

Advanced UV-C Excimer Light Source for Rapid Mineralization of Azo Dye in Wastewater

4.1 Introduction

To ensure compliance with environmental discharge regulations, wastewater quality assessment requires several components [Yaseen et al., 2019]. One significant issue that frequently causes wastewater to have a particular color is the presence of organic dyes. Textile effluents contain typical dye content ranging between 10 – 200 mg/L [Yaseen et al., 2019]. Many human and animal disorders have been traced due to the toxic and highly carcinogenic nature of textile dyes [Al-Tohamy et al., 2022a] [Al-Mamun et al., 2019]. A wide range of dyes exist, but due to their bright and long-lasting color, azo dyes ($-N=N-$) contribute 60 to 70% of the total dye consumed in the textile, paper, and leather industries [Benkhaya et al., 2020] [Allabakshi et al., 2023]. These dyes are frequently utilized in industrial procedures, such as manufacturing artificial dyes and coloring materials in sectors like textiles, dry cleaning, and others [Chandanshive et al., 2020]. Significant quantities of water are utilized in textile industries for dyeing processes. Subsequently, color-rich wastewater is released at the various stages of the dyeing process [Yaseen et al., 2019], necessitating the urgent development of closed-loop water supply systems to address concerns about resource usage. Also, since azo dyes are hydrolyzed [Science et al., 2001], they cannot be recovered for reuse and must, therefore, be degraded or eliminated before being released into the environment.

Various chemical, physical, and biological techniques are used to eliminate synthetic dyes from wastewater. Among them, AOPs such as ultraviolet light (UV) with H_2O_2/O_3 and photocatalysis are gaining popularity in removing complex organic pollutants from water and wastewater [Glaze, 1987; Pandis et al., 2022; Pignatello et al., 2006; Rajeshwar, 2011; Shekhawat et al., 2021]. AOP accelerates the elimination of hazardous contaminants by creating highly reactive $\bullet OH$ [95]. The $\bullet OH$ is an extremely powerful, non-selective oxidant that causes partial or total mineralization of organic dye substances [Tijani et al., 2014]. Among various AOPs, heterogeneous photocatalytic oxidation, particularly UV/ TiO_2 , is drawing a lot of attention [Rodríguez-Chueca et al., 2023]. TiO_2 is considered a more attractive choice for photo catalysts in environmental clean-up operations because of its low cost, high reactivity, high chemical stability, and non-toxic and insoluble nature [Prevot et al., 2001] [Vinodgopal et al., 1996b].

The most challenging problem in AOPs is the use of conventional UV light sources that often contain mercury, which is even more detrimental to the environment than the treated pollutants because of their routine replacement and often filament failure [Borchers et al., 2008] [Amos et al., 2014]. The best alternative to conventional mercury-based UV lamps could be the DBD based mercury-free plasma UV excilamp [Prakash et al., 2017]. Another difficulty related to AOPs is that, after the degradation process, the extraction and reuse of the catalysts from the treated matrix is quite challenging [Joseph et al., 2023b]. Recently, many research groups reported the immobilizing of photocatalysts directly onto the reactor walls to remove the organic dyes from the wastewater [Teixeira et al., 2016] [Chang et al., 2010], but the problem associated with this process is the decrease in photo activity after certain cycles as well as removal and replacement of photocatalysts from treated solution [Vaiano et al., 2023] [Vu et al., 2013]. So, there is a need for process optimization which eliminates the recovery and reuse of photocatalysts and simultaneously enhances the mineralization rate. Accordingly, excimer light sources based on

DBD combined with photocatalysts are being explored as a possible substitute to overcome these shortcomings.

In this chapter, the design and development of a mercury-free DBD-based modified XeI* excilamp is reported in which one of the electrodes is coated with TiO₂ nanoparticles to enhance the mineralization efficiency of the treated dye. This modified XeI*-excilamp generates 253 nm UV-C light and reactive oxygen species from TiO₂-coated electrode simultaneously. The transportation mechanism of different active ions and reactive species from the gas phase to the aqueous phase has been discussed. The developed modified excilamp is the first of its kind and has been utilized to degrade RB5 azo dye effectively. The effects of different concentrations of catalysts loading, initial concentrations of dye, solution pH, and different concentrations of H₂O₂ are examined at different treatment times for the degradation of RB5 dye. Instead of loading photocatalysts in the wastewater suspension, we coated the TiO₂ on the electrode of the excilamp and utilized H₂O₂ as a radical promoter with varying concentrations of 0.013% to 0.039% v/v. In order to determine the toxicity of dye wastewater treated using various processes, radish seeds were germinated in soil using the treated dye wastewater and deionized water, and the results were analyzed. An understanding of how reactive species in the gas and aqueous phases interact with wastewater constituents and an effective strategy to valorize treated effluent is discussed.

4.2 UV-C XeI* (253 nm) Excilamp Design and Development

The developed DBD-based XeI* UV-C excimer light source is shown in Figure 4.1. The inner and outer tube dimensions are 10 mm OD, 7 mm ID, 16 mm OD, and 13 mm ID, respectively, and the lamp length is 160 mm. A wire mesh of stainless steel having a thickness of 0.1 mm coated with TiO₂ nanoparticles is used on the outer surface of the larger OD quartz tube, which acts as the ground electrode. An aluminum rod inserted inside the smaller quartz tube acts as a high-voltage electrode in the co-axial DBD configuration. This electrode is hermetically sealed for electrical isolation. The photocatalytic activity of any catalyst strongly depends on its phase and crystalline size [Wang et al., 2014] [Chen et al., 2012]. In this study, the TiO₂ nanoparticles were prepared by the sol-gel method, and the detailed method of preparation is discussed in section 2.7 of Chapter 2 of this thesis.

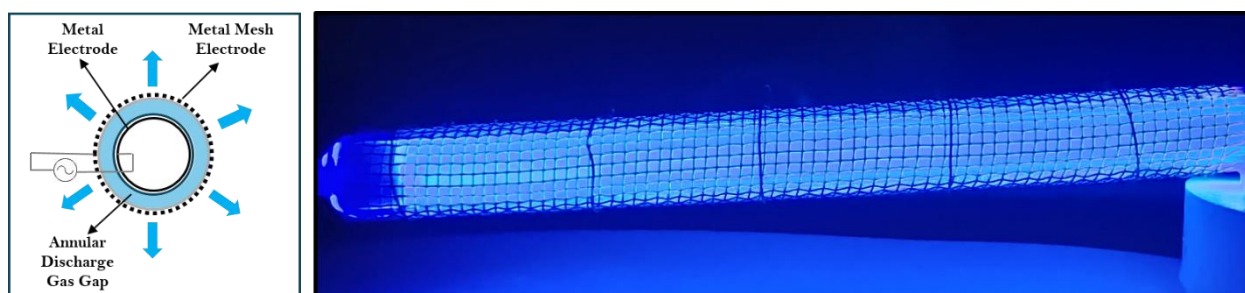


Figure 4.1: Cross-sectional and original view of developed 253 nm XeI* excilamp.

4.3 Procedure of Dye Degradation

All RB 5 degradation experiments were performed in the batch reactor, as described in section 2.8.1, and the reactor is shown in Figure 2.9 of Chapter 2. The dye degradation efficiency, energy yield, and COD reduction are estimated using the equations 2.3, 2.4, and 2.5. The toxicity effect of the untreated and treated dye effluents was assessed by employing their utility in the germination of radish seeds. The germination of the radish seeds was carried out using five different water samples, including DIW, untreated dye wastewater, treated dye wastewater with XeI* excimer/H₂O₂ (3 mM) for 3 min and 40 min, treated dye wastewater with XeI* excimer/TiO₂

(1 g/L). The pH of the used solution was neutral, so we did not perform the neutralization of the treated effluents. The seeds were directly sown in the soil, and treated wastewater was used to water the soil to see the effect of different liquids on the growth of the stem and root of the radish seeds. The study was carried out for three days, and the impact of the different treated and untreated dye wastewater on the germination rate, stem length, and root length of the radish seed was studied.

4.4 Electrical and Optical Characterization of XeI* Excilamp

The photocatalytic activity and dye degradation rate strongly depend upon the intensity and wavelength of the UV light source used [Reza et al., 2017]. The absolute intensity of the developed UV-C (253 nm) lamp is shown in Figure 4.2 (a) as a function of discharge power (W). It can be seen that the intensity increases linearly with increasing input power ($R^2 > 0.99$), and the time required to stabilize the UV intensity was about 30 s. A maximum of $2570 \mu\text{W}/\text{cm}^2$ UV-C intensity is obtained at 42.5 W. All the experiments of RB5 dye degradation are performed at an absolute UV intensity of $1050 \mu\text{W}/\text{cm}^2$ (optimized based on gas pressure, applied voltage, and lamp heating) until specifically mentioned. The optical emission spectra (OES) of the developed DBD-based excilamp is shown in Figure 4.2 (b). A prominent 253 nm spectral band corresponding to the B-X transition for XeI* along with some weak transition bands at 206 nm (D-X transition for I_2), 265 nm (C-A transition for XeI*), and 320 nm (B-A transition) can be seen in Figure 4.2 (b). Along with the 253 nm spectral band, these weak bands also participate in the process of degradation of dyes by enhancing the generation of $\bullet\text{OH}$.

