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Degradation of methylene blue dye by UV/H_2O_2 advanced oxidation process: reaction kinetics, residual H_2O_2 and specific energy consumption evaluation

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ABSTRACT

In the present study, the degradation of methylene blue (MB) dye, a common pollutant from textile and printing industries was observed using UV/H_2O_2 advanced oxidation process. Effect of process variables like pH (3–11), H_2O_2 dosage (2.5–12.5) mM and initial MB dose (10–100) mg/L on decolorization efficiency of dye was investigated. An acidic pH of 3 was found to be favorable for decolorization of MB. Degradation of MB followed pseudo-first-order removal kinetics. Rate constants of MB decolorization increased with increase in H_2O_2 concentration and decrease in initial dye concentration. The results showed that about 89.85% residual H_2O_2 remained in the system even after 75 min treatment time. To ensure the minimum residual H_2O_2 in effluent and optimum MB removal, H_2O_2 dose was optimized at 12.5 mM with specific energy consumption of 271.6 kWh/kg dye. Thus, in the described experimental range of conditions, UV/H_2O_2 oxidation of MB may be an efficient, inexpensive and clean alternative treatment for decolorization of textile wastewater containing this dye.

Keywords: Advanced oxidation process; Methylene blue; Removal kinetics; Residual H_2O_2; Specific energy consumption; UV/H_2O_2 process

1. Introduction

Synthetic dyes pose a major threat to the environment due to their toxicity and hardly biodegradable nature. About 54% of the dye effluents currently found in the environment across the world come from the textile sector as a result of the extensive use of dyes in various textile industry operations which leads to large amounts of dye wastewater [1]. There are various types of synthetic dyes used in textile industries such as reactive, acidic, basic, direct, disperse and mordant dyes [2]. These dyes create severe environmental pollution problems by releasing toxic and potentially carcinogenic substances into the aqueous phase [3].

One of the dyes which is widely used in textile industries is methylene blue (MB) dye. MB is a cationic thiazine dye that is basic in nature. It is a common water pollutant due to its high use in textile industries for dyeing wool and other fabrics [4]. Due to its high stability and the occurrence of aromatic amines in its structures, such as nitro-aromatic and phenolic compounds, MB is difficult to degrade [5].

For treating refractory organic pollutants found in various industrial wastewaters such as textile, paper and pulp, pharmaceuticals, advanced oxidation processes (AOPs) are the sustainable new technology [6]. The main advantage of AOP is high mineralization efficiency with minimal production of secondary pollutants [7]. AOP has proven to be a unique and outstanding technology for the degradation of environmentally hazardous materials over the last few years [8]. Various types of pollutants are treated by AOPs like chlorinated hydrocarbons [9], dimethyl phthalate [10], textile industry wastewater [11], drugs [12], and pharmaceutically active compounds [13].

Homogeneous chemical oxidation employing ultraviolet radiation (UV) in the presence of H_2O_2 is one of these

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approaches that has received a lot of attention [14]. H_2O_2 is regarded as an environmentally favorable oxidizing agent under suitable conditions as it is ultimately transformed into water or OH ions which are safe for the environment [15]. H_2O_2 has high oxidizing potential in the presence of UV radiation and can destroy organic dyes by generating $OH^•$ radicals [7]. Also, the UV/H_2O_2 process is a clean process as there is no formation of sludge [16].

Despite many advantages of the UV/H_2O_2 process, its high H_2O_2/pollutant ratio and energy consumption is the main obstacle in its widespread use. To treat the organic pollutants, this process requires more energy consumption or more H_2O_2 dose. Most of the recent studies achieved more than 98% removal efficiencies at very low H_2O_2/dye ratio (less than 30) by increasing the reaction time [15,17] or by increasing the light source power (more than 250 W) [7,18]. In some studies, high removal efficiency was achieved by increasing H_2O_2/dye ratio up to 2,045 in less than 15 min treatment time resulting in lower specific energy consumption (SEC) [19,20].

The main objective of the present study is to achieve energy-efficient MB removal at low H_2O_2/dye concentration ratio by UV/H_2O_2 AOP. The influence of parameters like pH, H_2O_2 concentration, and initial dye concentration on color removal efficiency of dye was investigated and removal kinetics of MB dye was studied. Residual H_2O_2 was determined to check H_2O_2 concentration in the effluent after treatment. Specific energy consumption (SEC) was also evaluated to make the process more economic.

2. Material and methods

2.1. Chemicals

All the chemicals used in this study were of analytical grade. MB (MW = 319.85 g/mol) was obtained from Central Drug House. Hydrogen peroxide (30%) was purchased from Merck. Other chemicals like potassium iodide and ammonium molybdate were procured from Merck. A 1,000 mg/L MB stock solution was prepared. pH was adjusted by using aliquots of 1 N H_2SO_4 and 1 N NaOH.

2.2. Experimental setup

Experiments were carried out in a cylindrical glass reactor of 700 mL capacity. Inside the glass reactor a quartz tube containing a UV-C lamp (Philips) of 11W was placed. Maximum wavelength (λ_{max}) of the UV tube was 254 nm. Glass reactors with UV-C lamps are used by different researchers to carry out UV/H_2O_2 experiments [15,21,22]. Glass reactor was covered with aluminum foil to prevent the loss of UV radiation. A magnetic stirrer was placed below the glass reactor. The experimental setup is shown in Fig. 1.

