants like dyes in waste water [18-20]. Effective advanced oxidation processes (AOPs) include cavitation (Acoustic & hydrodynamic), oxidation by photocatalysis, Fenton's reaction and Chemical oxidation [21-24]. Out of these techniques cavitational reactors seems attractive due to simplicity to design, operate and ability to destroy organic material from waste water [25-27].

Cavitation is defined as formation of micro bubbles, their growth and then violent collapse releasing very high-energy (about 10000 K and 1000 atm) in milliseconds. Cavity collapse produces highly reactive hydroxyl radicals (free radicals) useful for the oxidation of complex organic chemicals from wastewater [28-30]. Out of four different types of cavitation only acoustic and hydrodynamic cavitation (HC) are effective for desired chemical changes [28]. Cavitation through HC is produced by the passage of the liquid through an orifice, throttling valve or a venture [31]. When the liquid flows through the orifice, pressure decreases and at the same time kinetic energy of liquid increases results into millions of cavities. Subsequently collapse of cavities results into hot spot and production of OH° which diffuse into the liquid medium and oxidize organic pollutant [32]. Oxidization can also occur at the gas-liquid interface depending on nature of organic pollutant.

HC has been successfully implemented by many scholars for chemical/physical transformation. Mishra and Gogate [27] studied effect of various parameters like inlet pressure, orifice geometry, pH and temeperature of liquid medium for degradation of Rhodamine B in a closed loop HC setup. Suslick et al. [33] successfully studied oxidization of I to I_3 by HC generated by a jet fluidizer. Vichare et al. [34] have studied decomposition reaction of KI and efficiency of the different orifice geometries in generating the cavitation. Chakinala et al. [35] reported 60–80% removal of TOC of industrial wastewater effluents under optimized conditions by hydrodynamic cavitation combined with advanced Fenton process. Kalumuck and Chahine [36] verified effective degradation of p-nitrophenol by hydrodynamic cavitation jet configuration. Madhu et. al. [37] reported 100% degradation of malachite green and 95.22% degradation of violet dye with the help of hydrodynamic cavitation. Gogate and Bhosale [38] studied degradation of orange acid-II and brilliant green dye with hydrodynamic cavitation. Saharan et al. [39] reported first order kinetics and 75.72% degradation of Orange G dye at pH 2.0 by HC.

Objective of present work is to study decolorisation of dye with the help hydrodynamic cavitation with different orifice geometries. Emphasis was given towards optimization of geometry of orifice plate and various operational parameters. Attempt was also made to enhance cavitational effect by adding oxidizing agent H_2O_2. Reactive Red 120 (RR 120), extensively used in the textile industries, was selected as a model dye.

2. Materials and methods

2.1 Materials

Reactive Red-120 dye (RR 120) was purchased from Sigma-Aldrich. The structure of Reactive Red 120 dye is given in Fig. 1.

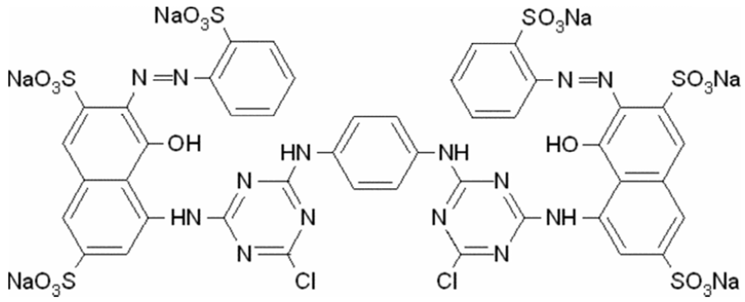

Fig. 1 Structure of Reactive Red 120 (RR120)

Hydrogen peroxide solution (30%, w/v) purchased from SD Fine Chem. Pvt. Ltd., Mumbai, India. The initial pH of the solution was adjusted using 1 N HCl and 1 N NaOH solution for each experimental run. All chemicals used were of analytical grade and suitably diluted with distilled water.

