CHAPTER 6

Synergistic Approach of Coupling Ozonation and Biological System for Efficient Azo Dye Mineralization: A Comprehensive Techno-Economic Evaluation

6.1 Introduction

In the textile industry, numerous toxic and potentially hazardous dyes get produced during unit operations and processes (Dias et al., 2019; Mohan and Oke, 2022; Punzi et al., 2015). Conventional dye wastewater treatment methods include a variety of biological, chemical, and physical processes. Among these methods, biological processes are considered the suitable option for dye treatment due to their environmentally friendly and cost-effective nature (Irani et al., 2021; Srinivasan and Sadasivam, 2021). However, several studies have shown the existence of non–biodegradable or low-biodegradable compounds in textile effluent (Malik et al., 2020). The existence of these non–biodegradable compounds causes a lower biodegradability index (BOD_5 : COD < 0.2) and makes biological treatment ineffective for the majority of industrial wastewater, including textile industry. The biological methods are typically effective for wastewater having BOD_5 : COD ratios greater than 0.4 (Bilińska and Gmurek, 2021).

The wastewater treatment industry faces significant challenges when treating wastewater that contains dye (Abidin et al., 2015). Depending on how they are distinct from other substances, it is crucial to develop a suitable technology for treating toxic dyes. In this context, new technologies for the treatment of textile wastewater have been developed (Zhao et al., 2018).

The principle of advanced oxidation processes (AOPs) is to produce strong oxidizing radicals, specifically the hydroxyl radical ($OH^{\bullet}$), which is having high oxidation potential ($E^{\circ} \cong 2.8\ V$) and is capable of oxidizing highly recalcitrant contaminants (Asghar et al., 2015; de Souza et al., 2010; Ledakowicz and Pázdzior, 2021; Tapalad et al., 2008). Hydroxyl radical ($OH^{\bullet}$) can be generated by individual processes which includes ozone (O_3), UV fenton, hydrogen peroxide (H_2O_2), UV/H_2O_2, $O_3/UV/H_2O_2$, and $O_3/TiO_2/H_2O_2$ system (Bilińska and Gmurek, 2021). Among all these existing advanced treatment processes, ozonation is preferred as a viable alternative for textile wastewater treatment owning to its high selectivity towards the chromophoric group of an azo dye, less sludge formation, and adaptability across a wide pH range (Chaturvedi and Jaiswal, 2022; Fanchiang and Tseng, 2009; Lu et al., 2009; Paździor et al., 2017). Ozone can quickly break the azo bond, removing colour in very short intervals. Meanwhile, it may improve the biodegradability of dye wastewater. However, ozonation is effective in colour removal of dye wastewater but it often shows low rate of mineralization (Abidin et al., 2015; Venkatesh et al., 2016).

Therefore, the application of biological process as a post-treatment of pre-ozonated dye wastewater could be an effective approach to achieve complete mineralization (Su et al., 2020). Biofilm systems have recently received significantly more attention than free cell systems due to their numerous advantages, including the ability to prevent cells from washing out under aerobic conditions, substantial biomass growth, and excellent removal efficiency (Tripathi et al., 2023a). Among biofilm technology, packed bed bioreactor (PBBR) is widely employed in recent years due to its several advantages such as; easy fabrication, longer retention time, and higher specific area. Application of PBBR for dye wastewater treatment is reported by several researchers (Bharti et al., 2019; Geed et al., 2017; Swain et al., 2021a).

The main motive of the present study was to assess the efficiency of an integrated treatment system (ozonation coupled with biodegradation) for simulated textile wastewater (STWW) treatment using Congo red dye as target pollutant. The utilization of ozonation as a pre-treatment prior to biodegradation has been explored for complete mineralization of dye wastewater. Although ozonation has been utilized to treat textile effluents in recent years, only a few papers have investigated the potentially toxic metabolites formed after ozonation. Furthermore, to the best of our understanding, only a few research studies based on an economic analysis of the suggested strategy have been conducted. Additionally, a degradation pathway was proposed based on the metabolites identified after the ozonation.

6.2 Materials and method

6.2.1 Ozonation procedure

Ozonation was used to pre-treat the CR dye wastewater before subjecting it to biological treatment. Ozonation was carried out in a tubular reactor (height = 65 cm; inner dia = 5 cm; working volume = 1.0 L) (**Fig. 6.1**). The ozone was generated via corona discharge method using a Faraday ozone generator (Model: L20G). The experimental setup of ozonation consists of oxygen concentrator (OXY-5L), faraday ozone generator, porous diffusor, peristaltic pump (MILTON ROY INDIA: A-11 SS), tubular reactor and an excess ozone trap containing 2% KI solution. Oxygen was supplied from the oxygen concentrator at a flowrate of 5.0 L/min. The final ozone dose was set to 69.9 ± 0.5 mg O_3/L. The concentration of gaseous ozone was determined using a 2% KI solution in the conical flask prior to the ozonation experiments (Method 2350E, APHA, 2012). The ozone gas flowrate was fixed at a rate of 1.0 L/min during the ozonation experiments, keeping the ozone dose constant. The unreacted ozone coming out from the column was collected in bottles containing a 2% KI solution. The reaction between the KI solution and extra ozone releases I_2, which is then titrated against standard thiosulphate using starch as an indicator. The ozonation experiments were performed using 500 mg/L of CR dye wastewater solution for various time intervals (5, 10, 15, 20, and 25 min), and samples were analyzed for BOD, COD, and CR concentration. All the experiments were conducted at ambient temperature.

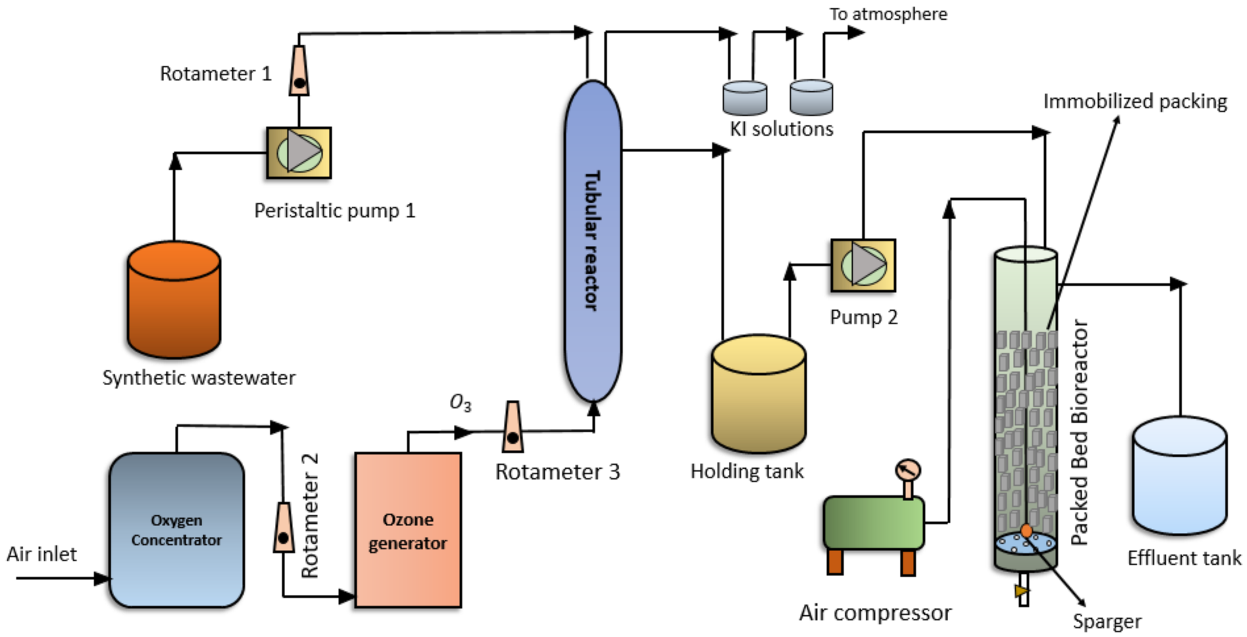

Fig. 6.1 Schematic diagram of coupling process (ozonation and biodegradation) for the treatment of STWW.

