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# Photodecomposition of crystal violet dye in water solution and suspensions of metal oxides

Tatiana Yurievna Zakharian
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# PHOTODECOMPOSITION OF CRYSTAL VIOLET DYE IN WATER SOLUTION AND SUSPENSIONS OF METALS OXIDES

An Abstract of a Thesis

Submitted

in Partial Fulfullment

of the Requirements for the Degree

Master of Arts

Tatiana Yurievna Zakharian

University of Northern Iowa

July 2000

ABSTRACT

Photodecomposition and photodecolorization of crystal violet dye were studied in water solution, hydrogen peroxide solution and suspensions of metal oxides. Spectroscopic evidence for the formation of methylated pararosanilines and demethylated derivatives of Michler's ketone as the reaction intermediates was obtained for the photodecomposition of crystal violet in water solution. The mechanism of formation of the intermediates was discussed in terms of charges of individual atoms calculated using Spartan software.

Photooxidation of crystal violet was shown to occur faster in hydrogen peroxide solution due to the higher oxidation potential of hydrogen peroxide and hydroxyl radicals. A mechanism similar to photooxidation in water solution was proposed since the formation of the same intermediates was observed.

The semiconducting oxides $TiO_2$ and ZnO were shown to be more efficient in crystal violet photodecomposition than any of the insulating oxides studied: $SiO_2$, $Al_2O_3$, and MgO. Adsorption and wavelength dependent studies of titanium dioxide suspensions are consistent with a pathway in which a dye is oxidized by the surface-bound hydroxyl radicals formed by injection of an electron from adsorbed hydroxyl groups to photogenerated holes. Photogenerated electrons are subsequently scavenged by molecular oxygen to form $O_2^-$ radical anions and ultimately hydroxyl radicals that can also oxidize the dye. Intermediates/products of photodecomposition were found to be adsorbed on the titanium dioxide surface, which could lower the catalytic efficiency of titanium dioxide as the reaction proceeds. Zinc oxide was found to be the most efficient oxide for crystal

violet photodecomposition, but its low photochemical stability makes it unsuitable for industrial catalysis. Photochemically inert oxides were shown to influence the rate of crystal violet photodecomposition. Acceleration of photodecomposition in the presence of aluminum oxide can be explained by stabilization of the excited state of the dye by the aluminum oxide surface, and inhibition of photodecomposition in the presence of silicon dioxide can be explained by the formation of dye clusters on the silicon dioxide surface. Fast decolorization in magnesium oxide suspensions is due to the reaction of crystal violet with hydroxide ion to form a carbinol base. Titanium dioxide was concluded to be the best prospective catalyst for crystal violet photodecomposition of those studied, since it is highly efficient, relatively cheap and chemically stable.

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This Study by: Tatiana Yurievna Zakharian

Entitled: Photodecomposition of Crystal Violet Dye in Water Solution and Suspensions of Metal Oxides

has been approved as meeting the thesis requirement for the

Degree of Master of Arts

June 15, 2000 — Date — Dr. Shoshanna R. Coon, Chair, Thesis Committee

6/15/00 — Date — Dr. Laura M. Hoistad, Thesis Committee Member

6/15/00 — Date — Dr. Paul E. Rider, Thesis Committee Member

June 15, 2000 — Date — Dr. Vyacheslav N. Pak, Thesis Committee Member

7/18/2000 — Date — Dr. John W. Somervill, Dean, Graduate College

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# CHAPTER I

## INTRODUCTION

Dyes are intensely colored chemical compounds which, being applied to a substrate, impart color to their substrate. Their ability to produce color arises from the absorption of light in the visible range (400-700 nm), as a result of the interaction of the radiation energy with the electron system of the molecule. The absorption spectrum depends on the electronic structure of the dye.

The efficiency of dyes in absorbing specific wavelengths and reflecting others is evaluated by the extinction coefficient, which is a measure of the fraction of light lost to scattering and absorption per unit distance in the dye. For dyes with higher extinction coefficients, lesser amounts are required to give the same depth of shade, which makes them more economical in industry.

Dyes can be classified on the basis of the functional groups present. Azo, carbonyl and triphenylmethane dyes are the most widely used classes of dyes.

Azo dyes contain azo groups (-N=N-) linked to two radicals, with at least one, but more usually both, being aromatic. Azo dyes have high extinction coefficients, cover all shades from yellow to navy and are relatively inexpensive, which makes them widely used for dyeing of apparel and household textiles. The disadvantage of azo dyes is that with bathochromic (red) shades, the ability to preferentially absorb light at only specific wavelengths is reduced, with the resulting dulling of the shade. Further, the light fastness of azo dyes is usually not very high: many of them undergo reductive and oxidative

photochemical reactions on exposure to strong light with the azo chromophore being destroyed which makes the molecule either colorless or at best pale yellow.

Carbonyl dyes contain at least one carbonyl group (-C=O). Carbonyl dyes in general are compact, which makes them excellent in obtaining high-quality dyeings in pale shades on difficult to dye fabrics, and have good to excellent lightfastness. The principal disadvantage of most carbonyl dyes is that they are tinctorially weak and based on complex and expensive chemicals and chemical processes.

Triphenylmethane dyes contain three phenyl rings connected to an $sp^2$-hybridized carbon. The formulas of some common triphenylmethane dyes are shown in Figure 1.

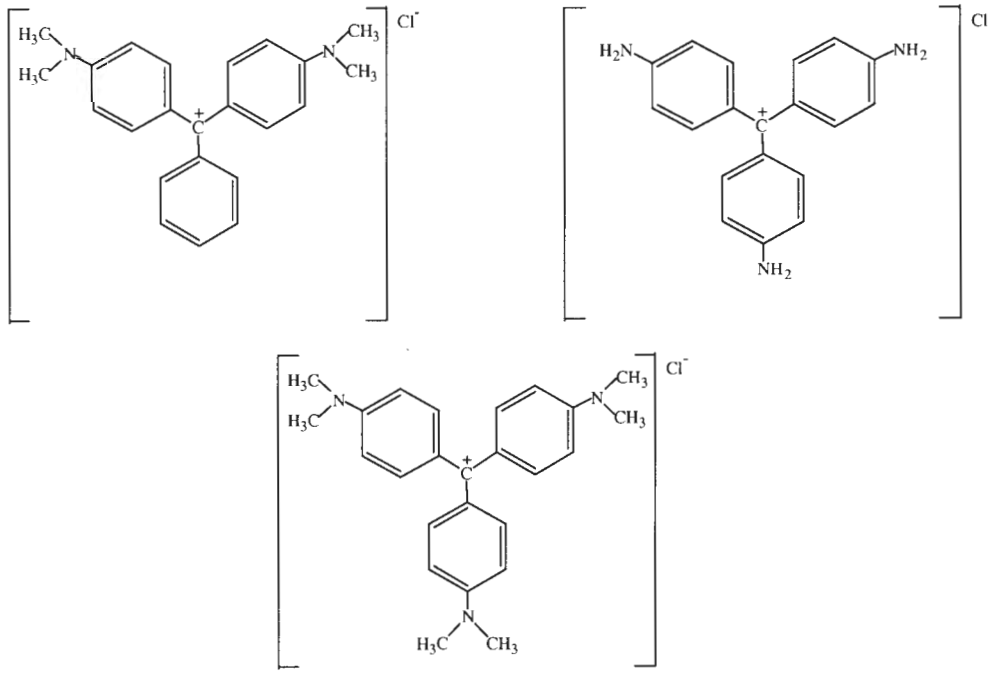



Figure 1. Structure of three triphenylmethane dyes (clockwise from upper left): Basic Green 4 (Malachite Green), Basic Red (Pararosaniline) and Basic Violet 3 (Crystal Violet).

Triphenylmethane dyes are of brilliant hue, exhibit high tinctorial strength and can be applied to a large range of substrates. However, they are seriously deficient in fastness properties, especially fastness to light and washing. Consequently, they are used in outlets where brightness and cost effectiveness rather than permanence are paramount, for example, the coloration of paper, waxes, plastics, drugs and ceramics.[1] Crystal violet, N,N,N',N',N",N"-hexamethylpararosaniline, is widely used in pulp and paper manufacture for coloration of paper and in laboratories for staining human and veterinary tissue cells.[2]

Because of the high extinction coefficients of dyes, their presence in waste-waters even at low concentrations may significantly lower transmission of sunlight—an important component of life for most organisms. In addition, many triphenylmethane dyes exhibit toxic effects toward microbial populations and can be toxic and mutagenic to animals.[3] Some dyes, including crystal violet, are known to be enzymatically degraded in the human digestive system to produce carcinogenic substances.[4] These environmental effects state the necessity of decolorization for nontoxic and noncarcinogenic dyes to form colorless and harmless dye derivatives and decomposition for the others to degrade them into nonhazardous compounds, preferably $CO_2$ and water.

Significant losses occur during manufacture and processing of dyes. Recent estimates indicate that 12% of the synthetic textile dyes used yearly are lost to waste streams.[5] Because of their hazardous environmental effect, contamination of drinking water supplies is of concern, and an efficient and cheap way of treating dye-contaminated waters should be found.

There are three groups of water treatment methods: physical, biological and chemical.[6]

Physical methods include adsorption, sedimentation, floatation, coagulation and reverse osmosis. These methods result in physical removal of the dye material from the effluent, which lowers the concentration of the dye but a waste disposal problem still remains.

Biological treatment can be aerobic or anaerobic.[7] The aerobic systems use free oxygen dissolved in the wastewater to convert wastes in the presence of microorganisms to carbon dioxide and water. The anaerobic process occurs in the absence of free oxygen and converts the waste to methane and carbon dioxide. Most biological methods are slow and not very effective due to the stability of modern synthetic dyes. Usually only a moderate amount (10-20%) of color can be removed using them.

Chemical methods include reduction and oxidation of contaminating dyes. Many dyes, particularly azo dyes, are susceptible to destructive reduction. For example, using zinc hydrosulfite for the decolorization of dyed paper stock resulted in decolorization of 98% for azo dyes.[8]

Chemical oxidation is one of the main methods to treat and decompose dyes in wastewater. Oxidizing agents such as chlorine and ozone are very efficient in dye degradation.[9, 10, 11,12] For example, complete decolorization of acid dyes was obtained with low concentration of chlorine at room temperature.[13] However, discharge of chlorinated organics into the environment is extremely undesirable. Ozonation, usually resulting in less hazardous products than chlorination, requires significant electrical

power and capital costs. A prospective oxidizing agent is hydrogen peroxide, which has an advantage of being not only a relatively strong chemical oxidant, but also an easily-storable, non-corrosive liquid, totally miscible in water. Ultraviolet light splits hydrogen peroxide molecules, producing free radicals with higher oxidation potential and, therefore, allowing a greater number of chemical products to be oxidized. Thus, ultraviolet/hydrogen peroxide systems are successfully used in decolorization of wastewater dyes in the paper industry.[14]

The use of visible/UV light and semiconducting metal oxides as catalysts[15,16,17] to induce oxidation or reduction of synthetic dyes is a very promising method of wastewater treatment. It has been noted that organic contaminants can be completely mineralized by irradiation in the presence of semiconducting metal oxides.[18] The advantages of this method are that semiconductors appear to be efficient, inexpensive, non-toxic and chemically stable.[19]

There are two main processes that can occur in the semiconductor-dye system[20]:

1. Photosensitization, when an adsorbed molecule injects an electron from its excited state into the conduction band of semiconductor particle and the oxidized form of the dye then undergoes the transformation to give stable products. The semiconductor in turn can reduce a different molecule adsorbed on the surface (Figure 2A).

2. Reduction and oxidation by the photoexcited semiconductor, when continuous band-gap irradiation excites an electron from the valence band of the semiconductor to the conduction band, creating an electron-hole pair which can initiate oxidation and reduction of the absorbed substrates (Figure 2B).