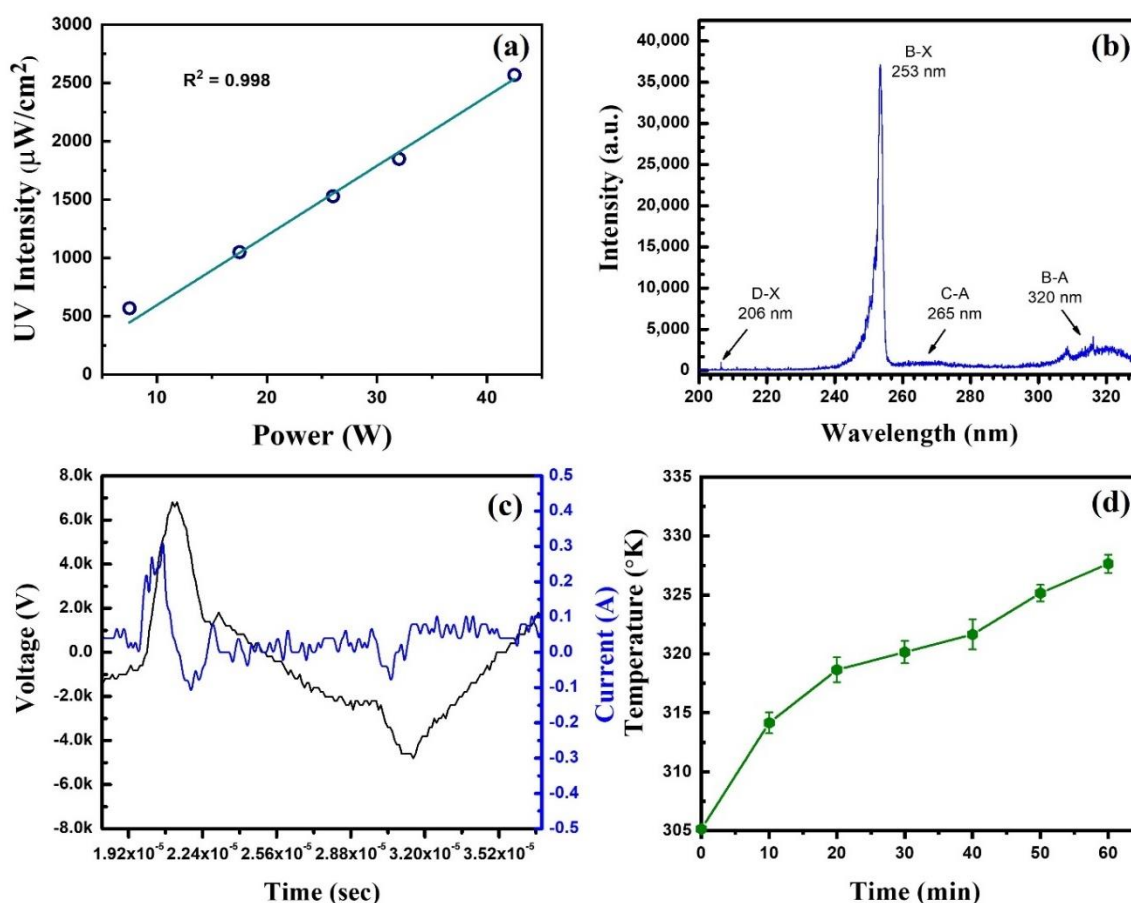


Figure 4.2: (a) Absolute XeI* excilamp intensity with respect to discharge power of the excimer source, (b) Emission spectra of excimer source dominating at wavelength 253 nm, (c) typical V-I characteristics of the developed source, and (d) temperature variation of treated solution as a function of XeI* excimer treatment time.

The typical voltage-current (V-I) characteristic is shown in Figure 4.2 (c) at an applied voltage of 7 kV and frequency of 25 kHz. The input power of the excilamp is estimated by multiplying the recorded voltage and current values in the V-I characteristics and then integrating them over time [Jangra et al., 2023a]. The input power is found to be 17.5 W for the developed mercury-free excilamp at the optimized parameters with 1050 $\mu\text{W}/\text{cm}^2$ of UV output. From the absolute intensity measurement, we found that the XeI* excimer light source has an instant start-up with full radiation output, in contrast to the mercury-based UV-C lamp, which has a start-up time of about 2.5 min [Chatterley et al., 2010]. Figure 4.2 (d) shows the temporal variation of temperature of the treated dye solution with respect to the treatment time. Even after 60 min of UV exposure to the dye solution, the solution temperature remains well below 330 K, indicating the non-thermal nature of the treated solution.

4.5 Characterization of TiO₂ Nanoparticles

The size and morphological characteristics of the nanoparticles are carried out prior to the dye degradation process using FE-SEM and HRTEM analysis, and results are shown in Figures 4.3 (a), 4.3 (b), and 4.3 (c). Figure 4.3 (a) shows the FE-SEM image of a segment of TiO₂-coated stainless steel wire mesh electrode at a magnification of 67x (scale bar: 1 mm). The coating of TiO₂ is clearly visible on the mesh electrode. A high magnification (80000x, scale bar: 1 μm) image has also been captured by focusing on the single wire of the mesh electrode [see Figure 4.3 (b)].

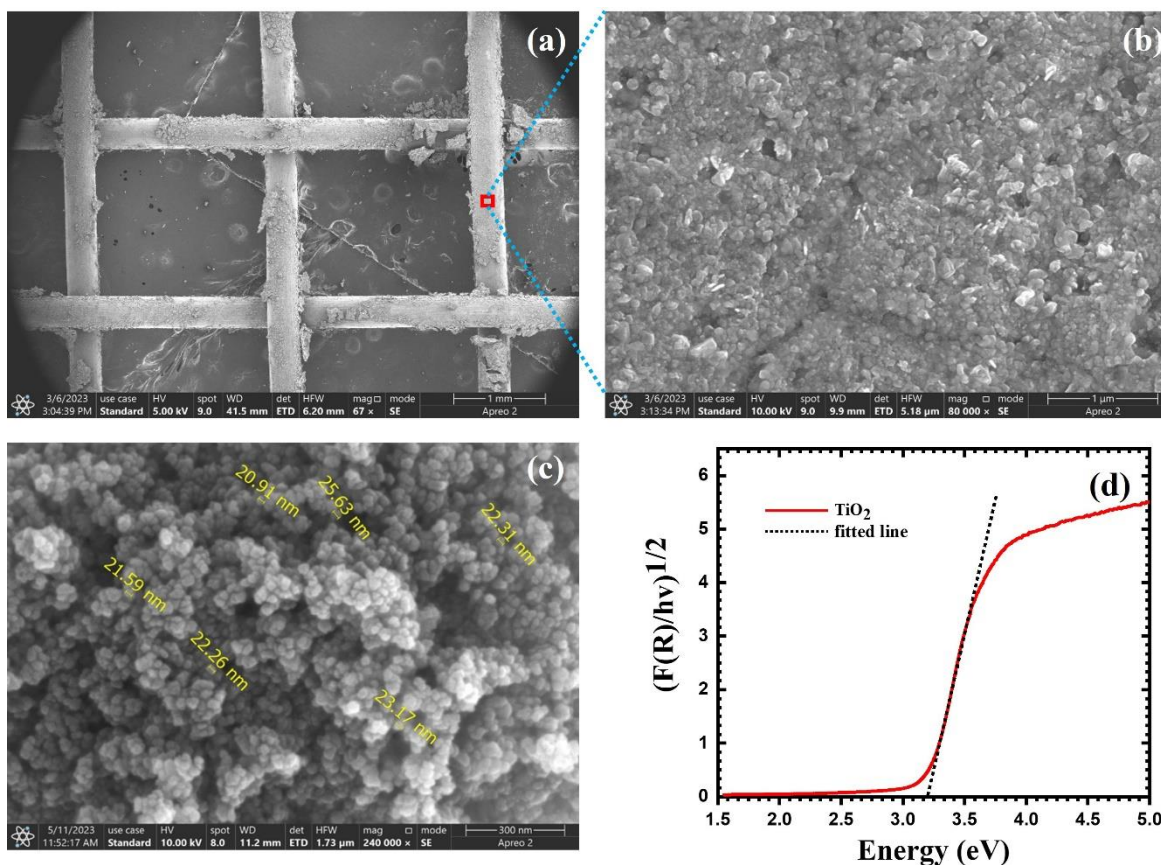


Figure 4.3: FE-SEM images of the TiO₂-coated outer mesh electrode (a) at a magnification of 67x, (b) at a magnification of 80,000x, (c) at a magnification of 2,40,000x, and (d) Kubelka-Munk plot of synthesized TiO₂ nanoparticles.

To confirm the size of the nanoparticles, the FE-SEM of the TiO₂ nano-powder is also performed, and the obtained image can be seen in Figure 4.3 (c). The average size of the nanoparticles is $\sim 23 \pm 2$ nm [as marked in Figure 4.3 (c)] and is quite suitable for photocatalytic applications [Khan et al., 2019]. The Kubelka-Munk plot of synthesized TiO₂ nanoparticles is shown in Figure 4.3 (d), which confirms that the band gap of synthesized TiO₂ is 3.2 eV, corresponding to the anatase phase [Reddy et al., 2003]. This phase of the TiO₂ nanoparticles is most suitable for photocatalytic applications in dye degradation [Pawar et al., 2018]. The XRD pattern of the synthesized TiO₂ nanoparticles is shown in Figure 4.4.

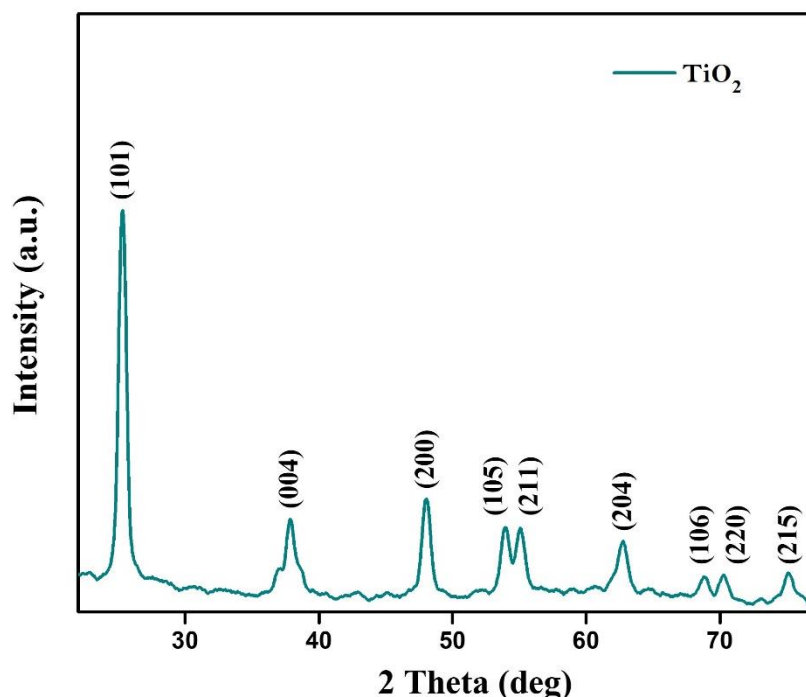


Figure 4.4: XRD pattern of synthesized TiO₂ nanoparticles.

The XRD pattern exhibited peaks at 25.31°, 37.89°, 48.02°, 53.96°, 55.09°, 62.73°, 68.81°, 70.29° and 75.11°. These peaks correspond to the crystal planes of (101), (004), (200), (105), (211), (204), (106), (220) and (215), respectively. The XRD pattern is well-matched to the pattern of anatase TiO₂ according to the reference JCPDS card 21-1272 [Chen et al., 2022b] [Wei et al., 2013].