6.2.2 Biological Treatment

Wastewater from textile manufacturing processes contains azo dyes and shows low biodegradability. To increase biodegradability, ozone was used to pre-treat the simulated wastewater. Subsequently, PBBR was used to remove the remaining dye and its intermediates from wastewater. The biological experiment was carried out in PBBR (height = 100 cm, dia = 5 cm) having a total capacity of ~1.9 L. The cubes of Low-density polyethylene (LDPE) were utilized as a packing material for the PBBR because it offers high surface area, good chemical resistance, and low water absorption.

The sheet of LDPE was cut into equal-size cubes ($1\ cm \times 1\ cm \times 1\ cm$), and washed with ethanol (70%) then dried in an oven at 50°C. The dried LDPE cubes are then packed into the reactor and run in batch mode for 20 days with bacterial culture and MSM to form biofilm. The solution's pH and temperature were maintained at 7.0±0.5 and 35±1°C, respectively during biological treatment. The flow rate of dye solution was adjusted between 10 – 25 mL/min. The outlet samples were withdrawn from the reactor's top on a regular interval.

6.2.3 Analytical methods

The absorbance of samples, chemical oxygen demand (COD), pH of the solution, and Biochemical oxygen demand (BOD_5) were continuously monitored at regular interval. The absorbance of the sample was measured in the range of 250–800 nm using a UV-VIS spectrophotometer (ELICO SL 159). COD (standard dichromate method) and BOD_5 (standard dilution method) were determined as per the standard method for water and wastewater (APHA, 2012). The iodometric method was used to calculate the amount of ozone. The morphological characteristics of the biofilm formed onto the LDPE surface was examined using microscopy (Nikon ECLIPSE Ni-E, Japan). The immobilized packing materials were first vacuum dried before the visual observation (**Fig 6.2**).

Metabolites formed after ozonation were analyzed using GC/MS. After degradation, the sample (15 mL) was drawn from the reactor and filtered via a 0.22 µm syringe filter. The filtrate was then extracted with an equal volume of ethyl acetate (1:1 V/V) in a separating funnel. Anhydrous Na_2SO_4 was used to remove excess water, and the sample was then evaporated in a rotary vacuum evaporator (at a temperature of 45-50°C). After evaporation, the residue was dissolved in methanol (HPLC-grade) for GC/MS analysis.

Agilent GC/MS (GC 7820A, 5977B GC/MSD) installed with HP- 5 MS column was used to carry out the GC/MS analysis, and helium was used as a carrier gas. The temperature of the injector was kept between 250 to 300°C. The final metabolites were identified using the corresponding mass spectra and retention time.

The removal efficiency of both color and COD were calculated using following equations:

$$\%\,Color\ Removal = \frac{C_i - C_f}{C_i} \tag{6.1}$$

$$\% \, COD \, Removal = \frac{COD_i - COD_f}{COD_i} \tag{6.2}$$

where C_i and C_f are initial and final concentration of CR dye (mg/L), respectively. COD_i and COD_f are the initial and final COD (mg/L), of samples, respectively.

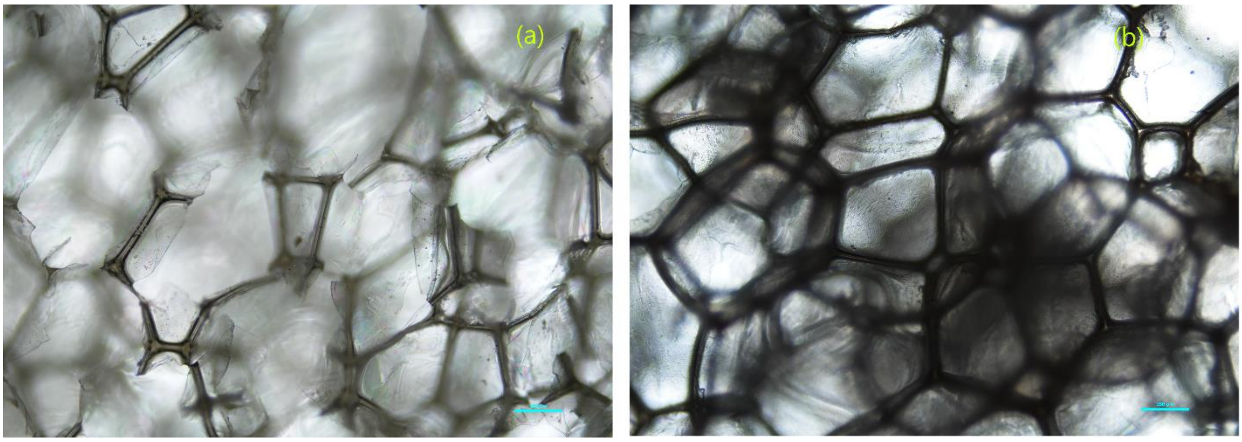

Fig. 6.2 Microscopic image of the packing material (a) before immobilization (b) after immobilization.

6.2.4 Toxicity assessment

The microcrustacean *Daphnia magna* was used in the acute toxicity test. It is a freshwater planktonic microcrustacean that functions as a primary consumer in the aquatic food chain, consuming the particulate organic material in the medium through filtration. The tests were carried out in an incubator chamber at 20 ± 2℃ under dark conditions. The tests involve young *D. magna* exposed to several dilutions of the test samples for 48 hours, and the acute toxicity was determined by EC_{50} (an effective concentration that leaves 50% of the test organisms immobile or dead after a period of 48 h). Two 50 mL beakers were used for the tests, as well as a control with dilution water. Each beaker contained ten young Daphnia (6–24 h of life). Synthetic effluents were tested at various concentrations before and after ozonation and biological treatment. The control test was carried out using Daphnia in a distilled water sample. The immobile bodies were counted after 48 hours of incubation to calculate the toxicity factor using Trimmed Spearman-Karber software (version 1.5.0).

6.2.5 Techno-economic assessment

Technical and economic evaluation of the developed technology is vital to evaluate its feasibility to scale up. Most of the studies related to the AOPs have been performed on a lab scale. There are several costs, related to the entire treatment process that must be considered when determining the process's economic viability. Keeping that in mind, a techno-economic analysis was carried out to find the economic viability of a hybrid process for the treatment of real textile wastewater.