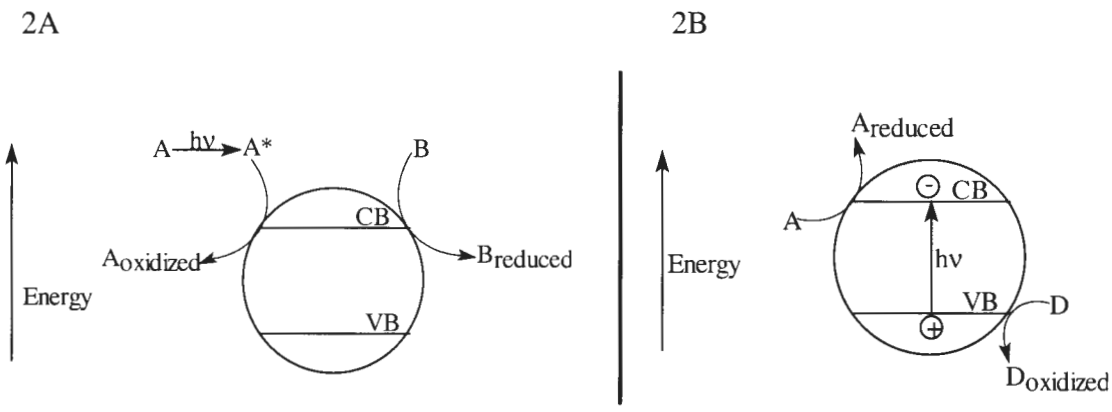



Figure 2. Photosensitization of dye-semiconductor system (A) and photoexcitation of a semiconductor surface (B).

Photoreduction of dyes in suspensions of semiconducting oxides can be carried out by the photoexcited electrons. It is usually a one-electron reduction to yield a semireduced dye, which then disproportionates to yield a two-electron reduction product (leuco dye). Thus, zwitterionic viologen, was reduced in a colloidal $In_2S_3$ suspension, producing leuco zwitterionic viologen.[21]

Photooxidation of dyes in water suspensions of metal oxides in the presence of oxygen could occur by different mechanisms:

1. Direct oxidation of adsorbate molecules by trapped holes.

2. Oxidation of hydroxide ions by trapped holes to produce hydroxyl radicals, which in turn can oxidize a dye in the solution.

3. Oxidation by perhydroxyl radicals produced by protonation of $O_2^{-\bullet}$ species, which are formed by the interaction of trapped electrons with preadsorbed molecular oxygen.

These oxidation routes are hard to differentiate. The chemical identification of hydroxylated oxidation intermediates and the ESR detection of hydroxyl radical appear to support the hydroxyl radical mechanism[22], but a recent diffuse reflectance flash photolysis experiment in nonaqueous solutions presented evidence in favor of direct oxidation by trapped holes.[23] A competitive mechanism, where an organic molecule and hydroxide adsorbed on the surface compete for the trapped holes, has also been proposed.[24]

In this investigation, crystal violet was selected to be a model compound to study photodecomposition and photodecolorization of dyes on metal oxide surfaces.

Photodecolarization and photodecomposition of crystal violet was previously studied both in the solutions of different solvents and adsorbed on different surfaces.[25] Crystal violet can be photooxidized or photoreduced depending on experimental conditions. Photoreduction may involve either an electron or hydrogen abstraction process. Thus, it is favored under anaerobic conditions and in the presence of compounds that are oxidized more readily than the dye, for example, protein substrates. Photoreduction of crystal violet is believed to proceed via a radical to form a leuco dye as a major product (Figure 3).[26]

Oxidation is usually favored under aerobic conditions and when the medium containing the crystal violet is more easily reduced than the dye itself. Thus, photooxidation is observed more frequently on nonprotein substrates and in liquids of poor electron and hydrogen donating ability. Several products of crystal violet photooxidation, including demethylated dyes, amino-substituted benzophenones

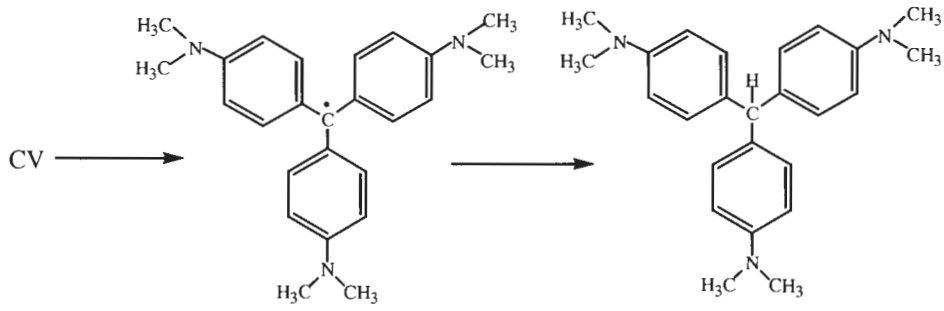



Figure 3. Reduction of crystal violet

and leuco dyes, have been identified.[27] The proposed mechanisms for the formation of these products will be discussed in this thesis.

Although photodecomposition of crystal violet has been intensively studied, little work has been done in terms of photodegradation and photodecolorization of crystal violet in the suspensions of semiconducting metal oxides. Effects of crystal violet concentration, amount of semiconductor, light intensity and pH have been investigated,[28] but the products of the reaction were not identified and the mechanism of photodecomposition was unclear.

The focus of this research was photoreactions of crystal violet dye in hydrogen peroxide solution and in water suspensions of metal oxides under illumination. The aim of the research was to determine the mechanism of photodecolorization and photodecomposition of crystal violet and to evaluate the efficiency of photooxidation. In order to do that, five oxides were studied and compared: zinc oxide and titanium dioxide,

which are semiconductors, and magnesium oxide, aluminum oxide and silicon dioxide, which are insulators. Photodecomposition of other triphenylmethane dyes was also studied.

# CHAPTER II

# EXPERIMENTAL SECTION

## Materials

Crystal violet (N,N,N′,N′,N″,N″-hexamethylpararosaniline (chloride), CI 42555, Sigma Chemical Co), Basic fuchsin (pararosaniline hydrochloride, CI 42500, Fisher Scientific Company) and Michler's ketone (4,4'-bis(dimethylamino)benzophenone, Acros) were of reagent grade and were used without further purification.

The following oxide powers were used: Degussa Fumed $TiO_2$ P-25 grade (80% anatase, 20% rutile, 21 nm average particle size), rutile $TiO_2$ (Rutile Titanium Dioxide, 94%, 0.3-1.0 μm particle size, Aremco Products, Inc.), ZnO (Zinc Oxide, 99.9%, 1-5 μm particle size, Aremco Products, Inc.), MgO (Magnesium Oxide, 99.9%, 1-5 μm particle size, Aremco Products, Inc.), $SiO_2$ (Cab-O-Sil, Amorphous fumed silica, 99.8%, 0.2-0.3 μm particle size, Cabot Co), $Al_2O_3$ (Aluminum Oxide, Baker Chemical Co). The powders were subjected to heating at 400°C for at least an hour before each experiment to remove $CO_2$ adsorbed on the surface.

## Light Source

All the experiments were performed in the sunlight passing through the window of the third floor of McCollum Science Hall at the University of Northern Iowa. The spectra of the sunlight and sunlight through the window, recorded using a spectroradiometer (Licor Model LI-1800), are shown in Figure 4 and 5. The plastic

housing from Rite Lite Professional Fluorescent Work Light #FL-915 from Wal-Mart was used to cutoff the UV wavelengths ($\lambda$<400nm).[29]

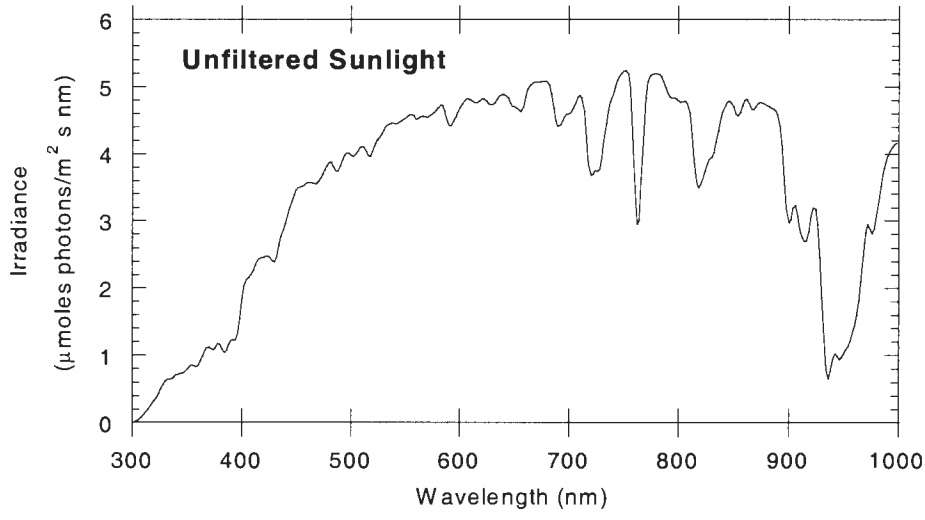



Figure 4. The spectrum of sunlight measured by a spectroradiometer with 2 nm resolution.

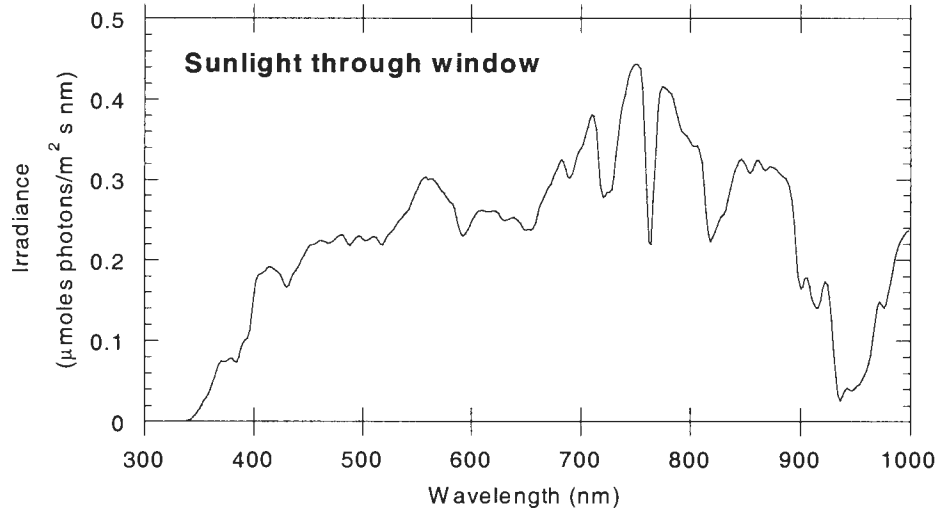



Figure 5. The spectrum of sunlight through the window of McCollum Science Hall, measured with a spectroradiometer with 2 nm resolution.

## Procedures and Analysis

Unless otherwise noted, aqueous oxide suspensions were prepared by adding 0.23 g of an oxide powder to 25ml of $5x10^{-5}$ M dye solution. Prior to irradiation, the suspensions were magnetically stirred in the dark for 30 minutes to ensure establishment of adsorption/desorption equilibrium of the dye on the oxide surface. At given irradiation time intervals, samples were collected and centrifuged to remove the catalyst. The supernatents were analyzed by UV-Vis spectroscopy with a Shimadzu UV-2101PC or UV-2401PC double beam spectrophotometer to monitor the loss of the dye and the possible formation of intermediate species.

All the comparisons, such as different catalysts, dyes and etc., were done in simultaneous trials to reassure that the differences in the reaction rates are due to the activities of reactants, not different sunlight intensities on different days.

Thin layer chromatography on silica plates was used to confirm some of the UV/vis data. The eluting solution was a 90:9:1 mixture of 1-propanol to water to acetic acid.

$TiO_2$ pellets used for diffuse reflectance spectroscopy experiments were produced by centrifugation and dried in the dark for several days prior to the measurements. Diffuse reflectance spectroscopy measurements were made using a Shimadzu UV2101PC double beam spectrophotometer with the ISR-260 intergrating sphere accessory. Spectra were referenced to Degussa P-25 $TiO_2$.

Molecular modeling was carried out using Spartan IBM Version 5.0.3 Open GL, running on the IBM RS6000 computers in the Chemistry Department at the University of

Northern Iowa. The geometry of the crystal violet and pararosaniline cations was optimized using the AM1 semi-empirical method, with the options set to "optcycle=500 maxcycle=500 hess=unit". Hartree-Fock *ab initio* calculations using the STO-3G basis set were then done on the optimized structure to estimate the charges on the individual atoms.

# CHAPTER III

# RESULTS AND DISCUSSION

Crystal violet undergoes photodecolorization and photodecomposition in water solution and in slurry with solid substrates. The rates of the reactions depend on the chemical properties of the substrates and on the wavelengths of illumination.

## Photodecomposition of Crystal Violet in Water Solutions

Crystal violet is relatively stable in water solution in the dark, but it decomposes when exposed to light, which indicates that excitation of the dye is necessary for the reaction to occur. When illumination of the crystal violet solution was carried out in the sunlight and monitored by UV-visible spectroscopy, both visible and UV bands underwent a hypsochromic shift and decreased in intensity (Figure 7). New species with absorbance at about 360nm were formed and then decomposed with further illumination (Figure 6 and 7).

