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Degradation of patent blue V using cavity-bubble oxidation reactor induced by glass balls

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ABSTRACT

A cavity-bubble oxidation reactor was used to study the degradation of patent blue V. The generation of cavity-bubbles by glass balls and flow-rate-induced jet were the degradation mechanisms used in this reactor. Initially, basic operating parameters were optimized by varying the initial concentration (10–40 ppm) and solution pH 2–12. The extent of degradation (22.6%) at 20 ppm was reduced to 11.4% when the initial concentration was increased to 40 ppm. Following that, combined treatment strategies for process intensification of the degradation process were investigated. It was found that lower initial concentrations and acidic conditions favored the degradation of patent blue V. Under the optimal conditions of a concentration of 20 ppm and a pH of 2, the combined effect of the cavity-bubble oxidation reactor and chemical oxidation processes, such as hydrogen peroxide, gave a 95.38% extent of degradation at optimum H_2O_2 loading (2.5 g/L), which was 4.5 times greater than that obtained using cavity bubble oxidation reactors alone. The highest degree of degradation (98.48%) was achieved with a cavity-bubble oxidation reactor coupled with an optimum loading of the Fenton reagent (0.125 g/L $FeSO_4$ and 2.5 g/L hydrogen peroxide). With the exception of the Fenton process, the kinetic analysis revealed that the degradation of patent blue V followed first-order reaction kinetics in all cases.

1. Introduction

Water covers a large portion of the globe and is a vital resource for humans and the environment. Water contamination has risen dramatically in recent years as a result of the direct and indirect addition of pollutants to water resources. The quality of drinking water is impacted by water contamination. As a direct consequence of this, it is detrimental to both the health of humans and the natural environment. Pollution from a single source is referred to as "point source pollution," while pollution from multiple sources is referred to as "nonpoint source pollution" [1]. Sewage, industrial waste, oil pollution, air pollution, marine dumping, radioactive waste, underground storage leaks, and global warming can contaminate water. Some of the toxic substances found in industrial

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waste may have a slight effect, while others could be lethal in terms of immune suppression, reproductive failure, and acute toxicity [2-4]. Due to the rapid expansion of food and other industries, the daily generation of hazardous waste is increasing. The environmental impact of this waste is immediate and dangerous. The release of such toxic chemicals into the atmosphere causes significant environmental harm. Dyes have a vibrant, complex, and penetrative color that necessitates a significant amount of mineralization. Furthermore, azo dyes and their derivatives have a significant carcinogenic influence on the environment [5-7]. The basic objective of wastewater treatment is to ensure that industrial effluents can be dealt with without causing severe harm to humans, other living organisms, or the environment. Therefore, long-term, sustainable process technology is needed to treat industrial effluent before its disposal. Several initiatives have been devoted to developing better industrial process technology. Membrane filtration, adsorption, precipitation, and biological treatment techniques have been developed to treat dye-containing wastewater [8]. However, each of these approaches, on its own, is inefficient due to the large salt levels produced by reactive dying; there is also a possibility that secondary waste will be produced in the process [9,10]. The biological treatment is inefficient for the processing of such dyes since it has a high carbon footprint, is less versatile when used in combination with other techniques, and takes more time than the other processes [11-12]. Adsorption, electrocoagulation, and flocculation are among the methods used to treat dye wastewater, but these methods produce secondary waste in the form of solids, making them inefficient [13-15]. As a result, it is necessary to develop a crucial system with enhanced approaches that will result in the total removal of these dyes from the effluent without the formation of secondary waste. Hydroxyl radical (OH^-) reactions are used to remove organic and inorganic pollutants from water and wastewater using advanced oxidation processes (AOPs). Because of this, OH reacts without discrimination once it has formed, and any contaminants that are present will be rapidly broken down and converted efficiently into small inorganic compounds [16]. The production of hydroxyl radicals requires the participation of at least one primary oxidant in addition to an energy source or catalyst. In order to obtain the highest possible yield of OH^-, it is necessary to use carefully calculated and predetermined dosages, sequences, and combinations of these reagents [17]. Advanced oxidation processes have been called the "water treatment process of the 21st century" because they can lower the pollutants from hundreds of parts per million (ppm) to less than five parts per million (ppm). This makes a big difference in chemical oxygen demand (COD) and total organic carbon (TOC). Even today, AOPs have yet to be widely adopted in the commercial sector owing to their relatively high costs. Despite this, AOPs are a popular tertiary treatment technique for removing organic and inorganic pollutants that are among the most difficult to deal with due to their high oxidative capability and efficiency. Cavitation has been recognized as a promising approach for the total removal of contaminants in wastewater for several decades [16-18]. Chemical substrates, such as chlorinated hydrocarbons, aromatic compounds, textile dyes, phenolic compounds, and esters, can be converted by the cavitation approach into short-chain organic acids, carbon dioxide, and inorganic ions as final products [20-22]. Cavitation is the phenomenon of the production, growth, and eventual collapse of microbubbles or cavities over extremely short time intervals (microseconds), releasing huge magnitudes of energy across a very small area. Cavitation is currently categorized into four types based on the manner of generation: ultrasonic, hydrodynamic, optic, and particle cavitation. Ultrasonic and hydrodynamic cavitation are the two most common methods of cavitation for treating wastewater in the shortest time. Optic and particle cavitations, on the other hand, are typical single-bubble cavitations that do not cause any physical or chemical changes in the bulk solution [23]. In a number of studies, it has been shown that acoustic and hydrodynamic cavitation can break down toxic and harmful chemicals. In addition to the frequently used orifice- or venturi-based cavitating devices, which also provide excellent flexibility due to variations in design and operation, a variety of recently developed hydrodynamic cavitation reactors are also being used by researchers to enhance advanced technologies. The creation of novel cavitating devices, such as high-speed homogenizers, swirling flow cavitation, and vortex diode-based cavitation, is currently the focus of many researchers [24-28]. The current study will concentrate on the treatment of dye-containing wastewater with a cavitation-based reactor, such as a cavity-bubble oxidation reactor. The degrading mechanism of the reactor is cavity-bubble production by glass balls and a flow-rate-induced jet. When liquid solution travels through the glass balls, liquid jets are cut into many smaller microscopic bubbles. When it collapses, extreme conditions will release vapour inside the cavity. Layer by layer of glass in the column reduces the bubbles' size [29-30]. Small cavity bubbles recombine to generate a larger bubble. When the tension between two bubbles approaches its limit, the larger bubble collapses, causing high temperature and pressure locally, this breaks water into OH^- and O_2^- radicals with strong oxidation abilities per the below reaction scheme.