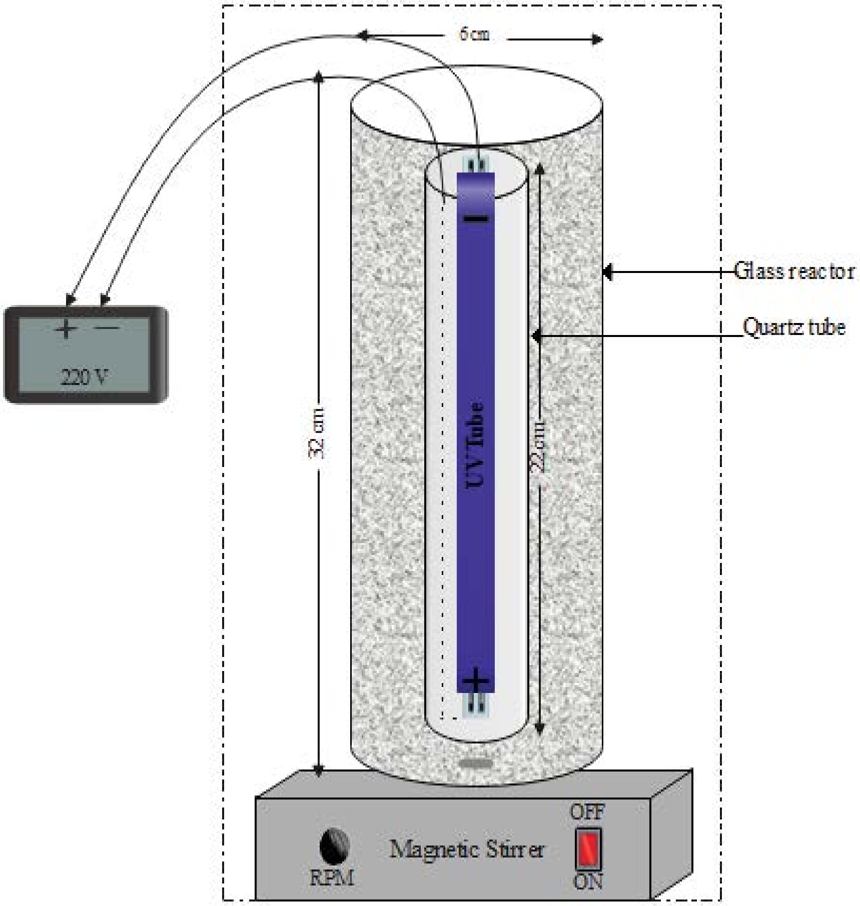


Fig. 1. Experimental set-up for UV/H_2O_2 process.

2.3. Experimental procedure

MB dye sample (500 mL) was taken in a reactor. The desired pH and H_2O_2 dose were added to the solution. Constant agitation was provided with a magnetic stirrer. The desired sample volume was taken to analyze color removal efficiency and residual H_2O_2 concentration measurement [23] at varied time intervals to suggest the best treatment conditions.

2.4. Analytical methods

pH was adjusted by using 3-point calibrated lab scale pH meter (LABTRONICS LT-501). For the analysis of MB concentration, absorption spectra of MB were studied from the range of 250 to 700 nm in UV-Vis spectrophotometer (Systronics 119). Maximum absorbance was observed at two wavelengths 293 and 664 nm (Fig. S1). To check color removal efficiency of MB, absorbance of the solution was taken at 664 nm.

Color removal efficiency was calculated by following equation [3]:

$$\text{Color removal efficiency}\left(\%\right)=\frac{C_i-C_f}{C_i}\times 100 \tag{1}$$

where C_i is the initial concentration of dye and C_f is the final concentration of dye.

To determine residual H_2O_2 concentration, the Iodide method given by [23] is used. This method is based upon the principle of oxidation of KI in the presence of H_2O_2. Due to the oxidation of potassium iodide, iodine is liberated as iodide which is measured spectrophotometrically at 352 nm. 2 mL of each Solution A and Solution B are mixed and then a sample is added to make a total volume of 10 mL. Flow chart of method and standard curve is shown in Fig. S2a and b, respectively.

Energy consumption and SEC were calculated by using Eqs. (2) and (3) respectively [13]:

$$\text{Energy}\left(\text{kWh/m}^3\right)=\frac{P\times t\times 1{,}000}{V} \tag{2}$$

$$\text{SEC}\left(\text{kWh/kg dye}\right)=\frac{P\times t\times 1{,}000}{V\left(C_i-C_f\right)} \tag{3}$$

where P is power of UV lamp (kW), t is treatment time (h), V is working volume of solution (L), C_i and C_f are initial and final dye concentration (mg/L), respectively.

Color characteristics of samples in terms of dominant wavelength, hue, luminance and purity before and after treatment were obtained by using Spectrophotometric Multi-wavelength method (2120-D) mentioned in Standard methods for the examination of water and wastewater respectively [24].

Transmittance values corresponding to wavelengths (10 ordinates) in Columns X, Y and Z in Table 2120: I [24] are used to find trichromatic coefficients (x and y) according to the following equations:

$$x=\frac{X}{X+Y+Z} \tag{4}$$

$$y=\frac{Y}{X+Y+Z} \tag{5}$$

where x and y are located on the chromaticity diagrams to determine color characteristics.

2.5. Removal kinetics

Pseudo-first-order reaction rate constants were calculated by following equation [7]:

$$\ln\frac{\left[C_t\right]}{\left[C_0\right]}=-k_{\text{obs}}t \tag{6}$$

where C_0 is the initial concentration of MB, C_t is the concentration of MB at time t and k_{obs} is the first order rate constant.