The techno-economical assessment was performed based on the estimated unit expense per volume of treated wastewater (UEX,$\$/m^3$) to evaluate the economics and feasibility of developed integrated treatment system. The annual operating expense (OpEX) and amortized capital expense (ACapEX) per volumetric flow rate (Q) are both considered by this parameter which is shown in Eq. 6.3. The treatment process was simulated using SuperPro Designer (v9.0, Intelligen Technology).

$$UEX = \frac{OpEX + ACapEX}{Q} \qquad (6.3)$$

Direct expense (DEX) is generally the sum of installation, equipment purchase, piping, insulation, building, etc. Indirect expenses (IEX) includes construction and engineering cost and other expense (OEX) includes contingency cost, which is a direct function of DEX (Supplementary data) (Martínez et al., 2018). Direct fixed capital expenses (DFCapEX) can be calculated as sum of direct expenses, indirect expenses, and other expenses (Eq. 6.4).

$$DFCapEX = DEX + IEX + OEX \qquad (6.4)$$

The total cost of raw materials, industry consumables, utilities, and additional costs like transportation and waste treatment or disposal was calculated as the annual operating expense (OpEX). Using a 20-year (n) amortization period and a 7% annual amortization rate (i) for the direct fixed capital expense (DFCapEX), the annual amortized capital expense (ACapEX) was calculated (Eq. 6.5).

$$ACapEx = \frac{DFCapEX*i}{\left[1-\left(\frac{1}{1+i}\right)^{n}\right]} \qquad (6.5)$$

The cost involved with the electricity consumption for the hybrid process was calculated using Eq. (6).

$$E_{EO} = \frac{P*t*1000}{V*\log\frac{C_i}{C_f}} \qquad (6.6)$$

where E_{EO} is electrical energy consumed per order kWh/m^3 to treat pollutants in 1 m^3 volume, *t* is the time req. for treatment (h), V is the treatment volume (m^3), C_i and C_f are initial and final dye concentration, respectively.

6.3 Results and discussion

6.3.1 Variation in pH with ozonation

One of the major factors that can influence ozonation treatment efficiency is the pH of the dye solution. As observed in **Fig. 6.3**, the initial pH values of 7, 9, and 11 decreases rapidly with ozonation time for 500 mg/L of CR dye solution. This demonstrates that ozone oxidation results in the formation of acidic byproducts (inorganic acids and organic anions). It is intriguing to observe that for an initial pH of 3 does not change significantly and is comparable to those demonstrated for the other pH values. A similar trend of pH variation is also reported by de Souza et al.(2010).

Ozone interacts with aromatic contaminants present in wastewater via two separate reaction mechanisms, namely direct and indirect. At low pH levels, molecular ozone serves as the primary oxidant in direct ozonation, whereas at high pH levels, hydroxyl radicals ($OH^{\bullet}$) are produced by the breakdown of ozone. The solution's pH tends to decrease during treatment due to the interaction of ozone with both hydroxyl anions and the breakdown products produced by oxidation by $OH^{\bullet}$ (typically carboxylic acids) (Somensi et al., 2010).

Another reason for pH reduction could be explained by carbon dioxide dissolution in the effluent. When ozone reacts via $OH^{\bullet}$ mechanism it oxidizes the organic pollutant and results in the formation of carbon dioxide and a part which dissolves in the effluent. According to Lei and Li, 2014, this dissolved carbon dioxide could results in the formation of carbonic acid (H_2CO_3), bicarbonate (${HCO_3}^-$), and H^+ (Eq. $6.7 - 6.9$), which results in reduction of pH of effluent sample.

$$H_2O + CO_2 \rightarrow H_2CO_3 \qquad (6.7)$$

$$H_2CO_3 \rightarrow {HCO_3}^- + H^+ \qquad (6.8)$$

$$HCO_3{}^- \rightarrow CO_3^{-2} + H^+ \qquad (6.9)$$

The reduction in pH is highly evident in the early stages of oxidation (especially for alkaline solutions) due to increased consumption of ozone and dye degradation/mineralization. Since molecular ozone targets specific chromophore groups, direct ozone attack at low pH favors the degree of decolorization. At higher pH, decolorization decreases and mineralization increases due to hydroxyl radical’s higher oxidative strength and lower selectivity compared to molecular ozone.

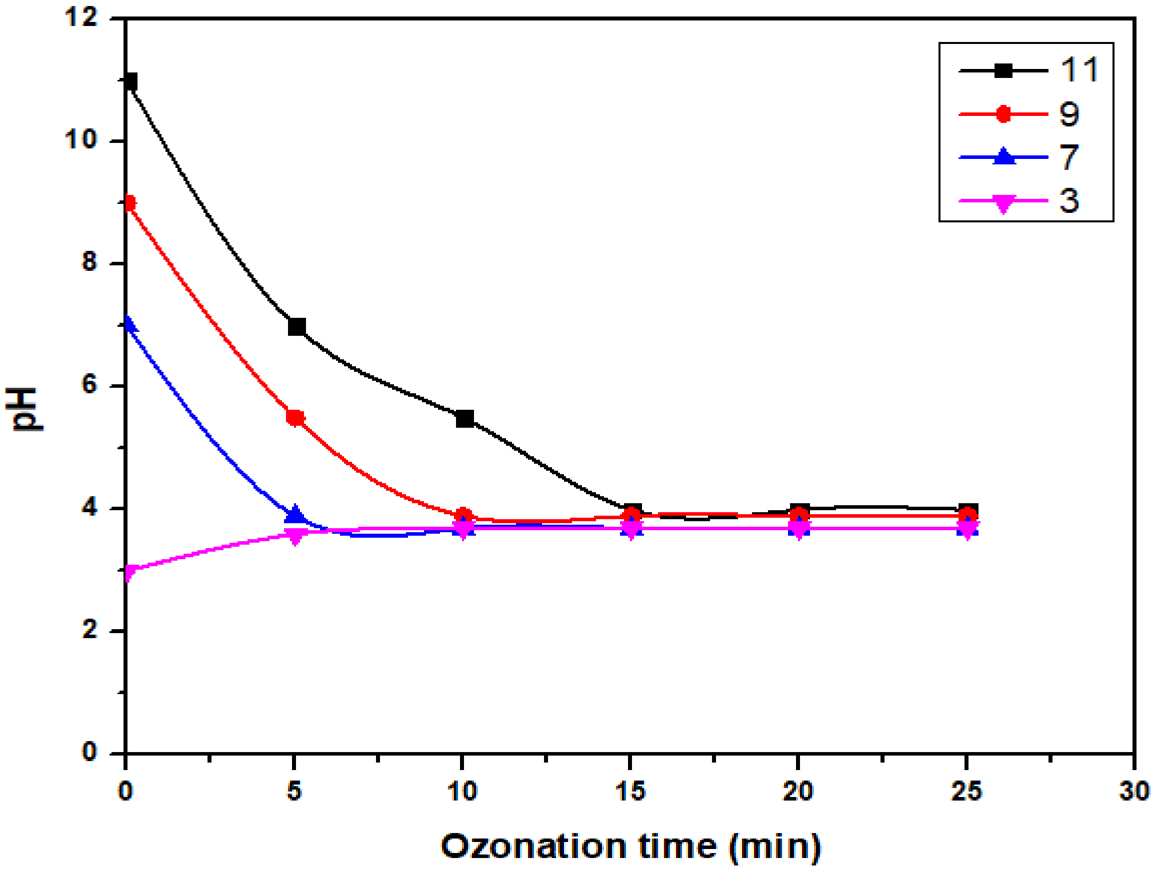

Fig. 6.3 Variation in the solution pH with the ozonation time (Initial dye concentration = 500 mg/L, Temperature = 35 °C)

6.3.2 Effect of ozonation time on color and COD removal

The UV-vis spectra of the initial STWW and ozonated STWW are illustrated in **Fig. 6.4** at various ozonation times. The UV-vis spectral absorption of the STWW solution (t=0 min) is constituted by one visible band corresponding to a maximum near 550 nm and a second band in the ultraviolet region corresponding to a maximum near 343 nm. The benzene and naphthalene rings of the primary molecule are responsible for these two peaks. The reduction of absorbance peak in regions of 300–350 nm and 500–550 nm is an indication of oxidation of the naphthalene group and chromophore group (-N=N-), respectively. From **Fig. 6.4**, it is clearly visible that the absorption peak in the range of 550 nm was rapidly reduced after 10 min of ozonation. The reaction of ozone with the conjugate system is highly selective in direct oxidation mechanism (acidic condition). **Fig 6.5** shows the color and COD removal (%) with the ozonation time at 500 mg/L of CR dye and pH of 11.0. The results show that COD removal is significantly higher than color removal up to 10 minutes of ozonation. In alkaline conditions, ozone reacts via a hydroxyl radical mechanism, which has greater oxidative power but is comparatively less selective than molecular ozone resulting in a high degree of mineralization. After 5 min of ozonation, 30% COD removal was achieved whereas only 18% color removal was found. As ozonation time increases, the solution pH changes from alkaline to acidic conditions resulting in a direct ozonation mechanism, which favors decolorization (Venkatesh et al., 2016). After 15 min of ozonation, more than 80% color removal was attained but COD removal was only 60%. Even though there is a tendency for COD to reduce with longer ozonation times, there are certain instances where the values rise, particularly for times of 20 and 25 minutes. The rise in COD may be caused by the ozonation of dye molecules, which produces small organic molecular fragments that cannot be further mineralized under the stated oxidative conditions. These fragments include acetic acid, aldehydes, and ketones, which may be the cause of the oxidative conditions that result in the increase in COD (de Souza et al., 2010).