2.2 Experimental set-up

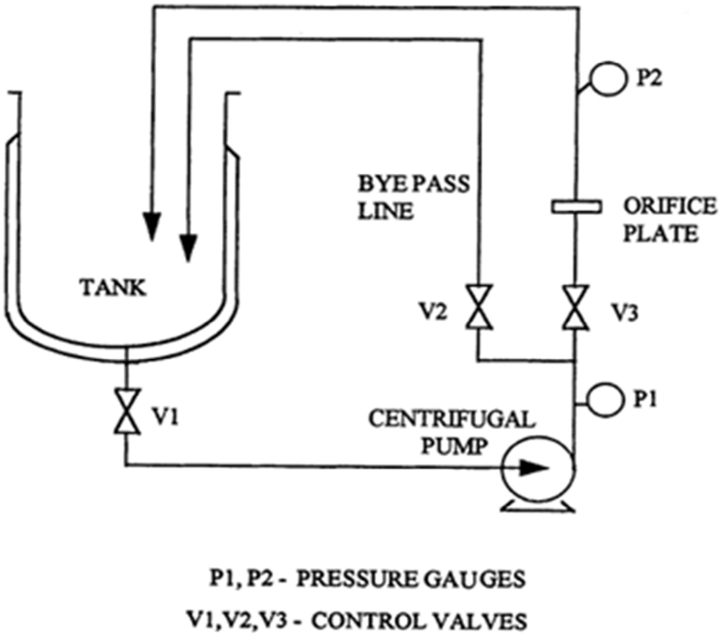

Fig. 2 hydrodynamic cavitation setup with orifice plate

Experimental setup of HC is shown in figure 2. Setup is designed to withdraw dye solution from a holding tank of 5 litre volume, passing through orifice plate through main pipe line and then returned back to the tank for recirculation. Other major components of setup include a centrifugal pump, control valve ($v_1 – v_3$) and replaceable orifice plates as shown in figure 3. Seven plates of different geometries have been used in order to study the cavitational effect of hydrodynamic cavitation. The properties of the orifice plates have been introduced in Table 1 and the geometry of orifice plate is shown in figure 3.

Table 1: Flow geometry of orifice plates

Plate No	Number of holes	Diameter of each hole (dh) mm	Flow area (mm^2)	α (mm^{-1})	β	Total perimeter of holes (mm)
Plate 1	1.00	1	0.785	4.00	0.4	3.14
Plate 2	5.00	1	3.925	4.00	2	15.70
Plate 3	9.00	1	7.065	4.00	3.61	28.26
Plate 4	1.00	2	3.14	2.00	1.6	6.28
Plate 5	3.00	2	9.42	2.00	4.81	18.84
Plate 6	1.00	3	7.065	1.33	3.61	9.42
Plate 7	1.00	4	12.56	1.00	6.41	12.56

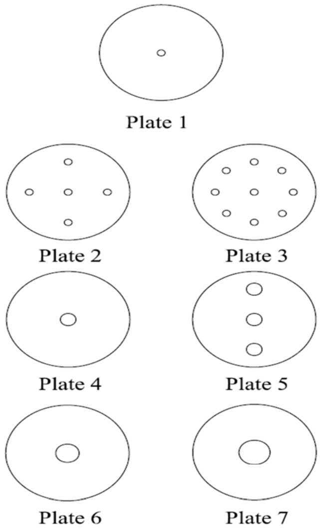

Fig. 3 Orifice plate geometry

2.3 Experimental procedure

Decolorisation of RR120 dye was carried out at different operating conditions using 5 l aqueous solution of RR120 and for a time period of 120 min. Samples were collected after 20 min interval from each experimental run for further analysis. Initially, to optimize orifice geometry, the effect of different geometries of orifice plates on the depolarization rate of RR120 has been studied at an inlet pressure varying from 1 kg/cm^2 to 3.5 kg/cm^2 using all the cavitating devices at natural pH of the solution. After optimizing orifice geometry and pressure further experiments were performed to study the effect of the other operating conditions such as initial dye concentration (10–25 mgl^{-1}), temperature (20–50°C), pH (2–10) and hydrogen peroxide concentration (30 – 150 mgl^{-1}). Each of the above parameters was altered keeping the other parameters constant. Analysis of initial sample and treated samples of RR120 were done by analysing absorbance using a UV–vis spectrophotometer (UV-1800 SHIMATZU, Japan). The percentage of decolorisation was calculated using equation (1).