Based on the HRTEM micrographs, spherical-like shapes with particle diameter of 20–30 nm could be seen for the synthesized TiO₂ nanoparticles [see Figure 4.5 (a)]. The variation in size between the nanoparticles obtained using the FE-SEM and HRTEM techniques might be attributed due to both particle aggregation phenomena and the loss of nanoparticle stability during the freezing-drying process. The image view software was used to analyse the particle size of the TiO₂, and measurement was taken over more than 60 particles. The historiographical representation of this measurement is shown in Figure 4.5 (b). To analyse the size, the Gaussian distribution was used. The surface property and the change in the chemical state can be evaluated using XPS. Figures 4.5 (c) and 4.5 (d) show the XPS spectrum recorded for synthesized TiO₂. Two spectrums are observed: one for O1s and the other for Ti2p. The peak observed at 529.52 eV in

Figure 4.5 (d) is mainly observed for TiO₂. Another peak observed at 531.20 eV is possibly attributed to the adsorbed hydroxyl and oxygen ion; a broad peak suggests they are weakly bound [Bharti et al., 2016]. Figure 4.5 (c) represents the spectrum of Ti2p, in which two doublet peaks are observed, Ti2p_{3/2} and Ti2p_{1/2}, at binding energies 458.32 eV and 463.98 eV, respectively. This observed doublet is because of the spin-orbit coupling interaction [Cottre et al., 2021]. Besides Ti and O, no other peak is observed, which suggests the phase purity of the synthesized TiO₂ nanoparticles.

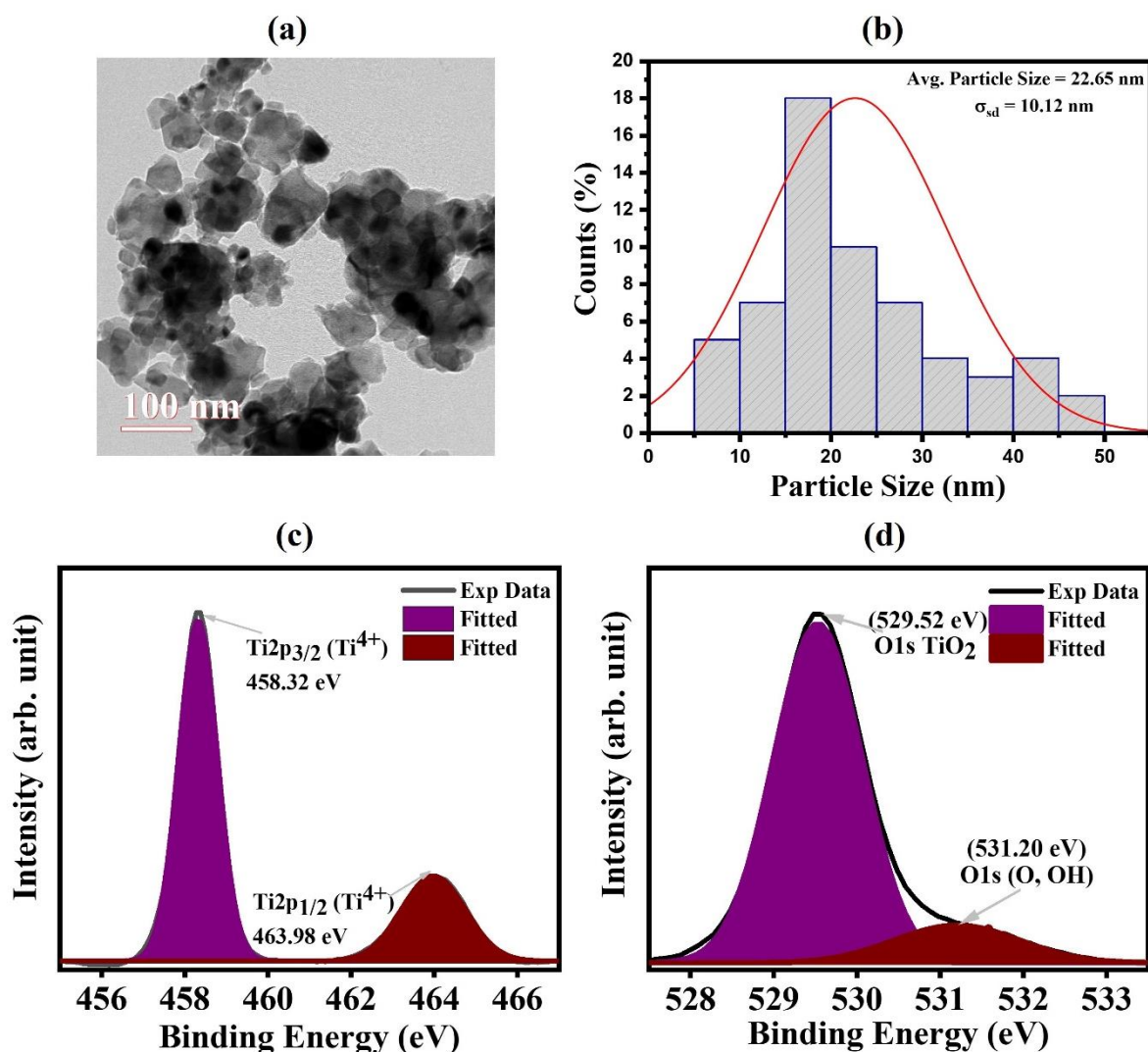


Figure 4.5: (a) Representative HRTEM micrographs of synthesized TiO₂ nanoparticles, (b) histogram representation with fitted Gaussian distribution for calculating TiO₂ nanoparticles average particle size. High-resolution XPS spectra of (c) Ti2p and (d) O1s in synthesized TiO₂ nanoparticles.

4.6 Effect of Different Parameters on the Dye Degradation Efficiency

The effect of different parameters (initial dye concentration, pH, H₂O₂, and catalyst loading) on the degradation of RB5 dye has been analyzed further. Figure 4.6 (a) shows the chemical structure of RB5 dye. The absorption spectra of the 50 mg/L RB5 dye solution as a function of different treatment times when exposed to excimer UV-C irradiation of intensity around 1 mW/cm² in the presence of 0.75 g/L TiO₂ loading at ambient pH is shown in Figure 4.6 (b). The RB5 dye has two broad and intense absorption bands at 312 nm in the UV region and 598 nm in the visible region; both have diminished when exposed to the developed mercury-free XeI* excimer source. The intensity of the band at 598 nm is characteristic of the chromophore azo double bond of RB5 dye. This intensity decreases rapidly when exposed to the UV-C excimer

light, confirming approximately 90% degradation of the dye within 60 min of the treatment time and complete degradation in 90 min. A weak band in the UV-B region (312 nm) was also observed after 40 min, probably due to aromatic by-products in the reaction medium [Kritikos et al., 2007].

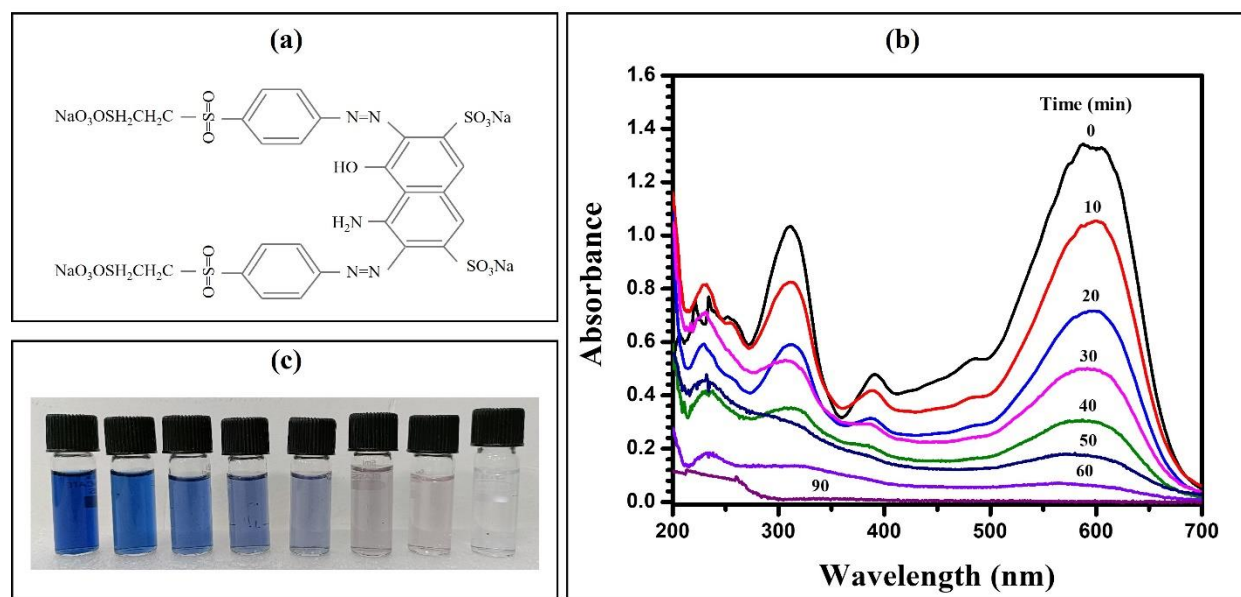


Figure 4.6: (a) Chemical structure of RB5 (M. W. 991.8), (b) UV-VIS absorbance spectrum of RB5 dye as a function of XeI* excimer light treatment time with 0.75g/L TiO₂ catalyst loading at ambient pH, and (c) pictorial representation of degradation of RB5 dye as a function of treatment time.

Figure 4.6 (c) shows the pictorial representation of decolorization of dyestuff at different exposure times by the developed excimer UV-C light source. A blank adsorption test was carried out in the dark by adding only 0.75g/L of TiO₂ in 50 mg/L of the dye suspension, and we found negligible degradation (< 1%) in the initial concentration of the RB5. The same test was performed in the visible light and found a < 2% reduction in the initial concentration of the dye after 60 min. It implies that the used dye is photostable in the visible range and agrees with the results published elsewhere [Kritikos et al., 2007].