Plot of ln (C_t/C_0) v/s time at pH 11.0 for 500 mg/L of Congo red dye ozonation is demonstrated in **Fig. 6.6**. According to the literature, ozonation of dye is a first-order kinetics reaction in terms of the concentration of dye. When ozone is available in excess (as in present study), it can be assumed to be constant throughout the reaction. The reaction rate in this situation can be described as pseudo-first order, making degradation kinetics only function of dye concentration (de Souza et al., 2010; Turhan et al., 2012).

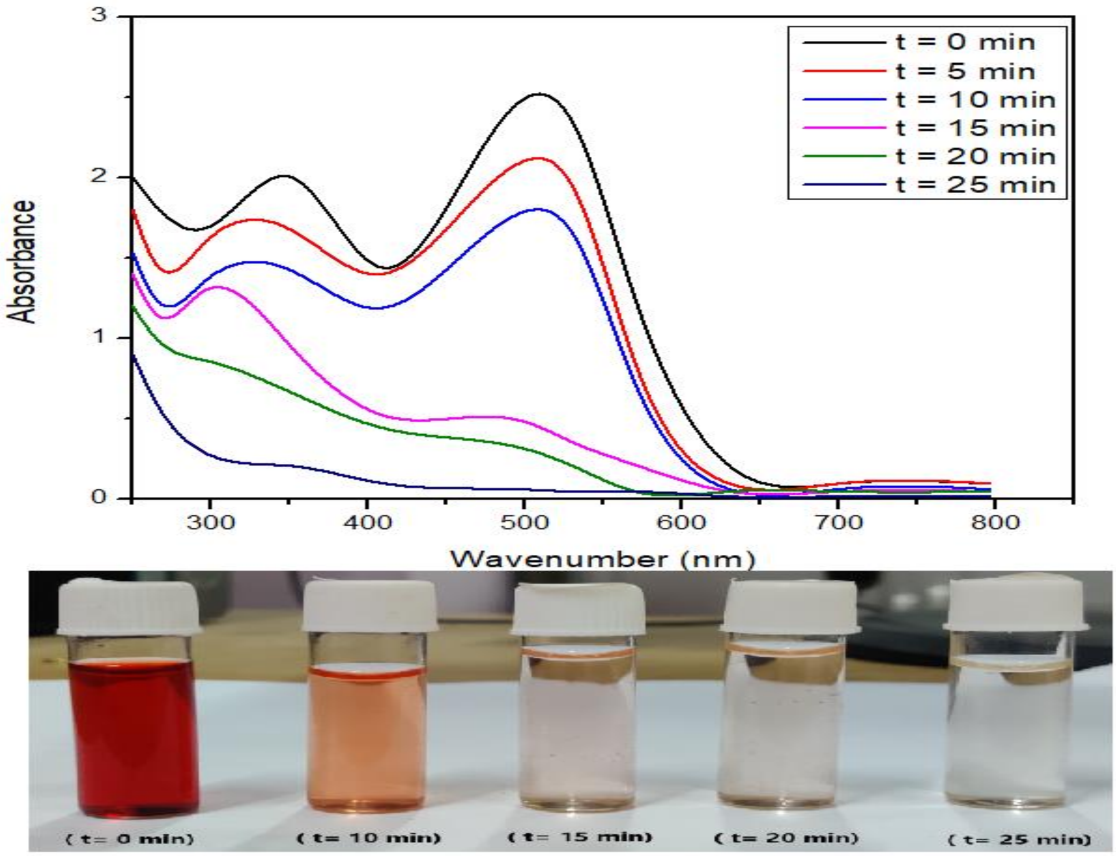

Fig. 6.4 Variation in the absorbance of the dye sample with the ozonation time (Initial dye concentration = 500 mg/L, Temperature = 35℃, pH = 11.0)

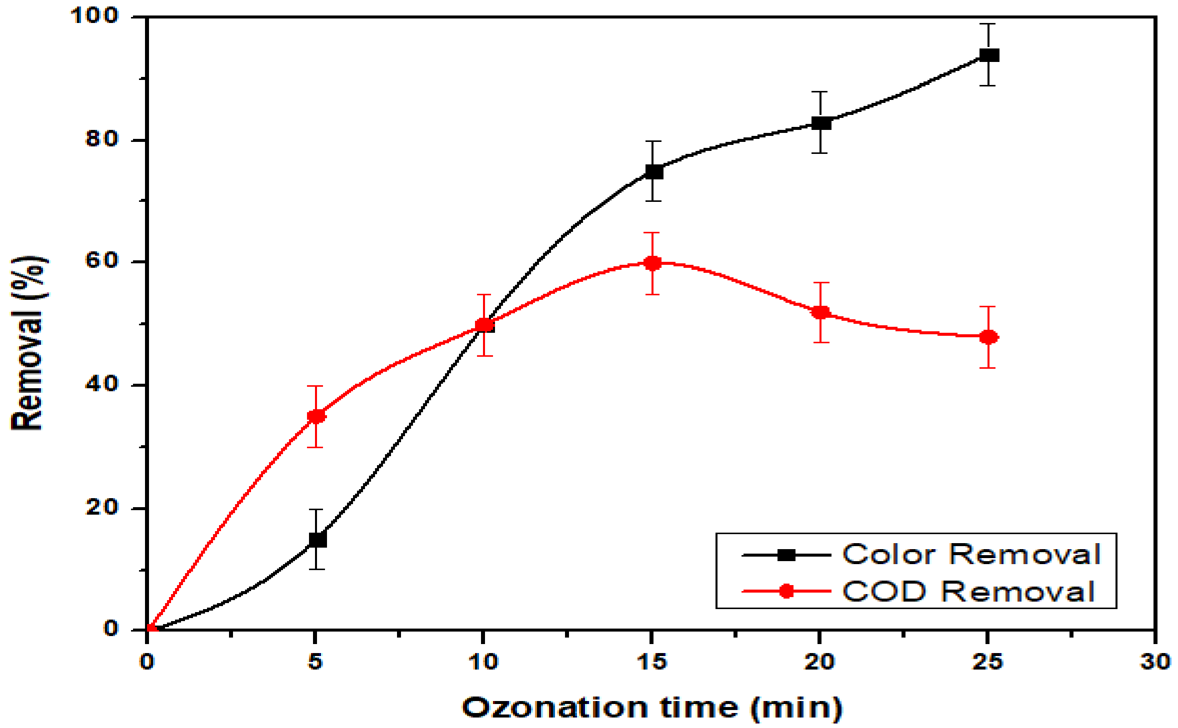

Fig. 6.5 Variation in Color and COD removal efficiency with the ozonation time (Initial dye concentration = 500 mg/L, Temperature = 35°C, pH = 11.0).