3. Results and discussion

3.1. Degradation of MB in different oxidation systems

Degradation experiments of MB were carried out in different oxidation systems: UV alone, H_2O_2 alone and combined UV/H_2O_2 to study the degradation kinetics (Fig. 2). Only 14.96% and 23.39% removal efficiency were obtained in UV alone and H_2O_2 alone processes respectively while in UV/H_2O_2 system 91% removal efficiency was obtained after 90 min treatment time. These results showed that the synergistic effect of UV and H_2O_2 is needed for the activation of hydroxyl radicals because in the presence of UV light, H_2O_2 molecules absorb the light quanta energy and converted it into hydroxyl radicals having high electrochemical potential [25]. Pseudo-first-order rate constants for UV alone, H_2O_2 alone, and UV/H_2O_2 are 0.096, 0.156 and 0.84 h^{-1} (0.0016, 0.0026 and 0.014 min^{-1}) respectively.

3.2. Effect of pH on MB removal

The effect of pH (3, 7, and 11) on decolorization of 50 mg/L MB was studied. Results showed that the decolorization of MB is highly dependent on pH. With increase in pH, color removal efficiency decreased. The highest decolorization of 91% was observed at pH 3 while at pH 11 decolorization was 50.99% in 90 min treatment time (Fig. 3). Acidic pH favors the production of more $OH^\bullet$ radicals. While, in alkaline conditions, H_2O_2 dissociates into HO^{2-} which quenches hydroxyl radicals and decreases their production [12]. Due to the reduction of hydroxyl radicals under alkaline conditions, degradation rate is slow [22]. Higher color removal efficiency of different dyes in the UV/H_2O_2 process at acidic pH has been observed by many researchers [25–27]. To confirm the optimum pH in the present study, experiments were also conducted at pH 3,4 and 5 for 100 mg/L dye at 30 min treatment time. About 59.26% color removal efficiency was obtained for pH 3, 37.56% for pH 4 and 33.16%

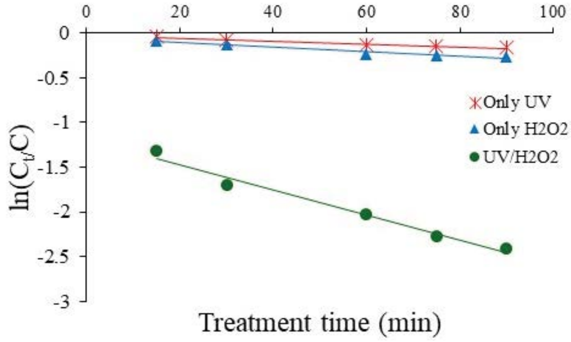


Fig. 2. Relative degradation of MB using UV only, H_2O_2 only and UV combined with H_2O_2. Experimental conditions: initial dye concentration = 50 mg/L, pH = 3 and H_2O_2 = 12.5 mM.

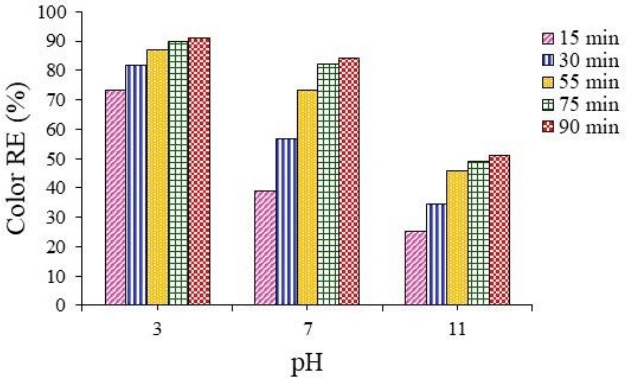


Fig. 3. Effect of pH on color removal efficiency of MB dye at different time intervals. Experimental conditions: initial dye concentration = 50 mg/L and H_2O_2 concentration = 12.5 mM.

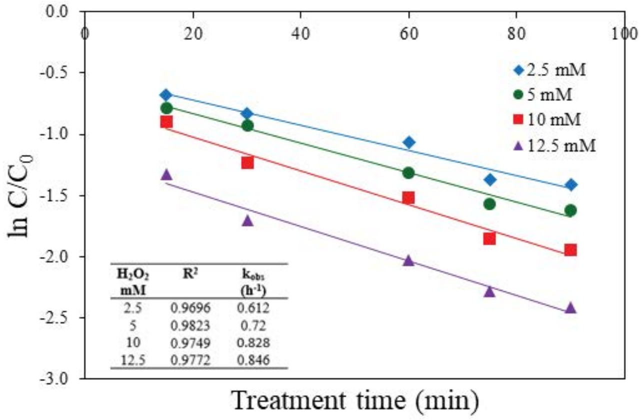
for pH 5 which showed the significant decrease in removal efficiency from pH 3 to pH 5 (Fig. S3). Hence, in the present study, pH 3 was selected to carry out experiments due to the production of more hydroxyl radicals in acidic pH.