4.6.1 Effect of Excimer UV-C Intensity

The effect of excimer UV-C light intensity on RB5 dye degradation for the case of 50 mg/L dye concentration and 1 g/L TiO₂ loading at ambient pH is shown in Figure 4.7 (a). The effect of variation in light intensity has been studied in the range of 550-2550 $\mu\text{W}/\text{cm}^2$. As can be seen in Figure 4.7 (a), the deterioration rate increases with increasing UV radiation intensity. This is because, with the increase in UV intensity, more UV-C photons fall on the catalyst surface, resulting in enhanced production of $\bullet\text{OH}$, which leads to a high degradation rate [Reza et al., 2017] [Toor et al., 2006]. Liu et al. [Liu et al., 2006] experimented with three different light intensities (1.24 mW/cm², 2.04 mW/cm², and 3.15 mW/cm²) and found that the decolorization rate of dye increases with increasing light intensity.

When the intensity was around 550 $\mu\text{W}/\text{cm}^2$, the dye completely degraded in about 90 min, and when the intensity was around 2550 $\mu\text{W}/\text{cm}^2$, the complete degradation of the dye took only 12 min. As mentioned above, for the developed mercury-free excilamp, the optimized UV-C intensity is 1050 $\mu\text{W}/\text{cm}^2$; therefore, all the experiments of RB5 dye degradation were performed at an absolute UV intensity of 1050 $\mu\text{W}/\text{cm}^2$.

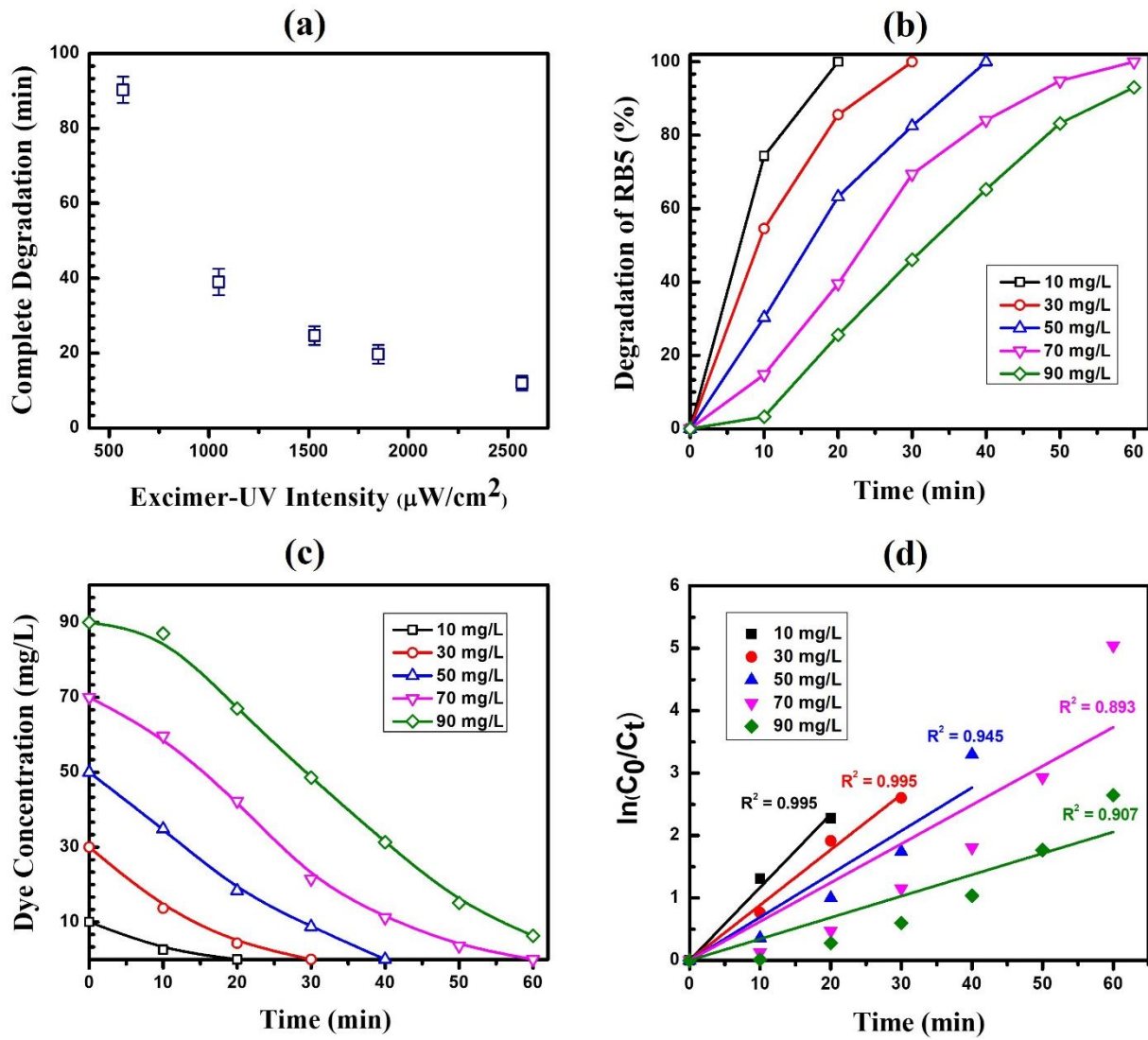
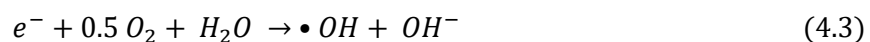
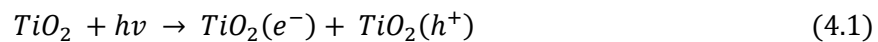
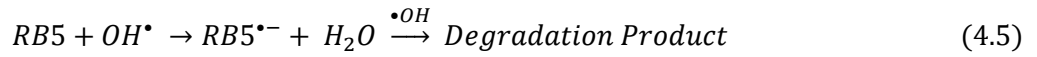


Figure 4.7: Effect of Xel* excimer light intensity on (a) complete degradation of RB5 dye (50 mg/L with 1g/L TiO_2 at ambient pH), (b) degradation as a function of exposure time with different initial concentrations of RB5 dye with 1g/L TiO_2 at ambient pH, (c) residue dye concentration at different times, (d) the degradation under Xel*/ TiO_2 processes based on a pseudo-first-order model.

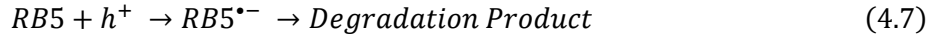
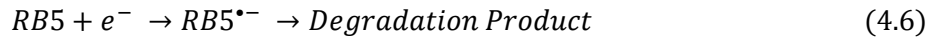
4.6.2 Effect of Initial Dye Concentration

The dependence of the photocatalytic process on the substrate concentration has also been investigated. The degradation is tested by varying the dye concentration from 10 mg/L to 90 mg/L and loading 1 g/L of TiO_2 catalyst at ambient pH. The acquired findings are shown in Figures 4.7 (b) and (c). For 50 mg/L, RB5 dye decomposed fully in just 40 min, whereas 90 mg/L degraded only ~ 65% in the same period. It is evident that the higher the dye concentration, the longer the treatment time [see Figures 4.7 (b) and 4.7 (c)]. For the increased dye concentration, lesser excimer UV-C photons could reach the photocatalyst surface, resulting in reduced $\bullet\text{OH}$ generation. The primary mechanism for $\bullet\text{OH}$ driven reactions is as follows,





In addition, there are indications that decolorization/degradation of suspension occurs by direct transfer of electrons and holes from the TiO₂ surface to the dye molecules [Tang et al., 2004] [Sohrabi et al., 2008] as,



So, as the dye concentration rises, photocatalyst activation decreases, resulting in fewer electrons available for direct reduction and fewer holes available for direct oxidation of the dye bond, further inhibiting degradation. The photocatalytic degradation of RB5 follows the pseudo-first kinetic model [see results in Figure 4.7 (d)] and is expressed as shown in equation 4.8 [Azizian, 2004].

$$\ln\left(\frac{C_0}{C_t}\right) = kt \quad (4.8)$$

Where, k is the first-order rate coefficient, C₀ is the initial concentration of RB5 dye, and C_t is the RB5 dye concentration at time t. The value of C_t is obtained from Figure 4.7 (c). The obtained k values for 10 mg/L, 30 mg/L, 50 mg/L, 70 mg/L, and 90 mg/L are 0.1173, 0.0886, 0.0692, 0.0623, and 0.0343, respectively. The rate coefficient demonstrated linearity and validated the behavior of first-order kinetics. At the low RB5 concentrations, the penetration of UV light into the aqueous solution is very high because of the lower concentration of dye molecules. However, when the dye concentration increases (70/90 mg/L), the degradation behavior deviates from first-order kinetics because of the lesser penetration of UV light in the aqueous phase. This is because, at high concentrations, the dye degradation rate is relatively slow at first. However, after 10 to 20 min of treatment, the rate of degradation increases because of reduced dye molecules. The obtained k values from this study are higher than the other reported k values for less than 75 mg/L dye concentration [Tang et al., 2004].

4.6.3 Effect of TiO₂ Loading

Another important parameter for dye degradation studies is the amount of the catalyst loading. In order to determine the optimal amount of the catalyst dose, experiments have been performed at ambient pH by varying the amount of catalyst from 0.5 g/L to 1.25 g/L in 50 mg/L initial dye concentration. The effect of different concentrations of TiO₂ is shown in Figure 4.8 (a), and the degradation efficiency increases continuously, with an increase in the catalyst loading. However, the dye degradation efficiency decreased when the catalyst dose exceeded 1g/L. At higher TiO₂ loading, the UV-C photon absorption increases, which results in more •OH production and increment of absorbance of dye molecules [Kritikos et al., 2007]. The increase in photocatalytic performance with increasing TiO₂ loading is evidence of a heterogeneous catalytic phase. This is because the amount of incident light absorbed by TiO₂ increases with increasing TiO₂ dosage in the suspension.

Interestingly, when the TiO_2 dose exceeded 1 g/L to 1.25 g/L, the dye degradation efficiency declined. Perhaps the increased XeI^* excimer light reflectance caused by the TiO_2 nanoparticles is mostly responsible for the decline in the RB5 dye degradation efficiency, as reported elsewhere [Muruganandham et al., 2006]. We could identify an optimized concentration of TiO_2 catalysts as 1 g/L for 50 mg/L dye degradation when our advanced photocatalytic mercury-free excimer UV-C lamp is used. In a previous report, the optimized concentration of TiO_2 loading was 2 g/dm³ in a solar/ TiO_2 process, and the complete degradation was achieved in 200 min when the dye concentration was 3.85×10^{-4} M [Muruganandham et al., 2006]. The reusability and stability experiments of prepared TiO_2 nanoparticles have also been performed, and it was found that the prepared catalyst maintained good stability and reusability after five cycles of dye degradation.