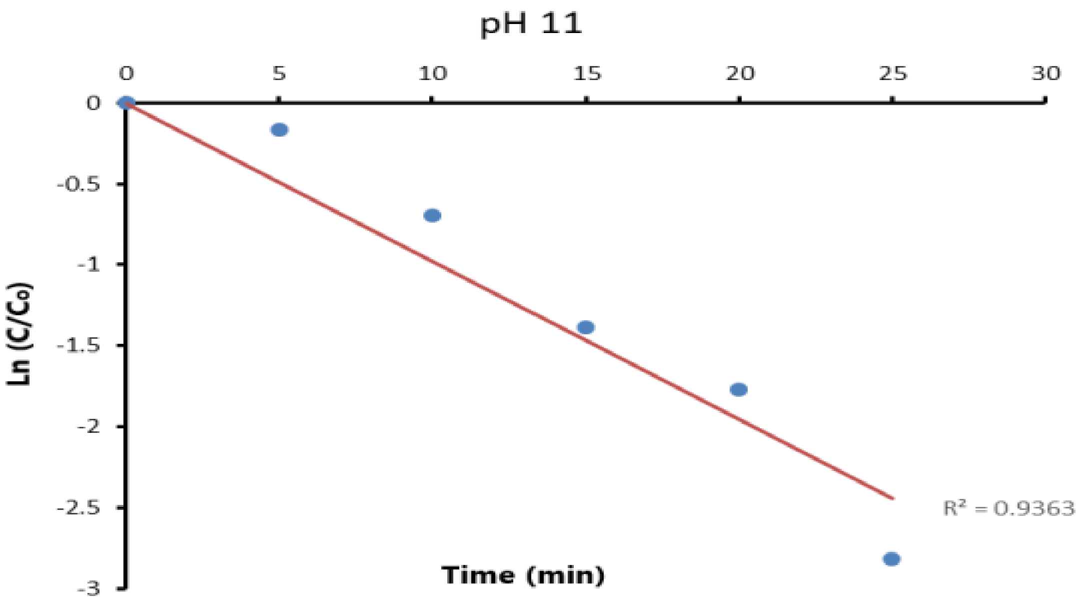

Fig. 6.6 Pseudo – first order kinetics plot for ozonation of Congo red dye.

6.3.3 Enhancement of biodegradability index (BOD_5/COD)

The biodegradability index of ozonated STWW can be determined by the BOD_5/COD ratio in addition to direct organic matter oxidation. COD and BOD_5 were determined to evaluate the biodegradability profile. The biodegradability ratio in this instance increased gradually because of the ozonation of wastewater. Before ozonation, the BOD_5 values of the dye solution were very low, and thus the dye solution BOD_5/COD ratio was 0.114. As the result shown in **Fig. 6.7**, the BOD_5/COD ratio was increased from 0.114 to 0.44 after 25 min of ozonation. The biodegradability ratio for dyes increased after ozonation, possibly due to metabolic activity caused by the presence of more readily degradable compounds. Venkatesh et al.(2015), reported that after 25 min of ozonation, the biodegradability index was increased for Acid red, Congo red, and Reactive black 5 dyes. According to Somensi et al. (2010), biodegradability index of real textile wastewater enhanced from 0.06 to 0.41 after 240 min of ozonation. Since ozonation is a costly process, it can be used only for partial oxidation which can be further completely mineralized by biodegradation. Using chemical oxidation in conjunction with bacterial degradation, rather than oxidation or biodegradation alone, may result in more advantageous and cost-effective process conditions.

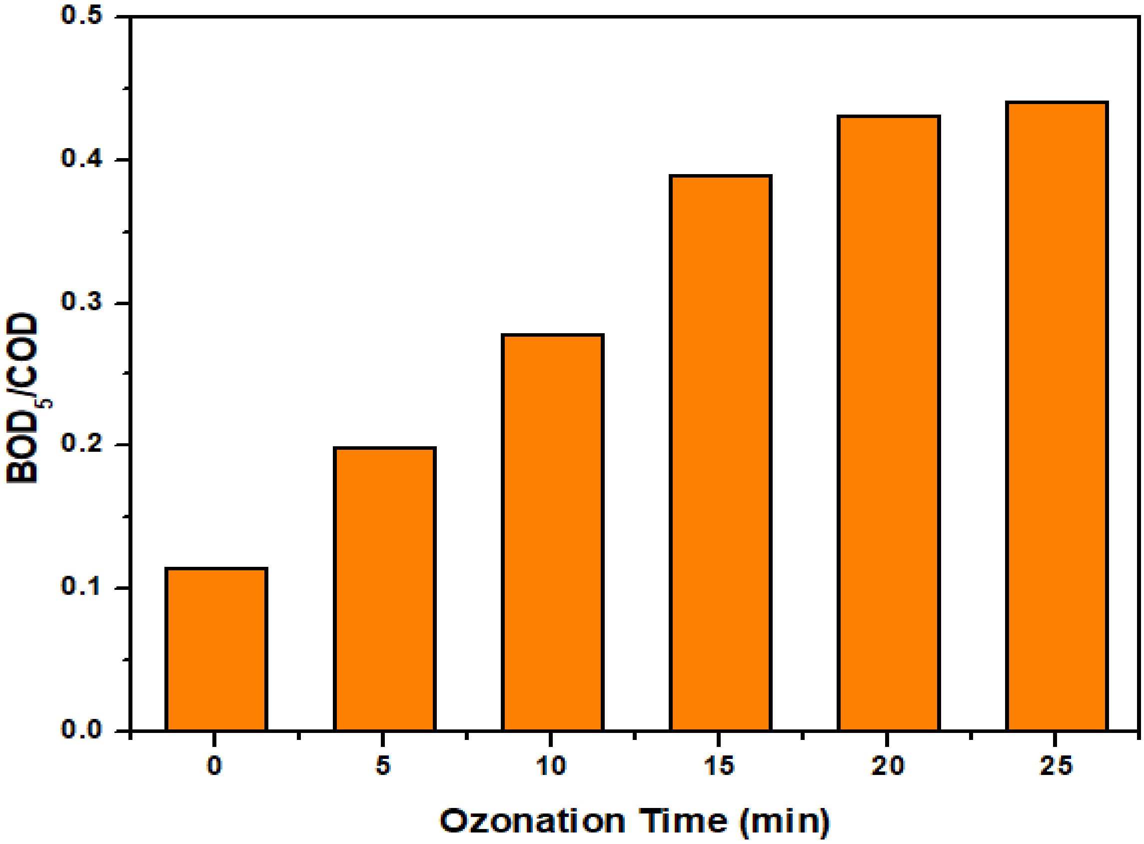

Fig. 6.7 Enhancement in the biodegradability of the sample with the ozonation time.

6.3.4 Coupling ozonation with biodegradation in PBBR

Ozonation of STWW not only reduced COD concentrations but also improved biodegradability. The treated wastewater solution was transferred into a holding tank, where the pH of the solution was adjusted to 7.0 prior to biological treatment. After that solution was transferred to the bioreactor for further mineralization. PBBR was run in batch mode with the bacterial sample to ensure the formation of the biofilm. **Fig. 6.8** shows the removal of color and COD in the combined process. Ozonation results in 90% of color removal and 45% of COD removal of and the corresponding biodegradability index also increases from 0.114– 0.44, which makes ozonated samples suitable for biodegradation. It is clearly visible that there is a gradual increase in the COD removal, and it reaches a maximum of 80% after 10 days of biodegradation (**Fig. 6.8**). The final solution after combined treatment of ozonation and biodegradation was having a COD concentration of 179 mg/L, which is well within the acceptable range as prescribed in the Environment (Protection) Rule (1986). An integrated system of ozonation and biodegradation has been employed by various researchers for the treatment of recalcitrant textile dyes. De Souza et al. (2010), have reported more than 90% of color removal for Remazol Black B dye. They found that ozonation as a pre-treatment for the coupling (Ozonation and Biodegradation) process has greater potential for color and COD removal. Dias et al. (2019), have also employed a moving bed bioreactor (MBBR) for the complete mineralization of pre-ozonated Reactive Red 239 dye solution.