Figure 8 displays the wavelength dependence of the crystal violet photodecomposition in water solution. Crystal violet decolorized with visible illumination ($\lambda < 400$ nm) slower than with full spectrum illumination.

Photodecomposition rate was observed to increase with increasing concentration of dissolved oxygen (Figure 9) indicating that photooxidation is a major pathway of photodecomposition.

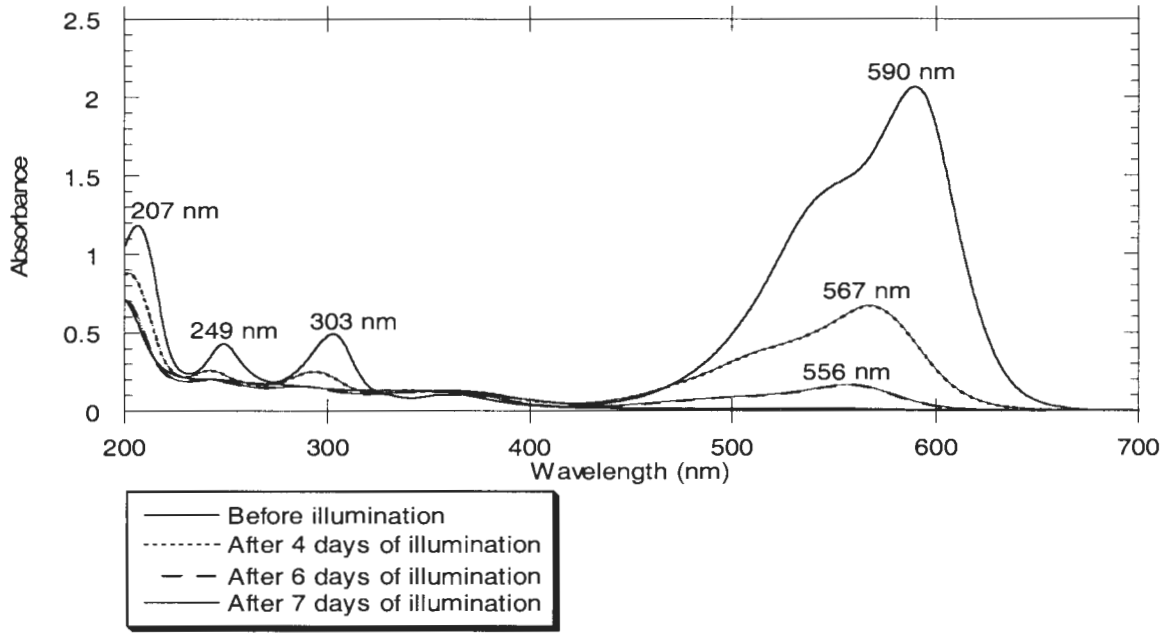



Figure 6. Photodecomposition of crystal violet in water solution under full spectrum illumination.

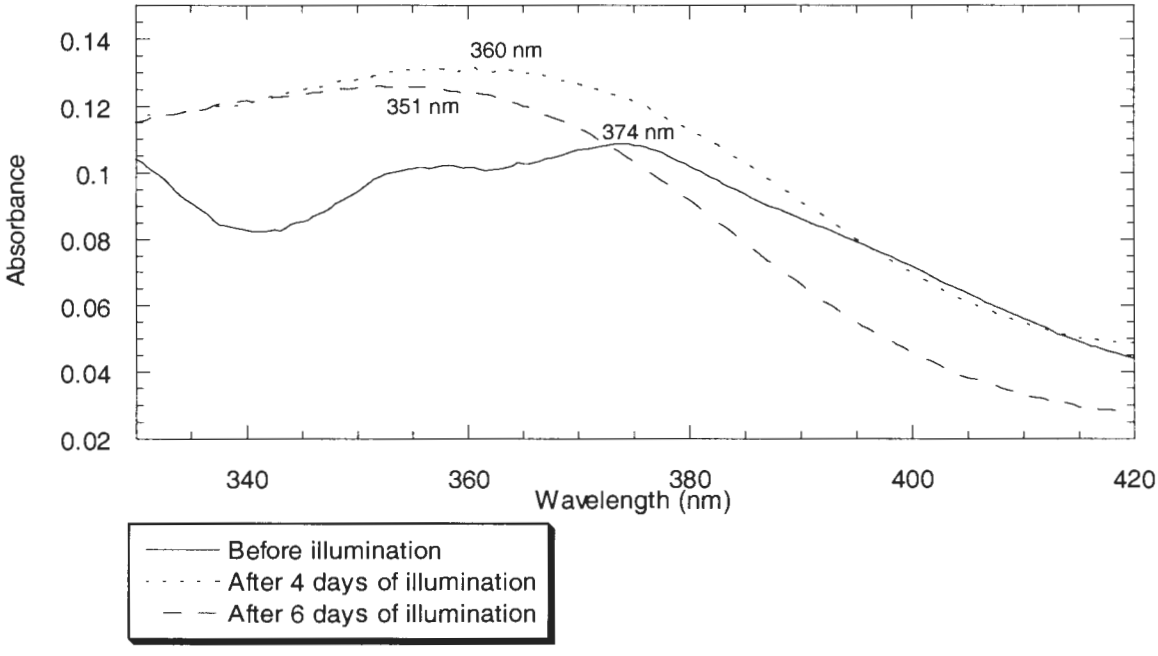



Figure 7. Photodecomposition of crystal violet in water solution under full spectrum illumination.

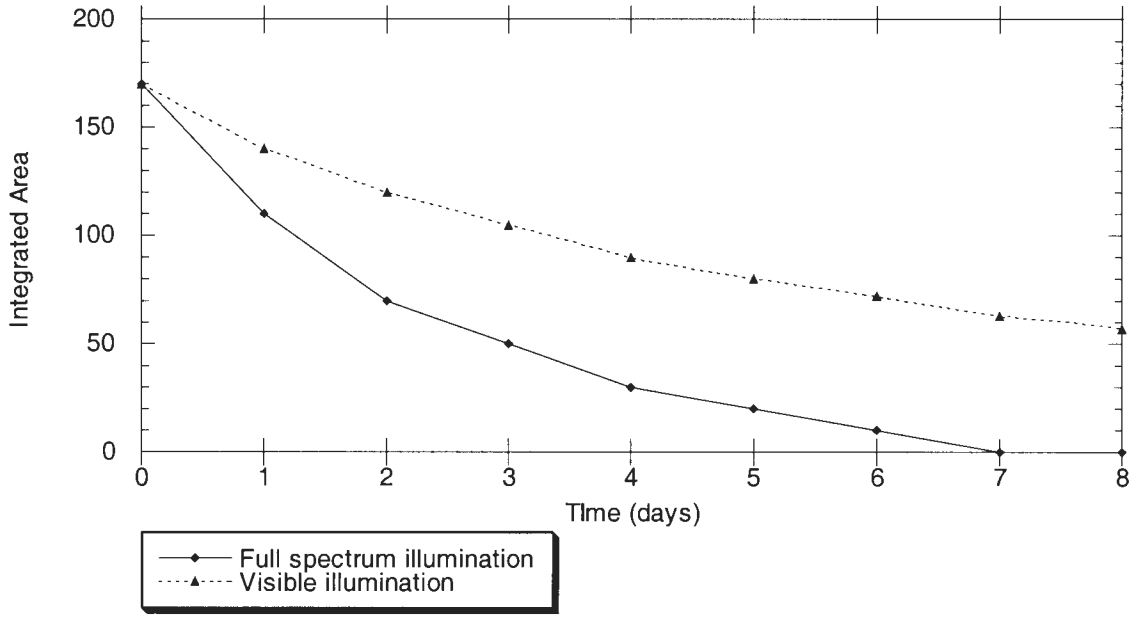



Figure 8. The decrease in the integrated area of the dye peak in the visible region as a function of time for the dye solutions under visible and full spectrum illumination (corrected by photon flux).

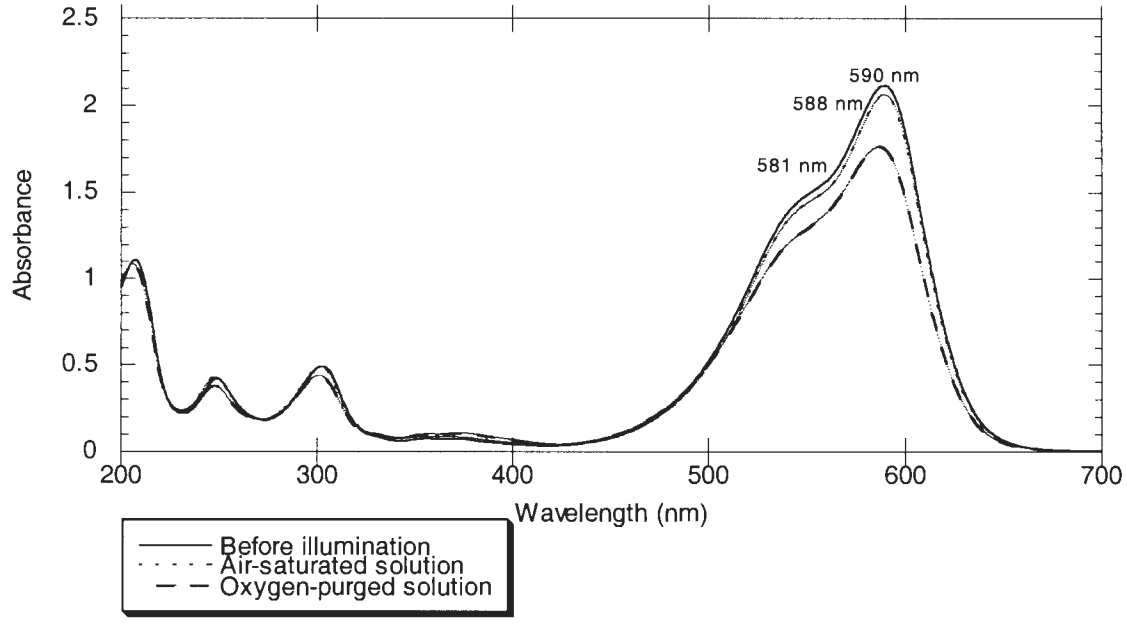



Figure 9. Photodecomposition of crystal violet in air-saturated and oxygen-purged water solutions after one day of full spectrum illumination.

The blue shift in the absorption spectra with illumination can be attributed to crystal violet demethylation to form methyl violet and other methylated parorosanilines, identified using TLC. Pararosaniline (see Figure 1), the final product of demethylation, was detected to be in the solution that had been irradiated for four days. The mechanism of demethylation has been proposed (Figure 10). [30]

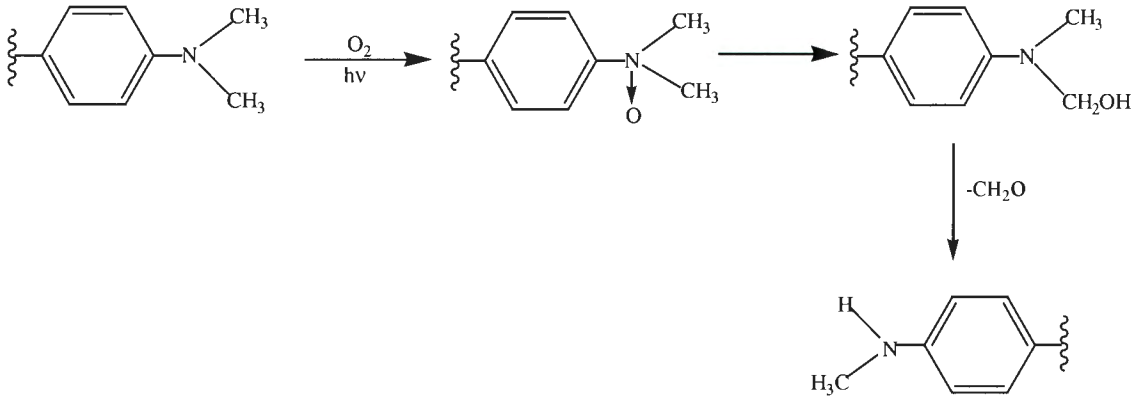



Figure 10. The mechanism of demethylation process.

In this mechanism, demethylation occurs via N-oxide precursors, which are too unstable to be detected. The final products of methyl group oxidation are carbon dioxide and water.

The overall decrease of absorbance in the visible region indicates that decomposition to colorless products is occurring concurrently with demethylation, thereby lowering the total concentration of methylated pararosanilines. The increase in absorbance at about 360 nm and then its decrease can be explained by the formation of intermediates in the decomposition to colorless products. The absorption spectra and a positive ketone test suggest that these intermediates are demethylated derivatives of

Michler's ketone, 4,4- bis(dimethylamino)benzophenone (Figure 11), which has $\lambda_{max}$ of 381nm. The blue shift in the absorption maximum of the intermediates with irradiation can be attributed to their further demethylation.