3.3. Effect of H_2O_2 concentration

Effect of H_2O_2 concentration from 2.5 to 12.5 mM on color removal efficiency of MB dye was studied. With increase in H_2O_2 dose, color removal efficiency of dye also increased. At concentrations of 2.5, 5, 10 and 12.5 mM, color removal efficiency was 56.64%, 60.29%, 70.89% and 81.76%, respectively for 50 mg/L dye solution in 30 min treatment time (Fig. S4). This increase in color removal results in the increase of rate constants from 0.612 to 0.84 h^{-1} (0.010 to 0.014 min^{-1}) (Fig. 4). Due to photolysis of H_2O_2 in the presence of UV, hydroxyl radicals are generated [Eq. (7)] which are used in the UV/H_2O_2 process to carry out the treatment of pollutants [28].

$$H_2O_2 + UV(hv) \rightarrow HO^\bullet + HO^\bullet \tag{7}$$

Increase in H_2O_2 concentration from 0.01 to 0.2 mM increased the color removal efficiency of 4.79 mg/L Rhodamine dye from 63% to 99% in 10 min [18]. Laftani et al. [17] also showed that decolorization efficiency of 50 mg/L Ponceau S (diazo dye) was increased from 59.07% to 98.50% when H_2O_2 concentration was increased from 0.46 to 2 mM due to the production of more hydroxyl radicals with increase in H_2O_2 concentration. Manikandan et al. [11] observed the increase in color removal efficiency of dye bath water from 63.76% to 98.77% with an increase in H_2O_2 dose from 100 to 400 mM. However, at very high concentrations above 400 mM, self-quenching of H_2O_2 occurred which resulted in decrease in removal efficiency. Self-quenching occurred due to the reaction of excess H_2O_2 with $OH^\bullet$ radicals which result in production of $HO_2^\bullet$ radicals and decrease removal efficiency [29] (Eq. 8)



H_2O_2 mM	R^2	k_{obs} (h^{-1})
2.5	0.9696	0.612
5	0.9823	0.72
10	0.9749	0.828
12.5	0.9772	0.846

Fig. 4. Degradation kinetics of MB dye at different H_2O_2 concentrations. Experimental conditions: initial dye concentration = 50 mg/L and pH = 3.

$$H_2O_2 + OH^\bullet \rightarrow H_2O + HO_2^\bullet \tag{8}$$

Self-quenching of H_2O_2 was not observed in the present study upto 12.5 mM H_2O_2 concentration and dose was not increased above 12.5 mM so that effluent contains less amount of residual H_2O_2.

Also, it was noted that there was no significant increase in color removal efficiency with increase in treatment time after 30 min. (Fig. S4). So, in the present case, treatment time beyond 30 min is not recommended to save energy.

3.4. Residual H_2O_2 concentration

Residual H_2O_2 after UV/H_2O_2 treatment was also investigated to optimize the H_2O_2 concentration so that minimum residue of H_2O_2 will be released in effluent. Residual H_2O_2 was calculated at different time intervals for different initial H_2O_2 doses (2.5, 5, 10 and 12.5) mM during the experiment (Fig. 5). For initial H_2O_2 doses of 2.5, 5, 10 and 12.5 mM, residual H_2O_2 was found to be 98.13%, 95.57%, 95.44% and 94.41%, respectively after 30 min treatment while even after 75 min, more than 89% residual H_2O_2 was remained in the effluent for all the initial H_2O_2 doses which indicates that only small amount of H_2O_2 was used in the treatment process.

Sarathy et al. [30] discussed the treatment of surface water by UV/H_2O_2 in which 10 mg/L (0.29 mM) H_2O_2 was used for

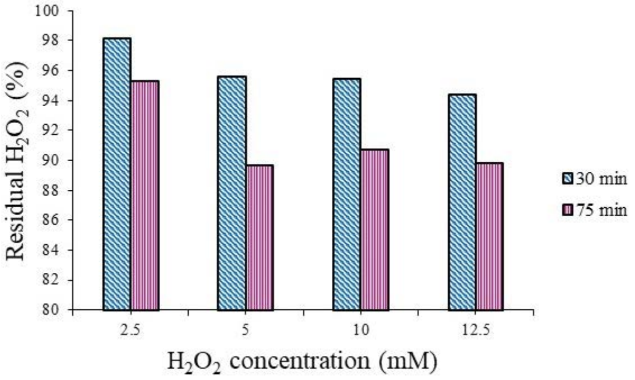


Fig. 5. Residual H_2O_2 during degradation of MB dye at different initial H_2O_2 doses. Experimental conditions: initial dye concentration = 50 mg/L and pH = 3.

treatment experiments. After treatment, about 90% of residual H_2O_2 was observed in water. Similarly, Giri et al. [31] discussed the removal of pharmaceutical compounds by UV/H_2O_2 process in which H_2O_2 dose ranged from 0–1.46 mM and only small fractions of H_2O_2 were used in the process after 30 min while more than 85% H_2O_2 remained in the system.

3.5. Removal kinetics of MB dye

Experiments were performed at different initial dye concentrations of 10, 25, 50 and 100 mg/L to study the removal kinetics. Increase in initial dye concentration showed a negative effect on color removal efficiency. With increase in initial dye concentration from 10 to 100 mg/L, color removal efficiency decreased from 96.57% to 59.26% in 30 min treatment time (Fig. S5). This decrease in color removal efficiency results in an increase in pseudo-first-order rate constants. At initial dye concentrations of 10, 25, 50 and 100 mg/L, rate constants were 1.46, 1.092, 0.846, 0.528 h^{-1} (0.0243, 0.0182, 0.0141 and 0.0088 min^{-1}) respectively (Fig. 6).

The reason for this negative effect of initial pollutant concentration on degradation is due to the fact that at higher pollutant concentrations, higher amounts of UV photons could be absorbed by pollutant molecules [21]. Hence there is reduction in the absorption of photons into the solution due to induction of inner filter effect which makes solution impenetrable to UV radiations and decreases the hydroxyl radical production [32]. Another possible reason for decrease in degradation could be the increase in intermediate concentration at higher pollutant concentration which reacts with hydroxyl radicals and quenches their effect [21].