$$\%\,Decolorisation = \frac{C_{A_0} - C_A}{C_{A_0}} \times 100 \qquad (1)$$

Where, C_{Ao} is initial concentration of RR 120 and C_A is the concentration of RR 120 at any time t.

3. Results and discussion

3.1 Hydraulic Characteristics

The cavitation number is mainly used to study hydraulic characteristics [42-45]. Cavitation number is calculated by equation (2):

$$C_V = \left(\frac{p_2 - p_2}{(1/2)\rho v_0^2}\right) \qquad (2)$$

Where, p_2 is downstream pressure of solution, p_v is vapor pressure of the solution, v_o is the velocity of the solution through the orifice and ρ is the density of the solution. To study the hydraulic characteristics of orifice plates used in this study, flow rate is measured by changing inlet pressure (1 to 3.5 kg/cm^2) and cavitation number calculated from equation (2). The variation of cavitation number with operating inlet pressure for different orifice plates is shown in figure 4. It was observed that the there is decrease in cavitation number with increase in operating inlet pressure. Main line flow rate increases by increasing pressure which subsequently increases the velocity (v_o) at the throat, results in decreasing cavitation number (eq. 2). Number of cavities produced and their collapsing rate increases as cavitation number decreases. Minimum cavitation number (C_v = 0.19) was obtained for plate 5 at operating inlet pressure of 3.5 kg/cm^2. Similar observations are made by Rajoriya et. al [44] and kumar et. al. [45].

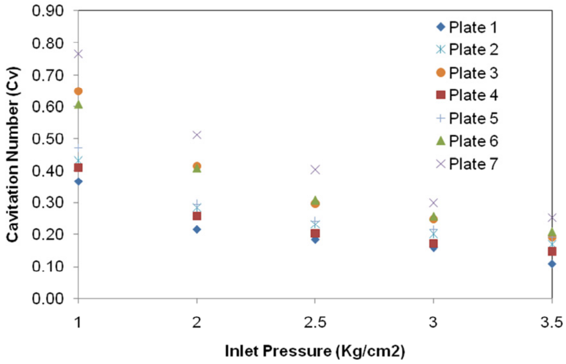

Fig. 4 Hydraulic characteristics of various cavitating devices

3.2 Optimization of geometry of orifice plates

The optimization of orifice plates is essential for getting the maximum decolorisation of dye using HC. The experiments were conducted at different inlet pressures to examine the percentage decolorisation with different orifice plates and also to determine extent of decolorisation at different cavitation number. Figure 5 shows the effect of geometry of orifice at different pressure on the decolorisation rate of RR 120. Figure 6 shows the effect of cavitation number on the decolorisation rate of RR 120. It was found that the decolorisation rate increased with a decrease in cavitation number till an optimum value and then further decreased for all orifice plates. It was observed that plate 5 gives maximum decolorisation of 62.5% at 3.5 kg/cm^2 pressure and C_v = 0.19. As the operating inlet pressure increases, the velocity at the constriction of the orifice plate also increases, and consequently the cavitation number decreases (as per Eq. (2)). The lower cavitation number generates more cavities resulting into a large amount of OH˚ radicals which enhances the decolorisation of the dye. But at very low cavitation number beyond an optimum value there is formation of cavitation cloud which decreases cavity collapse [46].