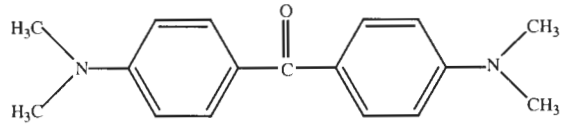



Figure 11. Structure of Michler's Ketone.

A similar shift is observed in water solution of Michler's ketone with illumination (Figure 12), which is consistent with the proposed mechanism.

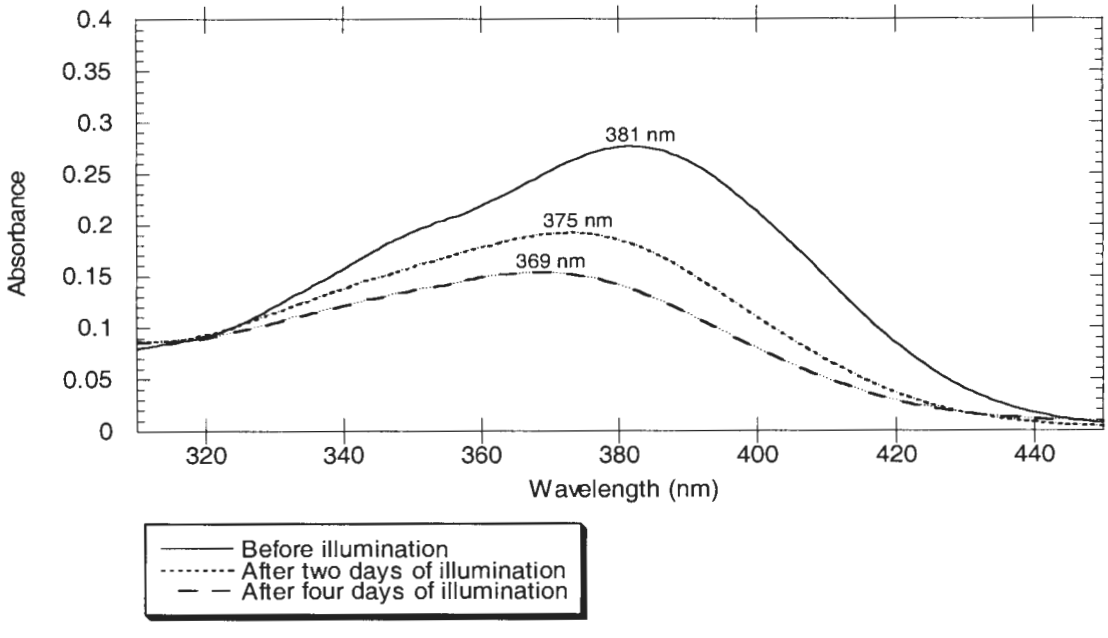



Figure 12. Photodecomposition of Michler's ketone under full spectrum illumination.

The other possible intermediates of the decomposition reaction are the aminophenols but no spectroscopic evidence of these was seen. Residual absorbance in the UV indicates that complete mineralization of organic compounds does not occur after 20 days of illumination.

In order to test these conclusions and to simplify interpretation of crystal violet decolorization data, photodecomposition of pararosaniline (Figure 1) was studied (Figure 13). No shifts in $\lambda_{max}$ were observed in any of the peaks since demethylation cannot occur. The peak with the absorption maximum at 336 nm can be assigned to 4,4'-diaminobenzophenone.

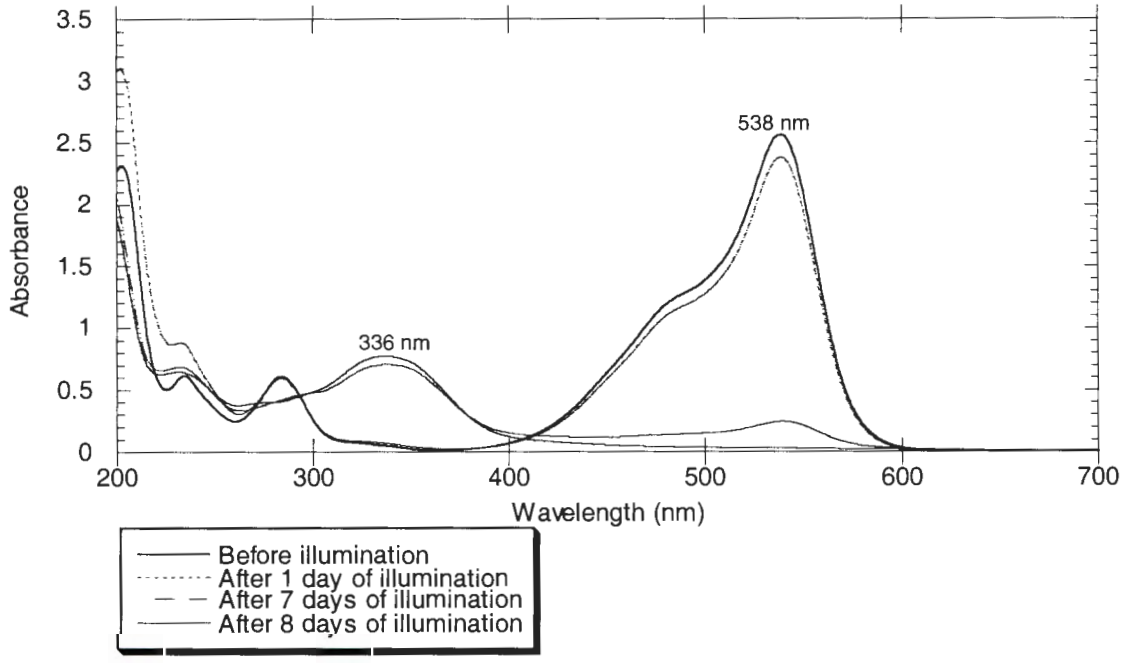



Figure 13. Photodecomposition of pararosaniline in the sun.

Complete decolorization was observed after 7 and 8 days of illumination for crystal violet and pararosaniline respectively. This result can be rationalized in terms of point charges of individual atoms (Table 1 and Table 2) calculated using Spartan.

Table 1. Charges of individual atoms in a crystal violet molecule (see Figure 1) calculated using Spartan

| *Atoms* | *Atom Charges* | |
|---|---|---|
| | Natural | Mulliken |
| Central C | 0.23 | 0.12 |
| Attaching C | -0.12 | -0.05 |
| Ortho C | 0.04 | -0.02 |
| Meta C | -0.12 | -0.1 |
| Para C | 0.24 | 0.17 |
| Ortho H | 0.05 | 0.08 |
| Meta H | 0.05 | 0.08 |
| N | -0.25 | -0.27 |
| N-C | 0.01 | -0.05 |
| $H_2C$-H | 0.06 | 0.08 |
| HC-$H_2$ | 0.05 | 0.07 |

Table 2. Charges of individual atoms in a pararosaniline molecule (see Figure 1) calculated using Spartan.

| *Atoms* | *Atom Charges* | |
|---|---|---|
| | Natural | Mulliken |
| Central C | 0.24 | 0.13 |
| Attaching C | -0.12 | -0.05 |
| Ortho C | 0.04 | -0.02 |
| Meta C | -0.12 | -0.09 |
| Para C | 0.27 | 0.19 |
| Ortho H | 0.06 | 0.09 |
| Meta H | 0.05 | 0.07 |
| N | -0.41 | -0.42 |
| N-H | 0.23 | 0.23 |

Because of the electron-donating methyl groups present in crystal violet molecule, the central carbon and the ring carbons in a crystal violet molecule have higher negative charge than the analogous atoms in the pararosaniline molecule. This makes crystal violet more susceptible to oxygen attack. The atoms with the highest negative charge, nitrogens and carbons attached to the central atom, are more likely to donate electrons to oxygen. The interaction between nitrogens and oxygen is consistent with the mechanism proposed for demethylation, and the interaction between the carbon adjacent to the central carbon and oxygen could be the first step in ketone formation. It would be consistent with the mechanism proposed by Kuramoto and Kitao,[31] in which the reaction proceeds through the formation of an unstable dioxeran intermediate, which decomposes to produce 4,4-bis(dimethylamino)benzophenone and p-(dimethylamino)phenol (Figure 14).

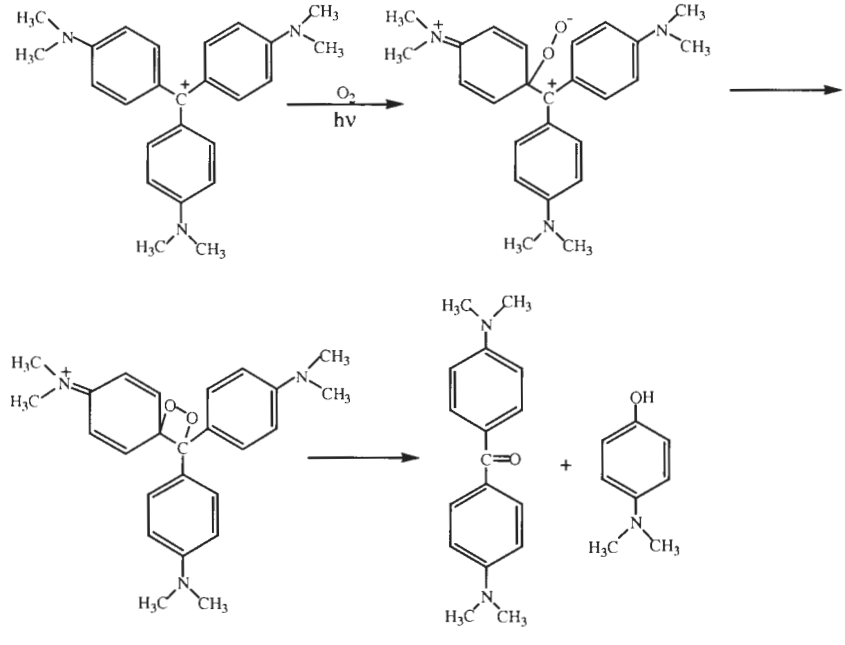



Figure 14. Mechanism of crystal violet photooxidation proposed by Kuramoto and Kitao.

No experimental evidence was obtained to support this mechanism and other mechanisms should also be considered.

The peak attributed to ketone formation is more intense in the case of pararosaniline photooxidation than in the case of crystal violet photooxidation. This indicates either higher stability of 4,4-diaminobenzophenone to further decomposition in comparison to its methylated derivatives or the higher yield of its formation. Further experiments are necessary to distinguish between the two possibilities.

All the above data is consistent with the following scheme of photodecomposition of crystal violet in water solution (Figure 15).[32]

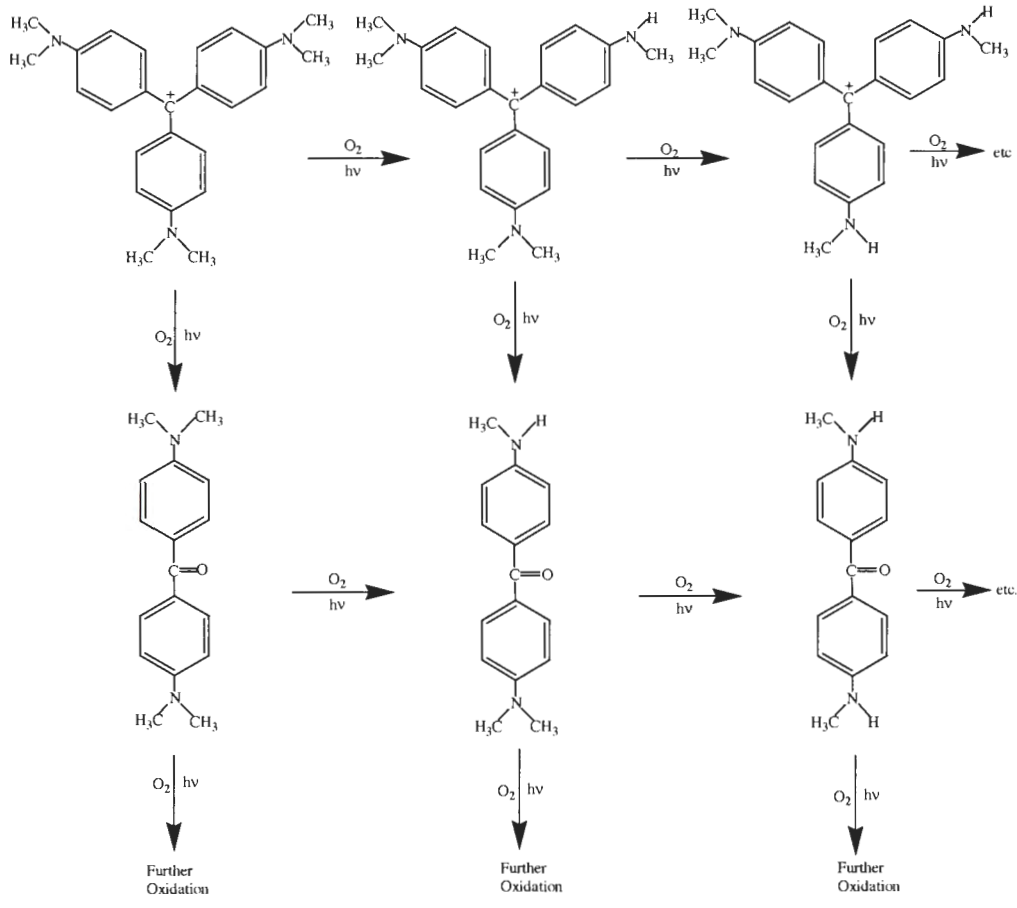



Figure 15. The mechanism of crystal violet photodecomposition in the water solution.