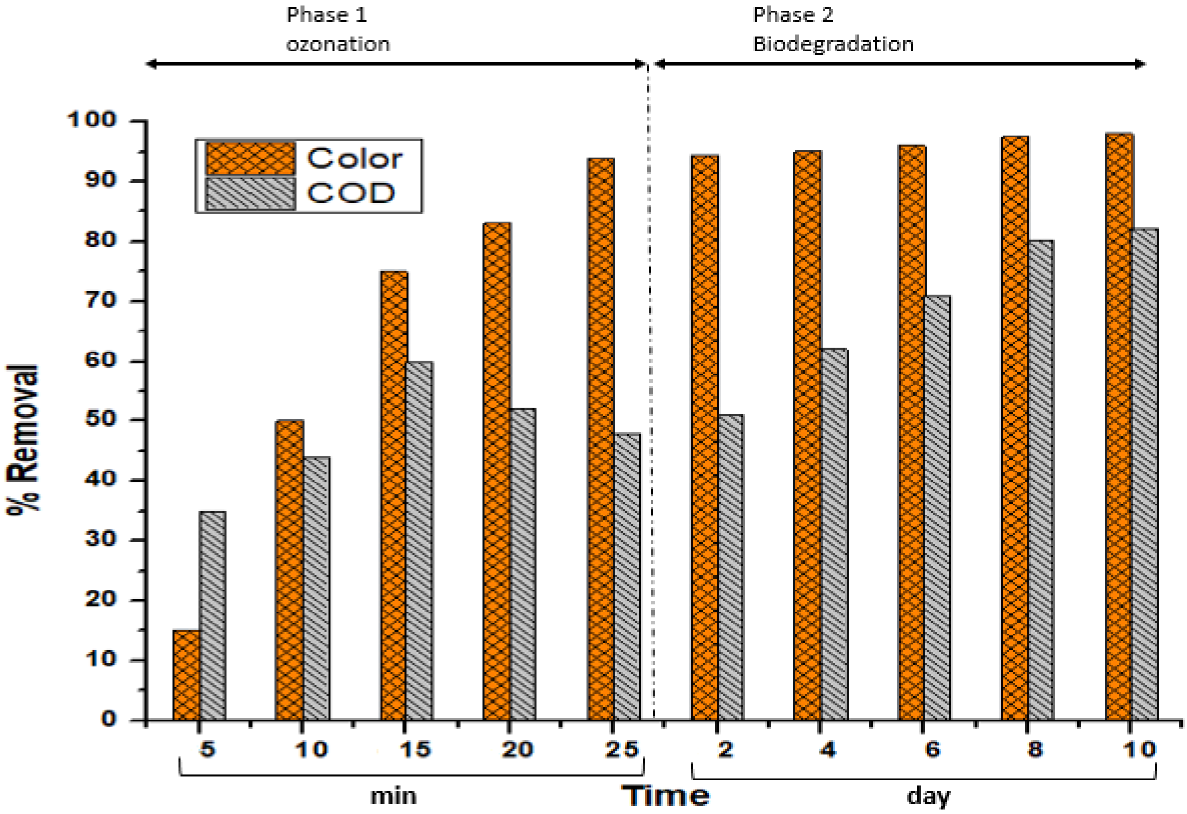

Fig. 6.8 Combined color and COD removal plot for coupling process (ozonation and biodegradation).

6.3.5 Assessment of toxicity

The acute toxicity tests conducted on STWW, ozonated samples, and biodegraded samples are shown in **Table 6.1**. The toxicity was evaluated after 48 hours of the bioindicator exposure, and the median effective concentration of the sample affected 50% of the organisms tested (EC_{50}). According to the findings, the toxicity of synthetic wastewater increased after ozonation (EC_{50} values decreased), whereas the ozonated sample's toxicity decreased after biological treatment (EC_{50}values increased). The presence of high toxicity is demonstrated by the decrease in EC_{50}values determined in tests for all samples.

For *Daphnia magna*, the EC_{50} value of synthetic wastewater (500 ppm) was 14 ± 0.5 mg/L, which reaches a very toxic level after 15 min of ozonation. This may be because ozonation results in toxic intermediate byproducts. The findings of this study are consistent with acute toxicity tests published in the literature which showed that ozonation results in an increase in toxicity (de Souza et al., 2010).

Table 6.1 Acute toxicity result for *Daphnia magna.*

Test Sample		pH	EC_{50}
Raw Synthetic wastewater sample			
100 ppm		7.05	51
300 ppm		7.06	32
500 ppm		7.02	14
Ozonated synthetic wastewater sample			
500 ppm	t = 5 min	7.0	16
500 ppm	t = 10 min	6.5	10
500 ppm	t = 15 min	4.0	Very toxic
500 ppm	t = 20 min	4.0	22
500 ppm	t = 25 min	4.0	17
Biological treatment of ozonated synthetic wastewater			
500 ppm	t = 2 day	7.05	22.5
500 ppm	t = 4 day	7.06	39.8
500 ppm	t = 6 day	7.02	44.6
500 ppm	t = 8 day	7.04	Non-toxic
500 ppm	t = 10 day	6.95	Non-toxic

6.3.6 GC-MS assessment of degraded metabolites

The metabolites formed after the ozonation of CR dye were assessed using GC-MS. Following ozonation of CR dye for 10 and 25 minutes, two samples were collected and extracted using ethyl acetate (1:1). The samples were dissolved in HPLC grade methanol for GC-MS analysis. The sample shows prominent peaks at the retention time (RT) of 23.3, 24.5, 25.2, 26.0, and 27.6 min under ozonation of 10 min. The major metabolites, namely (i) 4-Nitro-5,6,7,8-tetrahydronaphthalen-1-ol (m/z = 193), (ii) 2-Benzyl-5-oxocyclohexanecarboxylic acid (m/z = 232), (iii) pyridinecarboxylic acid (m/z = 284), and (iv) N-[2-(2,6-Dimethylphenoxy)ethyl]-N-methylamine (m/z = 179) were identified at RT of 23.3, 24.5, 25.2, and 27.6 min, respectively. A particular finding is confirmed by the analysis of these metabolites: oxidation by ozone leads to the formation of a byproduct of an acidic composition. Further, after 25 min of ozonation, the sample shows 3 major peaks at the retention time of 24.6, 27.3, and 28.4 min. A total of five metabolites were observed by a mass spectrometer, shown in **Fig 6.9**. At RT = 24.6 min, 3-[2-(Aminocarbonyl) phenyl]acrylic acid (m/z = 191) and Oxaluric acid (m/z = 132) were detected. At RT = 27.3 min, the third and fourth metabolites, benzeneacetaldehyde, -(methoxymethylene)-4-nitro- (m/z = 207), and ethenyl ester (m/z = 72), were detected. The final metabolite, 2-Amino-1-propanol (m/z = 75), was detected at RT = 28.4 minutes.