4.6.4 Effect of Different pH

The most important parameter that influences photocatalytic degradation is the pH of the solution [Tang et al., 2004]. Five different pH values in the acidic, ambient, and alkaline mediums have been studied to see the effect on the decolorization of the dye molecule at a fixed TiO_2 dose of 1 g/L. Figure 4.8 (b) shows the percentage degradation of RB5 under acidic, ambient, and alkaline conditions. It can be observed from Figure 4.8 (b) that degradation is much faster in the case of an alkaline medium than in an acidic medium. In just 20 min of treatment, the degradation has accelerated by two folds as the pH of a dye suspension rises from 2 to 10. This shows that the alkaline conditions are more favorable in our case. In general, the pH of the textile effluents is alkaline ($\sim 10 \pm 1$); [Rai et al., 2023] and hence, these results hold an excellent opportunity to degrade the textile effluents more effectively.

The point of zero charge (PZC) for TiO_2 is 6.8. The surface of the catalyst is positively charged when the pH is below PZC and negatively charged when the pH is above PZC [Abdellah et al., 2018]. The RB5 dye is fully in anionic form within the pH range studied, i.e., due to the presence of sulfonic groups. With increasing pH, the negative charges on TiO_2 are expected to repel the dye, and a decrease in photodegradation with increasing pH was expected. However, it has been observed that the RB5 dye degradation efficiency increases with increased pH. A similar result was reported earlier for the RB5 dye and acid blue 40 dye degradation [Tang et al., 2004]. This effect may be attributed to the more efficient generation of $\bullet\text{OH}$ by TiO_2 with an increasing concentration of hydroxide ions. At pH values of 10 and 6 (ambient), the complete degradation of RB5 took around 30 min and 40 min, respectively, making no significant contribution due to the alkalinity medium of the suspension. Accordingly, the ambient pH is selected for all the experiments until mentioned.

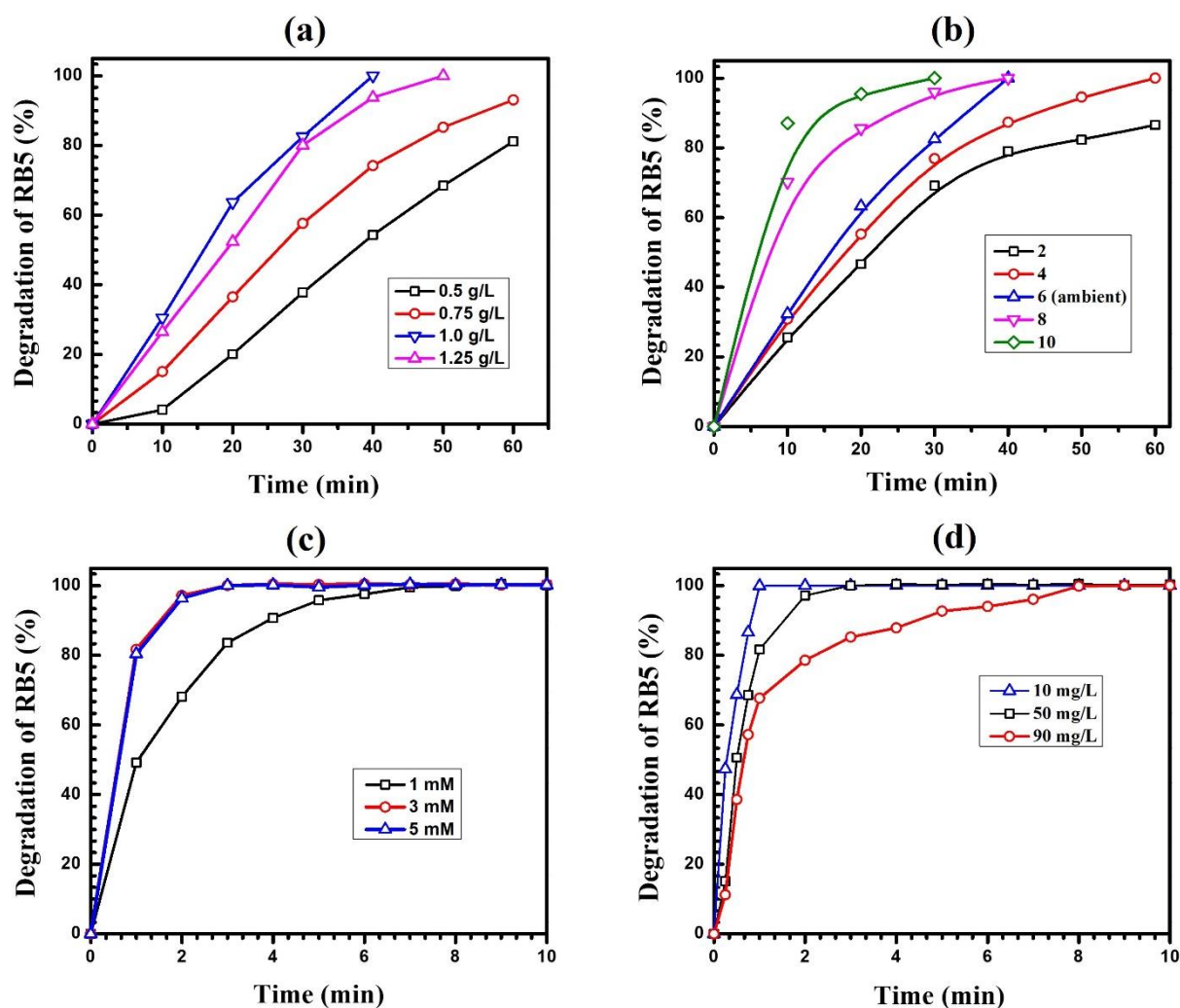


Figure 4.8: (a) Effect of different amounts of catalyst loading on RB5 dye degradation using Xel* excimer light source at 50 mg/L initial dye concentration, (b) Effect of different pH on RB5 dye degradation using Xel* excimer light source at 50 mg/L initial dye concentration, (c) Effect of different concentration of H₂O₂ on RB5 dye degradation using Xel* excimer light source at 50 mg/L initial dye concentration, (d) Time course dye degradation with 3 mM H₂O₂ addition on different dye concentrations.

4.6.5 Effect of the Addition of H₂O₂

Figure 4.8 (c) shows the percentage degradation of the 50 mg/L RB5 dye profiles when the concentration of H₂O₂ has been varied at ambient pH (without any TiO₂ loading). For 1 mM concentration of H₂O₂, the complete degradation occurs in 7 min. In contrast, the degradation rate becomes constant for further increases in the H₂O₂ concentration, i.e., 3 mM and 5 mM, and complete degradation occurs in just 3 min of treatment. When we increased the concentration of H₂O₂, the degradation time decreased because of the higher •OH generation in the suspension. However, after a certain limit, the degradation rate becomes constant because H₂O₂ itself scavenges •OH (equation 4.9). Therefore, a high concentration of H₂O₂ does not provide a high degradation rate.



The effect of H₂O₂ addition in a suspension containing 50 mg/L & 90 mg/L RB5 dye has been studied in further experiments. For 3 mM of H₂O₂ and the 90 mg/L dye solution, the

complete degradation occurs in 6 min. In contrast, when the same concentration of H₂O₂ in the 50 mg/L and 10 mg/L dyes is used, complete degradation occurs in 3 min and 1 min, respectively [see Figure 4.8 (d)]. These results are due to the powerful oxidizing nature of H₂O₂, reacting rapidly with excimer UV-C light to produce •OH [Tang et al., 2004] or reacting with electrons to produce •OH and OH⁻ [Prevot et al., 2001] through the following possible reactions,



A dark test was also performed to check the degradation with only H₂O₂, and negligible degradation occurred in the aqueous dye solution, showing that the RB5 dye is quite stable under bleaching conditions. Moreover, adding TiO₂ into this process reduces the degradation efficiency because H₂O₂ scavenges the photo-generated oxidizing species, i.e., •OH and valence band holes (see equations 4.9 and 4.12) [Asgari et al., 2022], which would otherwise be available for the oxidative destruction of the dye molecules. Accordingly, XeI*-excimer/H₂O₂ is considered a probable method of treating wastewater because of its ability to produce •OH (on-site) and also because it is a sludge-free operation with faster kinetics [Luo et al., 2021].

4.7 Comparison and Mechanism of Degradation

Figure 4.9 compares XeI*-excimer/ H₂O₂ performance with XeI*-excimer/TiO₂ and XeI*-excimer alone with different varying initial dye concentrations for complete degradation of RB5 dye. The time taken for complete degradation of RB5 dye (50 mg/L) by XeI*-excimer light source with TiO₂ is 40 min. On the other hand, with the XeI*-excimer source alone, it took around 360 min. When H₂O₂ is added to the dye suspension and irradiated with XeI*-excimer light, it shows exceptional results, and complete degradation of RB5 dye takes only 3 min. This is perhaps due to the more significant production of •OH in XeI*-excimer/ H₂O₂ because of the multiple electron transitions in the UV region [see Figure 4.2 (b)] and the reaction mechanism (4.9-4.12) explained above. According to Sun and Bolton [Sun et al., 1996], •OH generation rate and the quantum yield for the TiO₂ suspension are much lower than the H₂O₂ suspension, which is also one of the reasons for the higher removal rate in the case of H₂O₂ than TiO₂.

A comparison of different UV-based reactors operated at different powers for the degradation of RB5 dye is shown in Table 4.1. It reveals that the dye degradation time in advanced XeI*-excilamp/H₂O₂ is much less than that of the other UV-based reactors reported earlier in the literature.