Photodecomposition of Crystal Violet by Hydrogen Peroxide

Oxidation by hydrogen peroxide was used as a model system to lend evidence towards the mechanism of crystal violet photodecomposition in $TiO_2$ suspensions since hydroxyl radicals are believed to be the main oxidizing species in both systems.

Hydrogen peroxide is a strong oxidizing agent, which was found to be very efficient in crystal violet photodecomposition both in the light (Figure 16) and in the dark, the reaction in the light being much faster (Figure 17). Comparison of the rates of the reaction under visible and full spectrum illumination shows that UV irradiation significantly accelerates the reaction. This observation can be explained by the efficient splitting of hydrogen peroxide molecules by UV light to form hydroxyl radicals, which have higher oxidation potential.

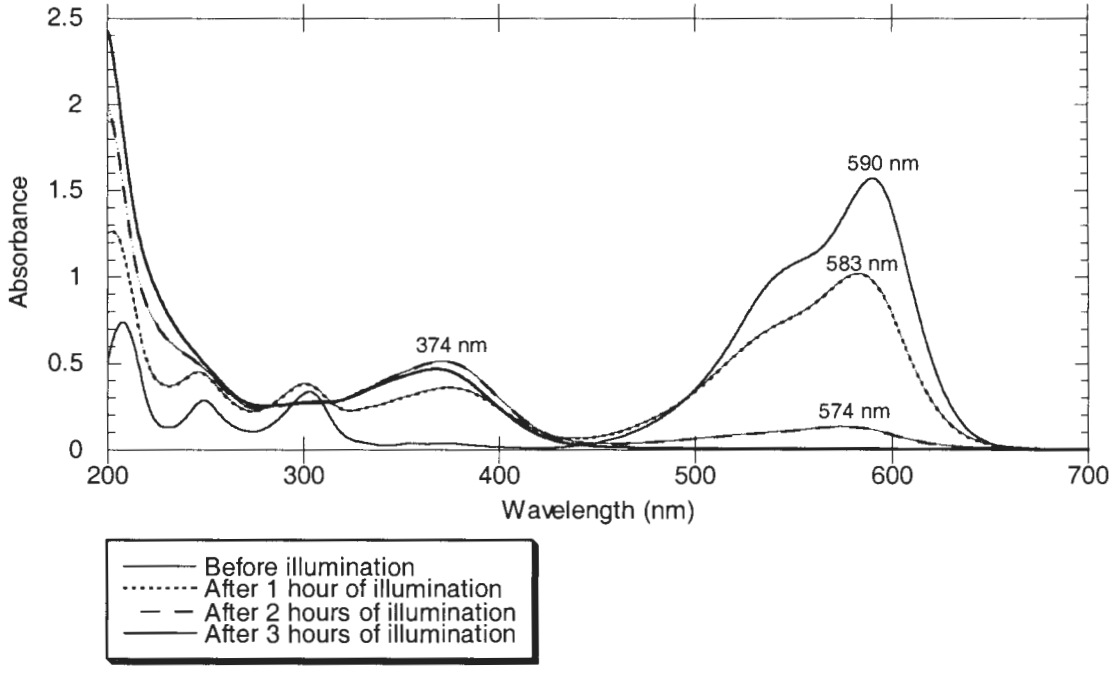



Figure 16. Photodecomposition of crystal violet in hydrogen peroxide solution under full spectrum illumination.

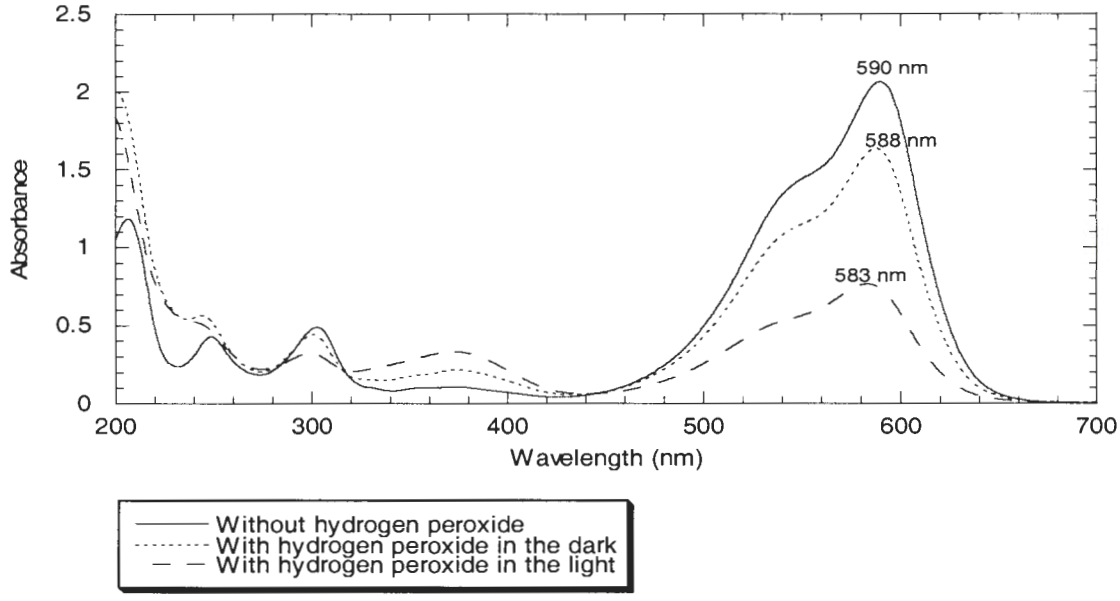



Figure 17. Decomposition of crystal violet in hydrogen peroxide solution in the dark and in the light (an hour reaction time).

Analysis of the absorption spectra indicates occurrence of both demethylation and decolorization reactions discussed in the previous section, with the rates of both reactions being higher in hydrogen peroxide solution. The higher demethylation rate can be explained by either higher concentration of active oxygen in the hydrogen peroxide solution formed by decomposition of hydrogen peroxide or by the oxidation being performed by hydroxyl radicals, which have higher oxidation potential than oxygen. Decolorization reaction has a significantly higher rate than demethylation in hydrogen peroxide solutions.

Figure 16 clearly shows that methylated diaminobenzophenones are intermediate species, whose concentration in the solution passes though a maximum as photooxidation takes place.

Figure 18 shows the effect of the increase of hydrogen peroxide concentration on the absorbance of crystal violet solution at 590 nm.

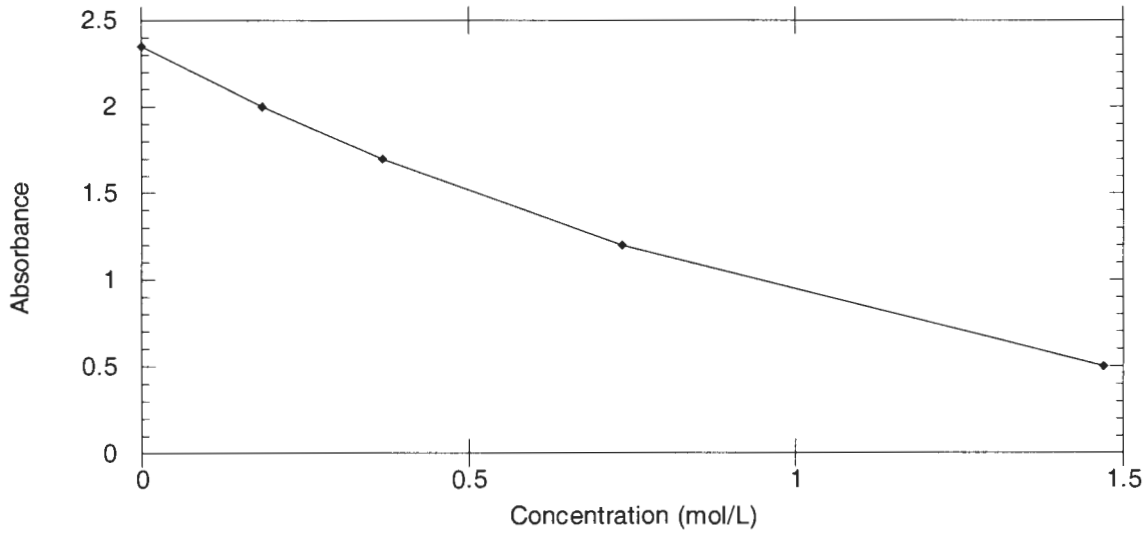



Figure 18. The decrease in absorbance at 590 nm for the solutions with different concentrations of hydrogen peroxide after 20 minutes of full spectrum illumination.

The spectrum of pararosaniline photooxidation in hydrogen peroxide solution is analogous to that in water solution, with rate of decolorization being much faster for the former even at relatively low hydrogen peroxide concentrations (Figure 19).

Based on these data it was concluded that the mechanism of the photoreaction of crystal violet with hydrogen peroxide is similar to the mechanism of photodecomposition of crystal violet in water solutions.

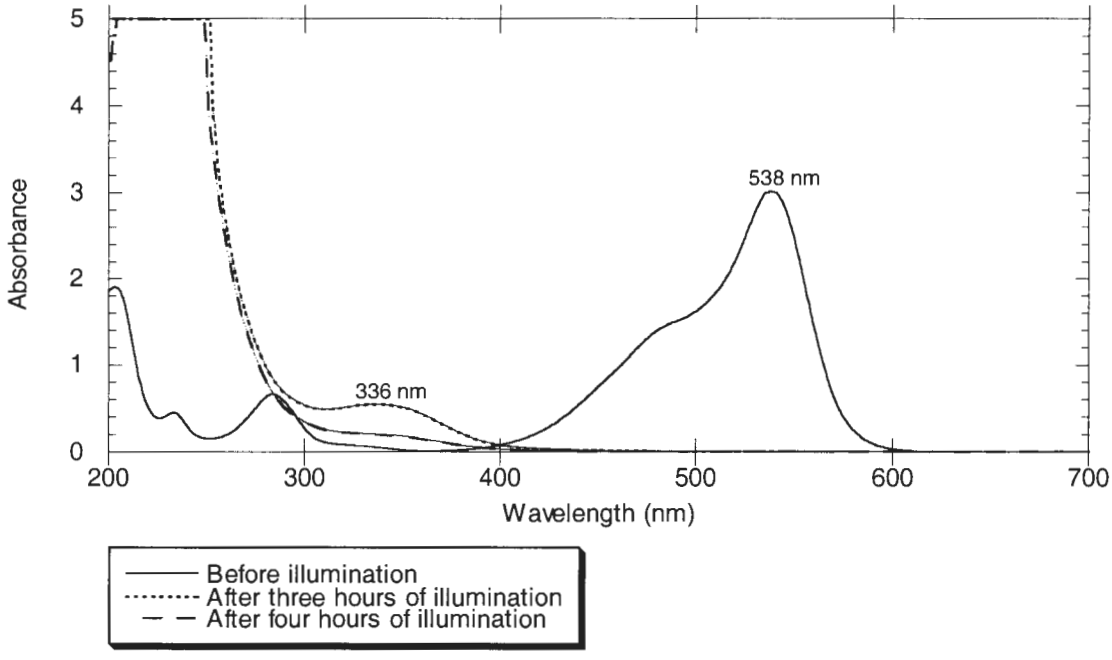



Figure 19. Photodecomposition of pararosaniline in hydrogen peroxide solution.