3.6. Absorption spectra of MB dye at different time interval

UV-Vis absorption spectra from 250 to 700 nm were taken to study the degradation of MB dye (10 mg/L). Absorption spectra were taken before treatment and after treatment at different time intervals from 15 to 90 min. Peak at 664 nm was due the chromophore of the dye formed by a conjugation system through sulfur and nitrogen between the aromatic rings and peak at 293 nm was due to the benzene rings [33].

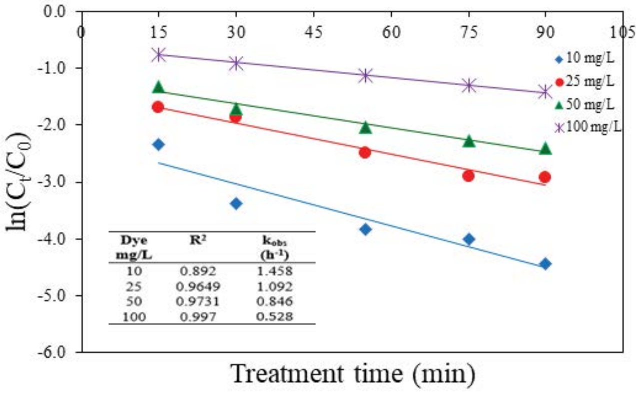


Fig. 6. Degradation kinetics of MB dye at different initial dye concentration. Experimental conditions: H_2O_2 concentration = 12.5 mM and pH = 3.

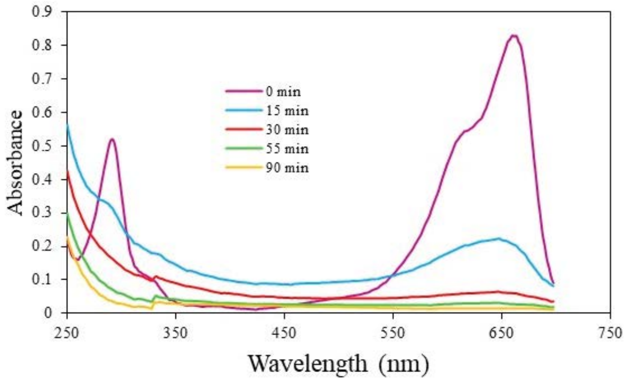


Fig. 7. UV-Vis absorption spectra of MB dye at different time intervals. Experimental conditions: initial dye concentration = 10 mg/L, pH = 3 and H_2O_2 = 12.5 mM.

Decrease in the height of characteristic peak was observed after UV/H_2O_2 treatment (Fig. 7) which showed the significant degradation of MB dye. Peak due to benzene rings which was observed at 293 nm was completely diminished at 15 min of treatment, whereas second peak (664 nm) which is due to chromophore of dye was drastically removed at 15 min of treatment, which further diminished at 30 min of treatment time.

The disappearance of the MB characteristic peak without the emergence of other new absorption bands indicated the complete removal of MB by catalytic degradation without any intermediate production [34]. Zhou et al., [35] also observed the disappearance of MB peaks after 40 min treatment without the formation of other new peaks which showed that MB was completely removed due to the destruction of benzene ring and hetero polyaromatic bonds.

Pathway of MB was discussed by [36] in which MB undergone demethylation by the OH and HO_2 radicals and converted into unstable intermediates like Azure A, Azure B and Thionine molecules which further converted into H_2O, Cl^-, CO_2, SO_4^{2-} and NO_3. UV-Vis spectra of dye confirmed the complete destruction of MB with the disappearance of characteristic peaks and no formation of new peaks. Similar

Table 1
Optimum process conditions with normalized energy consumption for removal of different types of dyes using UV/H_2O_2 process

S. No.	Type of pollutant	MW	Conc.	pH	H_2O_2 conc.	H_2O_2/dye conc.	Time	Vol.	Light source	Colour RE	k_{obs}	k_{obs}	Energy	SEC	Normalized SEC	References
		g/mol	mg/L		mM	mM/mM	min	mL	W	%	min^{-1}	h^{-1}	kWh/m^3	kWh/kg		
1	Alizarin Yellow R	309.21	250	4.9	250	309	60	400	8	92.7	0.075	4.5	20	86.3	1	Narayanasamy and Murugesan [22]
2	Remazol Brilliant Blue R	626.54	110	–	30	171	30	900	25	96	0.117	7.0	14	131.5	1.5	Cardoso et al. [38]
3	Methylene blue	319.85	50	3	12.5	80	30	500	11	81	0.014	0.85	11	271.6	3.1	Own study
4	Thiazole Yellow	695.72	45	4	0.18	3	10	250	6	30	0.037	2.2	4	296.3	3.4	Rauf et al. [29]
6	C.I. Acid Black 1	616.50	20	7.2	58.8	1,813	10	500	30	99.5	–	–	10	502.5	5.8	Kasiri and Khataee [20]
7	C.I. Acid Blue	695.60	20	–	58.8	2,045	10	500	30	93.5	–	–	10	534.7	6.2	Kasiri and Khataee [20]
8	C.I. Acid Red 88	400.38	20	7	25	500	2	100	30	77.9	–	–	10	641.9	7.4	Modirshahla et al. [40]
9	Malachite Green	364.91	15	4	0.18	4	10	250	6	40	0.027	1.6	4	666.7	7.7	Rauf et al. [29]
5	Reactive Orange 122	926.20	50	5	1.48	27	120	600	10	99.9	0.190	11	33	667	7.7	Çobanoğlu and N. Değermenci [15]
10	C.I. Basic Red 46	420.00	20	7	29.4	617	14	500	30	95	–	–	14	737	8.5	Khataee and Habibi [19]
11	Mordant Red	480.00	24	3	2.5	50	50	250	20	99	0.086	5.2	67	2,806	33	Elmorsi et al. [37]
12	Methyl Orange	327.33	10	6.5	8.8	288	1.5	20	25	99.9	1.056	63	31	3,128	36	Navarro et al. [39]
13	Ponceau S	760.60	50	–	2	30	40	500	250	99.5	–	–	333	6,700	78	Laftani et al. [17]
14	Methylene blue	319.85	10	–	0.88	28	20	250	250	98	0.264	16	333	34,014	394	Kumar et al. [7]
15	Methylene blue	319.85	30	4	49	522	30	100	300	50	0.013	0.78	1,500	100,000	1,159	Jian-Xiao et al. [25]
16	Rhodamine	479.00	5	7	0.05	5	15	50	300	95.6	0.106	6.4	1,500	327,565	3,796	Ding et al. [18]
	Min.		5	3	0.05	3	1.5	20	6	30	0.013	0.78	4	86.3		
	Max.		250	7.2	250	2,045	120	900	300	99.9	1.056	63	1,500	327,565		