$$H_2O \rightarrow OH^- + H^+ \quad (1)$$
$$OH^- + OH^- \rightarrow H_2O_2 \quad (2)$$
$$H^+ + O_2 \rightarrow HO_2^- \quad (3)$$
$$2HO_2^- \rightarrow H_2O_2 + O_2 \quad (4)$$
$$H_2O_2 + OH^- \rightarrow HO_2^- + H_2O \quad (5)$$

Xu et al. (2010) [29] reported air-bubble cavitation using small glass balls for the removal of the dye methyl orange. In this innovative cavitation approach, dye methyl orange was degraded up to 37.82% at 10 ppm of initial dye concentration, a 4.5 L/min air flow rate, and a pH of 6.8. They also investigated the degradation of Rhodamine B, Congo Red, Azo Fuchsin, and Acid Red B under similar operating process conditions. It was reported that the maximum degradation for Acid Red B was 76%, 71.75% for Azo Fuchsin, 64.52% for Congo Red, and 60.73% for Rhodamine B. Mahale et al. (2013) [31] used a similar air-bubble cavitation setup for the removal of patent blue V in batch mode. They reported that the maximum patent blue V degradation was 73.1% with a 36.6% COD removal without the addition of catalysts or additives at pH 7.2, 20 ppm initial concentration, 4.5 L/min air flow rate, and pH 6.8. However, with the addition of the catalysts, the degradation of patent blue V was reported as 77.1 % (49.5 % COD) for 0.3 g/L of ZnO, 83.4 % (60.5% COD) for 0.6 g/L of TiO_2, and 80.7 % (61.6 % COD) for 0.6 g/L of MnO_2 using the air-bubble cavitation method. Mohod et al. [30] investigated the removal of methyl violet 2B by employing a modified cavity bubble oxidation reactor. The authors explored the role of operational parameters on the extent of methyl violet 2B removal, like pH and initial dye concentration. A 96% removal of methyl violet 2B was accomplished with the addition of TiO_2 and MnO_2 as additives. The current study employs a cavity-bubble oxidation reactor that is comparable to the previous one but does not use ultraviolet irradiation. Patent blue V, an acidic dye also known as Food Blue 5 with the molecular formula $C_{27}H_{31}N_2O_7S_2$, has been investigated as a specific pollutant. The dye is used in cosmetics, textiles, and detergents and has a dark blue color. Even though patent blue has a wide range of applications, its presence in water can cause significant issues, which include harmful effects on microorganisms and severe allergic reactions in humans, such as anaphylaxis. Based on the application, the proportion of patent blue V in wastewater generated by processing industries generally varies from 10 to 100 mg/L. In light of these characteristics, developing effective treatment methods for patent blue V removal is of the utmost importance. For this reason, an approach based on the use of a cavity-bubble oxidation reactor on a continuous mode of operation without the use of UV irradiation was investigated for the first time as part of this study. The effect of initial dye concentration and pH on the extent of degradation of patent blue V dye was initially investigated to optimize the operating parameters; these optimized values were used in the subsequent intensification investigation. To the best of our knowledge, no previous study has evaluated the use of hydrogen peroxide (H_2O_2) and Fenton reagent coupled with a cavity-bubble oxidation reactor to study the efficacy of the coupled process. In addition, the mineralization and kinetic investigations were carried out under optimized conditions.

2. Materials and methods

2.1. Materials

Patent blue V dye was obtained from Loba Chem. Pvt. Ltd., Mumbai, India. Its molecular formula is $C_{27}H_{31}N_2NaO_6S_2$, and the molecular weight is 566.66 g/mole. The sodium hydroxide (NaOH), sulphuric acid (H_2SO_4) (98% pure), hydrogen peroxide (H_2O_2) (30% w/v), and ferrous sulphate ($FeSO_4.7H_2O$) (97%) were purchased from Merck Specialties Pvt. Ltd., Mumbai, India. In the laboratory, distilled water was used to prepare the dye solution. All other chemicals were of analytic grade and were utilized in their original form.

2.2. Experimental methodology

Figure 1 shows a schematic view of the cavity-bubble oxidation reactor setup. The reactor is made up of three chambers with a total height of 100 cm that are packed with glass marbles measuring 10 mm. The first chamber (Reducer 1) of the column is 15 cm in height and 7.62 cm in diameter, while the middle compartment is 70 cm in height. The bottom chamber (Reducer 2) is conical in shape, with a diameter of 7.62 cm that is reduced to 2.54 cm in size. The reactor is leak-proof, with adequately sealed input and output port connections. The glass balls used in all the experiments were the same size, and the packed portion with the glass balls was approximately 75% of the height of the reactor.