## Photodecomposition of Crystal Violet in Water Suspensions of Metal Oxides.

### Photodecompostion of Crystal Violet in Titanium Dioxide Water Suspensions

Titanium dioxide is a very efficient catalyst for crystal violet photodecomposition. After one hour of exposure of crystal violet water solution to sunlight in the presence and absence of $TiO_2$, a dramatic decrease in intensity and a hypsochromic shift were observed only for the sample containing $TiO_2$ (Figure 20), while the spectrum of homogeneous crystal violet solution exhibited almost no difference from the original spectrum. Since Degussa P-25 (80% anatase, 20% rutile) was found to be more active in crystal violet photodecomposition than rutile $TiO_2$, Degussa P-25 was used for further experiments.

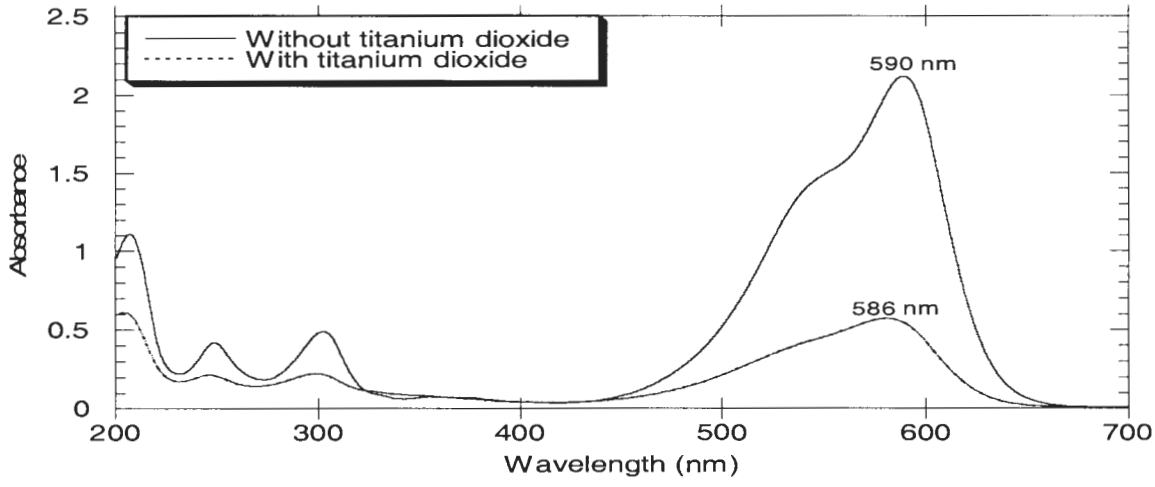



Figure 20. Photodecomposition of crystal violet in the absence and presence of titanium dioxide after an hour of illumination.

Mechanism of photodegradation. In order to distinguish between the two main processes that can occur in the semiconductor-dye system, photosensitization and oxidation/reduction by the photoexcited semiconductor, the rates of crystal violet photodecomposition under visible and full spectrum illumination were compared (Figure 21).

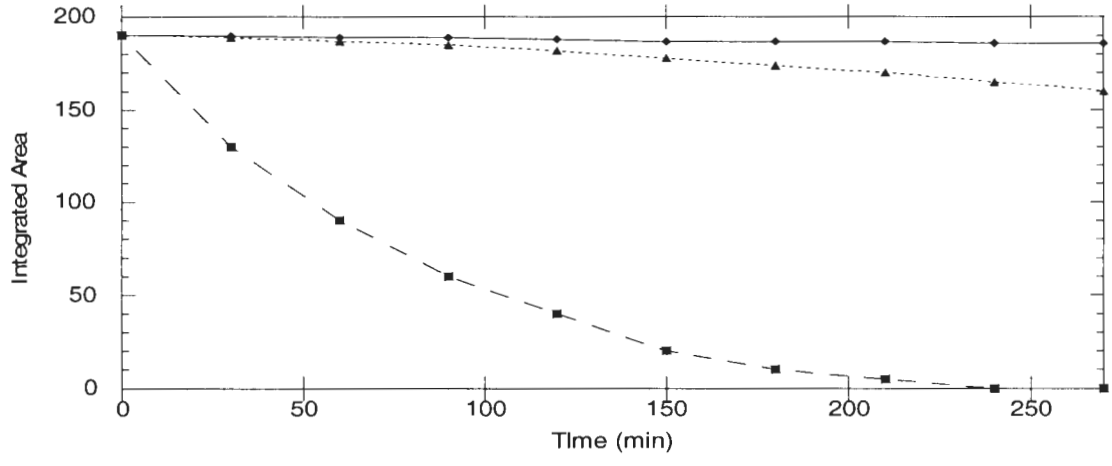



Figure 21. The decrease in the integrated area of the dye peak in the visible region as a function of time for crystal violet water solution and titanium dioxide suspension under visible and full spectrum illumination (corrected by photon flux).

Photosensitization does occur, since the presence of titanium dioxide accelerates decolorization of crystal violet under visible illumination, but the much higher rate of the reaction for the full spectrum illumination indicates that oxidation/reduction by the photoexcited semiconductor is the main mechanism of crystal violet photodecomposition.

Photoreduction by the photoexcited semiconductor surface would require efficient preadsorption of the dye to the $TiO_2$ lattice for the direct electron transfer to occur.[33] When $TiO_2$ was added to crystal violet solution and the mixture was kept in the dark, a small increase in crystal violet concentration was observed for the solution exposed to $TiO_2$ powder for a short period of time (Figure 22).

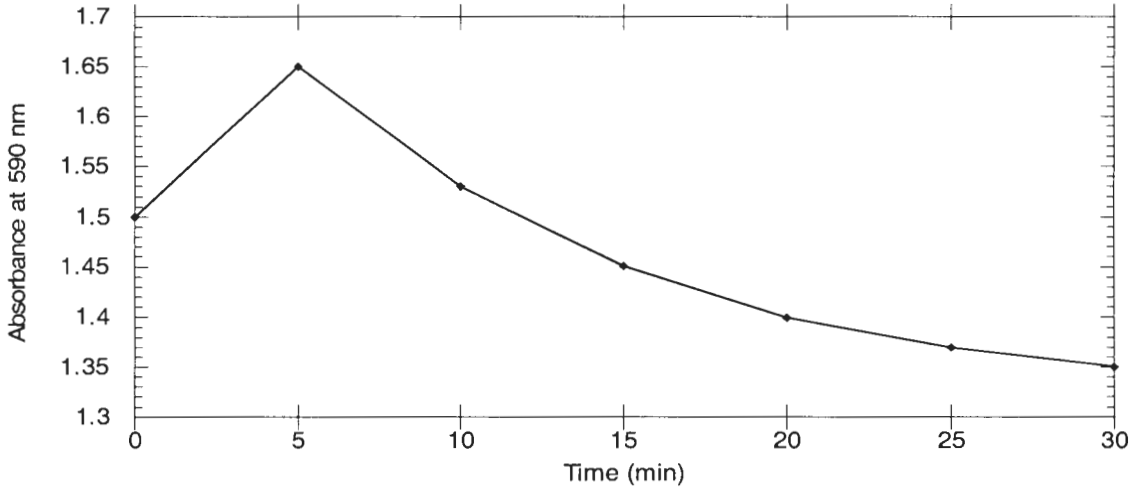



Figure 22. Absorbance of crystal violet solution as a function of stirring time with titanium dioxide powder (in the dark).

The initial increase in absorbance indicates that water is adsorbed on the $TiO_2$ lattice better than crystal violet. The subsequent decrease in the dye concentration indicates its secondary adsorption by the surface hydroxyl groups either formed by dissociation of water molecules on the $TiO_2$ surface or adsorbed from water solution.

Since water is adsorbed preferentially to crystal violet initially, and taking the low concentration of crystal violet into account, I conclude that crystal violet occupies only a small fraction of the surface-solution interface, with solvent occupying most of it. Moreover, no spectroscopic evidence for any reduction products was seen, either in the supernatent of the centrifuged $CV/H_2O/TiO_2$ solution or on the surface of $TiO_2$. These data rule out photoreduction as a possible mechanism of crystal violet photodecomposition in $TiO_2$ suspensions under illumination.

In the case of oxidation by the photoexcited semiconductor, one or more of several species could perform the oxidation:

1. trapped holes
2. hydroxyl radicals formed by the interaction of hydroxide ions with the photoexcited semiconductor
3. perhydroxyl radicals formed by the protonation of $O_2^{-\bullet}$.

Direct oxidation is expected to be less important than oxidation by hydroxyl radicals or by perhydroxyl radicals since it also requires strong adsorption of the dye at the semiconductor lattice, which was shown not to be the case with crystal violet.

Additional evidence for the importance of oxidation by hydroxyl radicals comes from the inhibition of crystal violet photooxidation by isopropanol, which is known as a

good OH• quencher,[34] and from the higher activity of anatase $TiO_2$ in photooxidation of crystal violet in comparison to rutile $TiO_2$. It has been shown that anatase $TiO_2$ abstracts water better and forms hydroxyl radicals more readily than rutile $TiO_2$.[35]

Since the solution after preadsorption in the dark decolorizes two times faster than the solution without preadsorption, secondary adsorbtion on the hydroxyl groups at the titanium dioxide surface has a great influence on the rate of the reaction. Besides, hydroxyl radicals are extremely reactive and are not likely to migrate far from the surface even at low concentrations of oxidizable reactants. Therefore, the oxidation of crystal violet in the solution by free hydroxyl radicals was concluded to be negligible.

The best explanation for the observations is photogeneration of surface-bound hydroxyl radicals, which oxidize molecules at the surface layer without diffusing into the bulk solution.

In order to keep the photoxidation process going, it is necessary to avoid accumulation of electrons in the conduction band of semiconductor particles, which would increase the electron-hole recombination rate and lower the quantum yield of the reaction. Because the conduction band of $TiO_2$ is nearly isoenergetic with the reduction potential of oxygen, adsorbed oxygen serves as a trap for photogenerated conduction electrons.[36] Since oxygen reacts slowly with the electrons of most semiconductors, including $TiO_2$, the rate of electron transfer from the particles to oxygen is usually both yield and rate-controlling in the photocatalytic process.[37] $O_2^{-\bullet}$ and $O_2^{2-}$ generated species can either directly oxidize the dye or protonate to form perhydroxyl and hydroxyl radicals:

$$O_2^{-\bullet} + H^+ \rightarrow HO_2^\bullet$$

$$HO_2^\bullet + HO_2^\bullet \rightarrow H_2O_2 + O_2$$

$$O_2^{-\bullet} + HO_2^\bullet \rightarrow O_2 + HO_2^-$$

$$HO_2^- + H^+ \rightarrow H_2O_2$$

$$H_2O_2 \rightarrow 2OH\bullet$$

To learn more about the impact of the reaction with oxygen into the overall rate of the photodecolorization process, a detailed kinetic study should be performed.

Intermediates and products. No absorption bands were observed in the supernatent of the centrifuged CV/$H_2O$/$TiO_2$ solution after six hours of full spectrum illumination. However, the $TiO_2$ pellet produced by centrifugation had a slight yellow color. Reflectance spectroscopy indicates the presence of a compound/compounds with absorption maximum at 376 nm, adsorbed on the surface of the titanium dioxide (Figure 23). Comparison of the reflectance spectra for different possible intermediates and products of the reaction reveals that the detected compounds are most likely to be demethylated derivatives of Michler's ketone, which is consistent with the proposal of oxidation by hydroxyl and perhydroxyl radicals to be the main mechanism of photodecomposition. It is not known whether demethylated derivatives of Michler's ketone are intermediates or the final products of photodecomposition in $TiO_2$ suspensions since their further decomposition was not studied.

On the basis of the above mentioned results and discussion, the mechanism shown in Figure 24 is proposed for the catalysis.