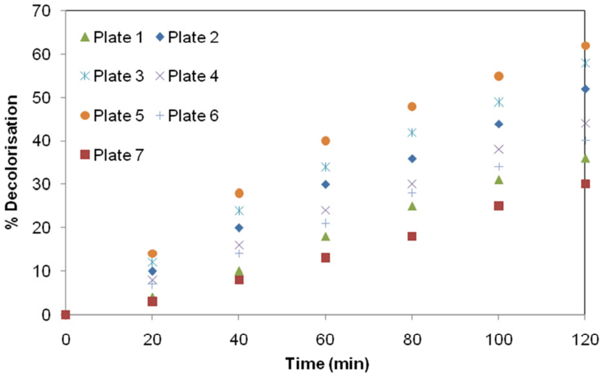

Fig. 5 Effect of geometry of orifice plate on %Decolorisation

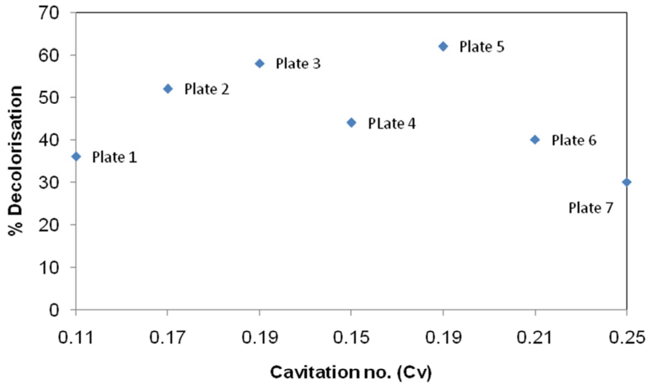

Fig. 6 Effect of cavitation number (C_v) on decolorisation at 3.5 kg/cm^2

3.2.1 Effect of α

A parameter α is defined as a ratio of throat perimeter to flow area. Orifice plate having higher value α for a same flow area (Plate 3 and Plate 6) generates more cavities resulting into higher decolorisation. For the plates having same value of α (Plate 1, Plate 2 and Plate 3), the extent of decolorisation is high for plate having higher no of holes. Rajoriya et. al [44] also shows increase in decolorisation of reactive blue 13. Sivakumar et. al [47] observed similar results for degradation of rodamine B. Decolorisation rate increases by increase in value of α up to 2 beyond which there is decrease in decolorisation rate.

3.5.2 Effect of β

Dimensionless geometrical parameter β calculated as a ratio of throat area to flow area. It can be observed that there is enhancement in percentage decolorisation with an increase in the value of β. Maximum 62% decolorisation was achieved with Plate 5 (β = 4.81). This is due to increasing flow area which increases the number of cavitational events and thereby resulting into higher decolorisation rate. Since with a higher throat area, velocity at the throat decreases which eventually decreases cavitation number resulting into lower degradation rate. Rajoriya et. al [44], they have reported maximum degradation of 44% for Reactive blue dye using orifice plate having maximum value of β (β = 0.025). Sivakumar et. al [47], also reported similar results for degradation of Rhodamine B dye by hydrodynamic cavitation. Since geometry of orifice plate 2 gives maximum decolorisation, further experiments are performed with orifice plate 2 geometry.

3.3 Effect of Inlet Pressure

Effects of inlet operating pressure on the decolorisation rate of RR120 investigated with 10 mgl^{-1} RR120 in aqueous solution at temperature 30^{o}C. The results were showed in figure 7. It was found that percentage decolorisation of RR 120 is increased with increasing pressure and maximum decolorisation of 62.5% is observed at inlet operating pressure of 3.5 kg/cm^2. Increase in pressure increases intensity of collapse of cavities thus cavitaional intensity is increased. This increase in cavitation intensity results into the enhancement of the hydroxyl radical production which subsequently increases the extent of decolorisation of RR 120. Wang et. al [48] investigated effect of pressure on degradation rate of rhodamine B and obtained similar results. Gogate et. al. [49] reported enhancement in degradation of triazophos with an increase in pressure till 5 bar beyond which it was decreased. Gogate and Bhosale [26] also observed maximum degradation of orange acid II dye till 5 kg/cm^2 beyond which it was decreased.