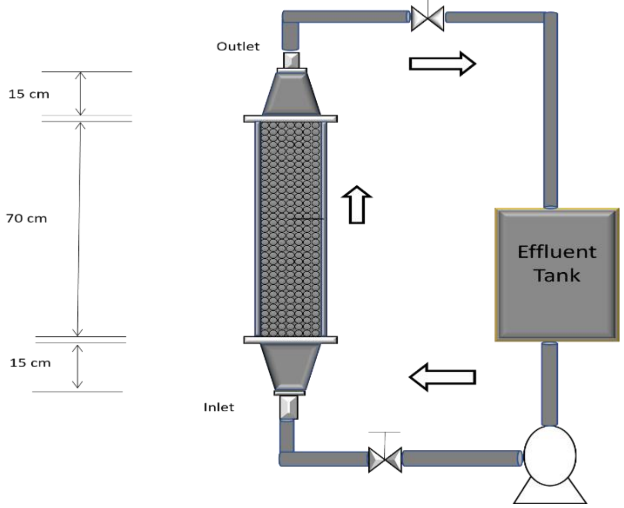

Fig. 1. Schematic representation of the experimental setup for the cavity-bubble oxidation reactor.

Initially, the required concentration solutions were prepared for the experimental runs using distilled water. With the help of a 1.5 HP regenerative pump (procured from Kirloskar Pvt. Ltd., Pune), the solution was fed at a flow rate of 104.328 L/h from the bottom of the reactor. The 20 mL samples were collected from the sampling valve at 30 min intervals. The samples were examined at a wavelength of 675 nm with the help of a UV-Vis spectrophotometer. Chemical Oxygen Demand (COD) was analysed using the standard method based on potassium dichromate. The experimental runs to investigate the influence of pH on patent blue V removal were carried out at various pH levels ranging from 2 to 12, which were adjusted using 1 N NaOH and conc. H_2SO_4 as needed. All tests were repeated at least twice to ensure reproducibility, and the average values are presented in the discussion. The statistics also include error bars to highlight the fluctuation, which was within 2% of the reported average value.

3. Results and discussion

3.1. Influence of initial concentration

Experiments were carried out in a range of initial concentrations of patent blue V (10–40 mg/L) to evaluate the effect of the initial concentration on the removal of patent blue V. The percentage removal of patent blue varied with reaction time at various initial concentrations, as shown in Figure 2. As the initial concentration of patent blue V increased from 10 to 20 mg/L, the extent of patent blue dye removal increased from 16.6% to 22.6%. However, as the initial concentration of patent blue V increased beyond 20 mg/L, the extent of degradation decreased up to 11.4%. Throughout the initial treatment period, the rate of removal of patent blue at 20 mg/L of the initial dye concentration was about twice that at 40 mg/L, as indicated in the figure. After 180 minutes of treatment, the highest removal of patent blue was 22.6 % at an optimal dye concentration of 20 mg/L and a pH of 7.

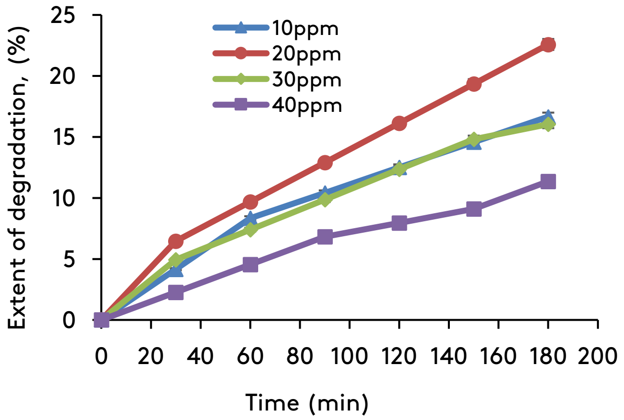

Fig. 2. Effect of initial dye concentration on the extent of degradation of patent blue v cavity-bubble oxidation reactor (pH 7).

The observed optimum trends can be due to the fact that initially, oxidizing species are abundant; as the concentration of these species increases, they are capable of degrading a larger amount of dye present in the solution, resulting in greater rates until the optimal loading level is reached. There is a reasonable steady state that exists between the dye molecules that can be exploited for degradation and the OH^- radicals that are formed in the solution, and it is vital to realize that the formation of OH^- radicals remains constant regardless of the operating process parameters [32,33]. There are fewer oxidizing radicals available to react with the excess dye molecules, resulting in a decrease in the degradation rate beyond the optimal concentration. At this point, the rate of hydroxyl radical generation becomes a limiting factor, resulting in a reduced overall extent of degradation. Another possible explanation for the vicinity of an optimum dye concentration is supported by the finding that the degradation rate is affected by the relative availability of hydroxyl radicals and dye molecules at the site of the reactions [34,35]. This hypothesis is supported by the observation that the optimum dye concentration can be explained by the occurrence of this phenomenon. There is an extremely high concentration of OH radicals available right at the surface of the bubble [36,37]. At very low dye concentrations, the possibility of OH^- radicals recombining to generate H_2O_2 dominates the surface, where radicals are abundant. This occurs even though the dye concentration is extremely low. On the contrary, the oxidation reaction that is responsible for the removal of dye takes place in the bulk of the solution. This is the location where the quantity of OH^- radicals is minimal, which can be attributed to the fact that only about 10% of the hydroxyl radicals produced in the bubble are able to diffuse into the bulk of the solution. The chance of a radical attack on the molecule of patent blue v increases in proportion to the dye concentration; as a consequence, the amount of patent blue that is removed also increases in proportion. When the concentration is substantially higher, there is a limited formation of OH^- radicals in comparison to the excess dye molecules that are present in the solution; as a result, the amount of dye that can be removed from the solution diminishes. The results obtained are consistent with the findings reported by Xu et al. [29], who observed that at significantly high initial concentrations, degradation was not achieved completely and required longer treatment times. According to the research by Xu et al. [29], the initial methyl orange dye concentration was changed from 5.0–25 mg/L, and they reported that a concentration of 10 ppm was the optimum concentration for methyl orange degradation. Ma et al. [38] reported that the maximum degradation (25%) of Acid Red B was obtained at 20 ppm using air-bubble cavitation.