Table 2
Color characteristics of MB before and after 30 min treatment

Color characteristics	Before treatment	After treatment (30 min)
Dominant wavelength	490 nm	580–590 nm
Hue	Blue green	Yellowish orange
Luminance	66.3	89.5
Purity	20%	less than 10%

formation of intermediates was observed by [33] during the photocatalytic degradation of MB dye occurred by demethylation.

In the present study, no new absorption peaks were observed after the degradation process resulted in the complete destruction of benzene rings and chromophore of MB by UV/H_2O_2 process without any stable intermediate formation.

Color characteristics of 10 mg/L MB dye were also determined before and after 30 min treatment. The dominant wavelength of dye before treatment was 490 nm with the blue green hue while after 30 min treatment visual discoloration of dye was observed with the dominant wavelength of 580–590 nm with yellowish-orange hue (Table 2). It showed that the dye was completely degraded by UV/H_2O_2 process after 30 min treatment which resulted in the change of dominant wavelength and hue of the sample.

3.7. Comparison of present study with literature

The color removal efficiency of dyes ranged from 30%–99.5% over a range of H_2O_2/dye concentration of 3–2045 along with optimum process conditions and normalized SEC is shown in Table 1.

Rauf et al. [29] used the lowest H_2O_2/dye concentration ratio of 3 and 4 for the degradation of Thiazole Yellow and Malachite Green dye respectively. But due to the very low ratio, only 30% and 40% color removal was achieved in 10 min with specific energy consumption (SEC) of 296 kWh/kg Thiazole Yellow and 666 kWh/kg Malachite Green. High color removal efficiency of 95.6% at very low H_2O_2/dye concentration ratio (5) was achieved by [18]. However, SEC (327,565 kWh/kg dye) was very high (highest in table) which is 1200 times more than present study. In earlier studies by [15,17,37] high removal efficiency (>98%) of dyes was achieved at H_2O_2/dye concentration ratio of 27 to 50 but SEC was relatively high (667; 6,700; 2,806 kWh/kg dye respectively) in these studies.

More than 90% decolorization of Alizarin yellow and Remazol BBR orange was obtained with SEC of 86.3 kWh/kg dye and 131.52 kWh/kg dye but at relatively high H_2O_2/dye ratio of 309 and 171 [22,38]. At a H_2O_2/dye concentration ratio of 288, high color removal efficiency of Methyl Orange (99.9%) was obtained at high SEC of 3,128.13 kWh/kg dye [39]. Compared to present study, equivalent dye removal efficiency was obtained by [40] at EC of 641.8 kWh/kg dye and H_2O_2/dye concentration ratio (500) which is higher than energy consumed (271.6 kWh/kg) and H_2O_2/dye concentration ratio (80) in the present work. At H_2O_2/dye concentration ratio of 617 color removal efficiencies of C.I. Basic Red was 95% with high SEC of 736.84 kWh/kg dye [19]. High color removal efficiency 93.5% for C.I. Acid blue was obtained by [20] with SEC (535 kWh/kg dye) at a very high H_2O_2/dye concentration ratio of 2045 (highest in table).