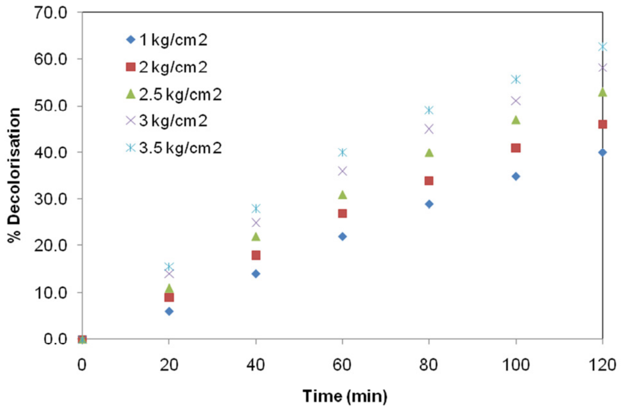

Fig. 7 Effect of Pressure on decolorisation of RR120 at 10 mgl^{-1}, 30^{o}C

3.4 Effect of initial dye concentration

The effect of initial dye concentration on the decolorisation rate of RR120 was obtained at temperature 30^{o}C and pressure 3.5 kg/cm^{2}. Figure 8 showed the kinetics of decolorisation for initial concentrations of RR120 from 10 – 25 mgl^{-1}. It was observed that the concentration of RR120 in aqueous solutions decreased with time and the decolorisation rate can be represented by the equation (3):

$$-\ln\left(\frac{C_A}{C_{A_0}}\right) = kt \tag{3}$$

Where, C_A is the concentration of RR120 at time t, C_{Ao} is initial concentration, k is decolorisation rate constant and t is decolorisation time. Figure 8 indicated that the decolorisation of RR120 follows first order reaction kinetics. It was also observed that degradation rate constant was decreased by increasing initial concentration of RR120. The degradation rate constants of RR120 were 8.315 x 10^{-3}, 6.526 x10^{-3}, 4.034 x10^{-3} and 1.306 x10^{-3} min^{-1} at initial concentration of 10, 15, 20 and 25 mgl^{-1} respectively. Similar results were obtained by others by hydrodynamic degradation of Reactive blue 13 [44], Rhodamine B [48] and reactive brilliant red K-2BP [50] in aqueous solution. Total quantity of dye molecules increases with increase in initial concentration, whereas total concentration of hydroxyl radicals remains constant in the system. Also intermediates formed during decolorisation compete with dye itself for hydroxyl radicals, results in decreased rate constant.

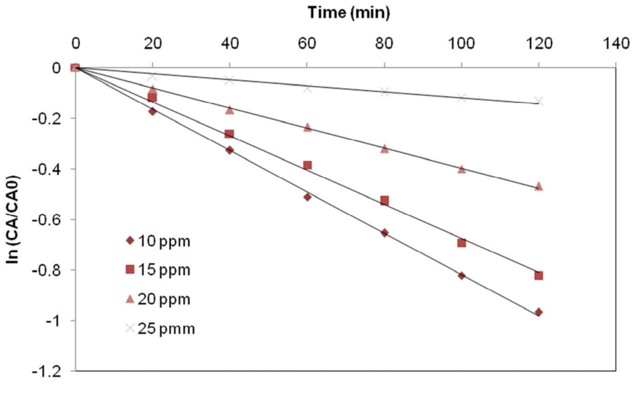

Fig. 8 Effect of initial concentration on decolorisation of RR120 at 30^{o}C and 3.5 kg/cm^{2}

3.5 Effect of operating temperature

Effect of temperature to the decolorisation rate of RR120 was investigated with 10.0 mgl^{-1} RR120 aqueous solution at 3.5 kg/cm^2 and the result was showed in figure 9. It was observed that percentage decolorisation increased from 20°C to 30°C and after that it decreases at higher temperature. Rise in temperature increases the vapour pressure of the solution results in more cavitation bubbles which accelerate decolorisation rate at higher temperature till 30°C. However further increase in temperature reduces the intensity of collapsing cavities which results in decreasing decolorisation rate. Therefore optimal operational temperature of 30°C was selected due to highest decolorisation efficiency. Similar results related to a change in decolorisation rate with rise in operating temperature have been reported in literature [48, 50, 57].