3.2. Effect of pH

Operating pH is one of the most critical factors in determining the physicochemical features of a solution, and it influences the ease with which hydroxyl radicals are generated as well as the type of pollutants produced. At a dye dosage of 20 mg/L, the influence of pH was examined over a range of solution pH of 2–12. The pH of the solution was adjusted to the necessary value using concentrated H_2SO_4 and 1 N NaOH solution. The obtained results concerning the effect of pH on the removal of patent blue V are shown in Figure 3. It is clear that there was a negative correlation between the increase in pH and the level of degradation occurring. The highest removal of patent blue V (27.3%) was recorded at a pH of 2, while the level of degradation was substantially lower under alkaline conditions. In acidic conditions, the generation of hydroxyl radicals increases more due to the decomposition of hydrogen peroxide. At the same time, the recombination reaction of hydroxyl radicals is hindered due to the higher rate of formation and accumulation of hydroxyl radicals. This results in an increase in the total amount of hydroxyl radicals. In addition, the ability of hydroxyl radicals to participate in oxidation is maximized under acidic conditions. It is possible that the formation of the oxidizing species hydroperoxy anion (HO_2^-) in an alkaline medium, which is the conjugate base of H_2O_2, is the cause of the decrease in the removal rate in the basic pH range. The rate at which dye oxidizes is slowed by the HO_2^- anion's propensity to react with both H_2O_2 molecules and the OH^- radical [39-41]. Also, in an alkaline medium, dye molecules can become ionized and remain in the bulk liquid. However, the number of oxidizing OH^- radicals in the bulk liquid is significantly lower than the number at the bubble water interface, which results in a reduced amount of dye being removed. According to the authors' previous findings [42], similar trends regarding the results of the effect of pH while studying patent blue V dye using a cavity-bubble induced oxidation reactor with UV irradiation. It was reported that the maximum degradation of methyl violet 2B dye was 73.14% obtained at a pH of 4.2, and a lower degradation was obtained at the basic pH of the solution when operated under a cavity-bubble induced oxidation reactor at a batch mode of operation with a capacity of 700 mL. Additionally, Zhang et al. [43] revealed that the best pH range for maximal C.I. acid orange breakdown was in the 2–4 range. However, Sun et al. [44] claimed that the extent of Acid Black 1 decolorization was raised from 5 to 98 % with a decrease in the working pH from 6 to 3.

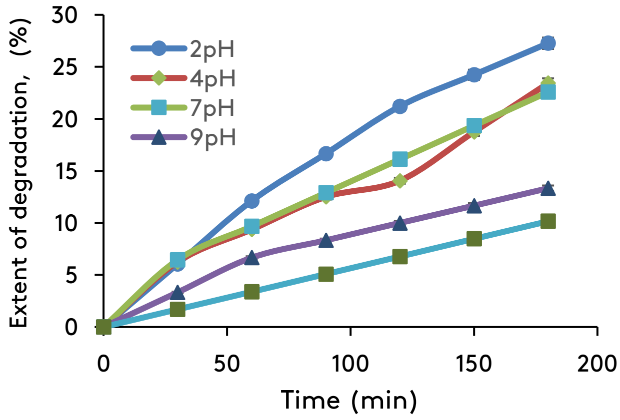

Fig. 3. Effect of initial pH on the extent of degradation of patent blue V cavity-bubble oxidation reactor (Concentration 20 ppm).

3.3. Effect of hydrogen peroxide

The addition of hydrogen peroxide is beneficial for raising the total quantity of hydroxyl radicals in the mixture. The dissociation of hydrogen peroxide results in the production of two moles of the hydroxyl radical. The experiment was carried out with hydrogen peroxide concentrations ranging from 0.5 to 3 g/L at an optimal initial concentration of 20 ppm and a pH of 2. Figure 4 depicts the obtained results of the effect of hydrogen peroxide loading on the degradation of patent blue V. The amount of degradation increased from 83.07 to 95.38.% with increasing hydrogen peroxide loading from 0.5 g/L to 2.5 g/L, as shown in the figure. However, as the hydrogen peroxide loading increased above the optimal level, the extent of patent blue V degradation decreased. It was also observed that when hydrogen peroxide was added, the extent of patent blue V degradation increased significantly. The addition of H_2O_2 to the cavity-based oxidation reactor increased the extent of patent blue V degradation, which could be explained by the decomposition of hydrogen peroxide into hydroxyl radicals. The loading of 2.5 g/L of H_2O_2 concentration resulted in the maximum extent of degradation after 180 minutes of treatment time. In the presence of hydrogen peroxide, the extent of degradation obtained was around 4.5 times greater than when merely employing a cavity-based oxidation reactor. The experiments were also conducted without marbles inside the column of a cavity-based oxidation reactor with an optimal hydrogen peroxide loading of 2.5 g/L. It was observed that only around 15% of the degradation of patent blue V was achieved using only hydrogen peroxide in the column without marbles. As a result, the presence of the marbles promoted the generation of hydroxyl radicals, which resulted in increased degradation. The results are also consistent with those of Gogate and Bhosale (2013) [45]; they used an orifice for hydrodynamic cavitation to evaluate the effect of H_2O_2 on dyes (Organe acid II and Malachite or brilliant green). Orange acid II degradation was enhanced from 60% to 96% with a 95.2 to 571.2 mg/l H_2O_2 concentration. The Malachite or bright green was degraded between 77% and 86% at equal H_2O_2 concentrations.