After analyzing these metabolites, a new pathway for CR dye degradation via ozonation was proposed (**Fig. 6.10**). Since the ozonation reaction was performed in an alkaline condition, then the ozone reacts via hydroxyl radical mechanism. The $OH^{\bullet}$ first attack on the azo bond of the CR dye results in the formation of carboxylic acid which further leads to form an amine and ultimately leads to the formation of an ester. Many researchers have reported the formation of 4-amino-3-naphthol-1-sulfonate (Li et al., 2013; Olukanni et al., 2013). Despite the fact that many by-products are anticipated to result from dye oxidation, it is difficult to identify each one because they are all less soluble in methanol.

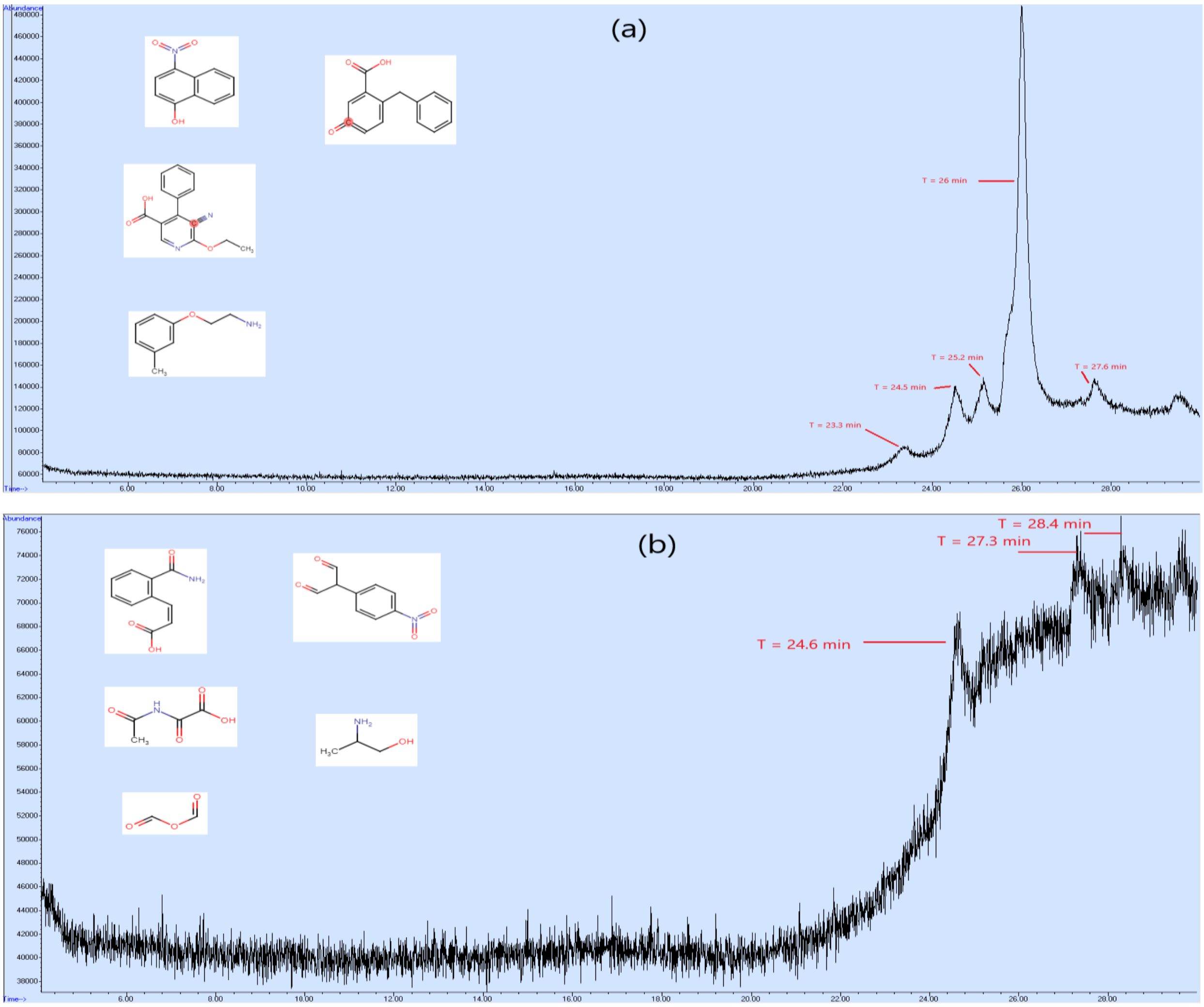

Fig. 6.9 GC – MS spectra of ozonated samples (a) After 10 min of ozonation (b) after 25 min of ozonation.

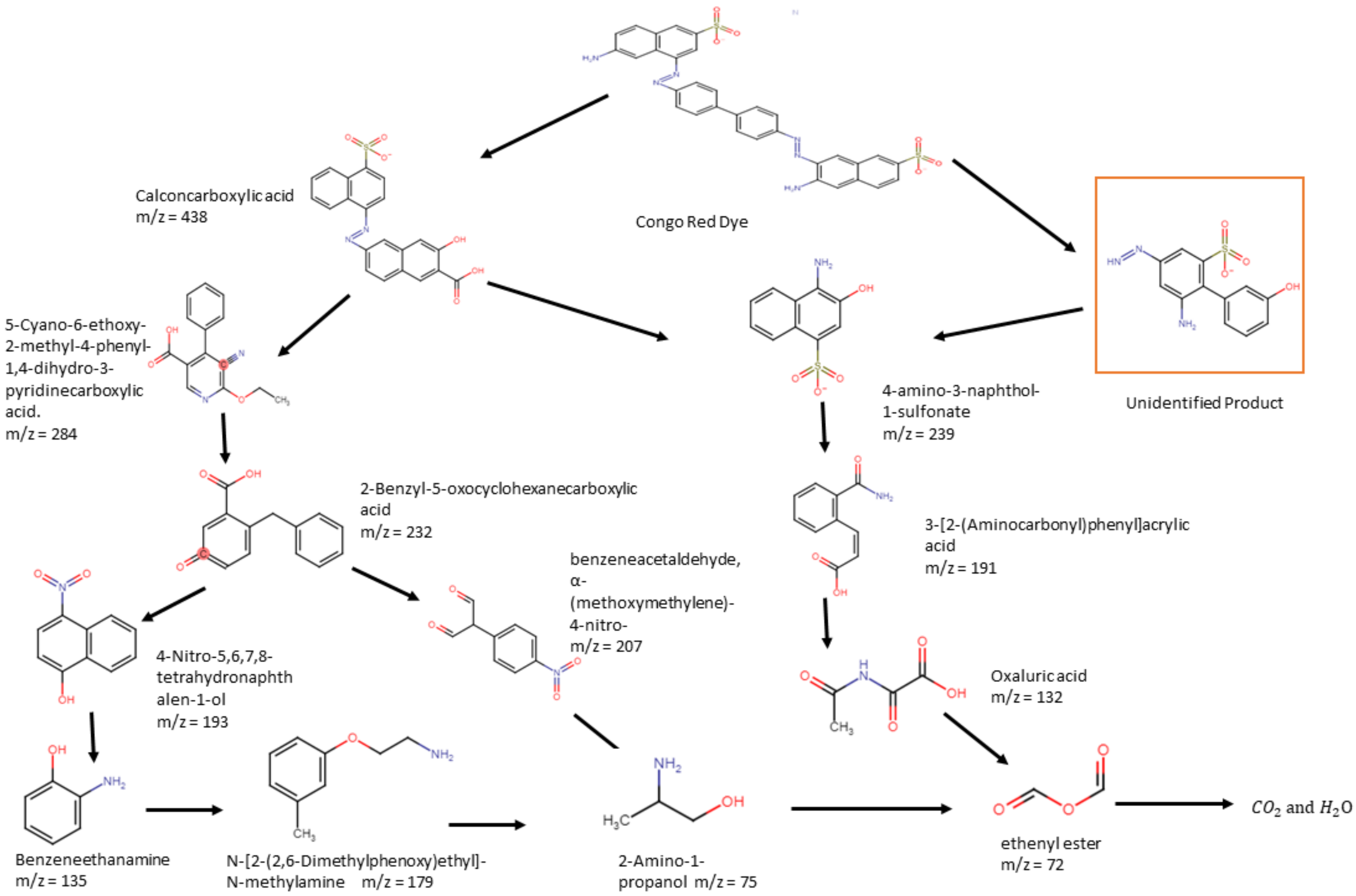

Fig. 6.10 Proposed pathway of Congo red dye degradation via ozonation.