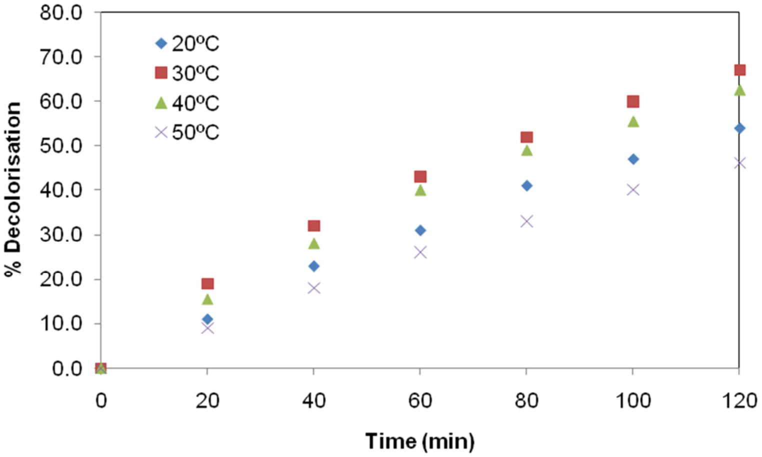

Fig. 9 Effect of operating temperature on decolorisation of RR120 at 3.5 kg/cm^2 and 10 mgl^{-1} of dye concentration

3.6 Effect of initial pH

The influence of initial pH of the solution on the decolorisation rate of RR 120 was obtained at pH value varying from 2.0–10.0 using 10 mgl^{-1} RR 120 aqueous solution at 40°C as shown in figure 10.

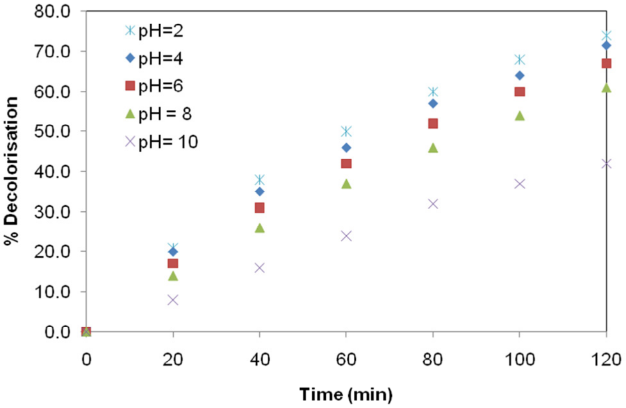

Fig. 10 Effect of initial pH on decolorisation of RR120 at 3.5 kg/cm^2, 30°C and 10 mgl^{-1} of dye concentration

It has been observed that acidic conditions i.e. decrease in pH is favourable for decolorisation of dye. Rajoriya et. al. [44] obtained maximum decolorisation of RB 13 at a solution pH of 2. Gogate et. al [49] obtained maximum degradation of triazophos using HC at pH 3. Saharan et. al. [55] have also studied the effect of solution pH on the decolorisation rate and reported maximum decolorisation rate at 2 pH. Higher decolorisation rate favoured by low pH because production of OH° and also the oxidation potential of OH° radicals is higher under acidic condition [52, 53]. Under acidic condition, RR120 becomes more hydrophobic due to its presence in molecular state and hence easily locate itself at the gas–liquid interface of the collapsing cavities where the concentration of hydroxyl radicals is maximum giving higher decolorisation rate. On other side, in the basic medium molecules of RR120 get ionic charge and thereby remain in the liquid. Since only 10% of generated hydroxyl radicals diffuse in the liquid decolorisation rate is less under basic condition [46, 54, 55]. The minimum decolorisation rate of 42% was obtained at pH of 10 in 120 min of reaction time, whereas the maximum rate of decolorisation of 74% was obtained at pH of 2.