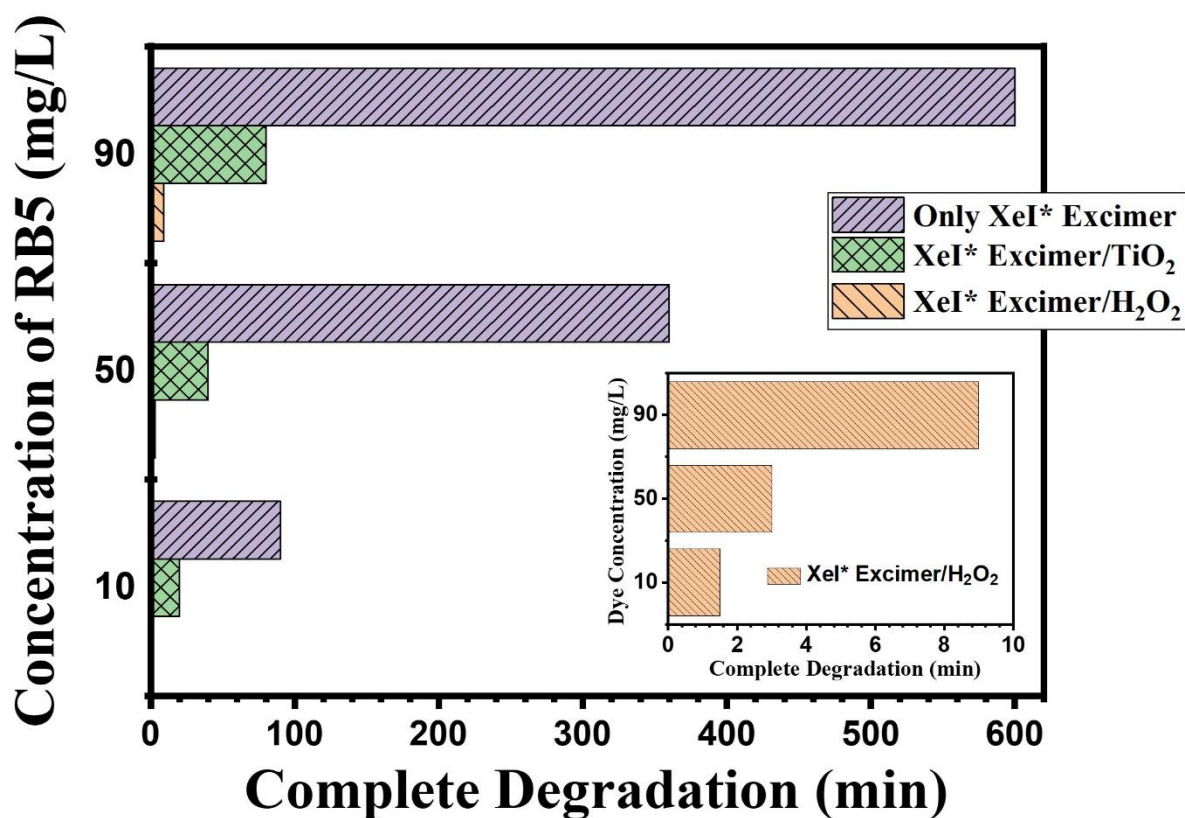


Figure 4.9: Time comparison of Xel*-excimer/H₂O₂ performance with Xel*-excimer/TiO₂ and Xel*-excimer alone at different varying initial dye concentrations for complete degradation of RB5 dye.

Table 4.1: Comparison of different reactors for the degradation of various organic dyes.

Dye	Dye Conc. (mg/L)	Sample Volume (ml)	pH	Light Source and Intensity	Power (W)	Process type & Loading	Time (min)	Energy Yield (mg/kWh)	Deg. (%)	Refs.
RB5	200	100	6	Medium Pressure UV Lamp	250	UV/TiO ₂ & 0.2 mg/L	240	-	96	[Bilal et al., 2018]
Acid Orange 7	10	28 ml/min		240 White LEDs	60	LED/N-TiO ₂ , Continuous flow	-	-	90	[Sannino et al., 2023]
Rhodamine B	40	500	4	High pressure mercury lamp (365 nm)	250	UV/TiO ₂ flow process & 1g/L	100	-	92	[Butman et al., 2020]
Methylene blue	20	-	6.8	-	19	Multineedle to plane liquid DBD Plasma	40	537	90 – 96	[Zhang et al., 2022b]
Brilliant Red 5B	-	100		-	95	Photo SDBD	14	401	> 99	[Allabakshi et al., 2023]

RB5	50	100	6	XeI* excilamp & 1.050 mW/cm ²	17.5	UV/TiO ₂ & 1g/L	40	428.6	> 99	[Ahla wat et al., 2024c]
RB5	50	100	6	XeI* excilamp & 1.050 mW/cm ²	17.5	UV/H ₂ O ₂ & 0.0137% v/v	3	5712	> 99	

In this study, the excitation of mesh electrode TiO₂ nanoparticles occurred when the XeI* excimer source transferred the energy (253 nm) to the surface of the catalyst. This reaction creates electron and hole pairs, which further react with atmospheric moisture (H₂O) and oxygen (O₂) to generate a pool of active ions and reactive species [Jiang et al., 2018]. The concentrations of active air ions have been measured using an air ion counter (AIC2, Alpha lab, USA) and found to be ~ 15000 ions/cm³. The negative air ions have been utilized for the on-site production of •OH and other reactive species. As reported by Jiang et al. [Jiang et al., 2018], the lifetime of these negative air ions was found to be 100 s to several min. Luts and Salm [A. Luts and J. Salm, 1994] identified that O₂⁻ is the primarily negatively charged ion and is more stable than other negative air ions. These photochemically generated negative air ions and reactive species can diffuse from the gas phase to the aqueous phase and further react with the different species present in the water as shown in Figure 4.10 (a). Various computational and experimental studies show the different scenarios of how these active ions and reactive species were transported from the gas phase to the aqueous phase [Verlackt et al., 2018] [Lu et al., 2016]. In the non-existence of electron and hole pairs in the suspension (because of absence of TiO₂), superoxide ions (from modified XeI* excimer source) react with H₂O₂ and produce •OH, which are subsequently used for the mineralization of organic wastewater. A separate experiment has been performed without a TiO₂ mesh electrode to see the effect of only UV light on the photolysis of H₂O₂ for the dye mineralization. Due to the low quantum yield of H₂O₂ at 253 nm [Liu et al., 2023b], the degradation rate decreases and results are shown in Figure 4.10 (b).

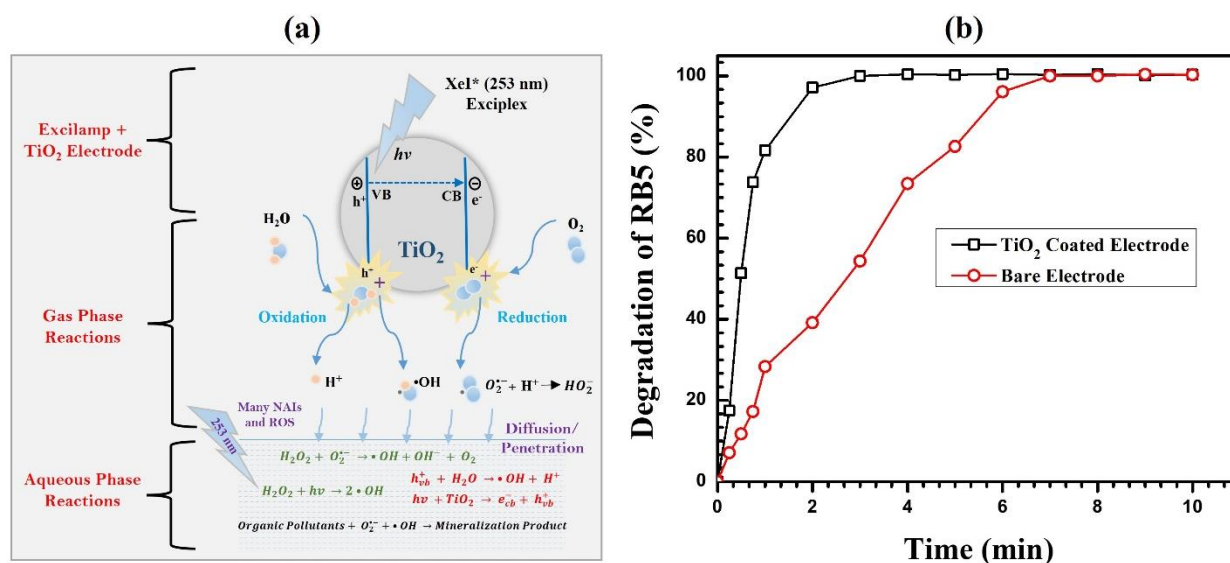


Figure 4.10: (a) The proposed mechanism for the aqueous azo dye degradation using modified XeI* excilamp, (b) The comparison of bare and TiO₂ coated mesh electrodes on the degradation of RB5 dye (initial RB5 concentration 50 mg/L, H₂O₂ loading 3 mM, and pH 6.0).

4.7.1 Radical Scavenging Effect

The modified XeI* excimer source-based degradation studies of the RB5 dye by adding H₂O₂ as a radical promotor are also confirmed by scavenging studies, as seen in Figure 4.11. These studies are used to examine the role of the reactive species in the modified XeI* excimer source-based degradation mechanism. Benzoquinone (BQ), ammonium oxalate (AO), and isopropanol (IPA) act as scavengers with active radicals $O_2^{\bullet-}$, h^+ , and $\bullet OH$, respectively [Wang et al., 2020]. The experiments are carried out using the modified XeI* excimer source without scavengers and with these three active radicals on RB5 dye in the presence of H₂O₂ as a radical promotor. It is found that adding different scavengers considerably reduces the rate of RB5 degradation. After the degradation, it exhibits 99.9%, 74.4%, 89.4%, and 17.7% of RB5 degradation for H₂O₂, BQ, AO, and IPA, respectively. Therefore, from this experiment, it is clearly observed that these three active radicals are involved in the degradation mechanism and the production of $\bullet OH$.

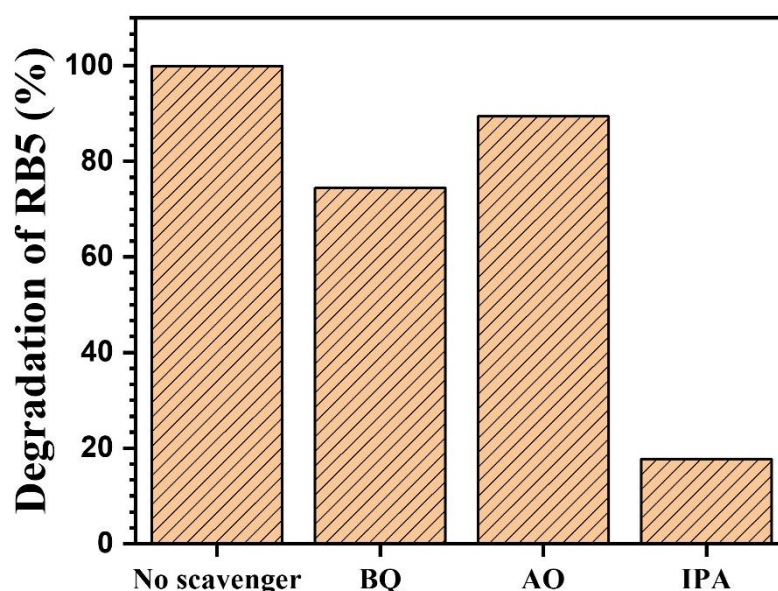


Figure 4.11: Quenching studies of reactive species during the modified XeI* excimer source based degradation of RB5 dye over H₂O₂ as a radical promotor.