6.3.7 Economic assessment

A techno-economic feasibility analysis was conducted for coupling ozonation with biodegradation in a packed bed bioreactor as compared to the single ozonation process for textile wastewater treatment. **Figure 6.1** depicts a simplified scheme of textile wastewater treatment using the coupling ozonation and biological process. A detailed flow chart and inventory of operation units for combined (ozonation + biodegradation) is shown in **Fig 6.11.** DEX, IEX, and other OEX were calculated based on equipment purchase cost (P) as mentioned in **Table 6.2**. The economic viability of both processes is tested on the basis of unit expense (UEX, \$/ m^3). The effluent flow capacity of a textile plant varies between 25 KLD- 500 KLD., In this study,50 KLD (2.08 m^3/h) effluent flow capacity was assumed. The total flow capacity for a textile plant operating 24 h/day for 322 days/year, would be 16136.06 $m^3/year$.

DFCapEx of the combined process ($2152938.28) was higher than the single ozonation process ($266941.3) mainly due to additional expense on the packed bed bioreactor which solely cost 80% of equipment purchase expense. Thus, annual amortized capital expense for the combined process ($203222.14) was much higher than the single ozonation process ($25197.37). OEX of the combined process was considerably low ($107060.9) in comparison to the single ozonation process ($453895.0). This difference was mainly due to the electricity consumption during the ozonation process. In the combined process, ozonation was carried out for a limited period of time in order to make the sample biodegradable. However, ozone was supplied for a longer period of time for complete degradation in single ozonation process. Due to this, OEX for the combined process only comprises 4.0% of total expense and for the single ozonation process, it comprises 60.0% of total expense. A major part of OEX corresponds to electricity consumption and the remaining consist of utility and waste management expense.

After comparing all the estimated costs, it can be said that coupling the biological process with the ozonation process can increase the direct fixed capital expense. However, operating expenses (utility and electricity consumption) could be significantly less for the coupling process than for the single ozonation process. As a result, the unitary expense of the coupling process per cubic meter of treated wastewater ($\$19/m^3$) can save 34 % with respect to those for a single ozonation process ($\$29/m^3$).

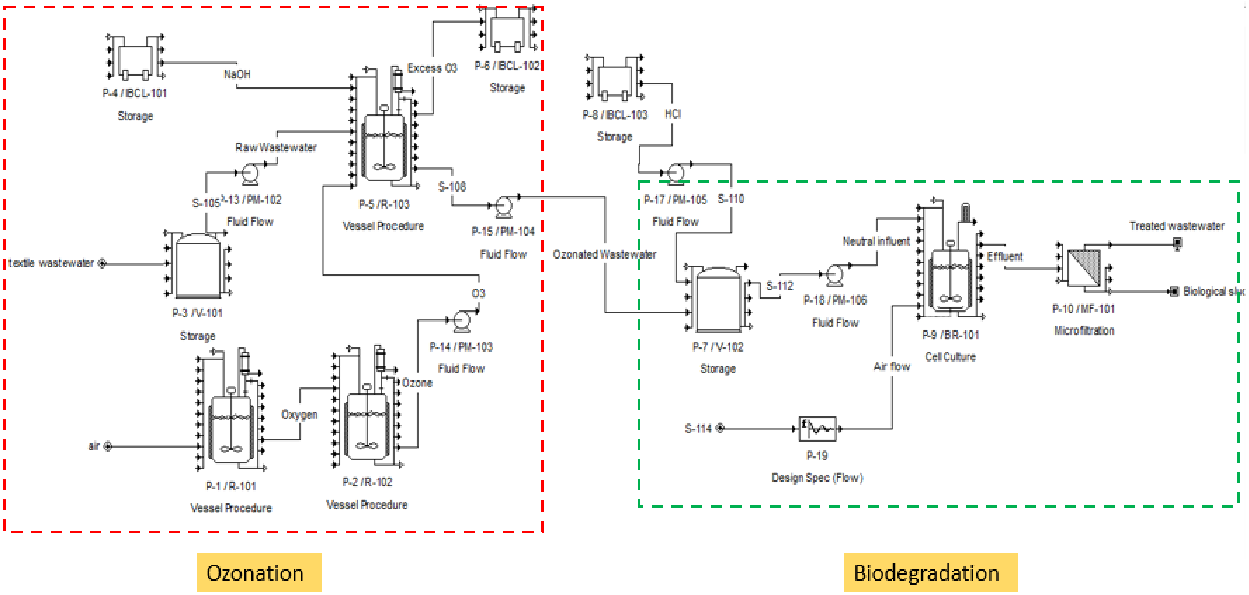

Fig. 6.11 A detailed flow chart of the coupling process (ozonation and biodegradation) for CR dye treatment.

Table 6.2 Operating expense (OpEX) and annual amortized capital expense (ACapEX) for the estimation of the unitary expense ($\$/m^3$) of each process strategy.

	Single Ozonation	Coupling Ozonation/Biological
Textile effluent flowrate ($m^3/year.$)	16136.06	
Equipment purchase P ($)	44230.73	356730.2
Total direct expense (DEX = 3.28 P), $/year	145076.8	1170075.0
Total indirect expense (IEX = 0.6 DEX), $/year	87046.08	702045.1
Total other expense (OEX = 0.24 DEX), $/year	34818.43	280818.0
Direct fixed capital expenses ($\mathrm{DFCapEX} = \mathrm{DEX} + \mathrm{IEX} + \mathrm{OEX}$), $/year	266941.3	2152938.0
Annual amortized capital expense ($ACapEx = \frac{DFCapEX*i}{\left[1-\left(\frac{1}{1+i}\right)^n\right]}$), $/year	25197.37	203222.1

Annual operating expenses (Raw material, Utilities, residue management, Transportation) OpEX, $/year	453895.0	107060.9
Unit expense $\mathrm{UEX} = \frac{\mathrm{OpEX} + \mathrm{ACapEX}}{\mathrm{Q}}$ $\$/m^3$	29.69	19.22

6.4 Conclusions

In this study, an effort was given to evaluate the feasibility of an integrated system (i.e., ozonation and biodegradation processes) for improved mineralization of Congo dye from wastewater. Ozonation of dye results in the formation of byproducts that are acidic in nature. This fact is confirmed by both pH and GC – MS analysis. Ozonation also results in improved biodegradability of dye sample, which was enhanced from 0.11 to 0.44. Thus, after 25 min of ozonation, more than 90% color and 50% COD removal was achieved. Acute toxicity test reveals that ozonated sample become more toxic than the simulated sample. Thus, biodegradation of ozonated sample becomes necessary. A total of nine metabolites formed after 25 min of ozonation, and a degradation pathway was proposed. Techno – economic assessment shows that the coupling of ozonation with biodegradation could save 34% unitary expense compared to single ozonation process. Thus, coupling of ozonation with biodegradation is the most efficient and economically viable option for dye degradation.