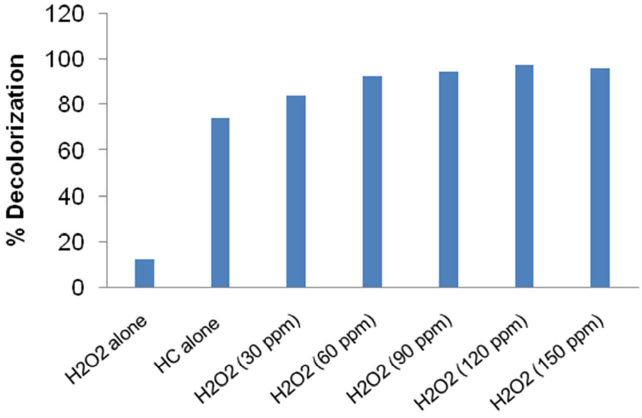

Fig. 11 Effect of addition of H_2O_2 on decolorisation of RR120 at 3.5 kg/cm^2, 30°C, pH 2 and 10 mgl^{-1} of dye concentration

3.7 Effect of H_2O_2

The effect of H_2O_2 concentration on decolorisation of RR120 was investigated in HC using 10 mgl^{-1} RR120 solutions at 40°C and pH 2 after 120 min. It was observed that the percentage decolorisation of RR120 increased significantly with the addition of H_2O_2 as shown in figure 11 up to optimum concentration of 120 mgl^{-1}, further increase in concentration of H_2O_2 decreases the percentage decolorisation. Decolorisation rate was found to be maximum at H_2O_2 concentration of 120 mgl^{-1}, at which about 97.5% decolorisation with a first order rate constant of 30.94×10^{-3} min^{-1} was achieved. Addition of H_2O_2 in Hydrodynamic cavitation enhances decolorisation of dye due to its high oxidation capacity (1.78 eV) and ability to dissociate easily into highly reactive hydroxyl radicals under cavitating conditions [52, 53, 56]. Beyond optimum concentration, the excess amount of H_2O_2 scavenges the hydroxyl radicals produced in the system therefore reduces the decolorisation rate. An experiment has also been carried out using H_2O_2 alone (in the absence of HC) at 120 ppm H_2O_2 concentration for 120 min of operation under same operating conditions with normal stirring. It was observed that only 12% decolorisation with a first order rate constant of 1.5×10^{-3} min^{-1} was achieved using H_2O_2 alone. Rajoriya et. al [44] reported 91% decolorisation with a first order rate constant of 46.6×10^{-3} min^{-1} in the presence of H_2O_2 at an optimum molar ratio of RB 13 to H_2O_2 (1:20). Wang et. al. [50] also observed degradation of K-2BP increased with increasing of H_2O_2 concentration up to 300 mgl^{-1}. Wang et. al. [51] found 99.1% degradation ratio of rhodamine B with addition of 150 mgL^{-1} H_2O_2 concentration.

4. Conclusions

The present work shows that HC combined with H_2O_2 effectively remove Reactive Red 120 dye from waste water. Efficiency of hydrodynamic cavitation is strongly influenced by the geometrical parameters of orifice plates such as α and β. It was found that higher fluid pressures, lower dye initial concentration, higher temperature, lower medium pH and addition of H_2O_2 up to 120 mgl^{-1} are favourable for the decolorisation of RR120. But the extent of decolorisation of RR120 is decreased when temperature of aqueous solution increase above 30°C and increase in concentration of H_2O_2 above 120 mgl^{-1}

5. References

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