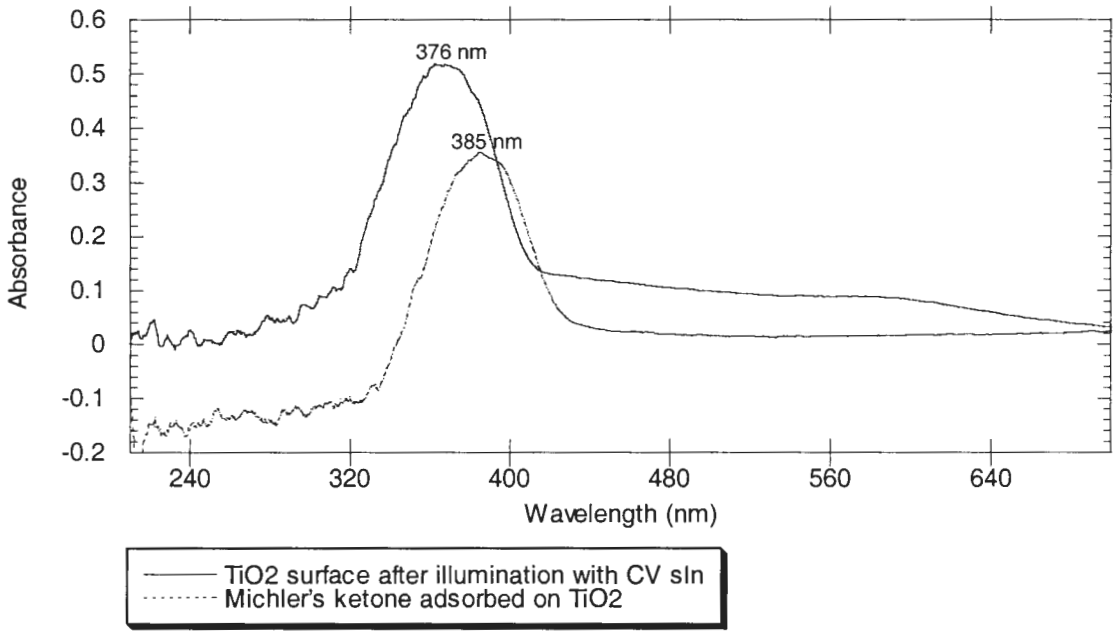



Figure 23. Absorbance spectra of $TiO_2$ surface after three hours of illumination and of Michler's ketone adsorbed on titanium dioxide surface.

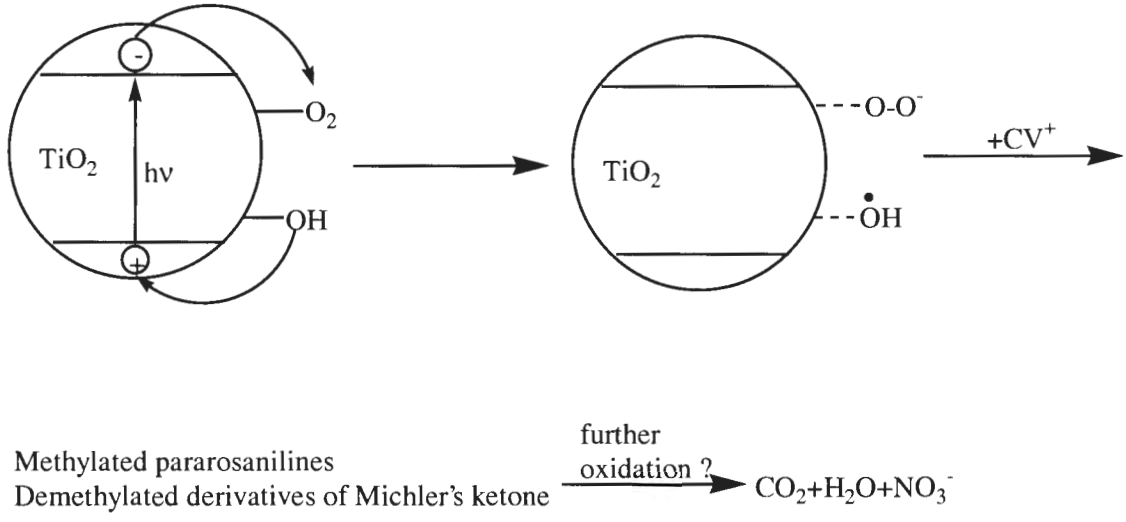



Figure 24. Proposed mechanism of crystal violet photodecomposition in titanium dioxide suspensions.

Photocatalysis starts by the excitation of the semiconductor by UV irradiation to produce electron-hole pairs on the surface of a semiconductor particle. An electron can be transferred from a surface hydroxyl group to a photogenerated hole on the $TiO_2$ particle to form surface OH•, which after its formation is still associated with the surface. Hydroxyl radicals can then oxidize crystal violet molecules to produce methylated pararosanilines and demethylated derivatives of Michler's ketone. Preadsorbed oxygen can be reduced by the conduction band electrons to form $O_2^{-\bullet}$ radicals, which can protonate to form perhydroxyl and hydroxyl radicals that most likely also oxidize crystal violet. Further studies should be carried out to determine the final products of crystal violet photodecomposition on $TiO_2$ surface.

Photodecomposition of Crystal Violet in Zinc Oxide Suspensions

Zinc oxide is another semiconducting oxide, which was shown to be even more efficient in photodecolorization of crystal violet than titanium dioxide. Zinc oxide was found to have higher initial adsorption of crystal violet and more efficient photosensitization than $TiO_2$ (Figure 25). The peak attributed to ketone formation was observed to be higher in ZnO suspensions than in $TiO_2$ suspensions. This result can be explained by either the higher rate of formation of demethylated benzophenones in ZnO suspensions or by lower adsorption of these intermediates on the ZnO surface. Demethylation was shown to be less efficient for ZnO than for $TiO_2$.

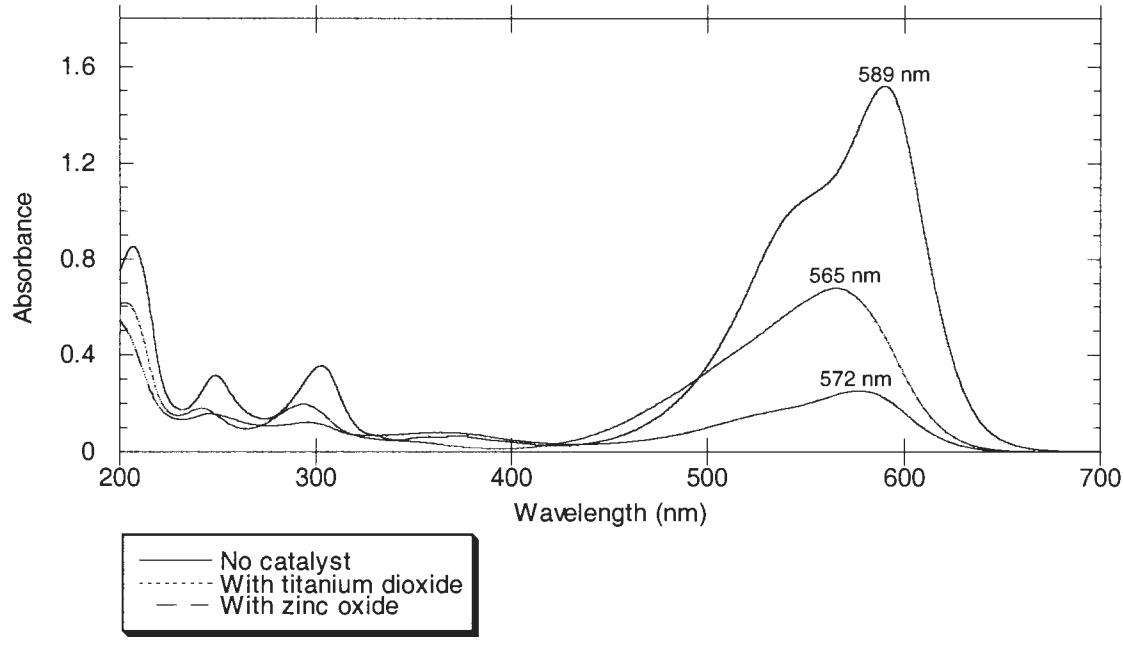



Figure 25. Photodecomposition of crystal violet in titanium dioxide and zinc oxide suspensions after three days of visible illumination. Faster decrease in the intensity of the main adsorption maxima in case of zinc oxide indicates the process of photosensitization being more efficient (the starting amount of adsorbed crystal violet is the same for ZnO and $TiO_2$).

Photodecomposition of Crystal Violet in Silicon Dioxide Suspensions

Silicon dioxide is an insulator with a band gap of at least 4.9 eV and therefore is a photochemically inert surface. The fast decrease in crystal violet concentration after the addition of silicon dioxide to a crystal violet solution and the bright purple color of the centrifuged $SiO_2$ powder indicate high adsorption of crystal violet on the surface of $SiO_2$. This is caused by the intense interaction of the cationic dye and negatively charged silanol groups. Strong localized surface interactions restrict the mobility of the adsorbed molecule, slowing down the diffusion of molecular oxygen to the dye layers stabilized by $\pi$-$\pi$ stacking and, consequently, decrease the rate of demethylation (Figure 26).

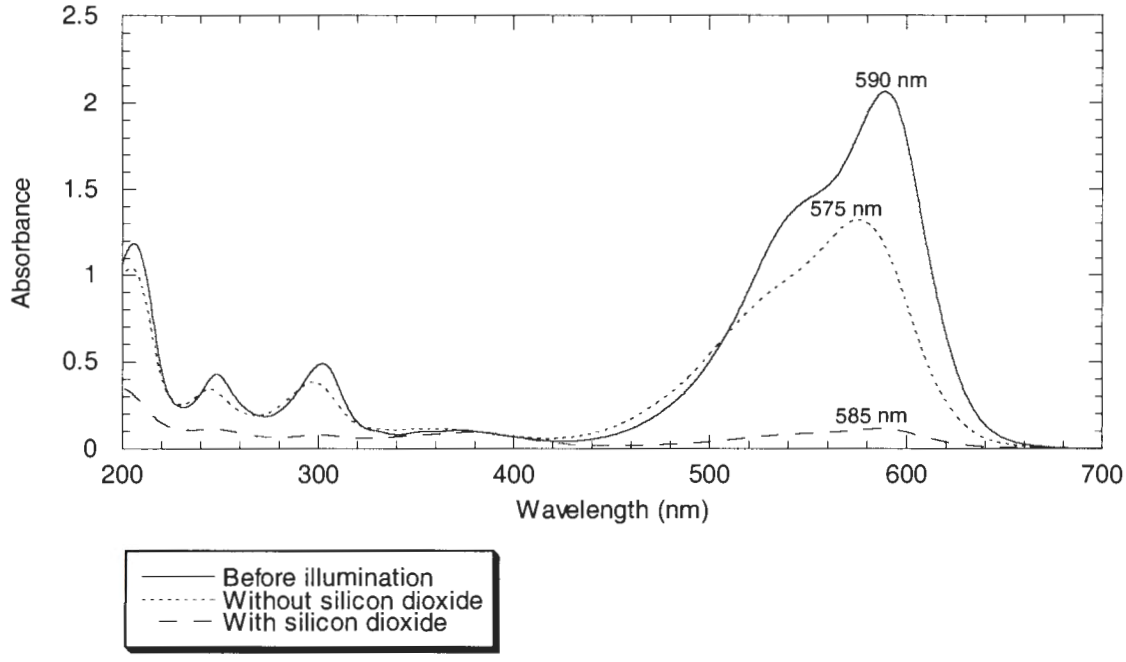



Figure 26. Photodecomposition of crystal violet in silicon dioxide suspension after three days of full spectrum illumination. Smaller hypsochromic shift indicates that $SiO_2$ slows down demethylation reaction.

Photodecomposition of Crystal Violet in Aluminum Oxide Suspensions

Aluminum oxide, an insulator, was found to accelerate the reaction of crystal violet with oxygen (Figure 27) since a larger hypsochromic shift is observed in the presence of $Al_2O_3$ than in homogeneous crystal violet solution after the same time of illumination. Aluminum oxide has been shown to stabilize the excited states of aromatic compounds,[38] which could enhance the efficiency of the reaction of crystal violet with oxygen since it is dependent on the lifetime of the excited state of the dye.