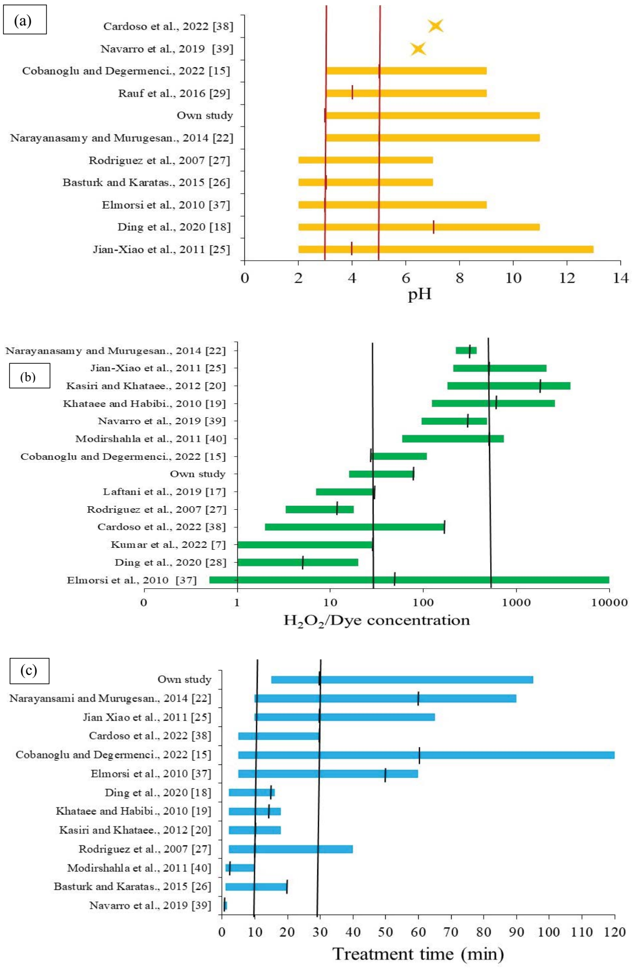


Fig. 8. Range and optimum (a) pH, (b) H_2O_2 concentration and (c) treatment time for UV/H_2O_2 process as per the literature review.

For methylene blue dye, Kumar et al. [7] used very low H_2O_2/dye concentration ratio (28) to obtain 98% removal efficiency but the process was highly energy-intensive with SEC of 34,014 kWh/kg. Jian-Xiao et al. [25] achieved only 50% degradation of MB dye at high H_2O_2/dye concentration ratio (522) and high SEC (100,000 kWh/kg dye). In the present work, 81.6% removal efficiency was obtained in 30 min with a low SEC of 271.6 kWh/kg dye at H_2O_2/dye ratio was found to be 80.

Maximum, minimum and optimum conditions are plotted in Fig. 8 for (a) pH, (b) H_2O_2/dye concentration and (c) treatment time as per literature review. As these are the important factors on which the UV/H_2O_2 process is highly dependent, they must be optimized to obtain maximum removal. The best operating range for the UV/H_2O_2 process for the removal of different dyes was found to be (3–5) for pH, (30–500) for H_2O_2/dye concentration, and (10–30) min for treatment time, as shown in Fig. 8, and is recommended for further investigations to obtain maximal dye removal.

4. Conclusion

Degradation of MB by UV/H_2O_2 process was investigated in the present study. Dye removal was caused due to the synergistic effect of UV and H_2O_2. Acidic pH was favorable for the treatment of dye. Maximum degradation was achieved at pH 3. The optimal H_2O_2 concentration was found to be 12.5 mM. It was found that for all the doses of H_2O_2, greater than 89% residual H_2O_2 remained in effluent after 75 min treatment time. Hence 12.5 mM was selected as optimum H_2O_2 concentration and dose was not increased above 12.5 mM to minimize the release of residual H_2O_2 in treated effluent. Color removal efficiency of 81.76% was observed for 50 mg/L MB dye in 30 min treatment time in optimized conditions with SEC of 271.6 kWh/kg dye. Degradation of MB obeyed pseudo-first-order removal kinetics. UV/H_2O_2 can be considered as economic and cleaner technology for the treatment of MB dye due to low energy consumption and no sludge formation.

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Authors contributions

M.S.B: Conceptualization, Methodology, Review, Visualization and Supervision, A. S: Experimentation, Methodology, Writing-Original draft.

Conflict of interest

Authors declare no conflict of interest.