4.8 Energy Yield and COD Analysis

Energy yield is a widely accepted parameter among the plasma-based water treatment methods to evaluate the energy efficiency of plasma-based reactors. In this study, the energy yield of DBD plasma-based mercury-free excilamp is computed for different methods by using equation 2.5. For the complete degradation of dye, the maximum energy yield in the case of XeI*-excimer/TiO₂ is found to be 428.6 mg/kWh for 50 mg/L dye concentration and 1g/L TiO₂. Whereas the maximum energy yield in the case of XeI*-excimer/H₂O₂ is found to be 5712 mg/kWh for 50 mg/L dye concentration and 3 mM H₂O₂. Figure 4.12 (a) shows the system's energy yield for different treatment methods used in this work. Allabakshi et al. [Allabakshi et al., 2023] used a surface dielectric barrier discharge (SDBD) system with UV-C light for dye mineralization and reported a maximum energy yield of 522 mg/kWh. According to the literature, the present XeI*-excimer/H₂O₂ system showed reasonably good energy efficiency than many other reported plasma reactors.

The mineralization and toxicity of treated RB5 dye are estimated by COD analysis of the untreated and treated dye solution. COD is a parameter that reflects the organic burden and, by extension, the chemical concentration of effluents. The transformation of organic compounds into inorganic compounds reduces the COD and is directly related to the degradation of organic matter [Deng et al., 2015]. COD concentrations of 50 mg/L untreated dye solution and treated

with XeI*-excimer/TiO₂ 40 min, XeI*-excimer/H₂O₂ 3 min, and XeI*-excimer/H₂O₂ 40 min, at ambient pH is shown in Figure 4.12 (b). It is found that the initial COD concentration was 246.7 mg/L, and it declined to 67.68 mg/L, after 40 min treatment with XeI*-excimer/TiO₂ process. When COD is reduced by up to 72.6%, at that treatment time the rate of RB5 dye removal is found to be ~ 99.9%. In the case of 50 mg/L dye concentration and 3 mM H₂O₂, the COD is reduced by 52.3% in the treatment time of 3 min, the rate of RB5 dye removal is found to be ~ 99.9%. For more than 95% COD reduction, it will take 40 min, in the case of 50 mg/L dye concentration and 3 mM H₂O₂. We find that for more mineralization, more treatment time is needed. Further, a significant decrease in COD values at the RB5 dye suspension treated with an excimer UV-C photocatalytic process indicated its potential for reactive azo dye degradation. The results hold a good promise for the rapid mineralization of the RB5 dye and can be an effective method for the treatment of RB5 dye.

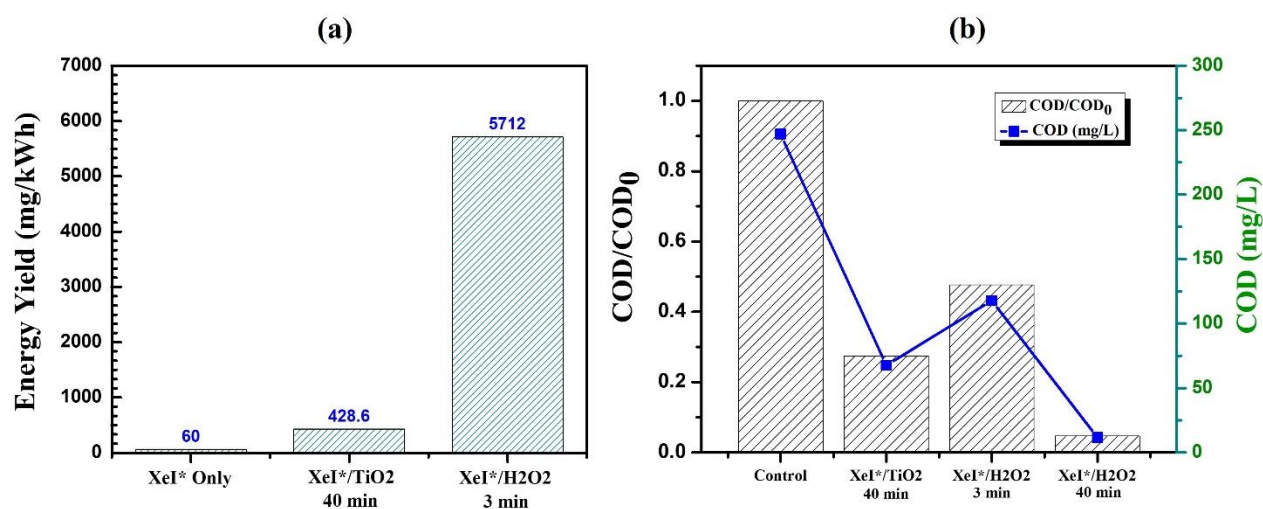


Figure 4.12: (a) Energy yield corresponding to different treatment methods for complete dye degradation (50 mg/L) and (b) COD removal as a function of treatment methods at ambient pH and initial RB5 dye concentration of 50 mg/L.

4.9 Possible Degradation Pathway of RB5 dye

Untreated and XeI*-excimer/H₂O₂ degraded RB5 dye samples are examined using HR-MS and FTIR techniques to determine a possible mechanism for RB5 dye degradation. The fragmentation data and m/z values obtained from mass spectroscopy analysis are used to identify the fragmented by-products. Based on the intermediates of its degradation and earlier publications [Bilal et al., 2018] [Plum et al., 2003] a possible mechanism for the degradation of RB5 dye is proposed and shown in Figure 4.13. Degradation of RB5 dye follows multiple steps like dissociation of azo (-N=N-) bond, rearrangement of functional group, ring opening, and finally its mineralization.

Initially, the breakage of the C-O bond in RB5 dye is caused by the •OH immediate interaction with organic contaminants that leads to the production of intermediate as shown in A: intermediate in Figure 4.13 (m/z 787). According to A: intermediate, the breakdown of the azo bond leads to the creation of products B (m/z 346) and C (m/z 280), which are related with the direct degradation of RB5 dye through the UV assisted photo-degradation process. Further, fragmentation of product B results in the formation of product D (m/z 189) by the dissociation of C-SO₃ bond. The fragmentation of product C results in the formation of product E (m/z 148), which mineralized into oxalic acid (m/z 90) through the ring opening mechanism of product E. The •OH attack on the benzene rings caused them to break, which then began RB5 dye to break down into less refractory intermediate molecules and eventually mineralized into CO₂ and H₂O.

It can be inferred that the degradation of dyes involves the cleavage of azo bonds, which results in the formation of aromatic amines, followed by their complete disintegration [Bilal et al., 2018] [El et al., 2016]. The analytical data showed that the azo (N=N) bond in RB5 dye has been degraded into several intermediate products.

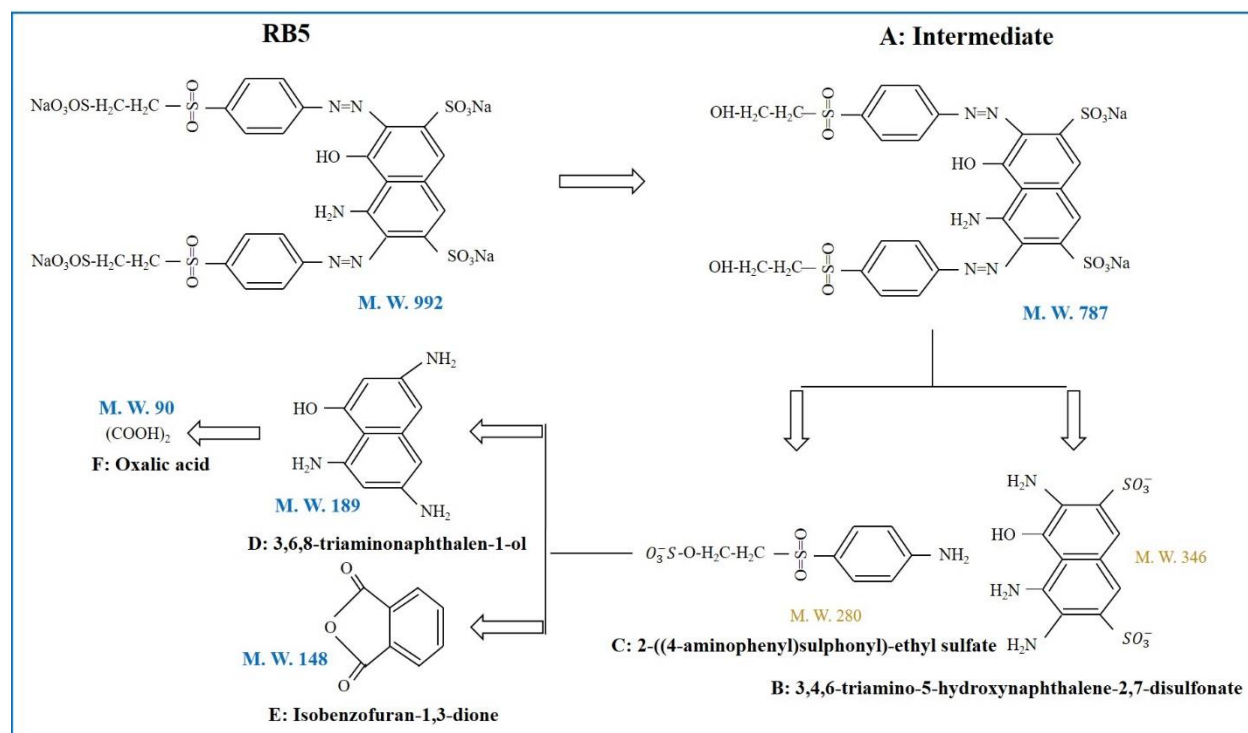


Figure 4.13: Possible degradation pathway of RB5 dye by XeI* excimer light-assisted photocatalytic reaction.