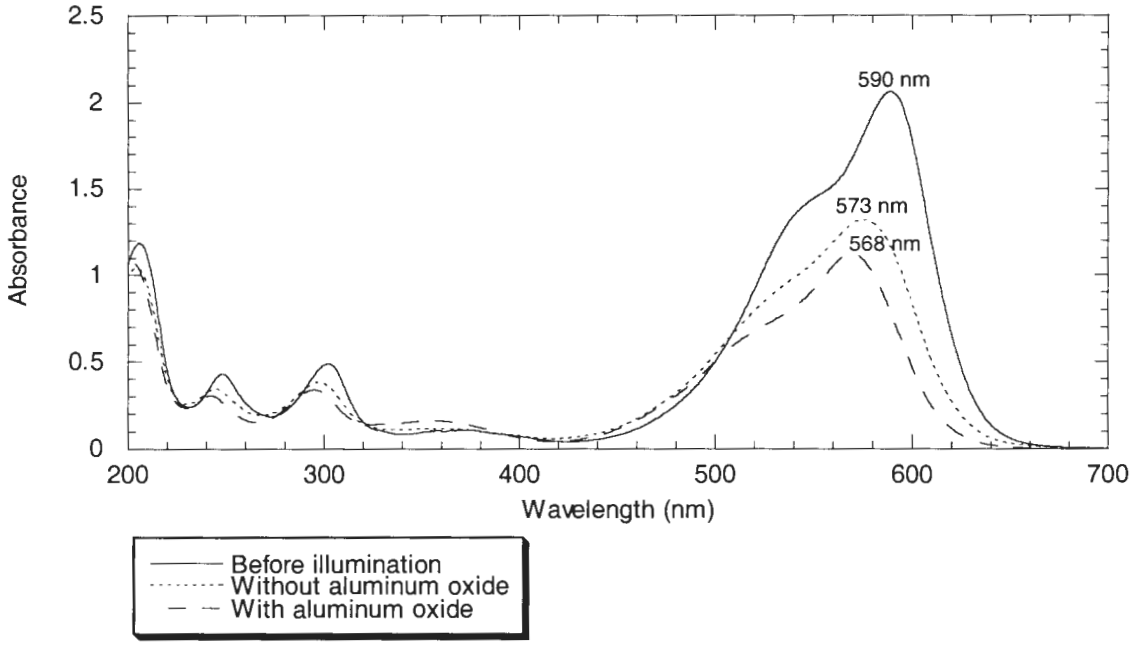



Figure 27. Photodecomposition of crystal violet in aluminum oxide suspension after three days of full spectrum illumination.

Photodecomposition of Crystal Violet in Magnesium Oxide Suspensions

Magnesium oxide was another insulator used to investigate possible influences introduced by photochemically inert oxides. Surprisingly, the crystal violet solution photodecolorized faster in the magnesium oxide suspension than in the suspension of titanium dioxide. The decolorization over MgO occurred with no change in $\lambda_{max}$ and no increase in absorbance at 360nm (Figure 28) and was attributed to the acid base reaction of crystal violet with hydroxide ions in solution (Figure 29), since a magnesium oxide suspension is basic (pH = 11).

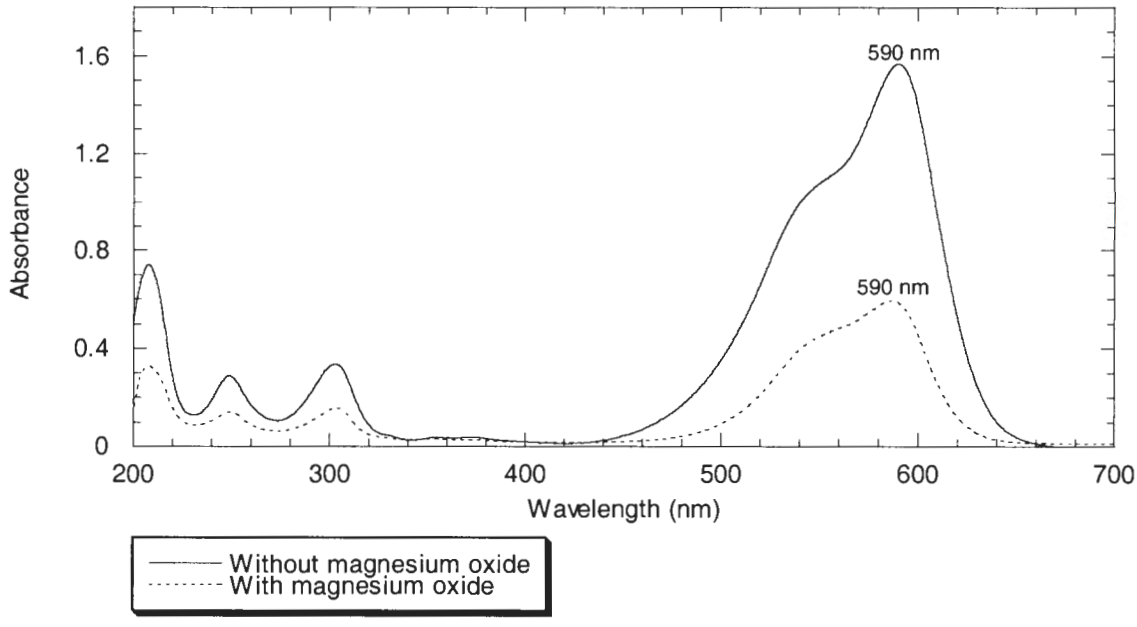



Figure 28. Decolorization of crystal violet solution half an hour after addition of MgO under full spectrum illumination.

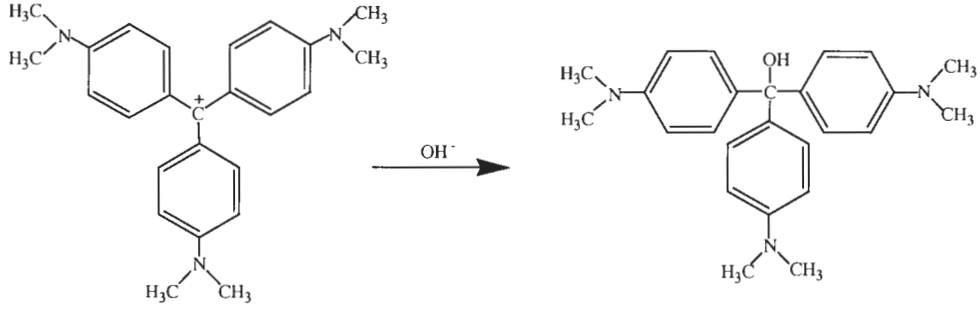



Figure 29. The reaction of crystal violet with base.

The formation of the colorless carbinol was supported by reverse reaction with acid to form crystal violet cation. The rate of the reaction in the dark was found to be lower than with illumination.

Pararosaniline was found to react faster with base than crystal violet does. It can be explained by the fact that pararosaniline, lacking electron-donating groups at the nitrogens, is more electron deficient than crystal violet, and therefore is more active in the reaction with the nucleophile.

According to the results of Spartan point charge calculations for individual atoms (Table 1), the central carbon in a pararosaniline molecule has higher positive charge than the analogous atom in a crystal violet molecule, which is in a good agreement with the proposed mechanism.

Comparison of Different Methods of Crystal Violet Photodecomposition

Hydrogen peroxide is efficient in crystal violet photodecomposition but it is consumed during the reaction and it absorbs only short UV wavelengths, utilizing only a very small part of solar radiation.

Anatase titanium dioxide is a cheap, chemically and biologically inert catalyst, and it can absorb short visible wavelengths (all wavelengths below 400 nm; from 2 to 5% of sunlight).[39] On the other hand, being a heterogeneous catalyst, titanium dioxide might adsorb the products of the reaction on its surface, which could result in lowering or even loss of its catalytic activity. The rate of photodecomposition of the intermediates, as well as the possible adsorption of the reaction products, should be taken into account when

discussing the possibility of using titanium dioxide for the treatment of dye-contaminated waste-waters on the industrial scale.

Zinc oxide was found to be more efficient than titanium dioxide in crystal violet photodecomposition, but it has been found that a significant quantity of $Zn^{2+}$ can be dissolved into solution during the photochemical reactions. It is known that ZnO electrode undergoes anodic photocorrosion according to the equation[40]

$$ZnO+2h^{+}\rightarrow Zn^{2+}+O*$$

Therefore, ZnO powder is not suitable to be a photocatalyst for wastewater treatment unless a means of removing $Zn^{2+}$ is also used.

None of the insulating oxides under investigation ($SiO_2$, $Al_2O_3$, MgO) are prospective catalysts for crystal violet photodecomposition because of the very low reaction rates.

# CHAPTER IV

# CONCLUSIONS

Dyes are among the most widely synthesized chemicals. Since some dyes, including crystal violet, are hazardous and significant losses occur during their manufacture and processing, efficient and easy ways of dye decomposition should be investigated. Chemical oxidation and photooxidation in the presence of semiconducting oxides have been shown to be one of the most prospective methods of treating dye-contaminated waters.

The focus of my research was to determine the mechanism of crystal violet photodecomposition in the presence of hydrogen peroxide and metal oxides, to study the influence of different factors on the rate of the reaction and to compare the efficiency of the photochemical processes.

Photodecomposition of crystal violet in water solutions was first studied in the absence of catalysts. It was shown that full spectrum illumination is more efficient in crystal violet decomposition than visible illumination and the increase in oxygen concentration accelerates the reaction. Two concurrent reactions, demethylation and ketone formation were found to occur to form demethylated dyes and demethylated derivatives of Michler's ketone. Point charges of individual atoms, calculated using Spartan, were used to identify the most probable mechanism of their formation.

Photoreaction of crystal violet with hydrogen peroxide was suggested to have the same mechanism as the reaction of crystal violet with oxygen. Its higher rate is due to the higher oxidation potential of hydrogen peroxide and hydroxyl radicals.

The results on the rates of photodecomposition were obtained and compared for the suspensions of several oxides: titanium dioxide and zinc oxide, which are semiconductors and magnesium oxide, aluminum oxide and silicon dioxide, which are insulators.

Semiconducting oxides were shown to be the most efficient in crystal violet photodecomposition in comparison to other oxides studied. Wavelength dependence and diffuse reflectance spectroscopy studies of the intermediates adsorbed on the surface allowed proposing oxidation by the photoexcited semiconductor as the main mechanism of crystal violet photodecomposition in titanium dioxide suspensions. It was concluded that surface-bound hydroxyl radicals perform the oxidation of crystal violet molecules preadsorbed by the surface hydroxyl groups. It was shown that oxygen is required for crystal violet photodecomposition since it serves as an electron acceptor, preventing accumulation of electrons on the semiconductor particles.

Studies of crystal violet photodecomposition in the presence of aluminum oxide and silicon dioxide indicate that a photochemically inert surface may influence the rate of the reaction. Aluminum oxide accelerates the reaction by stabilizing of the excited state of the dye and silicon dioxide inhibits crystal violet photodecomposition by forming dye clusters at the surface.

The reaction of crystal violet with hydroxide ion occurs in magnesium oxide suspensions (pH = 11) to form a carbinol base.

The efficiency of using different reagents and catalysts for treatment of crystal violet contaminated wastewaters was evaluated. Only hydrogen peroxide and

semiconducting oxides have a potential of being used in industry for this purpose, although they also have certain disadvantages: Hydrogen peroxide is consumed during the reaction; $TiO_2$ might adsorb products of the reaction on the surface; and ZnO is photochemically unstable. $TiO_2$ was concluded to be the most prospective industrial photocatalyst because of its cheapness, reasonable effectiveness, chemical and biological stability.

In future research on the photodegradation of crystal violet in water solutions and suspensions of metal oxides, I would suggest the following improvements and directions:

1. HPLC and Total Carbon Analysis should be performed to identify the intermediates and final products of photodecomposition.

2. Experiments with singlet and triplet state quenchers may provide the information about the role of the singlet and triplet states of crystal violet in its reaction with oxygen.

3. ESR studies should be performed in order to eliminate the possibility of the direct hole mechanism in semiconducting oxide suspensions and to detect the formation of hydroxyl radicals.

4. A detailed kinetic study is required to support the proposed mechanism of crystal violet photodecomposition in the suspensions of semiconducting oxides. The use of laser pulse photolysis to investigate the rapid recombination and trapping events occurring in and on the semiconductor photocatalyst may allow the measurements of the kinetic parameters.

Several changes can be made in the systems in order to make crystal violet photodecomposition more efficient:

1. A common feature of photocatalytic reactions occurring on metal oxides suspended in aqueous solution is dependence of the reaction rate on solution pH. Surface charge is expected to be positive at pH lower than isoelectric point and negative at pH higher than isoelectric point. The charge of a crystal violet molecule can also change significantly, which will definitely change the adsorptivity of the dye. Changes in adsorbtivity, in the bandgap positions of the semiconductor and redox potential of the dye will determine the photocatalytic activity at certain pH.

2. A simple and elegant approach to suppress the back electron transfer is to produce a long-distance charge separated state, with electrons and holes far from each other through the use of coupled, i.e. the combination of two or more, semiconductors with appropriate energy levels. In these coupled systems, for instance, ZnO/CdS, the energy levels of the semiconductors are such that the electrons, photogenerated or injected in CdS, are quickly transferred to the lower lying conduction band of ZnO. As a result, the electrons and holes are physically separated, thus reducing the possibility of back electron transfer and suppressing the wasteful charge recombination.

3. Metal deposition over the semiconductor catalyst is another method of enhancing of photoreaction efficiency. It improves the charge transfer rates to $O_2$ and consequently lowers the rate of wasteful recombination.

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