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Supporting information

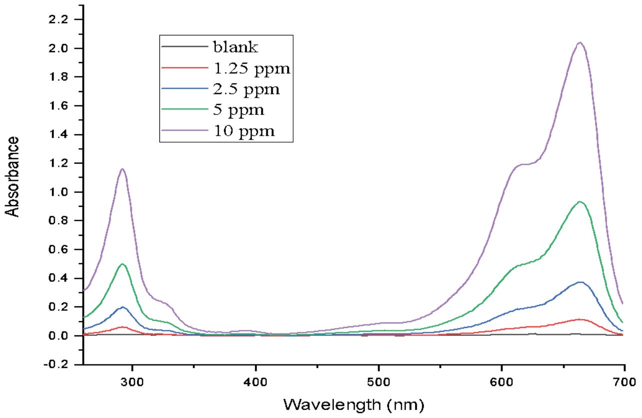
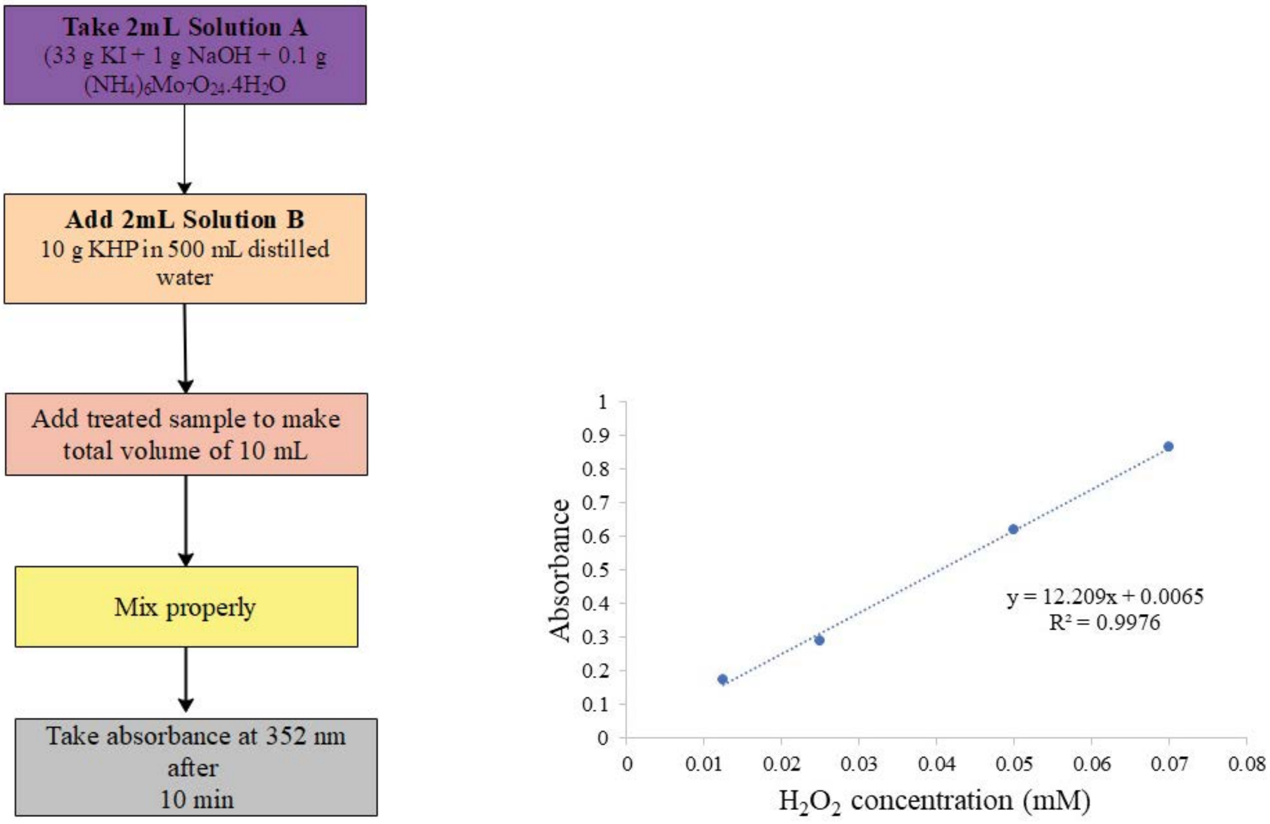


Fig. S1. Absorption spectra for methylene blue dye from 260 to 700 nm.



(a) (b)

Fig. S2. (a) Flow chart for the determination of H_2O_2 concentration and (b) standard curve for H_2O_2 at 352 nm.

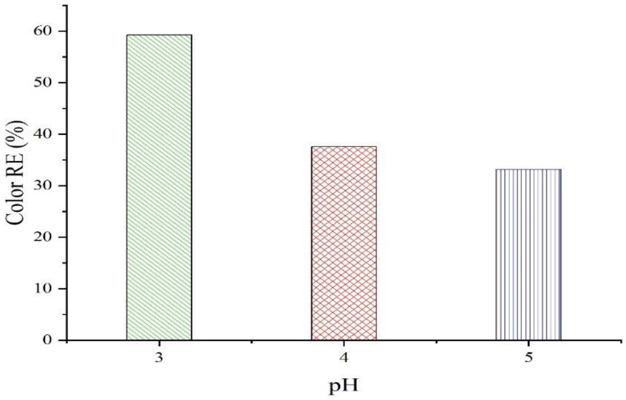


Fig. S3. Effect of pH on color RE of MB dye at 30 min. Experimental conditions: initial dye concentration = 100 mg/L and H_2O_2 concentration = 12.5 mM.

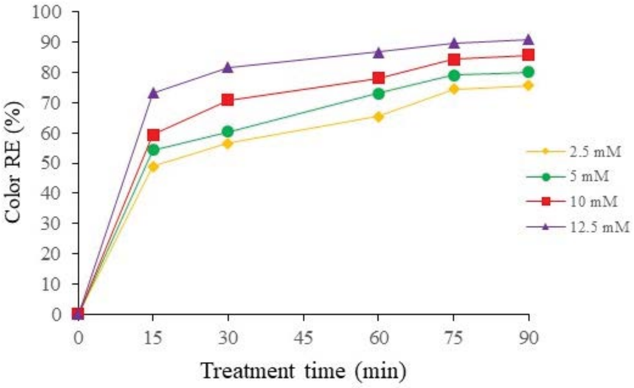


Fig. S4. Effect of H_2O_2 concentration on color removal efficiency of MB dye. Experimental conditions: initial dye concentration = 50 mg/L and pH = 3.

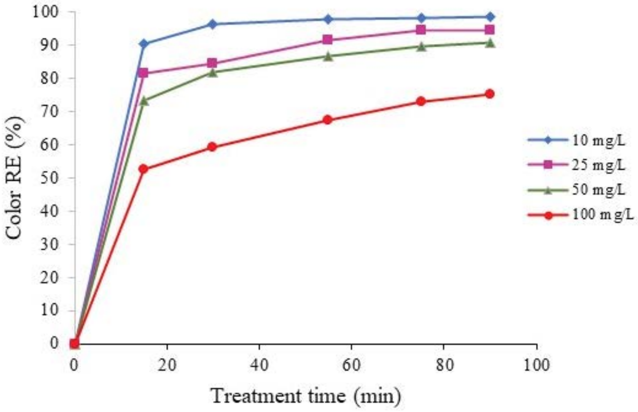


Fig. S5. Effect of dye concentration on color removal efficiency of MB. Experimental conditions: initial H_2O_2 concentration = 12.5 mM and pH = 3.