4.10 Degradation Comparison with Real Water Matrix

The widely used process for textile wastewater treatment is advanced photocatalytic oxidation. However, in this process, the extraction and reuse of the catalysts is challenging. We have eliminated the process of catalyst extraction and recovery by developing the modified XeI* excimer reactor for the faster degradation/mineralization of the azo dyes. The effects of the XeI* excimer reactor on the real water matrix (diluted seawater) have been investigated through a series of tests, and the outcomes are compared with the model RB5 degradation. Figure 4.14 compares the degradation of the model RB5 solution with diluted seawater to demonstrate the effectiveness of the employed approach. Sea water was chosen as a textile effluent alternative due to the presence of high concentrations of salts because, during the wet dyeing process, the textile industries use salts to enhance the penetration of the dye into the fabric and for dyeing efficiency [Sun et al., 2017]. TiO_2 and H_2O_2 -based XeI* excimer degradation rate of artificial textile water has been lower than that of the model RB5 solution prepared with DI water, as can be seen in Figure 4.14 (a) and (b).

Textile effluent generally contains dissolved organic matter, as well as ions such as CO_3^{2-} , Ca^{2+} , K^+ , Na^+ , HCO_3^- , and SO_4^{2-} , etc. All these components react with $\bullet\text{OH}$, thus reducing its concentration and making it less accessible for dye molecules. Also, $\bullet\text{OH}$ reacts with some inorganic ions, like HCO_3^- and SO_4^{2-} and forms the corresponding radicals, such as $\text{HCO}_3^\bullet$ and $\text{SO}_4^{\bullet-}$, which are less efficient for oxidation as compared to $\bullet\text{OH}$ itself [Zhao et al., 2022]. Still, the modified XeI* excimer reactor is very efficient, since the complete degradation has been achieved in just 7 min in the case of XeI*-excimer/ H_2O_2 . Since RB5 dye is an anionic dye, it has

been further demonstrated that the excimer reactor that has been built is a superior alternative to traditional techniques; the degradation of a cationic dye (methylene blue) has also been performed. The results of this experiment have shown that the modified XeI* excimer source using H₂O₂ as a radical promotor successfully acts on the cationic dye as well, and after just 8 min of treatment, 99.99% of the 50 mg/L of methylene blue has been degraded.

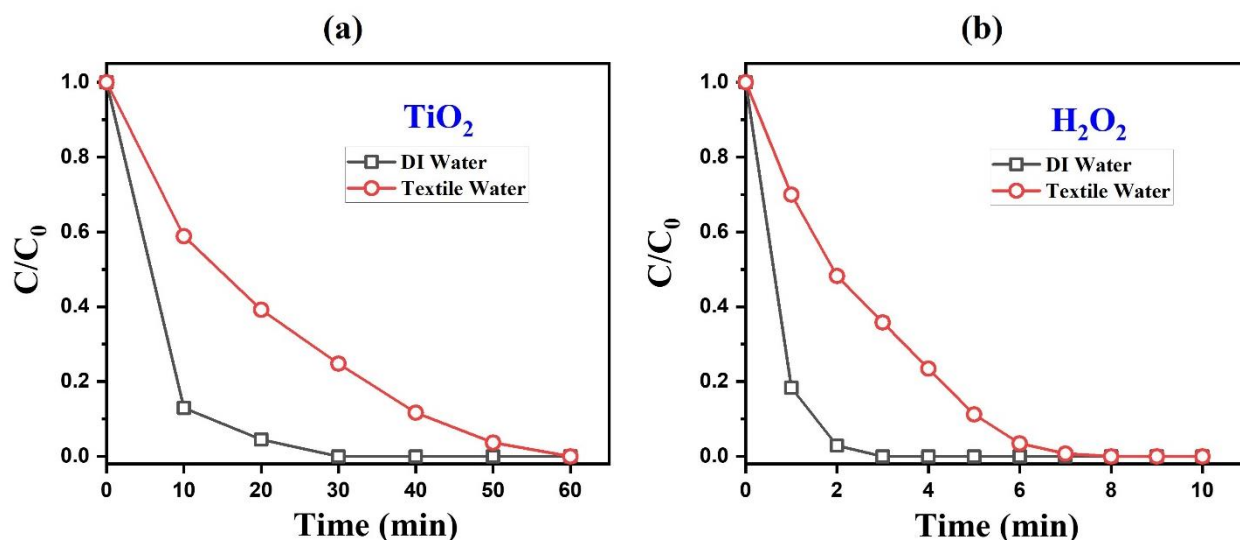


Figure 4.14: Comparison of degradation rates in DI water and textile water (a) with TiO_2 (initial RB5 concentration 50 mg/L, TiO_2 loading 1g/L, and pH 10.4) and (b) with H_2O_2 (initial RB5 concentration 50 mg/L, H_2O_2 loading 3 mM, and pH 10.4).

4.11 Toxicity Analysis of Treated Effluents and its Reusability for Agriculture Purposes

Radish seeds are first sown directly into soil to evaluate the germination ability of the treated and untreated dye wastewater. The water resulting from the separate treatments using XeI*-excimer/ TiO_2 and XeI*-excimer/ H_2O_2 are then used for watering the seeds. The germination process is allowed to proceed for 3 days under controlled conditions. The seed germination ability of DIW, untreated dye wastewater, XeI*-excimer/ H_2O_2 3 min treated dye wastewater, XeI*-excimer/ H_2O_2 40 min treated dye wastewater, and XeI*-excimer/ TiO_2 40 min treated dye wastewater is analyzed and compared by measuring stem and root length. Table 4.2 summarizes the germination percentage, root length, and stem length after 3 days of incubation.

Table 4.2: Effect of different treatments of dye wastewater on the radish seed germination.

	DI	Dye Wastewater	Treated with TiO_2	Treated with H_2O_2 for 3 min	Treated with H_2O_2 for 40 min
Stem Length (cm)	7.086±1.233	4.078±1.015	7.054±1.451	7.435±1.098	9.88±1.042
Root Length (cm)	1.277±0.212	1.1±0.183	1.222±0.229	1.643±0.209	2.16±0.361
Germination (%)	88	76	88	92	96

To illustrate it further, the images are captured for the growth of the stem and roots of radish seeds for continuous three days of incubation, which are shown in Figure 4.15. Figure 4.15 (a) shows the growth of the radish seeds in soil for 3 days consecutively, and Figure 4.15 (b) provides a visual representation of the impact of the various treatments on seed germination and growth (stem and root length) in a more natural and applicable context.



Figure 4.15: Photographic image of (a) the growth of the radish seeds in soil for 3 days and (b) stem and root length after 3 days.

The study demonstrates that treating dye wastewater separately using XeI*-excimer/TiO₂ and XeI*-excimer/ H₂O₂ under 253 nm light significantly enhances the degradation of dye molecules. The water resulting from these separate treatments shows positive effects on radish seed germination and growth when compared to untreated dye wastewater. UV/ H₂O₂ treated wastewater shows enhanced germination than DI water because some recent findings show that H₂O₂ can be used to increase the growth of the plant [Nurnaeimah et al., 2020] [Jafariyan et al., 2016]. On the other hand, when H₂O₂ dissolved wastewater is treated with a DBD-based modified XeI* excimer source, various reactive oxygen species are produced, which also helps in enhanced seed germination [Sivachandiran et al., 2017]. Germination of the seeds in the case of XeI*-excimer/ H₂O₂ (40 min) is 98%, whereas, in the case of XeI*-excimer/TiO₂, it is found to be near 89% despite having the same treatment time. This can be due to the presence of more non-degraded dye constituents in the XeI*-excimer/TiO₂ treated wastewater than the XeI*-excimer/ H₂O₂ treated wastewater. The root length in the case of dye wastewater is quite less because of nutritional deficiency in the dye wastewater due to the presence of more organic contaminants. The pH in all the experiments is found neutral; hence, no neutralization is required after treatment. In general, in direct atmospheric pressure cold plasma treatments, the pH of the treated effluents decreases, and it becomes acidic in nature [Allabakshi et al., 2023]. However, in the direct photolysis process, no neutralization is required [Cuerda-Correa et al., 2020], which is one of the advantages of this study. When we compare the growth in 3 min and 40 min by XeI*-excimer/H₂O₂ treatment, the treatment for 40 min displayed the highest germination percentage and enhanced growth of stems and roots because of the more demands of oxygen in the case of 3 min as compared to 40 min treatments [see Figure 4.12 (b)]. The above results suggest the potential

use of mercury-free plasma XeI*-excimer source for agricultural applications. Further research is needed to delve into the precise mechanisms underlying these effects and optimize the treatment process for wider environmental and agricultural applications.

4.12 Conclusion

In this chapter, an environmentally friendly XeI* excimer light source has been developed and used for the degradation of RB5 dye with an AOP using TiO₂ and H₂O₂. In the case of XeI*-excimer/TiO₂, the degradation of 50 mg/L of RB5 has been achieved in 40 min when the concentration of TiO₂ loading was 1 g/L at ambient pH. A faster degradation (within 3 min) of RB5 has been achieved by using the XeI*-excimer/H₂O₂ process in the case of 50 mg/L dye suspension at ambient pH. The mineralization of the dye has also been performed and more than 95% removal in the COD concentration has been achieved within 40 min of the treatment with XeI*-excimer/H₂O₂. The order of degradation/mineralization is found to be XeI*-excimer/H₂O₂ > XeI*-excimer/TiO₂ > XeI*-excimer alone. The developed process is environmentally friendly (because no mercury is used) and eliminates the process of recovery of catalysts from the treated water after degradation. The faster degradation occurs in the alkaline medium (pH 10), which makes this process more favorable to use for the treatment of wastewater since the textile effluents have an alkaline nature. The optimized method, i.e., XeI* excimer/H₂O₂, can be utilized for enhanced decolorization and mineralization of the unfixed dye in textile effluents. The results have been compared with existing dye degradation methods, and this environmentally friendly approach is found to be more effective in terms of time taken for degradation and energy yield. The treated water resulting from these separate treatments has been used on radish seeds, and the seed germination and root growth have shown a positive impact as compared to untreated dye wastewater. The wastewater used for seed germination is the same as obtained from the different processes. Large-scale textile wastewater treatment is possible with the intended reactor; however, in order to ensure that the reactor is applicable in practice, extensive pilot-scale testing of the design is required.