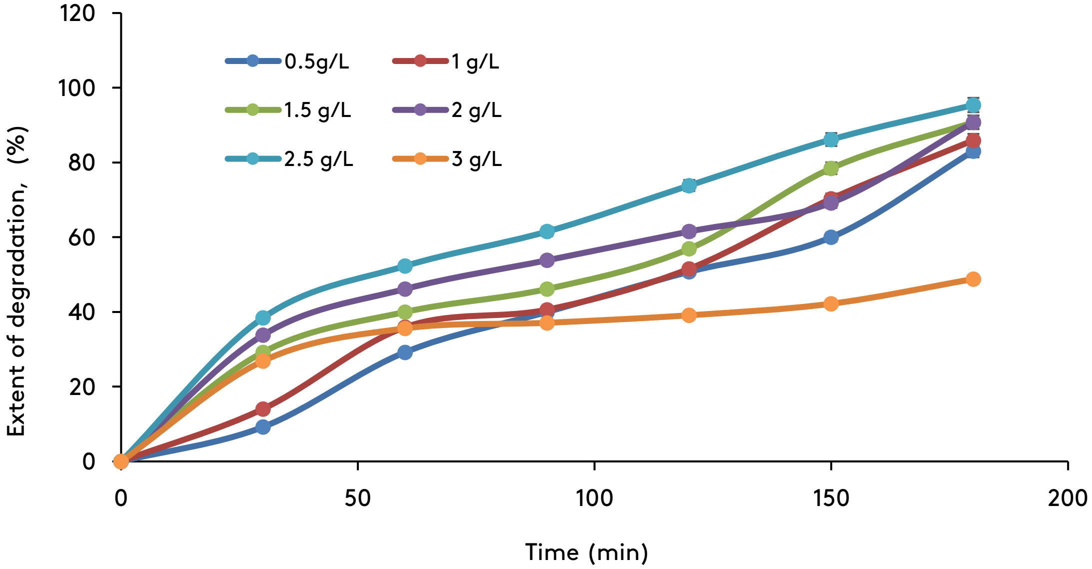

Fig. 4. Effect of H_2O_2 loading on the extent of degradation of patent blue V cavity-bubble oxidation reactor (Concentration 20 ppm, pH 2.0).

The presence of marble induced cavitation and the addition of hydrogen peroxide, resulting in increased degradation of patent blue V due to more free radical formation, provide strong evidence that the regulating mechanism of patent blue V degradation is free radical attack. When high doses of H_2O_2 are present, the rate of degradation slows down. This may be because H_2O_2 itself gets rid of more hydroxyl radicals, as the following reaction shows [29]:

$$H_2O_2 + \text{cavity} - \text{bubble collapse} \rightarrow 2OH^- \quad (6)$$

$$H_2O_2 + OH^- \rightarrow HO_2^- + H_2O \quad (7)$$

$$OH^- + HO_2^- \rightarrow H_2O + O_2 \quad (8)$$

$$OH^- + OH^- \rightarrow H_2O_2 \quad (9)$$

$$2HO_2^- \rightarrow H_2O_2 + O_2 \quad (10)$$

$$HO_2^- + HO_2^- \rightarrow H_2O_2 + O_2 \quad (11)$$

When H_2O_2 concentrations in the solution approach a threshold value, OH^- and H^- produced by the thermal oxidation of water selectively react with H_2O_2, which acts as an OH^- scavenger [47-48].

3.4. Effect of Fenton reagent

Figure 5 shows the results obtained for the effect of the Fenton reagent on patent blue dye removal. The figure shows that as the ferrous to H_2O_2 ratio decreased, the extent of patent blue V removal increased. The highest level of removal, 98.41 %, was achieved by using a mixture of ferrous sulphate (0.0125 g/L) and hydrogen peroxide (2.5 g/L).

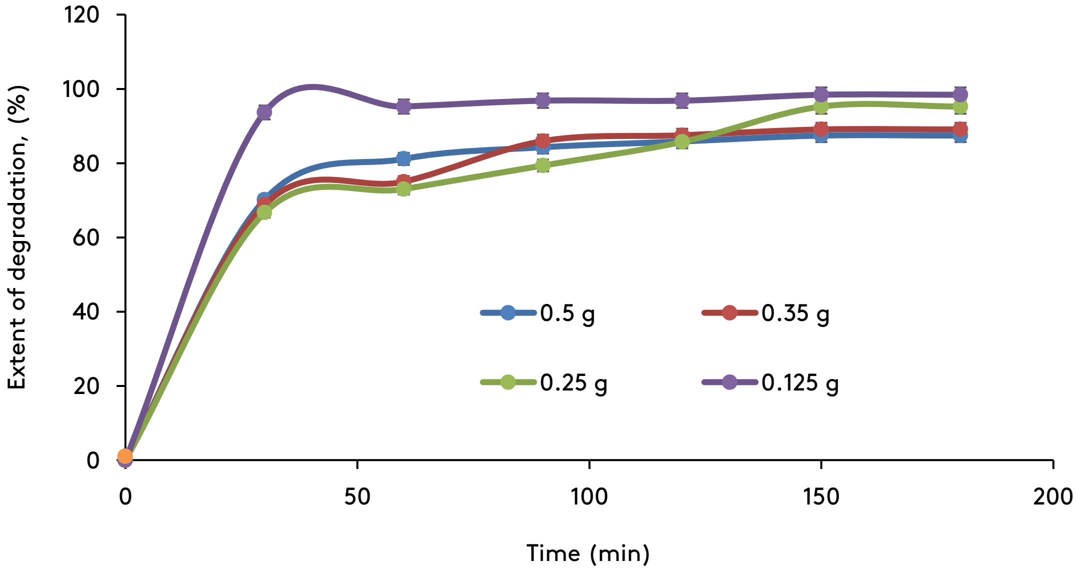

Fig.5. Effect of Fenton loading on the extent of degradation of patent blue v cavity-bubble oxidation reactor (Concentration 20 ppm, pH 2.0, 2.5 g/L H_2O_2).

The observed intensification could be attributed to the presence of Fe^{2+}, which enhanced the generation of the oxidizing species. The $FeSO_4$ dissociated into the ferrous ions (Fe^{2+}) and sulphate ions under the conditions that were brought about by the passage of air bubbles throughout the system [49]. The hydrogen peroxide produced during the treatment combined with the ferrous ions to produce more active OH^- radicals, perhaps significantly improving the dye degradation through the Fenton chemistry mechanism. Subsequently, the sulphate ions could react with water molecules to produce HO, which resulted in an enhanced degradation of patent blue V. The various processes that make up the increased formation of oxidizing species can be broken down into the following categories [50-52]:

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + OH^- \qquad (12)$$

$$Fe^{2+} + H_2O_2 \rightarrow Fe - OOH^{2+} + H^+ \qquad (13)$$

$$Fe - OOH^{2+} \rightarrow Fe^{2+} + \text{-}OOH^- \qquad (14)$$

$$Fe^{2+} + OOH^- \rightarrow Fe^{2+} + O_2 + H^+ \qquad (15)$$

According to the findings of Merouani et al. [53], the introduction of bivalent iron (Fe^{2+}) enhanced the process of Rhodamine B degradation to a greater extent than the introduction of trivalent iron (Fe^{3+}). It has also been found that an optimal Fe^{2+} concentration, when used together with ultrasonic irradiation, is advantageous for intensification [54, 55]. When the concentration of $FeSO_4$ was higher than the optimal concentration, the solution became saturated with Fe^{2+} ions, which led to the self-quenching of OH^- radicals [56-57]. The results were consistent with those of Ma et al., who reported that the degradation of Congo red dye increased up to 73.26% along with an 81.42% TOC reduction via the addition of Fe^{2+} ions (0.30 g/L), while a further increase in the loading of Fe^{2+} ions decreased the extent of degradation. Optimal concentration is defined as the concentration at which the reaction is most efficient. Because of this, there was no further improvement in the formation of HO radicals. In a more general sense, it is possible to establish that the beneficial effect of the combined approaches can only be obtained if the optimum level is not exceeded. This is the case regardless of the specific techniques involved.

4. Kinetic study

Kinetic analysis was performed to determine the rate constant and order of reaction for the various methodologies utilized in the study. The kinetics of patent blue V degradation were studied for a selected range of initial concentrations of dye (10 ppm-40 ppm), pH ranges (2 to 12), and different loadings of hydrogen peroxide over the range of (0.125 g/L–0.5 g/L) and ferrous salt loading (0.125 g/L–0.5 g/L) for a fixed loading of 2.5 g/L of hydrogen peroxide. The order and rate constants of the degradation reaction were calculated using the integral method of analysis. The following is the general rate equation.

$$\frac{-d[c]}{dt} = k'c^n \tag{16}$$

where c is the dye concentration in the solution, k' is the rate constant, and n is the order of reaction. For first order reactions, Equation (2) is obtained by putting n=1 and integrating Equation (1) for the bounds c = co at time t = 0 and c = c at time t = t.

$$\ln\frac{c_o}{c} = k't \tag{17}$$

For the second order reaction, Equation (3) is obtained by putting n=2 and integrating Equation (2) for the bounds c = co at time t = 0 and c = c at time t = t.

$$\frac{1}{c} - \frac{1}{c_0} = k't \tag{18}$$

where c_0 denotes the initial dye concentration at t=0 and cis the dye concentration at any time t=t. The degradation kinetics for various initial dye concentrations ranging from 10 ppm to 40 ppm were investigated, and the results are shown in Table 1.

Table 1. Optimized parameters of the study.

Parameter	**Range**	**Extent of Degradation (%)**	**COD Removal (%)**	**Rate Constant**	
				k (1/min)	**R^2**
Effect of initial dye concentration Reaction conditions (7 pH)	10	16.7	-	0.0011	0.962
	20	22.6	26.3	0.0015	0.982
	30	16.0	-	0.0011	0.962
	40	11.4	-	0.0007	0.983
Effect of pH Reaction conditions (20 ppm dye concen.)	2	27.3	-	0.0019	0.987
	4	23.4	-	0.0014	0.975
	7	22.6	-	0.0015	0.982
	9	13.3	-	0.0009	0.959
	12	10.2	-	0.0006	0.999
Effect of H_2O_2 Reaction conditions (20 ppm dye concen., 2 pH)	0.5	83.1	-	0.0075	0.855
	1	85.9	-	0.0086	0.872
	1.5	90.8	-	0.0105	0.864
	2	92.8	-	0.0102	0.864
	2.5	95.4	72.1	0.0141	0.915
	3	48.8	-	0.0041	0.665
Parameter	**Range (g/L)**	**Extent of Degradation (%)**		**Rate constant**	
				k (L/g. min)	**R^2**
Effect of Fenton reagent (g/L) Reaction conditions (2.5 g H_2O_2, 20 ppm dye concen., 2 pH)	0.125	98.4	76.4	0.0023	0.832
	0.25	95.2	-	0.0026	0.926
	0.35	89.1	-	0.0048	0.766
	0.5	87.4	-	0.0174	0.926

Reaction time 180 min

The data fit well into first-order kinetics, and the first-order rate constant increased until the optimum initial dye concentration of 20 ppm, then decreased as the initial dye concentration increased. Table 1 shows the rate constant and extent of degradation for various initial concentration ranges. The kinetic study with an initial optimum dye concentration of 20 ppm for a range of pH (2-12) and the rate constant and extent of degradation are summarized in Table 1. Despite changes in initial solution pH values ranging from 2 to 12, the degradation of Patent blue V dye followed first-order kinetics. The first-order rate constant decreased from 0.0019 to 0.0006 (1/min) as the pH of the dye solution increased from 2 to 12 pH. The kinetic analysis of the dye degradation process under different hydrogen peroxide loadings is depicted in Figure 6 and reported in Table 1. Regardless of hydrogen peroxide loading, kinetic data fit the first-order form.

It was observed that as the Fenton reagent loading decreased from 0.5 g/L to 0.125 g/L, the second-order rate constant increased from 0.0023 L/g. min to 0.0174 L/g.min. Figure 8 shows the UV spectra of the initial patent blue V and after degradation using the optimum loading of the Fenton reagent.

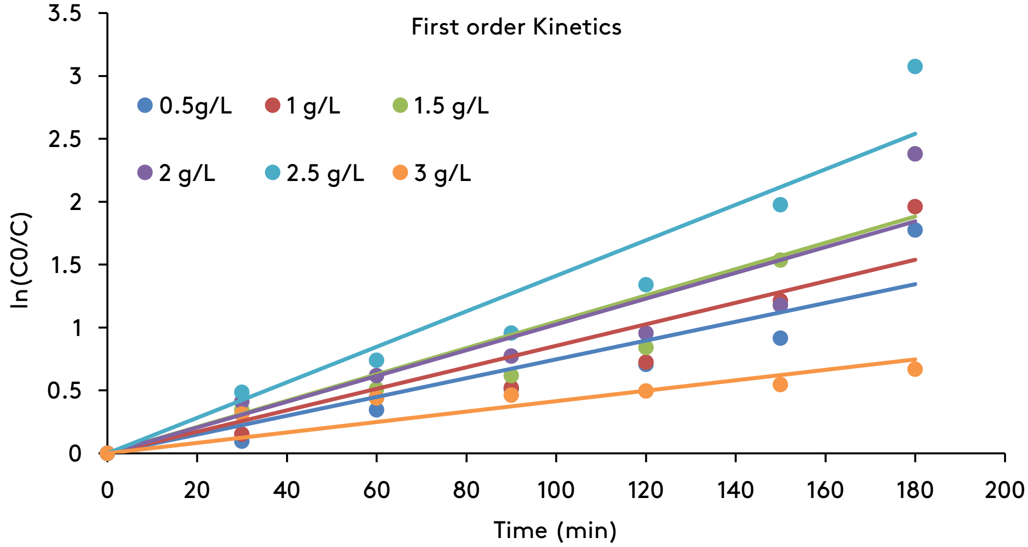

Fig. 6 .Kinetic study of H_2O_2 loading on the extent of degradation of patent blue V cavity-bubble oxidation reactor (Concentration 20 ppm, pH 2.0).

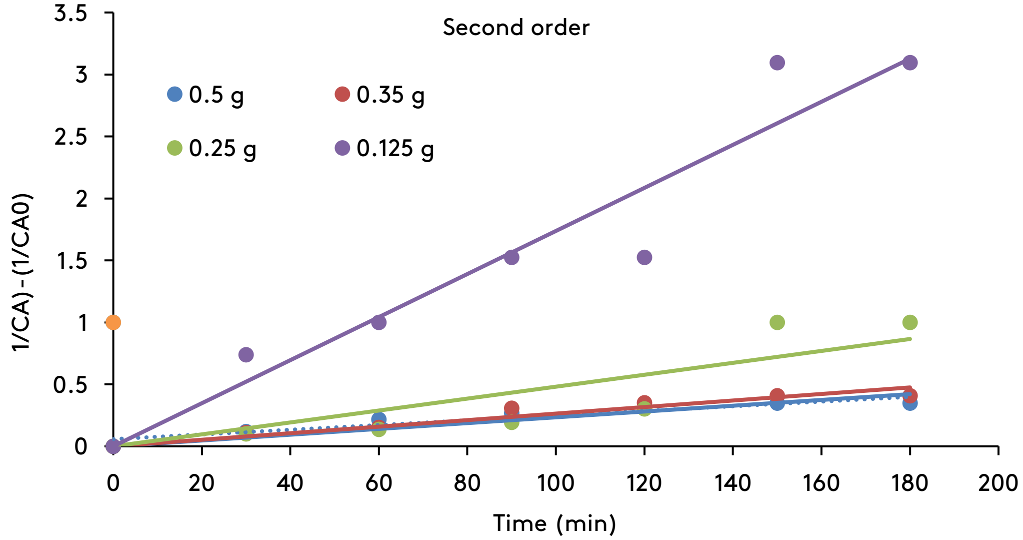

Fig. 7. Kinetic study of Fenton loading on the extent of degradation of patent blue V cavity-bubble oxidation reactor (Concentration 20 ppm, pH 2.0, 2.5 g/L H_2O_2).

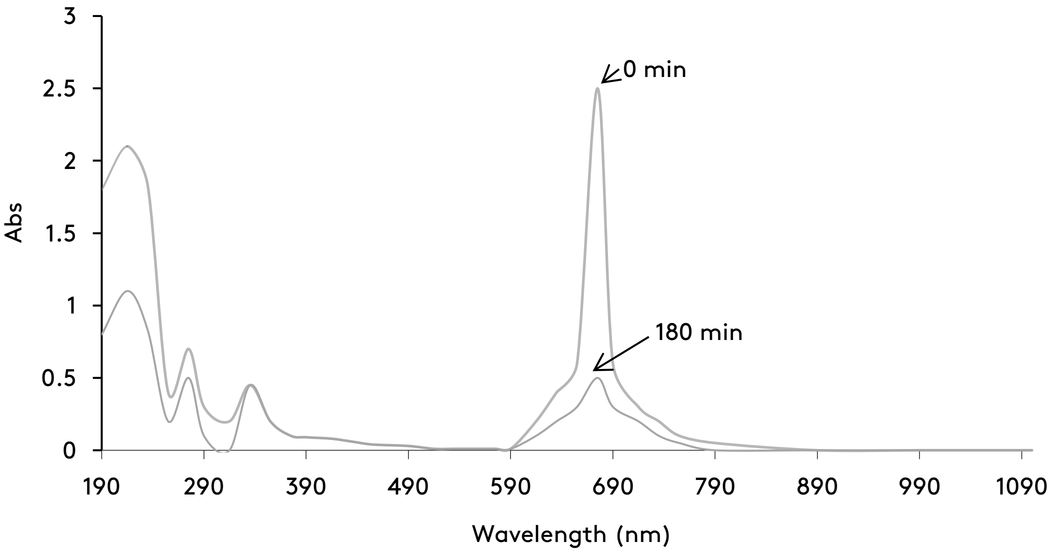

Fig. 8. UV spectra of Fenton loading on the extent of degradation of patent blue V cavity-bubble oxidation reactor (Concentration 20 ppm, pH 2.0, 2.5 g/L H_2O_2).

The figure clearly shows that the peak of patent blue V at 675 nm decreased after degradation in 180 min. The author's previous study [58] also reported pseudo-first-order reaction kinetics while studying methyl violet 2B degradation using a cavity-bubble induced oxidation reactor with UV irradiation.

5. Mineralization study

The level of mineralization was evaluated based on the percentage change in the COD for dye samples treated for 180 minutes in a cavity-bubble oxidation reactor under conditions designed to achieve maximum effectiveness. The results are displayed in Table 1. The COD reduction of 26.3% (20 ppm initial dye concentration, 7 pH) was achieved by employing a cavity-bubble oxidation reactor in the absence of any catalysts or additives in the solution, as is evident from the results. On the other hand, the results of COD removal that were achieved when additives and catalysts were introduced in the conditions of the reaction that were optimized have been fairly interesting. The maximum COD removal of 72.1 % was achieved in combination with optimal H_2O_2 catalyst loading (2.5 g/L), and the maximum COD removal of 76.4 % was achieved using Fenton (0.125 g/L $FeSO_4$ + 2.5 g/L H_2O_2) in 180 minutes of treatment. The extent of COD removal also followed a similar trend of improved outcomes for the treatment that was supported by ultrasound, which was comparable to what was seen with the degradation of pollutants. It is worth mentioning that AOPs are an efficient way to remove dyes. These processes involve the generation of highly reactive OH^- through chemical, UV, or any other type of alternative energy source. Due to their extremely effective production of oxidizing radicals, their most important feature is their capacity to completely destroy a wide range of dyes via OH^- formation [35,59,60]. In addition to producing the hydroperoxyl (HO_2^-) anion, which contributes to the breakdown of dyes found in industrial wastewater, AOPs are responsible for the production of hydroxyl radicals (OH^-) and other free oxidizing radicals. According to the general description of the degradation process, when cavitating conditions (such as high energy densities) are suitable, patent blue V dye is degraded through an oxidation process that begins with a free radical attack on the dye molecule, followed by a reaction with intermediates. According to Barka et al. [61], various reaction pathways, such as hydroxylation, desulfonation, deamination, desalkylation, and deshydroxylation, occurred during the oxidation process. They also reported that the primary products were obtained at HPLC retention times ranging from 2.33 to 48.00 minutes, with peak masses ranging from 94 m/z to 474 m/z; these products were subsequently mineralized into carbon dioxide, water, etc. According to the available published data, the hydroxyl radical attack on the dye molecules and the subsequent growth of their subsequent reactions were the first steps in the degradation pathway for the patent blue V dye that involves cavitation and photocatalysis.

6. Conclusions

The current study demonstrated that patent blue V dye could be successfully removed from water using a cavity-bubble oxidation reactor and that the efficiency could be increased by adding various additives. The rate of removal was substantially affected by operating parameters such as the initial concentration and pH of the patent blue V; it was demonstrated that the optimum initial concentration and acidic conditions were ideal for achieving a higher removal extent. The use of Fenton (H_2O_2 and $FeSO_4.7H_2O$) resulted in a higher extent of dye degradation, i.e., more than 90%. The strategy of optimum addition of $FeSO_4.7H_2O$ at a loading of 0.125 g $FeSO_4.7H_2O$ and 2.5g/L H_2O_2 of the solution resulted in a maximum removal of patent blue V dye of 98.41% (76.4% COD). Based on the findings, it is certain that cavity-bubble oxidation reactor treatment strategies enhanced with various additives provide a realistic option for dye degradation. The degradation of patent blue V followed first-order reaction kinetics for various H_2O_2 loadings, but a second-order reaction for the Fenton process.

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